PART I
SECTION I

THEORETICAL
Diagramatic representation of chalcones and related compounds derived from 2-hydroxy-4-ethoxyacetophenone.
SECTION I

CHALCONEs AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXYACETOPHENONE

In this section, chalcones and related compounds derived from 2-hydroxy-4-ethoxyacetophenone have been described. The acetophenone required for this purpose has been synthesised from resacetophenone which was prepared from resorcinol, glacial acetic acid and anhydrous zinc chloride.

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
& \quad \text{C}_2\text{H}_5\text{I} \quad \text{C}_2\text{H}_5\text{O} \\
& \quad \text{K}_2\text{CO}_3 \quad \text{CH}_3\text{COCH}_3 \\
\text{COCH}_3 & \quad \text{OH} \\
\end{align*}
\]

2-Hydroxy-4-ethoxyacetophenone was condensed with (1) benzaldehyde (2) 2-methoxybenzaldehyde (3) vanillin (4) 3-nitrobenzaldehyde (5) 4-chlorobenzaldehyde (6) 4-nitrobenzaldehyde (7) 2:4 dichlorobenzaldehyde.

Condensations were carried out using (a) different concentrations of potassium hydroxide and (b) phosphorus oxychloride. It was found after some trials that 40 per cent potassium hydroxide was the best to get an optimum yield of the chalcones. The reaction period used was about 24 hours.
Also, in these condensations only chalcones were isolated; all attempts to isolate a flavanone or other compounds have failed.

I CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXYACETOPHENONE AND BENZALDEHYDE:

The condensation was studied using different condensing agents:

(a) Potassium hydroxide solution of different concentrations
(b) Phosphorus oxychloride

(a) Potassium hydroxide:

The condensation has been investigated using different concentrations of alkali and for different reaction periods. The important conditions are tabulated below:

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium hydroxide per cent</th>
<th>Temperature °C</th>
<th>Reaction period (hr)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>25-30</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>40</td>
<td>100</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>25-30</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>40</td>
<td>100</td>
<td>4</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>40</td>
<td>25-30</td>
<td>24</td>
</tr>
</tbody>
</table>
Optimum yield of the chalcone was obtained with 50 per cent alkali as a condensing agent and by keeping the reaction mixture for 24 hours at the room temperature (25-30°C).

The product was crystallised from ethanol, ethyl acetate or benzene. No other product could be isolated.

(b) Phosphorus oxychloride:

In case of this condensing agent (1.0 ml) the mixture of ketone (1.98 gm) and aldehyde (1.17 gm) was kept at the room temperature for 24 hours. The chalcone was obtained in a yield of 1.7 gm.

The product obtained in all the above condensations has been assigned the structure, 2 ′-hydroxy-4′-ethoxylchalcone (I, R = H) on the following basis:

(1)(a) The compound is yellow in colour, and gives a characteristic red colour with concentrated sulphuric acid.

(b) It gives a deep brown colour with ethanolic ferric chloride indicating -OH and -CO groups in ortho position.

(c) It gives a benzoyl derivative (II, R = H).

(2)(a) The probable flavanone structure has been ruled out as the product could be isomerised to the corresponding flavanone (III, R = H) with dilute ethanolic sulphuric acid (1) which gives the following tests:
(b) It is insoluble in alkali as well as ethanolic alkali,

(c) It does not give any colour with ethanolic ferric chloride.

(3)(a) The product on bromination gives the corresponding dibromochalcone (IV, \( R = H \)) which on treatment with acetone and potassium iodide regenerates the original chalcone. The dibromide was also converted into the corresponding flavone (V, \( R = H \)) by the treatment of acetone and anhydrous potassium carbonate.

The flavone gives a bluish fluorescence in ethanol, and with the concentrated sulphuric acid an orange colour with a bluish fluorescence is obtained.

(b) The chalcone (I, \( R = H \)) was oxidised by selenium dioxide in \( n \)-amyl alcohol to the corresponding flavone (V, \( R = H \)) which was identical with the flavone, obtained as above(2).

(4) The chalcone on treatment with alkaline hydrogen peroxide gave the corresponding flavonol (VI, \( R = H \)) (3,4);

(a) It is soluble in alkali and gives a brown colour with ethanolic ferric chloride.

(b) It gives an orange colour with a greenish fluorescence with concentrated sulphuric acid.
(c) It gives an acetyl derivative (VII, R = H) with acetic anhydride.

(5) With ethyl acetoacetate in presence of sodium ethoxide it gives corresponding ethyl cyclohexenone carboxylate (VIII, R = H). This gives an orange colour with concentrated sulphuric acid (5,6). It has been hydrolysed and decarboxylated simultaneously by ethanolic sodium hydroxide to the corresponding cyclohexenone (IX, R = H).

(6) With hydroxylamine hydrochloride, the chalcone forms the corresponding isoxazoline derivative (IX, R = H). It gives an orange colour with concentrated sulphuric acid and gives no colour with ethanolic ferric chloride.

II CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXYACETOPHENONE AND 2-METHOXYBENZALDEHYDE

The condensation has been investigated under different conditions and the results obtained are as under:
TABLE II

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium hydroxide per cent</th>
<th>Potassium hydroxide ml</th>
<th>Reaction period (hr)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>24</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>20</td>
<td>24</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>24</td>
<td>3.0</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>24</td>
<td>2.7</td>
</tr>
</tbody>
</table>

It is clear from the above table that the maximum yield of the chalcone was obtained when 40 per cent 40 ml potassium hydroxide was used.

Phosphorus oxychloride was used as a condensing agent but the yield was poor.

The structure, 2'-hydroxy-2-methoxy-4'-ethoxychalcone (I, R = 2-OCH₃) has been assigned on the following basis:

(a) The product is yellow in colour and gives a brown colour with ethanolic ferric chloride while a red colour with concentrated sulphuric acid.

(b) It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali with an orange colour.
(c) It gives a benzoyl derivative (II, R = 2-OCH\textsubscript{3}) with benzoyl chloride.

(2) By treatment with dilute ethanolic sulphuric acid it has been cyclised to the corresponding flavanone (III, R = 2-OCH\textsubscript{3}), insoluble in alkali, not giving a ferric chloride test.

(3)(a) The product on bromination forms \(\alpha:\beta\) dibromo-chalcone (IV, R = 2-OCH\textsubscript{3}) which was debrominated into the original chalcone by acetone and potassium iodide treatment. It is also converted into the corresponding flavone (V, R = 2-OCH\textsubscript{3}) by treatment of acetone and anhydrous potassium carbonate.

(b) On Venkatraman oxidation by selenium dioxide in \textit{n}-amyl alcohol, it is converted into the corresponding flavone (V, R = 2-OCH\textsubscript{3}) which was identical with the flavone obtained as above. It gives a bluish fluorescence with concentrated sulphuric acid.

(4) It is also oxidised to the corresponding flavonol (VI, R = 2-OCH\textsubscript{3}) by treatment with alkali and hydrogen peroxide.

(a) It is soluble in alkali.

(b) It gives a brown colour with ethanolic ferric chloride and a greenish fluorescence with concentrated sulphuric acid.
(c) It gives an acetyl derivative (VII, R = 2-0CH₃) with acetic anhydride and pyridine.

(5) The chalcone forms corresponding ethyl cyclohexenone carboxylate (VIII, R = 2-0CH₃) with ethyl acetoacetate and sodium ethoxide which gives an orange colour with concentrated sulphuric acid. This carboxylate ester has been hydrolysed and simultaneously decarboxylated by dilute ethanolic alkali to the cyclohexenone (IX, R = 2-0CH₃).

(6) With hydroxylamine hydrochloride, it forms the corresponding isoxazoline derivative (X, R = H). It gives an orange colour with concentrated sulphuric acid.

III CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXYACETOPHENONE AND VANILLIN:

The condensation has been investigated using potassium hydroxide solution of different concentrations. The results obtained are as under:
TABLE III

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium hydroxide per cent</th>
<th>Potassium hydroxide ml</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>24</td>
<td>2.3</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>20</td>
<td>24</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>24</td>
<td>3.2</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>24</td>
<td>2.8</td>
</tr>
</tbody>
</table>

It is clear from the above table that maximum yield of the chalcone was obtained when 40 per cent 40 ml potassium hydroxide was used.

When phosphorus oxychloride was used as a condensing agent the yield of the chalcone was poor.

The product obtained in all the above condensations has been assigned the structure, 2'-4 dihydroxy-3-methoxy 4'-ethoxychalcone (I, R = 3-OCH₃, 4-OH) on the following basis.

(1)(a) The compound is yellow in colour. It gives a brown colour with ethanolic ferric chloride and a red colour with concentrated sulphuric acid.
(b) It is sparingly soluble in dilute alkali but
dissolves in ethanolic alkali with an orange colour.

(c) It gives a dibenzoyl derivative (II, R = 3-OCH₃,
4-OCOC₆H₅) with benzoyl chloride and pyridine.

(3) By treatment with dilute ethanolic sulphuric acid it
has been cyclised to the corresponding flavanone
(III, R = 3-OCH₃, 4-OH) insoluble in alkali not
giving ferric chloride test.

(3)(a) With bromine it forms β-dibromochalcone (IV,
R = 3-OCH₃, 4-OH) which could be debrominated by
treatment with potassium iodide and acetone. It is
also converted to corresponding flavone (V, R =
3-OCH₃, 4-OH) by treatment with acetone and anhydrous
potassium carbonate.

(b) It is oxidised by selenium dioxide in n-amyl alcohol
to the corresponding flavone (V, R = 3-OCH₃, 4-OH)
which is identical with the flavone obtained as
above. It gives a bluish fluorescence with concentrated
sulphuric acid.

(4) The chalcone is also oxidised to flavonol (VI, R =
3-OCH₃, 4-OH) by treatment with alkali and hydrogen
peroxide which is soluble in alkali, gives a brown
colour with ethanolic ferric chloride and a greenish
fluorescence with concentrated sulphuric acid. The
flavonol gives a diacetyl derivative (VII, \( R = 3-OCH_3, \ 4-OCH_3 \)) with acetic anhydride and pyridine.

(5) The chalcone forms corresponding ethyl cyclohexenone carboxylate (VIII, \( R = 3-OCH_3, \ 4-OH \)) with ethyl acetoacetate and sodium ethoxide. It gives an orange colour with concentrated sulphuric acid. This carboxylate ester has been hydrolysed and simultaneously decarboxylated by ethanolic alkali to the corresponding cyclohexenone (IX, \( R = 3-OCH_3, \ 4-OH \)).

(6) With hydroxylamine hydrochloride, it forms the corresponding isoxazoline derivative (X, \( R = 3-OCH_3, \ 4-OH \)). It gives an orange colour with concentrated sulphuric acid.

IV CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXYACETOPHENONE AND 3-NITROBENZALDEHYDE:

The condensation has been investigated using potassium hydroxide solution of different concentrations. The results obtained are as under:
TABLE IV

| 2-Hydroxy-4'-ethoxyacetophenone | 1.98 gm. |
| 3-Nitrobenzaldehyde | 1.66 gm. |
| Ethanol (Solvent) | 50 ml. |
| Temperature (Room temperature) | 25-30°C |

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium hydroxide per cent</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 ml</td>
<td>40</td>
<td>1.8</td>
</tr>
<tr>
<td>2</td>
<td>40 ml</td>
<td>20</td>
<td>2.4</td>
</tr>
<tr>
<td>3</td>
<td>40 ml</td>
<td>24</td>
<td>3.2</td>
</tr>
<tr>
<td>4</td>
<td>60 ml</td>
<td>40</td>
<td>2.8</td>
</tr>
</tbody>
</table>

It is clear from the above table that maximum yield of the chalcone was obtained when 40 per cent 40 ml potassium hydroxide was used.

When phosphorus oxychloride was used as a condensing agent the yield of the chalcone was poor.

The product obtained in all the above condensations has been assigned the structure, 2'-hydroxy-3-nitro-4'-ethoxy-chalcone (I, $R = 3-NO_2$) from the following facts:

1. The compound is brown in colour, gives a characteristic red colour with concentrated sulphuric acid, a brown colour with ethanolic ferric chloride and it
forms a benzoyl derivative (II, $R = 3-\text{NO}_2$).

(2) It has been cyclised to the corresponding flavanone (III, $R = 3-\text{NO}_2$) by treatment with dilute ethanolic sulphuric acid, not giving a ferric chloride test.

(3)(a) The product on bromination gives $\alpha:\beta$ dibromo chalcone (IV, $R = 3-\text{NO}_2$) which could be debrominated to the original chalcone. The dibromochalcone is also converted to the corresponding flavone (V, $R = 3-\text{NO}_2$) by treatment with acetone and anhydrous potassium carbonate.

(b) It is converted to the corresponding flavone (V, $R = 3-\text{NO}_2$) by oxidation with selenium dioxide in n-amyl-alcohol which was identical with the flavone obtained as above. With concentrated sulphuric acid it gives an orange colour with a bluish fluorescence.

(4) It gives corresponding flavonol on oxidation with alkaline hydrogen peroxide (VI, $R = 3-\text{NO}_2$). The flavonol gives following reactions:

(a) It is soluble in alkali and gives a brown colour with ethanolic ferric chloride.

(b) It gives an orange colour with a greenish fluorescence with concentrated sulphuric acid.

(c) It gives an acetyl derivative (VII, $R = 3-\text{NO}_2$) with acetic anhydride and pyridine.
(5) The chalcone gives corresponding ethyl cyclohexenone carboxylate with ethyl acetoacetate and sodium ethoxide (VIII, $R = 3-\text{NO}_2$) characterised by a yellow colour with concentrated sulphuric acid. It has been hydrolysed and simultaneously decarboxylated by ethanolic alkali to the corresponding cyclohexenone (IX, $R = 3-\text{NO}_2$).

(6) With hydroxylamine hydrochloride it forms the corresponding isoxazoline derivative (X, $R = 3-\text{NO}_2$). It gives an orange colour with concentrated sulphuric acid.

V CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXYACETOPHENONE AND 4-CHLOROBENZALDEHYDE:

The condensation has been investigated using different concentrations of alkali. The results obtained are as under:
### TABLE V

| 2-Hydroxy-4-ethoxyacetophenone | : 1.98 gm. |
| 4-Chlorobenzaldehyde            | : 1.54 gm. |
| Ethanol (Solvent)               | 50 ml     |
| Temperature (Room temperature)  | : 25-30°C |

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium hydroxide per cent</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>24</td>
</tr>
</tbody>
</table>

It is clear from the above table that maximum yield of the chalcone was obtained when 40 per cent 40 ml alkali was used.

Phosphorus oxychloride was used as condensing agent but the yield was poor.

The structure, 2'-hydroxy-4'-chloro-4'-ethoxychalcone (I, R = 4-Cl) has been assinged on the following basis:

1. The product is yellow in colour. It gives a brown colour with ethanolic ferric chloride and red colour with concentrated sulphuric acid.
(b) It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali giving an orange colour.

(c) It gives a benzoyl derivative (II, R = 4-Cl) with benzoyl chloride.

(2) It is cyclised to form corresponding flavanone (III, R = 4-Cl) by treatment with dilute ethanolic sulphuric acid which gives negative test with ethanolic ferric chloride.

(3)(a) With bromine it forms \( \alpha : \beta \) dibromochalcone (IV, \( R = 4-Cl \)) which could be debrominated by treatment with potassium iodide and acetone. It is also converted to corresponding flavone (V, \( R = 4-Cl \)) by treatment with acetone and anhydrous potassium carbonate.

(b) It is oxidised by selenium dioxide in \( \alpha \)-amyl alcohol to a flavone (V, \( R = 4-Cl \)) which is identical with the flavone obtained as above. It gives a bluish fluorescence with concentrated sulphuric acid.

(4) It is also oxidised to corresponding flavonol (VI, \( R = 4-Cl \)) by treatment with alkali and hydrogen peroxide.

(a) It is soluble in alkali.

(b) It gives a brown colour with ethanolic ferric chloride.
solution and a greenish fluorescence with concentrated sulphuric acid.

(c) It gives an acetyl derivative (VII, R = 4-Cl) with acetic anhydride and pyridine.

(5) The chalcone forms ethyl cyclohexenone carboxylate (VII, R = 4-Cl) with ethyl acetoacetate and sodium ethoxide. This carboxylate ester has been hydrolysed and simultaneously decarboxylated by ethanolic alkali to the corresponding cyclohexenone (IX, R=4-Cl).

(6) With hydroxylamine hydrochloride it forms the corresponding isoxazoline derivative (IX, R = 4-Cl). It gives an orange colour with concentrated sulphuric acid.

VI CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXYACETOPHENE AND 4-NITROBENZALDEHYDE:

The condensation has been investigated using potassium hydroxide solution of different concentrations. The results obtained are as under:
TABLE VI

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium hydroxide per cent</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>24</td>
</tr>
</tbody>
</table>

It is clear from the above table that maximum yield of the chalcones was obtained when 40 per cent 40 ml potassium hydroxide was used.

When phosphorus oxychloride was used as a condensing agent the yield of the chalcone was poor.

The product obtained in all the above condensations has been assigned the structure, 2'-hydroxy-4-nitro-4'-ethoxychalcone (I, R = 4-NO₂) from the following facts:

(1) The compound is brown in colour, gives characteristic red colour with concentrated sulphuric acid, a brown colour with ethanolic ferric chloride and it forms a benzoyl derivative (II, R = 4-NO₂).
(2) It is cyclised to the corresponding flavanone (III, \( R = 4-NO_2 \)) by treatment with dilute ethanolic sulphuric acid giving the usual characteristic tests.

(3) (a) The product on bromination gives \( \alpha: \beta \) dibromochalcone (IV, \( R = 4-NO_2 \)) which could be debrominated to the original chalcone. The dibromochalcone is also converted to the corresponding flavone (V, \( R = 4-NO_2 \)) by treatment with acetone and anhydrous potassium carbonate.

(b) It is converted to the corresponding flavone (V, \( R = 4-NO_2 \)) by oxidation with selenium dioxide in \( \eta \)-amyl alcohol which was identical with the flavone obtained as above. With concentrated sulphuric acid it gives an orange colour with a bluish fluorescence.

(4) It gives corresponding flavonol on oxidation with alkaline hydrogen peroxide (VI, \( R = 4-NO_2 \)).

(a) It is soluble in alkali and gives a brown colour with ethanolic ferric chloride.

(b) It gives an orange colour with a greenish fluorescence with concentrated sulphuric acid.

(c) It gives an acetyl derivative (VII, \( R = 4-NO_2 \)) with acetic anhydride and pyridine.

(5) The chalcone gives ethyl cyclohexemone carboxylate with ethyl acetoacetate and sodium ethoxide (VIII, \( R = 4-NO_2 \)) characterised by a yellow colour with
concentrated sulphuric acid. It has been hydrolysed and simultaneously decarboxylated by ethanolic alkali to the corresponding cyclohexenone (IX, R = 4-N\textsubscript{2}).

(6) With hydroxylamine hydrochloride it forms the corresponding isoxazoline derivative (X, R = 4-N\textsubscript{2}). It gives an orange colour with concentrated sulphuric acid.

VII CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-ACETOPHENONE AND 2-4 DICHLOROBENZALDEHYDE:

The condensation has been investigated using potassium hydroxide solution of different concentrations. The results obtained are as under:

**TABLE VII**

<table>
<thead>
<tr>
<th>Potassium hydroxide per cent</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>40</td>
<td>2.3</td>
</tr>
<tr>
<td>40</td>
<td>20</td>
<td>2.8</td>
</tr>
<tr>
<td>40</td>
<td>40</td>
<td>3.6</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>3.1</td>
</tr>
</tbody>
</table>

The condensation has been investigated using potassium hydroxide solution of different concentrations. The results obtained are as under:
If is clear from the above table that the maximum yield of chalcone was obtained when 40 per cent 40 ml potassium hydroxide was used.

When phosphorus oxychloride was used as condensing agent the yield of the chalcone was poor.

The product obtained in all the above condensations has been assigned the structure, 2'-hydroxy-2,4'-dichloro 4'-ethoxychalcone (I, = 2,4'-Cl) on the following basis:
(1)(a) The product is yellow in colour. It gives a brown colour with ethanolic ferric chloride solution and a red colour with concentrated sulphuric acid.
(b) It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali with an orange colour.
(c) It gives a benzoyl derivative (II, R = 2,4'-Cl) with benzoyl chloride and pyridine.

(2) It is cyclised to the corresponding flavanone (III, R = 2,4'-Cl) when treated with dilute ethanolic sulphuric acid which gives a negative test with an ethanolic ferric chloride solution.

(3)(a) With bromine it forms α:β dibromochalcone (IV, R = 2,4'-Cl) which could be debrominated to the original chalcone when treated with potassium iodide and acetone. The dibromide is also converted into the corresponding flavone (V, R = 2,4'-Cl) when treated with anhydrous potassium carbonate and acetone.
(b) The chalcone is also directly oxidised to flavone (V, R = 2,4-(Cl)₂) when treated with selenium dioxide in n-amyl alcohol which is identical with the flavone obtained as above. The flavone gives a bluish fluorescence with concentrated sulphuric acid.

(4) The chalcone is also oxidised by alkaline hydrogen peroxide giving the corresponding flavonol derivative (VI, R = 2,4-(Cl)₂).

(6) It is soluble in alkali.

(b) It gives a brown colour with ethanolic ferric chloride solution and gives a greenish fluorescence with concentrated sulphuric acid.

(c) It gives an acetyl derivative (VII, R = 2,4-(Cl)₂) with acetic anhydride and pyridine.

(5) The chalcone gives ethyl cyclohexenone carboxylate (VIII, R = 2,4-(Cl)₂) with ethyl acetoacetate and sodium ethoxide. This carboxylate ester has been hydrolysed and decarboxylated simultaneously by ethanolic alkali (IX, R = 2,4-(Cl)₂).

(6) With hydroxylamine hydrochloride it forms the corresponding isoxazoline derivative, (X, R = 2,4-(Cl)₂). It gives an orange colour with concentrated sulphuric acid and no colour with ethanolic ferric chloride.
EXPERIMENTAL

SECTION - I

CHALCONEs AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXYACETOPHENONE:

RESACETOPHENONE:

Resacetophenone was prepared from resorcinol, glacial acetic acid and anhydrous zinc chloride according to the method of Copper(13), Robinson and Shah(14).

Fused zinc chloride (40 gm) was dissolved in glacial acetic acid (40 ml) by warming. To the hot solution resorcinol (25 gm) was added and the mixture was heated just to boiling and allowed it to boil for a minute. It has been sufficiently cooled and poured in the mixture of 40 ml concentrated hydrochloric acid and 40 ml water. Resacetophenone slowly separated from the solution in flake needles was collected, washed thoroughly with water and dried, m.p. 142°C. Yield: 22 gm.

Ethyl iodide

It was prepared from ethyl alcohol, red phosphorus, and iodine (F.G. Mann and B.C. Saunders, 105).

2-HYDROXY-4-ETHOXYACETOPHENONE:

Resacetophenone (15.2 gm, 0.1 mol), anhydrous potassium
carbonate (56 gm., 0.4 mol) and ethyl iodide (15.6 gm. 0.1 M), in dry acetone (100 ml) were refluxed for eight hours. Acetone was removed. Then the residue was diluted with water and concentrated hydrochloric acid was added till there was effervescences of carbon dioxide. Solid separated was collected, washed with water and crystallised from ethanol, m.p. 160°C. Yield: 10 gm. Pierre Chabrier, Henry Najer, Rane Giudicelli and Eva Joanic Voisinet(16) give the same m.p.

I CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXYACETOPHENONE AND BENZALDEHYDE

CONDENSATION OF 2-HYDROXY-4-ETHOXYACETOPHENONE WITH

BENZALDEHYDE:

2'-HYDROXY-4'-ETHOXYCHALCONE:

2-Hydroxy-4-ethoxyacetophenone, (1.98 gm) benzaldehyde (1.17 gm), ethanol (50 ml) and potassium hydroxide (40 ml : 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture changed from yellow to orange. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was collected, washed with water, dried and crystallised from ethanol, yellow needles, m.p. 98°C. Yield: 2.7 gm.
It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali giving an orange colour. It gives a brown colour with ethanolic ferric chloride and a deep red colour with concentrated sulphuric acid. It gives a red colour with Wilson's boric acid reagent.

Analysis:

Found: C, 75.80%; H, 5.90%

C\textsubscript{17}H\textsubscript{16}O\textsubscript{3} requires C, 75.95%; H, 5.97%

(II) PHOSPHORUS OXYCHLORIDE METHOD:

The above acetophenone (1.98 gm), benzaldehyde (1.17 gm) and phosphorus oxychloride (1.0 ml) were mixed and warmed together till a clear solution was obtained. It was corked and left at the room temperature (25-30\°C) for about 24 hours. It was then washed with petroleum ether (40-60) benzene mixture (5:1) to remove the unreacted aldehyde and phosphorus oxychloride. The residual product was then crystallised as described above, m.p. and mixed m.p. 98\°C. Yield: 1.7 gm.

BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 5 hours. It was then cooled, and treated with ice water containing dilute sulphuric acid (10 per cent).
The white solid separated was collected, washed with dilute sodium bicarbonate solution, to remove benzoic acid if any, then with water, dried and crystallised from petroleum ether (40-60) yellow plates m.p. 122°C. Yield : 0.4 gm. Analysis:

Found : C, 77.02 %; H, 5.32 %

\[ C_{24}H_{20}O_4 \] requires C, 77.43 %; H, 5.37 %

**CYCLIC-ISOMERISATION OF 2'-HYDROXY-4'-ETHOXYCHALCONE:**

7'-ETHOXYFLAVANONE:

To the hot solution of chalcone (0.5 gm) in ethanol (40 ml), dilute sulphuric acid (20 ml; 10 per cent) was added. The clear solution was refluxed on a boiling water bath for 30 hours. Excess of ethanol was distilled off and the residual solution was then filtered hot and left at the room temperature. The brown solid obtained was collected, washed with water, dried and crystallised from ethanol brown needles, m.p. 165°C. Yield : 0.21 gm.

Analysis:

Found : C, 76.00 %; H, 5.90 %

\[ C_{17}H_{16}O_3 \] requires C, 75.95 %; H, 5.97 %
BROMINATION OF 2'-HYDROXY-1'-ETHOXYCHALCONE:

2'-HYDROXY-1'-ETHOXY-α:β-DIBROMOCHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and bromine in acetic acid (5 ml : 10 per cent) was added to it with constant stirring. The mixture was kept in an ice bath for 4 hours. Then it was treated with ice water. The yellow solid separated was collected, washed with water, dilute sodium thiosulphate solution and again with water, dried and crystallised from acetone, yellow needles, m.p. 171°C. Yield : 0.28 gm.

Analysis:

Found : Br, 37.00 %
C₁₇H₁₆O₃Br₂ requires Br, 37.39 %

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

The mixture of above dibromo-chalcone (0.3 gm), acetone (20 ml) and potassium iodide (0.3 gm) was refluxed on a water bath at 70°C for 3 hours. It was then filtered hot and acetone was removed. The yellow solid obtained was washed with dilute sodium thiosulphate solution, then with water, dried and crystallised from ethanol, yellow needles, m.p. and mixed m.p. with original chalcone 98°C.
CYCLISATION OF 2'-HYDROXY-4'-ETHOXYCHALCONE : 7'-ETHOXYFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate on the δ:β Dibromochalcone:

The dibromochalcone (0.5 gm) in acetone (20 ml) was mixed with anhydrous potassium carbonate (0.5 gm). The reaction mixture was then refluxed on a water bath at 70°C for 4 hours. The solution was then filtered hot, acetone was removed. The yellow solid obtained was washed with water, dried and crystallised from ethanol, yellow plates, m.p. 118°C. Yield: 0.22 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

To a solution of chalcone (0.5 gm) in n-amylalcohol (20 ml), selenium dioxide (0.5 gm) was added and the reaction mixture was refluxed on an oil bath at 150°C for 24 hours. Selenium was then filtered off from the hot reaction mixture and excess of n-amyl alcohol was removed by steam distillation. The yellow solid obtained was washed with petroleum ether (40-60) to remove traces of alcohol and crystallised from ethanol, yellow plates, m.p. 118°C. Yield: 0.24 gm.

Analysis:

Found: C, 76.36 %; H, 5.21 %

C_{17}H_{14}O_3 requires C, 76.68 %; H, 5.26 %
OXIDATION OF 2'-HYDROXY-4',-ETHOXYCHALCONE : 7-ETHOXYFLAVONOL

(a) By Action of Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml : 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml : 20 vol.) was added to it and the reaction mixture was kept cool in the ice bath for 4 hours, and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to greenish yellow. It was then treated with ice water and acidified with dilute hydrochloric acid (1:1), yellow solid separated was collected, washed with water, dried and crystallised from ethanol, yellow needles m.p. 91°C. Yield : 0.40 gm.

(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of chalcone (0.5 gm) and sodium peroxide (0.5 gm) in ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was collected, washed with water, dried and crystallised from ethanol, yellow needles, m.p. 91°C. Yield : 0.38 gm.

Analysis:

\[
\text{Found: C, 71.12 \%; H, 4.82 \%} \\
\text{C}_{17}H_{14}O_{4} \text{ requires C, 72.33 \%; H, 4.94 \%}
\]
ACETYL DERIVATIVE OF FLAVONOL:

A mixture of flavonol (0.5 gm), acetic anhydride (1 ml) and a drop of pyridine was refluxed on a boiling water bath for 4 hours. It was then treated with ice water and yellowish solid separated was collected, washed with water, dried and crystallised from ethanol, yellowish granules, m.p. 95°C. Yield: 0.22 gm.

Analysis:

Found: C, 70.17 %; H, 4.78 %
C₁₉H₁₆O₅ requires C, 70.37 %; H, 4.93 %

CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-4'-ETHOXYCHALCHONE; ETHYL-2-PHENYL-4'-(2"-HYDROXY-4"-ETHOXYPHENYL) -Δ⁴ - CYCLOHEXENE-6-ONE-1-CARBOXYLATE:

Sodium metal (0.2 gm) was dissolved in absolute ethanol (15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml). To this solution ethyl acetoacetate (1 ml) was added and the mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and diluted with ice water (100 ml), then acidified with dilute hydrochloric acid (1:1). The yellow solid separated was collected, washed with water, dried and crystallised from ethanol, yellow plates, m.p. 180°C.
Yield: 0.31 gm.

Analysis:

Found: C, 72.28 %; H, 6.58 %
C₂₃H₂₄O₅ requires C, 72.63 %; H, 6.32 %
HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE
ETHYL CYCLOHEXENONE CARBOXYLATE : 2-PHENYL-4-(2'-HYDROXY-
4''-ETHOXYPHENYL)-Δ₄'-CYCLOHEXENE-6-ONE :

A solution of above ethyl diphenyl cyclohexenone
carboxylate derivative (0.5 gm) in ethanol (20 ml) was
mixed with sodium hydroxide (10 ml: 5 per cent) and the
mixture was refluxed on a boiling water bath for 5 hours.
It was then diluted with ice water (100 ml) and acidified
with dilute hydrochloric acid (1:1). The yellow solid
separated was collected, washed with water dried and
crystallised from ethanol, pale yellow needles, m.p. 240°C.
Yield : 0.28 gm.

Analysis:
Found : C, 78.08 % ; H, 6.63 %
C₂₀H₂₀O₃ requires : C, 77.91 % ; H, 6.49 %

ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-4'-
ETHOXYCHALCON : 3-(2-HYDROXY-4'-ETHOXYPHENYL)-5-
PHENYLISOXAZOLINE :

2'-Hydroxy-4'-ethoxychalcone (1.0 gm) was dissolved
in pyridine (5 ml) and hydroxylamine hydrochloride (1.0 gm)
in water (5.0 ml) was added to it. The reaction mixture was
refluxed on a boiling water bath for 4 hours. It was then
cooled and acidified with dilute acetic acid (1:1). A
colourless product obtained was washed with water, dried and crystallised from ethanol, m.p. 225°C. Yield: 0.68 gm.

Analysis:

Found: N, 4.68 %

\[ \text{C}_{17}\text{H}_{17}\text{O}_3\text{N} \] requires N, 4.95 %

II  CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHoxyACETOPhENONE AND 2-METHOXYBENZALDEHYDE

CONDENSATION OF 2-HYDROXY-4-ETHOXYACETOPhENONE WITH

2-METHOXYBENZALDEHYDE : 2'-HYDROxy 2-METHOxy-4'

ETHOxyChALCONE :

2-Hydroxy-4-ethoxyacetophenone (1.98 gm) and 2-methoxybenzaldehyde (1.49 gm), ethanol (50 ml) and potassium hydroxide (40 ml: 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture changed from yellow to orange. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was collected, washed with water, dried and crystallised from ethanol, yellow needles, m.p. 110°C. Yield: 3.0 gm.

It has also been prepared by phosphorus oxychloride method.
The product is sparingly soluble in aqueous alkali, but dissolves in ethanolic alkali giving an orange colour. It gives a characteristic red colour with concentrated sulphuric acid. It also gives a red colour with Wilson's boric acid test reagent.

Analysis:

**Found**: C, 72.12%; H, 6.58%

**C_{18}H_{18}O_{4}** requires C, 72.49%; H, 6.04%

**BENZOYL DERIVATIVE**:

The chalcone (0.5 gm), a drop of pyridine and benzoyl chloride (1.0 ml) were mixed and the reaction mixture was heated on a boiling water bath for 5 hours. Pyridine was removed by treatment with cold dilute sulphuric acid. The yellow solid separated was filtered, washed with dilute sodium bicarbonate solution (5 per cent), to remove benzoic acid if any, and finally with water. It was dried and crystallised from petroleum ether (100-120), yellowish plate. m.p. 98°C. Yield: 0.42 gm.

Analysis:

**Found**: C, 74.50%; H, 5.68%

**C_{25}H_{22}O_{5}** requires C, 74.61%; H, 5.47%
CYCLO-ISOMERISATION OF 2'-HYDROXY-2-METHOXY-4'-ETHOXYCHALCONE:

7'-ETHOXY-2'-METHOXYFLAVANONE:

To the hot solution of chalcone (0.5 gm) in ethanol (40 ml), dilute sulphuric acid (20 ml : 10 percent) was added. The clear solution was then refluxed on a boiling water bath for about 30 hours. Excess of ethanol was distilled off and the residual solution was then filtered hot and left at the room temperature. The pale yellow solid obtained was collected, washed with water, dried and crystallised from ethanol, pale yellow needles, m.p. 105°C. Yield : 0.22 gm.

Analysis:

Found : C, 72.41 %; H, 6.14 %

C₁₈H₁₆O₄ requires : C, 72.49 %; H, 6.04 %

BROMINATION OF 2'-HYDROXY-2-METHOXY-4'-ETHOXYCHALCONE:

2'-HYDROXY-2-METHOXY-4'-ETHOXY α:β-DIBROMOCHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and bromine in acetic acid (5 ml : 10 per cent) was added to it with constant stirring. The mixture was kept cool in an ice bath for 4 hours. Then it was treated with ice water. The yellow solid separated was collected, washed with water, dilute sodium thiosulphate solution and again with water, dried and crystallised from acetone, yellow needles, m.p. 165°C. Yield : 0.30 gm.
Analysis:

Found: Br, 34.58%  
C_{18}H_{18}O_{4}Br_{2} requires Br, 34.93%  

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:  

The mixture of above dibromochalcone (0.3 gm) acetone (20 ml) and potassium iodide (0.3 gm) was refluxed on a water bath at 70°C for 3 hours. It was then filtered hot and acetone was removed. The yellow solid obtained was washed with dilute sodium thiosulphate solution, then with water, dried and crystallised from ethanol, yellow needles, m.p. and mixed m.p. with original chalcone 110°C.

CYCLISATION OF 2'-HYDROXY-2-METHOXY-4'-ETHOXYCHALCONE:  
7'-ETHOXY-2'-METHOXYFLAVONE:  

(a) By Action of Acetone and Anhydrous Potassium Carbonate on the α:β Dibromochalcone:  

The dibromochalcone (0.5 gm) in acetone (20 ml) was treated with anhydrous potassium carbonate (0.5 gm). The reaction mixture was then refluxed on a water bath at 70°C for 4 hours. The solution was then filtered hot, acetone was removed. The brown solid obtained was washed with water, dried and crystallised from ethanol, brown plates, m.p. 262°C. Yield: 0.21 gm.
(b) **By Selenium Dioxide Oxidation of The Chalcone**:

To a solution of chalcone (0.5 gm) in n-amyl alcohol (20 ml), selenium dioxide (0.5 gm) was added and the reaction mixture was refluxed on an oil bath at 150°C for 24 hours. Selenium was then filtered off from the hot reaction mixture and excess of n-amyl alcohol was removed by steam distillation. The yellow solid obtained was washed with petrol (40-60) ether to remove traces of alcohol and crystallized from ethanol, yellow plates, m.p. 262°C. Yield: 0.22 gm.

**Analysis:**

Found: C, 73.01%; H, 5.33%

C_{18}H_{16}O_4 requires C, 72.98%; H, 5.40%

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**Oxidation of 2'-Hydroxy-2-Methoxy-4'-Ethoxychalcone:**

7'-Ethoxy-2'-Methoxyflavonol:

(a) **By Action of Alkaline Hydrogen Peroxide**:

Chalcone (0.5 gm) in methanol (60 ml) was mixed with sodium hydroxide (20 ml: 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml: 20 vol) was added and the reaction mixture was kept cool in the ice bath for 4 hours, and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to
greenish yellow. It was then treated with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was collected, washed with water, dried and crystallised from ethanol, yellow needles, m.p. 100°C. Yield: 0.32 gm.

(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of chalcone (0.5 gm) and sodium peroxide (0.5 gm) in ethanol (20 ml) was refluxed on boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was collected, washed with water, dried and crystallised from ethanol, yellow needles, m.p. 100°C. Yield: 0.34 gm.

Analysis:

Found: C, 69.38%; H, 5.21%

C₁₉H₁₆O₅ requires C, 69.23%; H, 5.12%

Acetyl Derivative of Flavonol:

A mixture of flavonol (0.5 gm), acetic anhydride (1 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water and white solid separated was collected, washed with water, dried and crystallised from ethanol, white granules, m.p. 180°C. Yield: 0.20 gm.
**Analysis:**

*Found: C, 67.92 %; H, 5.12 %*

C$_{20}$H$_{18}$O$_6$ requires C, 67.79 %; H, 5.09 %

**CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-2 METHOXYETHYL CHALCONE : ETHYL-2-(2'-METHOXYPHENYL)-4-(2'-HYDROXY-4''-ETHOXYPHENYL)-∆$^4$-CYCLOHEXENE-6-ONE-1-CARBOXYLATE :**

Sodium metal (0.2 gm) was dissolved in absolute ethanol (15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml). To this solution ethyl acetoacetate (1 ml) was added and the mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and diluted with ice water (100 ml), then acidified with dilute hydrochloric acid (1:1). The brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown needles. m.p. 157°C. Yield: 0.28 gm.

**Analysis:**

*Found: C, 70.62 %; H, 6.52 %*

C$_{24}$H$_{26}$O$_6$ requires C, 70.25 %; H, 6.34 %
HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE
ETHYL CYCLOHEXENONE CARBOXYLATE : 2-(2'-METHOXYPHENYL)-
(2''-HYDROXY-4''-ETHOXYPHENYL)- Δⁿ-CYCLOHEXENE-6-ONE :

A solution of above ethyl diphenyl cyclohexenone
carboxylate derivative (0.5 gm) in ethanol (20 ml) and
sodium hydroxide (10 ml : 5 per cent) was refluxed on a
boiling water bath for 5 hours. It was then diluted with
ice water (100 ml) and acidified with dilute hydrochloric
acid (1:1). The yellow solid separated was collected, washed
with water, dried and crystallised from ethanol, pale yellow
needles, m.p. 240°C. Yield : 0.19 gm.

Analysis:
Found : C, 74.32 % ; H, 6.42 %
C_{21}H_{22}O_{4} requires C, 74.56 % ; H, 6.50 %

ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-2-
METHOXY-4'-ETHOXYCHALCONE : 3(2-HYDROXY-4-ETHOXYPHENYL)-5-
(2-METHOXYPHENYL) ISOXAZOLINE :

2'-Hydroxy-2-methoxy-4'-ethoxychalcone (1.0 gm) was
dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride
(1.0 gm) in water (5.0 ml) was added. The reaction mixture
was refluxed on a boiling water bath for ½ hours. It was
then cooled and acidified with dilute acetic acid (1:1).
A yellowish product obtained was collected, washed with
water, dried and crystallised from ethanol, yellow needles, m.p. 118°C. Yield: 0.69 gm.

Analysis:

Found: N, 4.78%  
C₁₈H₁₉O₄N requires N, 4.47%  

III CHALCONE AND RELATED COMPOUNDS DERIVED FROM  
2-HYDROXY-4-ETHOXY ACETOPHENONE AND VANILLIN  

CONDENSATION OF 2-HYDROXY-4-ETHOXY ACETOPHENONE WITH  
VANILLIN: 2'-4'-DIHYDROXY-3-METHOXY-4'-ETHOXY CHALCONE:  

2-Hydroxy-4-ethoxyacetophenone (1.98 gm), vanillin (1.67 gm), ethanol (50 ml) and potassium hydroxide (40 ml: 40 percent) were mixed in a tightly corked flask and left at the room temperature for about 24 hours. The mixture was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was collected, washed with water, dried and crystallised from ethanol, yellow needles, m.p. 54°C. Yield: 3.2 gm. The colour of the reaction mixture changed from yellow to orange.

The chalcone was also prepared by phosphorous oxychloride method.

The chalcone is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali giving an orange colour.
It gives a brown colour with ethanolic ferric chloride while red colour with concentrated sulphuric acid.

Analysis:

Found : C, 68.53 % ; H, 5.88 %

\[
\text{C}_{18}\text{H}_{18}\text{O}_5 \text{ requires } \text{C}, 68.80 \% ; \text{H}, 5.73 \%
\]

**BENZOYL DERIVATIVE** :

A mixture of chalcone (0.5 gm), a drop of pyridine, and benzoyl chloride (1.0 ml) was refluxed on a boiling water bath for 5 hours. It was then cooled and treated with ice water containing dilute sulphuric acid. The yellowish white solid separated was collected, washed with water, dilute sodium bicarbonate solution and again with water, dried and crystallised from petroleum ether (40-60), pale yellow plates, m.p. 108°C. Yield : 0.42 gm.

Analysis:

Found : C, 73.66 % ; H, 4.88 %

\[
\text{C}_{32}\text{H}_{26}\text{O}_7 \text{ requires } \text{C}, 73.55 \% ; \text{H}, 4.98 \%
\]

**CYCLO-ISOMERISATION OF 2'-4'-DIHYDROXY-3'-METHOXY-4'-ETHOXY CHALCONE : 7-ETHOXY-3'-METHOXY-4'-HYDROXYFLAVANONE** :

To a solution of chalcone (0.5 gm) in hot ethanol (40 ml) was added sulphuric acid (20 ml : 10 per cent). The reaction mixture was refluxed on a boiling water bath for 30 hours. Excess of ethanol was distilled off and the
residual solution was then filtered hot and left at the room temperature. The brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown plates. m.p. 165°C. Yield: 0.21 gm.

Analysis:

Found: C, 68.31%; H, 5.42%

C_{18}H_{18}O_{5} requires C, 68.80%; H, 5.73%

BROMINATION OF 2'-4'-DIHYDROXY-3-METHOXY-4'-ETHOXYCHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml). The bromine in acetic acid (5 ml: 10 per cent) was added with constant stirring. Then the mixture was kept cool for 4 hours. Then it was treated with ice water. The yellow solid separated was collected, washed with water, dilute sodium thiosulphate solution and again with water, dried and crystallised from acetone, yellow needles, m.p. 88°C. Yield: 0.42 gm.

Analysis:

Found: Br, 33.31%

C_{18}H_{18}O_{5}Br_{2} requires Br, 33.79%
DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

The mixture of above dibromochalcone (0.3 gm), acetone (20 ml) and potassium iodide (0.3 gm) was refluxed on a water bath at 70°C for 3 hours. It was filtered hot and acetone was removed. The yellow solid obtained was washed with dilute sodium thiosulphate solution, then with water, dried and crystallised from ethanol, brown needles, m.p. and mixed m.p. with original chalcone 54°C.

CYCLISATION OF 2',4'-DIHYDROXY-3-METHOXY-4'-ETHOXYCHALCONE:
7'-ETHOXY-3'-METHOXY-4'-HYDROXYFLAVONE:

By Action of Acetone and Anhydrous Potassium Carbonate on the α:β Dibromochalcone:

The dibromochalcone (0.5 gm) in acetone (20 ml) was treated with anhydrous potassium carbonate (0.5 gm). The reaction mixture was then refluxed on a water bath at 70°C for 4 hours. The solution was then filtered hot, acetone was removed. The brown solid obtained was washed with water, dried and crystallised from ethanol, brown plates. m.p. 210°C Yield: 0.20 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

To a solution of chalcone (0.5 gm) in n-amyl alcohol (20 ml), selenium dioxide (0.5 gm) was added and the reaction mixture was refluxed on an oil bath at 150°C for 24 hours.
Selenium was then filtered off from the hot reaction mixture and excess of n-amyl alcohol was removed by steam distillation. The brown solid obtained was washed with petroleum ether (40-60) to remove traces of alcohol and crystallised from ethanol, brown plates, m.p. 210°C. Yield: 0.23 gm.

Analysis:

Found: C, 69.31%; H, 5.31%

C_{18}H_{16}O_{5} requires C, 69.23%; H, 5.13%

**Oxidation of 2'-4-Dihydroxy-4'-methoxy-4'-ethoxychalcone:**

7'-Ethoxy-3'-methoxy-4'-hydroxyflavonol:

(a) By Action of Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml: 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml: 20 vol) was added and the reaction mixture was kept cool in ice bath for 4 hours and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to greenish yellow. It was then treated with ice water and acidified with dilute hydrochloric acid (1:1), brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown needles, m.p. 45°C. Yield: 0.18 gm.
(b) **Using Sodium Peroxide in Ethanic Solution**

A mixture of chalcone (0.5 gm) and sodium peroxide (0.5 gm) in ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was diluted with ice water and acidified with dilute hydrochloric acid (1:1). The brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown needles, m.p. 45°C. Yield: 0.22 gm.

**Analysis:**

\[
\begin{align*}
\text{Found: } & \ C, 65.38\% ; H, 4.48\% \\
\text{C}_{18}H_{16}O_6 \text{ requires: } & \ C, 65.86\% ; H, 4.87\%
\end{align*}
\]

**Acetyl Derivative of Flavonol**

A mixture of flavonol (0.5 gm), acetic anhydride (1 ml) and a drop of pyridine was refluxed on a boiling water bath for 4 hours. It was then treated with ice water and yellowish white solid separated was collected, washed with water, dried and crystallised from ethanol, yellowish white granules. m.p. 80°C. Yield: 0.18 gm.

**Analysis:**

\[
\begin{align*}
\text{Found: } & \ C, 64.18\% ; H, 4.38\% \\
\text{C}_{22}H_{20}O_8 \text{ requires: } & \ C, 64.08\% ; H, 4.85\%
\end{align*}
\]
CONDENSATION OF ETHYL ACETOACETATE WITH 2'-4' DIHYDROXY-3-
METOXY-4'-ETHOXYCHALCONE : ETHYL-2-(3'-METOXY-4'--
HYDROXYPHENYL)-4-(2''-HYDROXY-4''-ETHOXYPHENYL)- $\Delta^4$-
CYCLOHEXENE-6-ONE-1-CARBOXYLATE :

Sodium metal (0.2 gm) was dissolved in absolute ethanol
(15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml).
To this solution ethyl acetoacetate (1 ml) was added and
the mixture was refluxed on a boiling water bath for 5
hours. It was then cooled and diluted with ice water (100
ml), then acidified with dilute hydrochloric acid (1:1). The
brown solid separated was collected, washed with water,
dried and crystallised from ethanol, brown needles. m.p.
64°C. Yield : 0.23 gm.
Analysis :

Found : C, 67.48 %; H, 6.18 %
C$_{24}$H$_{26}$O$_7$ requires C, 67.62 %; H, 6.09 %

HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE
ETHYL CYCLOHEXENONE CARBOXYLATE : 2-(3'-METOXY-4'-HYDROXY-
PHENYL)-4-(2''-HYDROXY-4''-ETHOXYPHENYL)- $\Delta^4_2$CYCLOHEXENE-
6-ONE :

To a solution of above ethyl diphenyl cyclohexenone
carboxylate derivative (0.5 gm) in ethanol (20 ml) sodium
hydroxide (10 ml : 5 per cent) was added and the mixture was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was collected, washed with water, dried and crystallised from ethanol, pale yellow needles, m.p. 280°C. Yield : 0.18 gm. Analysis:

Found : C, 71.38 %; H, 6.48 %

C_{21}H_{22}O_{5} requires C, 71.19 %; H, 6.22 %

**ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-4 DIHYDROXY-3-METHOXY-4'-ETHOXYCHALCONE : 3-(2-HYDROXY-4-ETHOXYPHENYL)-5-(3-METHOXY-4-HYDROXYPHENYL) ISOXAZOLINE :**

2'-4 Dihydroxy-3-methoxy-4'-ethoxychalcone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added to it. The reaction mixture was refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A colourless product obtained was collected, washed with water, dried and crystallised from ethanol, white granules, m.p. 105°C. Yield : 0.79 gm.

Analysis:

Found : N, 4.31 %

C_{18}H_{19}O_{5}N requires N, 4.25 %
IV  CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXYACETOPHENONE  AND 3-NITROBENZALDEHYDE

CONденSATION OF 2-HYDROXY-4-ETHOXYACETOPHENONE WITH

3-NITROBENZALDEHYDE : 2'-HYDROXY-3-NITRO-4'-ETHOXYCHALCONE;

2-Hydroxy-4-ethoxyacetophenone (1.98 gm), 3-nitrobenzaldehyde (1.66 gm), ethanol (50 ml) and potassium hydroxide (40 ml : 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture changed from yellow to orange. The mixture was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown plates, m.p. 116°C. Yield : 3.2 gm.

The chalcone was also prepared by phosphorus oxychloride method.

The chalcone is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali giving an orange colour. It gives a brown colour with ethanolic ferric chloride, while a red colour with concentrated sulphuric acid.

Analysis:

Found : C, 65.12 % ; H, 4.54 % ; N, 4.24 %

C_{17}H_{15}O_5N  requires  C, 65.18 % ; H, 4.79 % ; N, 4.47 %
BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 5 hours. It was then cooled and treated with ice water containing dilute sulphuric acid. The yellow solid separated was collected, washed with water, dilute sodium bicarbonate solution and again with water. It was dried and crystallised from petroleum ether (40-60) yellow plates. m.p. 105°C. Yield: 0.38 gm.

Analysis:

Found: N, 3.12%
C_{24}H_{19}O_6N requires N, 3.36%

CYCLO-ISOMERISATION OF 2'-HYDROXY-3'-NITRO-4'-ETHOXYCHALCORE:

7'-ETHOXY-3'-NITROFLAVANONE:

To the hot solution of chalcone (0.5 gm) in ethanol (40 ml), dilute sulphuric acid (20 ml: 10 per cent) was added. The precipitated solid was dissolved in more ethanol (20 ml) and the clear solution was refluxed on a boiling water bath for 30 hours. Excess of ethanol was distilled off and the residual solution was then filtered hot and left at the room temperature. The brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown needles. m.p. 310°C. Yield: 0.23 gm.
Analysis:

**Found:** N, 4.32 %

C_{17}H_{15}O_N requires N, 4.47 %

**BROMINATION OF 2'-HYDROXY-3-NITRO-4' -ETHOXYCHALCONE:**

2'-HYDROXY-3-NITRO-4' -ETHOXY- \( \alpha : \beta \) - DIBROMOCHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml). The bromine in acetic acid (5 ml: 10 per cent) was added to it with constant stirring. The mixture was kept cool in an ice bath for 4 hours. Then the mixture was treated with ice water. The brown solid separated was collected, washed with dilute sodium thiosulphate solution, then with water and crystallised from acetone, brown needles, m.p. 146°C. Yield: 0.32 gm.

Analysis:

**Found:** N, 2.88 %; Br, 33.58 %

C_{17}H_{15}O Br_N requires N, 2.95 %; Br, 33.83 %

**DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:**

The mixture of above dibromochalcone (0.3 gm) potassium iodide (0.3 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. The solution was then filtered hot and acetone was removed. The brown solid obtained was washed with dilute sodium thiosulphate solution, then with
water, dried and crystallised from ethanol, brown plates, m.p. and mixed m.p. with original chalcone 116°C.

**CYCLISATION OF 2'-HYDROXY-3'-NITRO-4'-ETHOXYCHALCONE:**

**7'-ETHOXY-3'-NITROFLAVONE:**

(a) **By Action of Acetone and Anhydrous Potassium Carbonate on the α:β Dibromochalcone:**

The dibromochalcone (0.5 gm) in acetone (20 ml) was treated with anhydrous potassium carbonate (0.5 gm) and the reaction mixture was then refluxed on a water bath at 70°C for 4 hours. The solution was then filtered when hot and acetone was removed. The brown solid obtained was washed with water, dilute sodium thiosulphate solution and again with water, dried and crystallised from ethanol, brown granules. m.p. 108°C. Yield : 0.23 gm.

(b) **By Selenium Dioxide Oxidation of the Chalcone:**

A mixture of chalcone (0.5 gm), n-amyl alcohol (20 ml) and selenium dioxide (0.5 gm) was refluxed on an oil bath at 150°C for 24 hours. Selenium was then filtered off from the hot reaction mixture and n-amyl alcohol was removed by steam distillation. The brown solid obtained was washed with petroleum ether (40-60) to remove traces of alcohol, crystallised from ethanol, brown granules. m.p. 108°C. Yield : 0.18 gm.
Analysis:

Found: N, 4.68%

C_{17}H_{13}O_{5}N requires N, 4.50%

OXIDATION OF 2'-HYDROXY-3'-NITRO-4'-ETHOXYCHalcone:

7'-ETHOXY-3'-NITROFLAVONOL:

(a) By Action Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml: 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml: 20 vol) was added to it, and the reaction mixture was kept cool in the ice bath for 4 hours, and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to greenish yellow. It was then treated with ice water and acidified with dilute hydrochloric acid (1:1). Yellowish solid separated was collected, washed with water, dried and crystallised from ethanol, pale yellow needles. m.p. 145°C. Yield: 0.31 gm.

(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of chalcone (0.5 gm), sodium peroxide (0.5 gm) and ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellowish solid
separated was collected, washed with water and crystallised from ethanol pale yellow needles. m.p. 145°C. Yield: 0.27 gm.

Analysis:

Found: N, 4.51%

C₁₇H₁₃O₆N requires N, 4.28%

Acetyl Derivative of Flavonol:

A mixture of flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water and a yellow solid separated was collected, washed with water, dried and crystallised from ethanol, yellow needles. m.p. 105°C. Yield: 0.21 gm.

Analysis:

Found: N, 3.62%

C₁₉H₁₅O₇N requires N, 3.79%

Condensation of Ethyl Acetoacetate with 2'-Hydroxy 3-Nitro-4' -Ethoxychalcone: Ethyl-2(3'-Nitrophenyl)-4(2''-Hydroxy-4''-Ethoxyphenyl)-Δ⁴-Cyclohexene-6-One-1-Carboxylate:

Sodium metal (0.2 gm) was dissolved in absolute ethanol (15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml). To this solution ethyl acetoacetate (1.0 ml) was added and the mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and diluted with ice water (100 ml),
then acidified with dilute hydrochloric acid (1:1). The brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown plates. m.p. 118°C. Yield: 0.31 gm.

Analysis:

Found: N, 3.38%

C_{23}H_{23}O_7N requires N, 3.29%

HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL CYCLOHEXENONE CARBOXYLATE: 2-(3’-NITROPHENYL)-4-(2”-HYDROXY-4”-ETHOXYPHENYL)-Δ^4-CYCLOHEXENE-6-ONE:

A mixture of above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm), ethanol (20 ml) and sodium hydroxide (10 ml: 5 per cent) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The yellowish solid separated was collected, washed with water, dried and crystallised from ethanol, pale yellow plates. m.p. 128°C. Yield: 0.18 gm.

Analysis:

Found: N, 3.88%

C_{20}H_{19}O_5N requires N, 3.96%
ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-3-
NITRO-4'-ETHOXYCHALCONE : 3(2-HYDROXY-4'-ETHOXYPHENYL)-5-
(3-NITROPHENYL)ISOXAZOLINE :

2'-Hydroxy-3-nitro-4'-ethoxychalcone (1.0 gm) was
dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride
(1.0 gm) in water (5.0 ml) was added. The reaction mixture
was refluxed on a boiling water bath for 4 hours. It was
then cooled and acidified with dilute acetic acid (1:1).
A brown coloured product obtained was collected, washed
with water, dried and crystallised from ethanol, brown
needles, m.p. 136°C. Yield : 0.76 gm.
Analysis:

Found : N, 8.32 %
C_{17}H_{16}O_{2}N_{2} requires N, 8.54 %

V CHALCONE AND RELATED COMPOUNDS DERIVED FROM
2-HYDROXY-4'-ETHOXYACETOPHENONE AND 4-CHLOROBENZALDEHYDE :

CONDENSATION OF 2-HYDROXY-4'-ETHOXYACETOPHENONE WITH
4-CHLOROBENZALDEHYDE : 2'-HYDROXY-4'-CHLORO-4'-ETHOXYCHALCONE :

2-Hydroxy-4'-ethoxyacetophenone (1.98 gm) 4-chlorobenz-
zaldehyde (1.54 gm), ethanol (50 ml) and potassium hydroxide
(40 ml : 40 per. cent) were mixed in a tightly corked flask
and left at the room temperature for 24 hours. The colour
of the reaction mixture changed from a yellow to orange. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was collected, washed with water, dried and crystallised from ethanol, yellow plates. m.p. 98°C. Yield: 3.2 gm.

The chalcone was also prepared by phosphorus oxychloride method.

The chalcone is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali giving an orange colour. It gives a brown colour with ethanolic ferric chloride and a red colour with concentrated sulphuric acid.

Analysis:

Found: C, 66.28; H, 4.82; Cl, 11.29%

C_{17}H_{15}O_3Cl requires C, 66.21; H, 4.86; Cl, 11.52%

BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 5 hours. It was then cooled and treated with ice water containing dilute sulphuric acid. The yellow solid obtained was filtered, washed with water, dilute sodium bicarbonate solution and finally with water, dried and crystallised from petroleum ether (40-60), yellow needles. m.p. 90°C. Yield: 0.38 gm.
Analysis:

**Found:** Cl, 8.21%

\[ C_{21}H_{19}O_4Cl \] requires Cl, 8.74%

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**Cyclo-isomerisation of 2'-hydroxy-4'-chloro-4'-ethoxychalcone:**

**7'-ethoxy-4'-chloroflavanone:**

To the hot solution of chalcone (0.5 gm) in ethanol (40 ml), dilute sulphuric acid (20 ml : 10 per cent) was added. The precipitate so formed was dissolved in more ethanol (20 ml) and the clear solution was refluxed on a boiling water bath for 30 hours. Excess of ethanol was distilled off and the residual solution was then filtered hot and left at the room temperature. The brown solid separated was collected, washed with water and crystallised from ethanol, brown plates. m.p. 240°C. Yield: 0.18 gm.

Analysis:

**Found:** Cl, 12.00%

\[ C_{17}H_{15}O_3Cl \] requires Cl, 11.52%

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**Bromination of 2'-hydroxy-4'-chloro-4'-ethoxychalcone:**

**2'-hydroxy-4'-chloro-4'-ethoxy-\( \alpha:\beta \)-dibromochalcone:**

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml), The bromine in acetic acid (5 ml : 10 per cent) was added to it with constant stirring. The mixture was kept
cool in ice bath for 4 hours. Then the mixture was poured into ice water. The yellow solid separated was collected, washed with water, dilute sodium thiosulphate solution and again with water, dried and crystallised from acetone, yellow needles, m.p. 155°C. Yield: 0.38 gm.

Analysis:

Found: Halogen, 42.41 %

\[ \text{C}_{17}\text{H}_{15}\text{O}_3\text{Br}_2\text{Cl} \] requires Halogen, 42.27 %

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

The mixture of above dibromochalcone (0.3 gm), potassium iodide (0.3 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. The solution was then filtered hot, and acetone was removed. The yellow solid obtained was washed with dilute sodium thiosulphate solution, then with water, dried and crystallised from ethanol. Yellow needles, m.p. and mixed m.p. with original chalcone 98°C.

CYCLISATION OF 2'-HYDROXY-4'-CHLORO-4'-ETHOXYCHALCONE:

7'-ETHOXY-4'-CHLOROFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate on the \( \alpha: \beta \) Dibromochalcone:

The \( \alpha: \beta \) dibromochalcone (0.5 gm) in acetone (20 ml)
was treated with anhydrous potassium carbonate (0.5 gm) and the reaction mixture was refluxed on a water bath at 70°C for 4 hours. The solution was then filtered hot and acetone was removed. The yellowish brown solid separated was collected, washed with dilute sodium thiosulphate solution and then with water. It was crystallised from ethanol, yellowish brown plates. m.p. 280°C. Yield : 0.16 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

A mixture of chalcone (0.5 gm), n-amyl alcohol (20 ml) and selenium dioxide (0.5 gm) was refluxed on an oil bath at 150°C for 24 hours. Selenium was then filtered off from the hot reaction mixture and n-amyl alcohol was removed by steam distillation. The brown solid obtained was washed with petroleum ether (40-60) to remove traces of alcohol and crystallised from ethanol, yellowish brown plates. m.p. 280°C. Yield : 0.21 gm.

Analysis:

Found : Cl, 11.71 %

C_{17}H_{13}O_{5}Cl requires Cl, 11.81 %
OXIDATION OF 2'-HYDROXY-4'-CHLORO-4'-ETHOXYCHALCONE :

7'-ETHOXY-4'-CHLOROFLAVONOL :

(a) By Action of Alkaline Hydrogen Peroxide :

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml : 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml : 20 vol) was added and the reaction mixture was kept cool in the ice bath for 4 hours and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to greenish yellow. It was then treated with ice water and acidified with dilute hydrochloric acid (1:1). A brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown granules, m.p. 108°C. Yield : 0.21 gm.

(b) Using Sodium Peroxide in Ethanolic Solution :

A mixture of chalcone (0.5 gm), sodium peroxide (0.5 gm) and ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The brown solid obtained was collected, washed with water, dried and crystallised from ethanol, brown granules, m.p. 108°C. Yield : 0.23 gm.

Analysis:

Found : Cl, 11.28 %

C_{17}H_{13}O_{4}Cl requires Cl, 11.21 %
ACETYL DERIVATIVE OF FLAVONOL:

A mixture of flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water, a colourless solid separated was collected washed with water, dried and crystallised from ethanol, white granules, m.p. 118°C. Yield: 0.21 gm.

Analysis

Found: Cl, 9.78 %

C_{19}H_{15}O_{5}Cl requires Cl, 9.91 %

CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-4'-CHLORO-
4'-ETHOXYCHALCONE : ETHYL-2(4'-CHLOROPHENYL)4-(2''-HYDROXY-
4''-ETHOXYPHENYL)-Δ^4-CYCLOHEXENE-6-ONE-1-CARBOXYLATE:

Sodium metal (0.2 gm) was dissolved in absolute ethanol (15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml). To this solution ethyl acetoacetate (1 ml) was added and the mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The light brown solid separated was collected, washed with water, dried and crystallised from ethanol. Light brown granules, m.p. 180°C. Yield: 0.28 gm.
HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL CYCLOHEXENONE CARBOXYLATE: 2-((4'-CHLOROPHENYL)-4(2''-HYDROXY-4''-ETHOXYPHENYL)-Δ⁴-CYCLOHEXENE-6-ONE:

A mixture of above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm), ethanol (20 ml) and sodium hydroxide (10 ml : 5 percent) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The brown coloured solid separated was collected, washed with water, dried and crystallised from ethanol, brown granules, m.p. 140°C. Yield : 0.21 gm.

Analysis:

Found : Cl, 10.13 %  
C₂₀H₁₉O₃Cl requires Cl, 10.36 %
ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-4-
CHLORO-4'-ETHOXYCHALCONE : 3-(2-HYDROXY-4-ETHOXYPHENYL) -
5-(4-CHLOROPHENYL) ISOXAZOLINE :

2'-Hydroxy-4-chloro-4'-ethoxychalcone (1.0 gm) was
dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride
(1.0 gm) in water (5.0 ml) was added. The reaction mixture
was refluxed on a boiling water bath for 4 hours. It was
then cooled and acidified with dilute acetic acid (1:1).
A brown solid separated was collected, washed with water,
dried and crystallised from ethanol, brown plates, m.p. 160°C.
Yield : 0.81 gm.

Analysis:

Found : Cl, 12.04 %; N, 4.23 %
C_{17}H_{16}O_{3}N Cl requires : Cl, 11.18 %; N, 4.40 %
VI CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXYACETOPHENONE AND 4-NITROBENZALDEHYDE :  
CONDENSATION OF 2-HYDROXY-4-ETHOXYACETOPHENONE WITH 4-
NITROBENZALDEHYDE : 2'-HYDROXY-4-NITRO-1'-ETHOXYCHALCONE:

2-Hydroxy-4-ethoxyacetophenone (1.98 gm), 4-nitrobenzaldehyde (1.66 gm), ethanol (50 ml) and potassium hydroxide (40 ml : 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture changed from yellow to orange. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown plates, m.p. 180°C. Yield : 3.4 gm.

The chalcone was also prepared by phosphorus oxychloride method.

The chalcone is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali giving an orange colour. It gives a brown colour with ethanolic ferric chloride, while a red colour with concentrated sulphuric acid.

Analysis:

Found : C, 65.38 %; H, 4.73 %; N, 4.42 %
C_{17}H_{15}O_{5}N requires C, 65.18 %; H, 4.79 %; N, 4.47 %
BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 5 hours. It was then cooled and treated with ice water containing dilute sulphuric acid. The yellow solid separated was collected, washed with water, dilute sodium bicarbonate solution, and again with water. It was dried and crystallised from petroleum ether (40-60), yellow plates, m.p. 110°C. Yield: 0.32 gm.

Analysis:

Found: N, 3.38%

C_{24}H_{19}O_{6}N requires N, 3.36%

CYCLO-ISOMERISATION OF 2'-HYDROXY-4'-NITRO-4'-ETHOXYCHALCONE:

7'-ETHOXY-4'-NITROFLAVANONE:

To the hot solution of chalcone (0.5 gm) in ethanol (40 ml), dilute sulphuric acid (20 ml: 10 per cent) was added. The precipitate so formed was dissolved in more ethanol (20 ml) and the clear solution was refluxed on a boiling water bath for 30 hours. Excess of ethanol was distilled off and the residual solution was then filtered hot and left at the room temperature. The brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown needles, m.p. 142°C. Yield: 0.21 gm.
BROMINATION OF 2'-HYDROXY-4'-NITRO-4'-ETHOXYCHALCONE :

2'-HYDROXY-4'-NITRO-4'-ETHOXY-α:β'-DIBROMOCHALCONE :

The chalcone (0.5 gm) was dissolved in acetic acid (30ml). The bromine in acetic acid (5 ml : 10 per cent) was added with constant stirring. The mixture was kept cool in an ice bath for 4 hours and then left at the room temperature. Then the mixture was treated with ice water. The brown solid separated was collected, washed with dilute sodium thiosulphate solution, then with water and crystallised from acetone, brown needles, m.p. 210°C. Yield : 0.31 gm. Analysis :

Found : N, 3.01 % ; Br, 33.88 %

C_{17}H_{15}O_5Br_2N requires N, 2.95 % ; Br, 33.83 %

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE :

The mixture of the above dibromochalcone (0.3 gm) potassium iodide (0.3 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. The solution was then filtered hot and acetone was removed. The brown solid obtained was washed with dilute sodium thiosulphate solution,
then with water, dried and crystallised from ethanol, brown plates, m.p. 180°C.

**CYCLISATION OF 2'-HYDROXY-4'-NITRO-4'-ETHOXYCHALCONE :**

**7'-ETHOXY-4'-NITROFLAVONE :**

(a) **By Action of Acetone and Anhydrous Potassium Carbonate on the α:β Dibromochalcone :**

The dibromochalcone (0.5 gm) in acetone (20 ml) was treated with anhydrous potassium carbonate (0.5 gm) and the reaction mixture was refluxed on a water bath at 70°C for 4 hours. The solution was then filtered hot and acetone was removed. The brown solid obtained was washed with water, dilute sodium thiosulphate solution and again with water, dried and crystallised from ethanol, brown granules, m.p. 280°C. Yield : 0.18 gm.

(b) **By Selenium Dioxide Oxidation of the Chalcone :**

A mixture of chalcone (0.5 gm), n-amyl alcohol (20 ml) and selenium dioxide (0.5 gm) was refluxed on an oil bath at 150°C for 24 hours. Selenium was then filtered off from the hot reaction mixture and n-amyl alcohol was removed by steam distillation. The brown solid obtained was washed with petroleum ether (40-60) to remove traces of alcohol, and crystallised from ethanol, brown granules, m.p. 280°C. Yield : 0.23 gm.
Analysis:

Found: N, 4.39%

C_{17}H_{13}O_{5}N requires N, 4.50%

OXIDATION OF 2'-HYDROXY-4'-NITRO-4'-ETHOXYCHALCONE:

7'-ETHOXY-4'-NITROFLAVONOL:

(a) By Action of Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml: 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml: 20 vol) was added, and the reaction mixture was kept cool in the ice bath for 4 hours, and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to greenish yellow. It was then treated with ice water and acidified with dilute hydrochloric acid (1:1). Yellowish solid separated was collected, washed with water, dried, and crystallised from ethanol, pale yellow needles, m.p. 208°C. Yield: 0.18 gm.

(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of chalcone (0.5 gm) and sodium peroxide (0.5 gm) in ethanol was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellowish solid separated was collected, washed with water and crystallised
from ethanol, pale yellow needles, m.p. 308°C. Yield: 0.23 gm.

Analysis:

Found: N, 4.52%

C₁₇H₁₃O₆N requires N, 4.28%

ACETYL DERIVATIVE OF FLAVONOL:

A mixture of flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water and a brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown needles, m.p. 278°C. Yield: 0.23 gm.

Analysis:

Found: N, 3.96%

C₁₉H₁₅O₇N requires N, 3.79%

CONDENSATION OF ETHYL ACETOACETATE WITH

2'-HYDROXY-4'-NITRO-4'-ETHOXYCHALCONE: ETHYL-2(4'-NITROPHENYL)-4-(2''-HYDROXY-4''-ETHOXYPHENYL)-Δ⁴-CYCLOHEXENE-6-ONE-1-CARBOXYLATE:

Sodium metal (0.2 gm) was dissolved in absolute ethanol (15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml). To this solution ethyl acetoacetate (1 ml) was added and the mixture was refluxed on a boiling water bath for 5 hours.
It was then cooled and diluted with ice water (100 ml), then acidified with dilute hydrochloric acid (1:1). The brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown plates, m.p. 115°C. Yield: 0.21 gm.

Analysis:

Found: N, 3.12 %

C_{23}H_{23}O_7N requires N, 3.29 %

HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL CYCLOHEXENONE CARBOXYLATE: 2-(4'-NITROPHENYL)-4(2''-HYDROXY-4'' ETHOXYPHENYL)-Δ^1-CYCLOHEXENE-6-ONE:

A solution of above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml) and sodium hydroxide (10 ml; 5 per cent) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The yellowish brown solid separated was collected, washed with water, dried and crystallised from ethanol, pale yellow plates, m.p. 230°C. Yield: 0.29 gm.

Analysis:

Found: N, 3.88 %

C_{20}H_{19}O_5N requires N, 3.96 %
ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-4'-NITRO-
4'-ETHOXYCHALCONE : 3(2-HYDROXY-4'-ETHOXYPHENYL)-5-(4-
NITROPHENYL) ISOXAZOLINE :

2'-Hydroxy-4-nitro-4'-ethoxychalcone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added. The reaction mixture was refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A brown solid obtained was collected, washed with water, dried and crystallised from ethanol, brown needles, m.p. 120°C.
Yield : 0.58 gm.
Analysis:

Found : N, 8.38 %
C_{17}H_{16}O_{5}N_{2} requires N, 8.54 %
VII CHALCONE AND RELATED COMPOUNDS DERIVED FROM
2-HYDROXY-4-ETHOXYACETOPHENONE AND 2-4 DICHLOROBENZALDEHYDE :
CONDENSATION OF 2-HYDROXY-4-ETHOXYACETOPHENONE WITH 2-4 DICHLOROBENZALDEHYDE :
2'-HYDROXY 2-4 DICHLORO-4'-ETHOXYCHALCONE :

2-Hydroxy-4-ethoxyacetophenone (1.98 gm), 2-4 dichlorobenzaldehyde (1.93 gm), ethanol (50 ml) and potassium hydroxide (40 ml ; 40 per cent) were mixed in a tightly corked flask and left at the room temperature for 24 hours. The colour of the reaction mixture changed from yellow to red. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was collected, washed with water, dried and crystallised from ethanol, yellow needles, m.p. 161°C. Yield : 3.6 gm.

The chalcone was also prepared by phosphorus oxychloride method.

The product is sparingly soluble in aqueous alkali, but dissolves in ethanolic alkali giving an orange colour. It gives a characteristic red colour with concentrated sulphuric acid.

Analysis:

Found : C, 60.39 % ; H, 4.24 % ; Cl, 20.99 %
C_{17}H_{14}O_3Cl_2 requires C, 60.53 % ; H, 4.15 % ; Cl, 21.07 %
BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), a drop of pyridine and benzoyl chloride (1.0 ml) was heated on a boiling water bath for 5 hours. Then it was treated with ice water containing dilute sulphuric acid. The white solid separated was collected, washed with water, then with dilute sodium bicarbonate solution and again with water, dried and crystallised from petroleum ether (40-60) white plates, m.p. 108°C. Yield: 0.42 gm.

Analysis:

Found: Cl, 16.31%

C_{24}H_{18}O_{4}Cl_{2} requires Cl, 16.20%

CYCLO-ISOMERISATION OF 2'-HYDROXY-2'-4'-DICHLORO-4'-ETHOXY-CHALCONE: 7'-ETHOXY-2'-4'-DICHLOROFLAVANONE:

To the hot solution of chalcone (0.5 gm) in ethanol (40 ml), dilute sulphuric acid (20 ml: 10 per cent) was added. The precipitate so formed was dissolved in excess of ethanol (20 ml) and the clear solution was refluxed on a boiling water bath for 30 hours. Then it was filtered hot and ethanol was distilled off and left at the room temperature. The brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown needles, m.p. 188°C. Yield: 0.18 gm.
Analysis:

Found: Cl, 21.18 %

C_{17}H_{14}O_{3}Cl_2 requires Cl, 21.07 %

**BR0MINATION OF 2'-HYDROXY-2-CHLORO-4'-ETHOXYCHALCONE :**

2'-HYDROXY-2-CHLORO-4'-ETHOXY-CHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml). The bromine in acetic acid (5 ml : 10 per cent) was added to it with constant stirring and the mixture was kept cool in an ice bath for 4 hours. Then the mixture was treated with ice water. The yellow solid separated was filtered, washed with water, sodium thiosulphate solution and again with water, dried and crystallised from acetone, yellow needles, m.p. 112°C. Yield: 0.35 gm.

Analysis:

Found: Halogen, 47.52 %

C_{17}H_{14}O_{3}Br_2Cl_2 requires Halogen, 47.67 %

**DEBROMINATION OF THE ABOVE DIBROMOCHALCONE :**

The mixture of the above α:β dibromochalcone (0.3 gm), potassium iodide (0.3 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. The solution was then filtered hot and acetone was removed. The yellow solid obtained was washed with dilute sodium
thiosulphate solution, then with water, dried and crystallised from ethanol, m.p. and mixed m.p. with original chalcone 161°C.

CYCLISATION OF 2'-HYDROXY-2,4-DICHLORO-4'-ETHOXYCHALCONE:

7-ETHOXY-2'-4'-DICHLOROFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate on the α:β-Dibromochalcone:

The dibromochalcone (0.5 gm) in acetone (20 ml) was treated with anhydrous potassium carbonate (0.5 gm) and the reaction mixture was refluxed on a water bath at 70°C for 4 hours. Then the solution was then filtered hot and acetone was removed. The brown solid obtained was washed with water, then with dilute sodium thiosulphate solution and again with water, dried and crystallised from ethanol, brown granules, m.p. 155°C. Yield: 0.21 gm.

(b) By Selenium Dioxide Oxidation of The Chalcone:

To a solution of a chalcone (0.5 gm) in n-amyl alcohol (20 ml), selenium dioxide (0.5 gm) was added and the reaction mixture was refluxed on an oil bath at 150°C for 24 hours. Selenium was then filtered off from the hot solution and n-amyl alcohol was removed by steam distillation. The brown solid obtained was washed with petroleum ether.
(40-60) and crystallised from ethanol, brown granules, m.p. 155°C. Yield : 0.18 gm.

Analysis:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Found</th>
<th>Required</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>21.32</td>
<td>21.19</td>
</tr>
</tbody>
</table>

**C₁₇H₁₂O₃Cl₂** requires Cl, 21.19 %

**Oxidation of 2'-Hydroxy-2,4-dichloro-4'-ethoxychalcone**:

7'-Ethoxy-2'-4'-dichloroflavonol:

(a) By Action of Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml : 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml : 20 vol) was added and the reaction mixture was kept cool in the ice bath for 4 hours, and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to greenish yellow. It was then treated with ice water and acidified with dilute hydrochloric acid (1:1). The brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown plates, m.p. 132°C. Yield : 0.21 gm.
(b) Using Sodium Peroxide in Ethanol Solution:

A mixture of chalcone (0.5 gm), sodium peroxide (0.5 gm) and ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The brown solid separated was collected washed with water, dried and crystallised from ethanol, brown plates, m.p. 182°C, Yield: 0.18 gm.

It is soluble in alkali, gives a brown colour with ethanolic alkali and a greenish fluorescence with concentrated sulphuric acid.

Analysis:

Found: Cl, 20.38 %

C₁₇H₁₂O₄Cl₂ requires Cl, 20.23 %

Acetyl Derivative of Flavonol:

A mixture of flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water, and brown solid separated was collected, washed with water, dried and crystallised from ethanol, brown granules, m.p. 184°C. Yield: 0.23 gm.

Analysis:

Found: Cl, 18.21 %

C₁₉H₁₄O₄Cl₂ requires Cl, 18.07 %
CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-2-4-
DICHLOOR-4'-ETHOXYCHALCONE : ETHYL-2(2 4'-DICHLOROPHENYL)-
4-(2-HYDROXY-4'-ETHOXYPHENYL) - \( \Delta^4 \) -CYCLOHEXENE-6-ONE-1-
CARBOXYLATE :

Sodium metal (0.2 gm) was dissolved in ethanol (15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml). To this solution ethyl acetoacetate (1.0 ml) was added and the clear solution was refluxed on a boiling water bath for 5 hours. It was then cooled and treated with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1) yellowish white solid separated was collected, washed with water, dried and crystallised from ethanol, yellowish white granules, m.p. 184°C. Yield : 0.21 gm.

Analysis:

Found : Cl, 15.55 %

C\(_{23}\)H\(_{22}\)O\(_7\)Cl\(_2\) requires Cl, 15.81 %

HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE

ETHYL CYCLOHEXENONE CARBOXYLATE : 2-(2 4'-DICHLOROPHENYL)-
4-(2-HYDROXY-4'-ETHOXYPHENYL) - \( \Delta^4 \) -CYCLOHEXENE-6-ONE :

A solution of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml) and sodium
hydroxide (10 ml : 5 per cent) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). A brown solid separated was collected, dried and crystallised from ethanol, brown needles, m.p. 180°C. Yield : 0.18 gm.

Analysis:

Found : Cl, 18.64 %

C_{20}H_{18}O_3Cl_2 requires Cl, 18.84 %

**ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-2,4-DICHLORO-4'-ETHOXYCHALCONE : 3(2-HYDROXY-4-ETHOXYPHENYL)-5-(2,4-DICHLOROPHENYL) ISOXAZOLINE :**

2'-Hydroxy-2,4-dichloro-4'-ethoxychalcone (1.0 gm) was dissolved in pyridine (5 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added. The reaction mixture was refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A brown product obtained was collected, washed with water, dried and crystallised from ethanol, brown granules, m.p. 144°C. Yield : 0.73 gm.

Analysis:

Found : Cl, 20.28 %; N, 3.81 %

C_{17}H_{15}O_3NCl_2 requires Cl, 20.18 %; N, 3.97 %
SECTION II

THEORETICAL
2-Hydroxy-4-ethoxy-5-nitroacetophenone was condensed with (1) benzaldehyde (2) 2-methoxy benzaldehyde (3) vanillin (4) 4-chlorobenzaldehyde (5) 4-nitrobenzaldehyde (6) 4-methoxybenzaldehyde (7) 2,4 dichlorobenzaldehyde (8) 3-nitrobenzaldehyde.

Condensations were carried out using (a) different concentrations of potassium hydroxide and (b) phosphorus
oxychloride. It was found after some trial that 40 percent potassium hydroxide is the best to get an optimum yield of the chalcones. The reaction period used was about 24 hours.

Also, in these condensations only chalcones were isolated, all attempts to isolate a flavanone, or other compounds have failed.

I CHalcone AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE : AND BENZALDEHYDE

The condensation was studied using different condensing agents: (a) potassium hydroxide solution of different concentrations and (b) phosphorus oxychloride.

(a) Potassium Hydroxide:

The condensations have been investigated using different concentrations of alkali and for different reaction periods. The important conditions are tabulated below.
TABLE I

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium hydroxide per cent</th>
<th>Temperature °C</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>25-30</td>
<td>24</td>
<td>2.6</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>100</td>
<td>4</td>
<td>1.9</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>25-30</td>
<td>24</td>
<td>3.1</td>
</tr>
<tr>
<td>4</td>
<td>40</td>
<td>100</td>
<td>4</td>
<td>2.1</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>25-30</td>
<td>24</td>
<td>2.4</td>
</tr>
</tbody>
</table>

From the above table it is found that optimum yield of the chalcone was obtained with 40 per cent alkali as a condensing agent and by keeping the reaction mixture for 24 hours at the room temperature (25-30°C).

The product was crystallised from ethyl alcohol, ethyl acetate or benzene. No other product could be isolated.

(b) Phosphorus oxychloride:

In case of this condensing agent (1.0 ml) the mixture of ketone (2.48 gm) and aldehyde (1.17 gm) was kept at the room temperature for 24 hours. The chalcone was obtained in a yield of 2.0 gm.
The product obtained in all the above condensations has been assigned the structure, 2'-hydroxy-4'-ethoxy-5'-nitrochalcone (I, R = H) on the following basis:

(1) (a) The compound is yellow in colour. It gives a brown colour with ethanolic ferric chloride and a red colour with concentrated sulphuric acid.

(b) It is sparingly soluble in dilute alkali but dissolves in ethanolic alkali with an orange colour.

(c) It gives a benzoyl derivative (II, R = H) with benzoyl chloride and pyridine.

(2) By treatment with dilute ethanolic sulphuric acid it has been cyclised to the corresponding flavanone. (II, R = H) which is insoluble in alkali and does not give ferric chloride test.

(3) (a) With bromine it forms \( \alpha: \beta \) dibromochalcone (IV, R = H) which could be debrominated by treatment with potassium iodide and acetone. The dibromide was converted to flavone (V, R = H) by treatment with acetone and anhydrous potassium carbonate.

(b) It is oxidised by selenium dioxide in \( \eta \)-amyl alcohol to the corresponding flavone (V, R = H) which is identical with the flavone obtained as above. It gives a bluish fluorescence with concentrated sulphuric acid.

(4) The chalcone is also oxidised to the corresponding flavonol (VI, R = H) by treatment with alkali and
hydrogen peroxide, which is soluble in alkali, gives a brown colour with ethanolic ferric chloride and greenish fluorescence with concentrated sulphuric acid. The flavonol gives an acetyl derivative (VII, R = H) with acetic anhydride and pyridine.

(5) The chalcone forms corresponding ethyl cyclohexenone carboxylate derivative (VIII, R = H) with ethyl acetoacetate and sodium ethoxide. It gives an orange colour with concentrated sulphuric acid. This carboxylate ester has been hydrolysed and simultaneously decarboxylated by ethanolic alkali to the corresponding cyclohexenone (IX, R = H).

(6) With hydroxylamine hydrochloride, the chalcone forms the corresponding isoxazoline derivative (X, R = H) which gives an orange colour with concentrated sulphuric acid.

II CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE AND 2-METHOXYBENZALDEHYDE:

The condensation was carried out in the same manner as in the previous case using 40 per cent potassium hydroxide as the condensing agent. The condensation was investigated to obtain the maximum yield of the chalcone as under:
TABLE II

2-Hydroxy-4-ethoxy-5-nitroacetophenone : 2.48 gm.
2-Methoxybenzaldehyde : 1.49 gm.
Ethanol (solvent) : 50 ml
Temperature (Room temperature) : 25-30°C

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium hydroxide per cent</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>2.4</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>20</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>2.4</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>2.9</td>
</tr>
</tbody>
</table>

It clearly indicates that the maximum yield of the chalcone was obtained when the concentration of alkali was 40 per cent.

Phosphorus oxychloride was used as a condensing agent but it was found that the yield of the chalcone was poor.

The structure, 2'-hydroxy-2-methoxy-4'-ethoxy-5'-nitrochalcone (I, R = 2-OCH₃) has been assigned on the following ground:

(1)(a) The product is coloured and gives a characteristic brown colour with ethanolic ferric chloride and red colour with concentrated sulphuric acid.

(b) It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali with an orange colour.
(c) It gives a benzoyl derivative when treated with benzoyl chloride and pyridine (II, R = 2-0CH₃).

(2) It could be cyclised in presence of dilute ethanolic sulphuric acid to the corresponding flavanone (III, R = 2-0CH₃) which gives the following tests:
(a) It is insoluble in alkali.
(b) It does not give any colour with ethanolic ferric chloride.

(3)(a) The product on bromination gave α:β dibromochalcone (IV, R = 2-0CH₃) which was debrominated by acetone and potassium iodide. The product was also converted into the corresponding flavone (V, R = 2-0CH₃) by acetone and anhydrous potassium carbonate.
(b) On Venkatraman oxidation by selenium dioxide in η-amyl alcohol, it was converted into the corresponding flavone (V, R = 2-0CH₃) which was identical with the flavone obtained as above. It does not give any colour with ethanolic ferric chloride. It gives a bluish fluorescence in ethanol and with concentrated sulphuric acid an orange colour with a bluish fluorescence is obtained.

(4) The chalcone was oxidised by alkaline hydrogen peroxide to the corresponding flavonol (VI, R = 2-0CH₃) which
(a) dissolves in dilute alkali.
(b) gives a brown colour with ethanolic ferric chloride.
(c) gives a greenish fluorescence with concentrated sulphuric acid and
(d) gives an acetyl derivative \((\text{VII}, R = 2\text{-OCH}_3)\) with acetic anhydride and pyridine.

(5) It gives corresponding ethyl cyclohexenone carboxylate \((\text{VIII}, R = 2\text{-OCH}_3)\) with ethyl acetoacetate and sodium ethoxide, characterised by an orange colour with concentrated sulphuric acid. It has been hydrolysed and decarboxylated to the corresponding cyclohexonone \((\text{IX}, R = 2\text{-OCH}_3)\).

(6) With hydroxylamine hydrochloride, the chalcone forms the corresponding isoxazoline derivative \((\text{X}, R = 2\text{-OCH}_3)\), which gives an orange colour with concentrated sulphuric acid.
III CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE AND VANILLIN:

The condensation has been investigated using potassium hydroxide solution of different concentrations. The results obtained are as under:

TABLE III

<table>
<thead>
<tr>
<th>No</th>
<th>Potassium hydroxide per cent</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>2.0</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>20</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>3.6</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>2.8</td>
</tr>
</tbody>
</table>

It clearly indicates that the maximum yield of the chalcone was obtained when the concentration of alkali was 40 per cent.

Phosphorus oxychloride was used as a condensing agent but it was found that the yield of the chalcone was poor.

The structure, 2'-4 dihydroxy-3-methoxy-4'-ethoxy-5'-nitrochalcone (I, R = 3-0CH$_3$, 4-OH) has been assigned on the following ground:
(1) (a) The compound is brown in colour. It gives a brown colour with ethanolic ferric chloride and red colour with concentrated sulphuric acid.

(b) It is sparingly soluble in dilute alkali but dissolves in ethanolic alkali with an orange colour.

(c) It gives a dibenzoyl derivative \((\text{II}, R = 3\text{-OCH}_3, 4\text{-OC}_6\text{H}_5)\) with benzoyl chloride and pyridine.

(2) By treatment with dilute ethanolic sulphuric acid it has been cyclised to the corresponding flavanone \((\text{III}, R = 3\text{-OCH}_3, 4\text{-OH})\) which is insoluble in alkali and does not give a ferric chloride test.

(3) (a) With bromine it forms a \(\alpha:\beta\) dibromochalcone \((\text{IV}, R = 3\text{-OCH}_3, 4\text{-OH})\) which could be debrominated by treatment with potassium iodide and acetone. The dibromide was converted to flavone \((\text{V}, R = 3\text{-OCH}_3, 4\text{-OH})\) by treatment with acetone and anhydrous potassium carbonate.

(b) It is oxidised by selenium dioxide in \(n\)-amyl alcohol to the corresponding flavone, \((\text{V}, R = 3\text{-OCH}_3, 4\text{-OH})\) which is identical with the flavone obtained as above. It gives a bluish fluorescence with concentrated sulphuric acid.

(4) The chalcone is also oxidised to the corresponding flavonol \((\text{VI}, R = 3\text{-OCH}_3, 4\text{-OH})\) by treatment with alkali and hydrogen peroxide which is soluble in
alkali, gives a brown colour with ethanolic ferric chloride and a greenish fluorescence with concentrated sulphuric acid. The flavonol gives a diacetyl derivative (VII, R = 3-OCH$_3$, 4-0.COOCH$_3$) with acetic anhydride and pyridine.

(5) The chalcone forms corresponding ethyl cyclohexenone carboxylate derivative (VIII, R = 3-OCH$_3$, 4-OH) with ethyl acetoacetate and sodium ethoxide. It gives an orange colour with concentrated sulphuric acid. This carboxylate ester has been hydrolysed and simultaneously decarboxylated by ethanolic alkali to the corresponding cyclohexenone (IX, R = 3-OCH$_3$, 4-OH).

(6) With hydroxylamine hydrochloride the chalcone forms the corresponding isoxazoline derivative (X, R = 3-OCH$_3$, 4-OH) which gives an orange colour with concentrated sulphuric acid.

IV CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-
ETHOXY-5-NITROACETOPHENONE AND 4-CHLOROBENZALDEHYDE :

The condensation has been investigated using different concentrations of alkali. The results obtained are as under:
TABLE IV

2-Hydroxy-4-ethoxy-5-nitroacetophenone : 2.48 gm.
4-Chlorobenzaldehyde : 1.51 gm.
Ethanol (Solvent) : 50 ml.
Temperature (Room temperature) : 25-30°C

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium hydroxide per cent</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>24</td>
</tr>
</tbody>
</table>

It is clear from the above table that the maximum yield of the chalcone was obtained when 40 per cent 40 ml alkali was used.

The chalcone was also prepared by using phosphorus oxychloride as condensing agent.

The structure of the chalcone 2'-hydroxy-4-chloro-4'-ethoxy-5'-nitrochalcone (I, R = 4-Cl) has been assigned on the following basis:

(a) The product is yellow in colour. It gives a brown colour with ethanolic ferric chloride and a red colour with concentrated sulphuric acid.

(b) It is sparingly soluble in aqueous alkali but
dissolves in ethanolic alkali giving an orange colour.

(c) It gives a benzoyl derivative (II, R = 4-Cl) with benzoyl chloride.

(2) It is cyclised to the corresponding flavanone (III, R = 4-Cl) by treatment with dilute ethanolic sulphuric acid which gives a negative test with ethanolic ferric chloride.

(3)(a) With bromine it forms a \( \alpha : \beta \) dibromochalcone (IV, R = 4-Cl) which could be debrominated by treatment with potassium iodide and acetone. The dibromide was converted to the corresponding flavone (V, R = 4-Cl) by treatment with acetone and anhydrous potassium carbonate.

(b) It is oxidised by selenium dioxide in \( n \)-amyl alcohol to a flavone (V, R = 4-Cl) which is identical with the flavone obtained as above. It gives a bluish fluorescence with concentrated sulphuric acid.

(4) It is also oxidised to the corresponding flavonol (VI, R = 4-Cl) by treatment with alkali and hydrogen peroxide.

(a) It is soluble in alkali.

(b) It gives a brown colour with ethanolic ferric chloride solution and greenish fluorescence with concentrated sulphuric acid.
(c) It gives an acetyl derivative (VII, \( R = 4\text{-Cl} \)) with acetic anhydride and pyridine.

(5) The chalcone forms corresponding ethyl cyclohexenone carboxylate derivative (VIII, \( R = 4\text{-Cl} \)) with ethyl acetoacetate and sodium ethoxide. This carboxylate ester was hydrolysed and simultaneously decarboxylated by ethanolic alkali to the corresponding cyclohexenone (IX, \( R = 4\text{-Cl} \)).

(6) With hydroxylamine hydrochloride, the chalcone forms the corresponding isoxazoline derivative (X, \( R = 4\text{-Cl} \)) which gives an orange colour with concentrated sulphuric acid and a negative test with ethanolic ferric chloride.

V CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-
ETHOXY-5-NITROACETOPHENONE AND 4-NITROBENZALDEHYDE:

The condensation was carried out in the same manner as in the previous case using 40 per cent potassium hydroxide as the condensing agent. The condensation was investigated to obtain the maximum yield of the chalcone as under:
TABLE V

2-Hydroxy-1-f-ethoxy-5-nitroacetophenone : 2.48 gm.
4-Nitrobenzaldehyde : 1.66 gm.
Ethanol (Solvent) : 50 ml.
Temperature (Room temperature) : 25-30°C

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium hydroxide</th>
<th>Reaction period</th>
<th>Yield of chalcone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>per cent</td>
<td>ml</td>
<td>(hrs)</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>20</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>24</td>
</tr>
</tbody>
</table>

It clearly indicates that the maximum yield of the chalcone was obtained when the concentration of alkali was 40 per cent.

Phosphorus exychloride was used as a condensing agent but it was found that the yield of the chalcone was poor.

The structure, 2'-Hydroxy-1'-ethoxy-4'-5'-dinitrochalcone (I, $R = \text{4-NO}_2$) has been assigned on the following grounds:

(1)(a) The product is brown coloured and gives a characteristic brown colour with ethanolic ferric chloride and a red colour with concentrated sulphuric acid.

(b) It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali with an orange colour.
(c) It gives a benzoyl derivative when treated with benzoyl chloride and pyridine (II, R = 4-NO\textsubscript{2}).

(2) It could be cyclised in presence of dilute ethanolic sulphuric acid to the corresponding flavanone (III, R = 4-NO\textsubscript{2}) which gives the following tests:

(a) It is insoluble in alkali.

(b) It does not give any colour with ethanolic ferric chloride.

(3)(a) The product on bromination gave α:β dibromochalcone (IV, R = 4-NO\textsubscript{2}) which was debrominated by acetone and potassium iodide. The dibromochalcone was also converted into the corresponding flavone (V, R = 4-NO\textsubscript{2}) by acetone and anhydrous potassium carbonate.

(b) On Venkatraman oxidation by selenium dioxide in n-amyl alcohol, it was converted into the corresponding flavone (V, R = 4-NO\textsubscript{2}) which was identical with the flavone obtained as above. It does not give any colour with ethanolic ferric chloride. It gives a bluish fluorescence in ethanol and with concentrated sulphuric acid an orange colour with a bluish fluorescence is obtained.

(4) The chalcone was oxidised by alkaline hydrogen peroxide to the corresponding flavonol (VI, R = 4-NO\textsubscript{2}) which
(a) is soluble in alkali and gives a brown colour with ethanolic ferric chloride

(b) gives a greenish fluorescence with concentrated sulphuric acid and

(c) gives an acetyl derivative (VII, R = 4-NO₂) with acetic anhydride and pyridine.

(5) It gives corresponding ethyl cyclohexenone carboxylate derivative (VIII, R = 4-NO₂) with ethyl acetoacetate and sodium ethoxide, characterised by an orange colour with concentrated sulphuric acid. It has been hydrolysed and decarboxylated to the corresponding cyclohexenone (IX, R = 4-NO₂).

(6) With hydroxylamine hydrochloride, the chalcone forms the corresponding isoxazoline derivative (X, R = 4-NO₂) which gives an orange colour with concentrated sulphuric acid.

VI CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE AND 4-METHOXYBENZALDEHYDE:

The condensation was carried out in the same manner as in the previous case using potassium hydroxide as the condensign agent. The condensation was investigated to obtain the maximum yield of the chalcone as under:
TABLE VI

<table>
<thead>
<tr>
<th>No</th>
<th>Potassium hydroxide per cent</th>
<th>Potassium hydroxide ml</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>24</td>
<td>1.4</td>
</tr>
<tr>
<td>2</td>
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<td>20</td>
<td>24</td>
<td>2.4</td>
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<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>24</td>
<td>3.2</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>24</td>
<td>2.9</td>
</tr>
</tbody>
</table>

It clearly indicates that the maximum yield of the chalcone was obtained when the concentration of alkali was 40 per cent.

Phosphorus oxychloride was used as a condensing agent but it was found that the yield of the chalcone was poor.

The structure, 2'-hydroxy-4'-methoxy-5'-ethoxy-5'-nitrochalcone (I, R = 4-OCH₃) has been assigned on the following ground:

(a) The product is coloured and gives a characteristic brown colour with ethanolic ferric chloride and a red colour with concentrated sulphuric acid.

(b) It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali with an orange colour.
(c) It gives a benzoyl derivative when treated with benzoyl chloride and pyridine (II, R = 4-OCH₃).

(2) It could be cyclised in presence of dilute ethanolic sulphuric acid to the corresponding flavanone (III, R = 4-OCH₃) which gives the following tests:
(a) It is insoluble in alkali.
(b) It does not give any colour with ethanolic ferric chloride.

(3)(a) The product on bromination gave \( \alpha:\beta \) dibromochalcone (IV, R = 4-OCH₃) which was debrominated by acetone and potassium iodide. The dibromochalcone was converted into the corresponding flavone (V, R = 4-OCH₃) by acetone and anhydrous potassium carbonate.
(b) On Venkatramanan oxidation by selenium dioxide in \( \eta \)-amyl alcohol it was converted into the corresponding flavone (V, R = 4-OCH₃) which was identical with the flavone obtained as above. It does not give any colour with ethanolic ferric chloride. It gives a bluish fluorescence in ethanol and with concentrated sulphuric acid an orange colour with a bluish fluorescence is obtained.

(4) The chalcone was oxidised by alkaline hydrogen peroxide to the corresponding flavonol (VI, R = 4-OCH₃) which
(a) is soluble in alkali and gives a brown colour with ethanolic ferric chloride
(b) gives a greenish fluorescence with concentrated sulphuric acid and
(c) gives an acetyl derivative (VII, R = 4-OCH₃) with acetic anhydride and pyridine.

(5) It gives corresponding ethyl cyclohexenone carboxylate derivative (VIII, R = 4-OCH₃) with ethyl acetoacetate and sodium ethoxide, characterised by an orange colour with concentrated sulphuric acid. It has been hydrolysed and decarboxylated to the corresponding cyclohexenone (IX, R = 4-OCH₃).

(6) With hydroxylamine hydrochloride the chalcone forms the corresponding isoxazoline derivative (X, R = 4-OCH₃), which gives an orange colour with concentrated sulphuric acid.

VII CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE AND 2-4 DICHLOROBENZALDEHYDE:

The condensation has been investigated using different concentrations of alkali. The results are tabulated below:
TABLE VII

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium hydroxide per cent</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>2.4</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>20</td>
<td>3.2</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
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<td>4.0</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>3.6</td>
</tr>
</tbody>
</table>

The best yield of the chalcone was obtained with 40 per cent potassium hydroxide.

Phosphorus oxychloride was used as a condensing agent but it was found that the yield of the chalcone was poor.

The structure, 2'-hydroxy-2-4'-dichloro-4'-ethoxy-5'-nitrochalcone (I, \( R = 2,4\)-(Cl)\(_2\)) has been assigned on the following basis:

(1)(a) The product is yellow in colour. It gives a brown colour with ethanolic ferric chloride solution and a red colour with concentrated sulphuric acid.

(b) It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali with an orange colour.
(c) It gives a benzoyl derivative (II, $R = 2,4'$-$(Cl)_2$) with benzoyl chloride and pyridine.

(2) It is cyclised to the corresponding flavanone (III, $R = 2,4'$-$(Cl)_2$) when treated with dilute ethanolic sulphuric acid which gives a negative test with ethanolic ferric chloride solution.

(3)(a) With bromine it forms dibromochalcone (IV, $R = 2,4'$-$(Cl)_2$) which could be debrominated to the original chalcone when treated with potassium iodide and acetone. The dibromide is also converted into flavone (V, $R = 2,4'$-$(Cl)_2$) when treated with anhydrous potassium carbonate and acetone.

(b) The chalcone is also directly oxidised to flavone (V, $R = 2,4'$-$(Cl)_2$) when treated with selenium dioxide in n-amyl alcohol which is identical with the flavone obtained as above. The flavone gives a bluish fluorescence with concentrated sulphuric acid.

(4) The chalcone is also oxidised by alkaline hydrogen peroxide giving a flavonol derivative (VI, $R = 2,4'$-$(Cl)_2$).

(a) It dissolves in alkali.

(b) It gives a brown colour with ethanolic ferric chloride solution and greenish fluorescence with concentrated sulphuric acid.
(c) It gives an acetyl derivative (VII, $R = 2,4-(\text{Cl})_2$) with acetic anhydride and pyridine.

(5) The chalcone gives corresponding ethyl cyclohexenone carboxylate (VIII, $R = 2,4-(\text{Cl})_2$) with ethyl acetoacetate and sodium ethoxide. This carboxylate ester hydrolysed and simultaneously dehydroxylated by ethanolic alkali to the corresponding cyclohexenone (IX, $R = 2,4-(\text{Cl})_2$).

(6) With hydroxylamine hydrochloride the chalcone forms the corresponding isoxazoline derivative (X, $R = 2,4-(\text{Cl})_2$) which gives an orange colour with concentrated sulphuric acid.

VIII CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-

$4$-ETHOXY-5-NITROACETOPHENONE AND 3-NITROBENZALDEHYDE:

The condensation has been investigated as before using different concentrations of alkali.
TABLE VIII

2-Hydroxy-4-ethoxy-5-nitroacetophenone : 2.48 gm.
3-Nitrobenzaldehyde : 1.66 gm.
Ethanol (Solvent) : 50 ml.
Temperature (Room temperature) : 25-30°C

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium hydroxide per cent</th>
<th>ml</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>24</td>
<td>2.0</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>20</td>
<td>24</td>
<td>2.9</td>
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<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>24</td>
<td>3.7</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>24</td>
<td>3.0</td>
</tr>
</tbody>
</table>

It is clear from the above table that the maximum yield of the chalcone was obtained when 40 per cent 40 ml potassium hydroxide was used.

The chalcone was also prepared using phosphorus oxychloride as a condensing agent but the yield was poor.

The product has been assigned the structure, 2'-hydroxy-4'-ethoxy-3,5'-dinitrochalcone (I, R = 3-NO₂) from the following facts:

(1) The compound is brown in colour, gives a characteristic red colour with concentrated sulphuric acid, a brown colour with ethanolic ferric chloride and it forms a benzoyl derivative (II, R = 3-NO₂).
(2) It has been cyclised to the corresponding flavanone (III, R = 3-NO₂) by treatment with dilute ethanolic sulphuric acid. The flavanone does not give the colour reaction with ethanolic ferric chloride.

(3) (a) The product on bromination gives α: β dibromo-chalcone (IV, R = 3-NO₂) which could be debrominated to the original chalcone. The chalcone dibromide is also converted to the corresponding flavone (V, R = 3-NO₂) by treatment with acetone and anhydrous potassium carbonate.

(b) It is converted to the corresponding flavone (V, R = 3-NO₂) by oxidation with selenium dioxide in n-amyl alcohol which was identical with the flavone obtained as above. With concentrated sulphuric acid it gives an orange colour with a bluish fluorescence.

(4) It gives a flavonol on oxidation with alkaline hydrogen peroxide (VI, R = 3-NO₂). The flavonol gives following reactions.

(a) It is soluble in alkali and gives a brown colour with ethanolic ferric chloride.

(b) It gives an orange colour with a greenish fluorescence with concentrated sulphuric acid.

(c) It gives an acetyl derivative (VII, R = 3-NO₂) with acetic anhydride and pyridine.
The chalcone gives corresponding ethyl cyclohexenone carboxylate ester with ethyl acetoacetate and sodium ethoxide (VIII, R = 3-NO₂), characterised by a yellow colour with concentrated sulphuric acid. It has been hydrolysed and simultaneously decarboxylated with alkali to the corresponding cyclohexenone (IX, R = 3-NO₂).

With hydroxylamine hydrochloride, the chalcone forms the corresponding isoxazoline derivative (X, R = 3-NO₂) which gives an orange colour with concentrated sulphuric acid.
SECTION II

EXPERIMENTAL
EXPERIMENTAL

SECTION II

CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE:

2-Hydroxy-4-ethoxyacetophenone (4 gm), dissolved in glacial acetic acid (20 ml) was kept in an ice bath and concentrated nitric acid (24 ml) was added to it dropwise taking care that the temperature should not rise more than 5°C. The mixture was left overnight at the room temperature and diluted with ice water, solid separated was collected washed with water and crystallised from ethanol, light red needles, m.p. 132°C. Yield: 3.4 gm.

Analysis:

Found: C, 53.14%; H, 4.78%; N, 6.18%

C_{10}H_{11}O_{2}N requires C, 53.33%; H, 4.90%; N, 6.22%

CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY

5-NITROACETOPHENONE AND BENZALDEHYDE:

CONDENSATION OF 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE

WITH BENZALDEHYDE:

2'-HYDROXY-4'-ETHOXY-5'-NITROCHALCONE:

2-Hydroxy-4-ethoxy-5-nitroacetophenone (2.48 gm), benzaldehyde (1.17 gm), ethanol (50 ml) and potassium
hydroxide (40 ml : 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture changed from a yellow to red. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The solid separated was filtered, washed with water, dried and crystallised from ethanol, yellow needles, m.p. 152°C. Yield : 3.1 gm.

Analysis:

\[
\text{Found : C, 65.38 \%; H, 4.88 \%; N, 4.28 \%}
\]

\[
\text{C}_{17}H_{15}O_2N \text{ requires } \text{C, 65.18 \%; H, 4.80 \%; N, 4.47 \%}
\]

**BENZOYL DERIVATIVE:**

A mixture of the chalcone (0.5 gm) a drop of pyridine and benzoyl chloride (1.0 ml) was heated on a boiling water-bath for 5 hours. It was then cooled and treated with ice water containing dilute sulphuric acid. The pale yellow solid separated was filtered, washed with dilute sodium bicarbonate solution, to remove benzoic acid if any, and finally with water, dried and crystallised from petroleum ether (40-60), pale yellow needles, m.p. 102°C. Yield : 0.32 gm.

Analysis:

\[
\text{Found : N, 3.21 \%}
\]

\[
\text{C}_{24}H_{19}O_6N \text{ requires } \text{N, 3.36 \%}
\]
CYCLO-ISOMERISATION OF 2'-HYDROXY-4'-ETHOXY-5'-NITROCHALCONE:

7'-ETHOXY-6'-NITROFLAVANONE:

To the mixture of chalcone (0.5 gm) in hot ethanol (40 ml) dilute sulphuric acid (20 ml: 10 per cent) was added and the reaction mixture was refluxed an a boiling water bath for 30 hours. It was then filtered hot and left at the room temperature, ethanol was removed. The brown product obtained was filtered, washed with water, dried and crystallised from ethanol, light brown needles, m.p. 222°C.

Yield: 0.31 gm.

Analysis:

\[
\text{Found: N, 4.52\%} \\
\text{C}_{17}H_{15}O_\text{N} \text{ requires N, 4.47\%}
\]

BROMINATION OF 2'-HYDROXY-4'-ETHOXY-5'-NITROCHALCONE:

2'-HYDROXY-4'-ETHOXY-5'-NITRO \( \alpha : \beta \) DIBROMOCHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and the bromine in acetic acid (5 ml: 10 per cent) was slowly added to it. The reaction mixture was kept in an ice bath for 4 hours. Then it was treated with ice water. The yellow solid separated was filtered, washed with sodium thiosulphate solution, then again with water, dried and crystallised from acetone, yellow needles, m.p. 104°C.

Yield: 0.38 gm.
Analysis:

\[
\text{Found: Br, 33.68 \% ; N, 3.04 \% .}
\]

\[
\text{C}_{17}H_{19}O_{5}NBr_2 \text{ requires Br, 33.83 \% ; N, 2.96 \%.}
\]

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

A mixture of the above dibromochalcone (0.3 gm), potassium iodide (0.3 gm) and dry acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. Acetone was removed and the product obtained was washed with dilute sodium thiosulphate solution, then with water and crystallised from ethanol, brown needles, m.p. and mixed m.p. with original chalcone 152°C.

CYCLISATION OF 2'-HYDROXY-4'-ETHOXY-5'-NITROCHALCONE:

7'-ETHOXY-6-NITROFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate on the \(\alpha:\beta\) Dibromochalcone:

A mixture of dibromochalcone (0.5 gm) anhydrous potassium carbonate (0.5 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 4 hours. It was then filtered hot. Acetone was removed and the product obtained was washed with dilute sodium thiosulphate solution, then with water and crystallised from ethanol, white needles, m.p. 176°C. Yield: 0.21 gm.
(b) **By Selenium Dioxide Oxidation of the Chalcone:**

A mixture of the chalcone (0.5 gm), selenium dioxide (0.5 gm) and n-amyl alcohol (20 ml) was refluxed on an oil bath at 150°C for 24 hours. It was then filtered hot to remove selenium. On cooling the filtrate, a product precipitated was filtered, washed with petrol ether, and crystallised from ethanol, white needles, m.p. 176°C.

Yield : 0.18 gm.

**Analysis:**

- Found : N, 4.21%
- C_{17}H_{13}O_{2}N requires N, 4.50%

**Oxidation of 2'-Hydroxy-4'-ethoxy-5'-Nitrochalcone:**

**7-Ethoxy-6-Nitroflavonol:**

(a) **By Action of Alkaline Hydrogen Peroxide:**

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml : 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml : 20 vol) was added to it and the reaction mixture was kept cool in the ice bath for 4 hours and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to yellow. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1) a pale
yellow solid obtained was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 169°C. Yield: 0.28 gm.

(b) Using Sodium Peroxide in Ethanol Solution:

A mixture of the chalcone (0.5 gm) and sodium peroxide (0.5 gm) in ethanol (20 ml), was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The solid separated was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 169°C. Yield: 0.31 gm.

Analysis:

Found: N, 4.38%  
C_{17}H_{13}O_{6}N requires N, 4.28%

Acetyl Derivative of Flavonol:

A mixture of the flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water and the solid separated was filtered, washed with water, dried and crystallised from ethanol, white needles, m.p. 180°C. Yield: 0.28 gm.

Analysis:

Found: N, 3.68%  
C_{19}H_{15}O_{6}N requires N, 3.79%
CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-4'-ETHOXY-5'-NITROCHALCONE: ETHYL-2-PHENYL-4-(2''-HYDROXY-4''-ETHOXY-5''-NITROPHENYL)-$\Delta^4$-CYCLOHEXENE-6-ONE-1-CARBOXYLATE:

To a solution of sodium (0.2 gm) in ethanol (1.5 ml), ethyl acetoacetate (1.0 ml) and the chalcone (0.5 gm) in ethanol (20 ml) were added. The reaction mixture was refluxed on a boiling water bath for 5 hours. It was then cooled, diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The yellow solid obtained was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 188°C. Yield: 0.37 gm.

Analysis:

Found: N, 3.18%
C$_{23}$H$_{23}$O$_{7}$N requires N, 3.29%

HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL CYCLOHEXENONE CARBOXYLATE: 2-PHENYL-4-(2''-HYDROXY-4''-ETHOXY-5''-NITROPHENYL)-$\Delta^4$-CYCLOHEXENE-6-ONE:

A solution of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml) was mixed with sodium hydroxide (10 ml: 5 per cent) and the mixture was refluxed on a boiling water bath for 5 hours. It was then diluted with cold water (100 ml) and acidified with
dilute hydrochloric acid (1:1). A pale yellow solid separated was filtered, washed with dilute sodium bicarbonate solution and then with water. It was crystallised from ethanol, brownish needles, m.p. 182°C. Yield : 0.31 gm. Analysis:

Found : N, 4.08 %
C₂₀H₁₉O₅N requires N, 3.97 %

ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-4'-ETHOXY-5'-NITROCHALCONE : 3-(2-HYDROXY-4'-ETHOXY-5'-NITROPHENYL)-5-PHENYLSOXAZOLINE :

2'-Hydroxy-4'-ethoxy-5'-nitrochalcone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5 ml) was added to it. The reaction mixture was refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A colourless product obtained was washed with water, dried and crystallised from ethanol, colourless granules, m.p. 222°C. Yield : 0.58 gm. Analysis:

Found : N, 8.23 %
C₁₇H₁₆O₅N₂ requires N, 8.54 %
II CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-
4-ETHOXY-5-NITROACETOPHENONE AND 2-METHOXYBENZALDEHYDE : 
CONDESATION OF 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE 
WITH 2-METHOXYBENZALDEHYDE : 
2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-NITROCHALCONE : 

2-Hydroxy-4-ethoxy-5-nitroacetophenone (2.48 gm), 2-methoxybenzaldehyde (1.49 gm), ethanol (50 ml) and potassium hydroxide (40 ml : 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture was changed from a yellow to red. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The solid separated was filtered, washed with water, dried and crystallised from ethanol, pale brown needles, m.p. 186°C. Yield : 3.5 gm.

Analysis:

Found : C, 63.18 % ; H, 4.90 % ; N, 4.12 %
C₁₈H₁₇O₆N requires C, 62.98 % ; H, 4.96 % ; N, 4.08 %

BENZOYL DERIVATIVE :

The chalcone (0.5 gm) a drop of pyridine and benzoyl chloride (1.0 ml) were mixed and the reaction mixture was heated on a boiling water bath for 5 hours. It was then
cooled and treated with ice water containing dilute sulphuric acid. The pale yellow solid separated was filtered, washed with dilute sodium bicarbonate solution to remove benzoic acid if any, and finally with water, dried and crystallised from petroleum ether (40-60), pale yellow needles, m.p. 110°C. Yield : 0.39 gm.

Analysis:

Found : N, 3.28 %

C₂₉H₂₁O₇N requires N, 3.13 %

**CYCLO-ISOMERISATION OF 2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-NITROCHALCONE : 7-ETHOXY-6-NITRO-2'-METHOXYFLAVANONE :**

To the solution of chalcone (0.5 gm) in ethanol (40 ml), dilute sulphuric acid (20 ml : 10 per cent) was added and the reaction mixture was refluxed on a boiling water bath for 30 hours. It was then filtered hot and ethanol was removed. The brown colour product obtained was filtered, washed with water, dried and crystallised from ethanol, brown needles, m.p. 142°C. Yield : 0.31 gm.

Analysis:

Found : N, 4.21 %

C₁₅H₁₂O₆N requires N, 4.08 %
BROMINATION OF 2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-NITROCHALCONE:  

2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-NITROCHALCONE:  

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and the bromine in acetic acid (5 ml : 10 per cent) was added to it. The reaction mixture was kept in an ice bath for 4 hours, it was then treated with ice water. The yellow solid separated was filtered, washed with dilute sodium thiosulphate solution, then again with water, dried and crystallised from acetone, yellow needles, m.p. 178°C.  

Yield : 0.32 gm.  

Analysis:  

Found : Br, 31.70 %; N, 2.51 %  

C_{15}H_{17}O_{6}NBr_{2} requires Br, 31.81 %; N, 2.78 %  

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:  

A mixture of the above dibromochalcone (0.3 gm), potassium iodide (0.3 gm) and dry acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. Acetone was removed and the product obtained was washed with dilute sodium thiosulphate solution, then with water and crystallised from ethanol, brown needles, m.p. and mixed m.p. with original chalcone 186°C.
CYCLISATION OF 2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-NITROCHALCONE:
7-ETHOXY-6-NITRO-2'-METHOXYFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate

on the α : β Dibromochalcone:

A mixture of dibromochalcone (0.5 gm), anhydrous potassium carbonate (0.5 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 4 hours. It was then filtered hot. Acetone was removed and the product obtained was washed with water and crystallised from ethanol, white needles, m.p. 270°C. Yield: 0.23 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

A mixture of the chalcone (0.5 gm), selenium dioxide (0.5 gm) and n-amyl alcohol (20 ml) was refluxed on an oil bath at 150°C for 24 hours. It was then filtered hot to remove selenium. On cooling the filtrate, a product precipitated was filtered, washed with petroleum ether (40-60) and crystallised from ethanol, white needles, m.p. 270°C. Yield: 0.17 gm.

Analysis:

Found: N, 4.28 %

C_{18}H_{15}O_{6}N requires N, 4.10 %
OXIDATION OF 2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-NITROCHALCONE:

7'-ETHOXY-6-NITRO-2'-METHOXYFLAVONOL:

(a) By Action of Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was mixed with sodium hydroxide (20 ml : 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml : 20 vol) was added and the reaction mixture was kept cool in the ice bath for 4 hours and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to yellow. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1). A pale yellow solid obtained was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 210°C. Yield: 0.31 gm.

(b) Using Sodium Peroxide in Ethanol Solution:

A mixture of the chalcone (0.5 gm) and sodium peroxide (0.5 gm) in ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The solid separated was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 210°C. Yield: 0.38 gm.
Analysis:

Found: N, 3.69%

C_{18}H_{15}O_{7}N requires N, 3.92%

ACETYL DERIVATIVE OF FLAVONOL:

A mixture of the flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water and the solid separated was filtered, washed with water, dried and crystallised from ethanol, white needles, m.p. 198°C. Yield: 0.21 gm.

Analysis:

Found: N, 3.68%

C_{20}H_{17}O_{8}N requires N, 3.50%

CONDENSATION OF ETHYL ACETOACETATE WITH: 2'-HYDROXY-2'-METHOXY-2'-ETHOXY-5'-NITROCHALCONE:

ETHYL-2(2'-METHOXYPHENYL)-4-(2''-HYDROXY-4''-ETHOXY-5''-NITROPHENYL)-\Delta^1-CYCLOHEXENE-6-ONE-1-CARBOXYLATE:

To a solution of sodium (0.2 gm) in ethanol (20 ml), ethyl acetoacetate (1.0 ml) and the chalcone (0.5 gm) in ethanol (20 ml) was added. The reaction mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and
diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The pale yellow solid obtained was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 192°C. Yield: 0.28 gm. Analysis:

\[ \text{Found: N, 3.67%} \]
\[ \text{C}_{24}\text{H}_{25}\text{O}_{8}\text{N requires N, 3.77%} \]

**HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE**

**ETHYL CYCLOHEXENONE CARBOXYLATE : 2(2'-METHOXYPHENYL)-4-(2''-HYDROXY-4''-ETHOXY-5''-NITROPHENYL)-\( \Delta^4 \)-CYCLOHEXENE-6-ONE :**

A solution of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml) and sodium hydroxide (10 ml : 5 per cent) were refluxed on a boiling water bath for 5 hours. It was then diluted with cold water (100 ml) and acidified by dilute hydrochloric acid (1:1). A pale yellow solid separated was filtered, washed with dilute sodium bicarbonate solution and then with water. It was crystallised from ethanol, brownish needles, m.p. 320°C. Yield: 0.38 gm. Analysis:

\[ \text{Found: N, 3.46%} \]
\[ \text{C}_{21}\text{H}_{21}\text{O}_{6}\text{N requires N, 3.66%} \]
ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-NITROCHALCONE:

3-(2-HYDROXY-4-ETHOXY-5-NITROPHENYL)-5-(2-METHOXYPHENYL)-ISOXAZOLINE:

2'-Hydroxy-2-methoxy-4'-ethoxy-5'-nitrochalcone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added. The reaction mixture was refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A colourless product obtained was filtered, washed with water, dried and crystallised from ethanol, colourless needles. m.p. 175°C. Yield : 0.48 gm.

Analysis:

Found : N, 7.39 %

C₁₈H₁₈O₆N₂ requires N, 7.28 %
III CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE AND VANILLIN :

CONDENSATION OF : 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE

WITH VANILLIN : 2'-4-DIHYDROXY-3-METHOXY-4'-ETHOXY-5'-

NITROCHALCONE :

2-Hydroxy-4-ethoxy-5-nitroacetophenone (2.48 gm), vanillin (1.67 gm), ethanol (50 ml) and potassium hydroxide (40 ml : 40 per cent) were mixed in a tightly corked flask. The reaction mixture was left at the room temperature for about 24 hours. The colour of the reaction mixture changed from a yellow to red. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The solid separated was filtered, washed with water dried and crystallised from ethanol, pale brown needles, m.p. 142°C. Yield : 3.6 gm.

Analysis:

Found : C, 60.21 % ; H, 4.70 % ; N, 3.78 %

C$_{18}$H$_{17}$O$_7$N requires C, 60.17 % ; H, 4.81 % ; N, 3.89 %

BENZOYL DERIVATIVE :

A mixture of the chalcone (0.5 gm), a drop of pyridine, and benzoyl chloride (1.0 ml) was refluxed on a boiling water
bath for 5 hours. Then the reaction mixture was cooled and poured in cold water containing dilute sulphuric acid. The pale yellow product obtained was filtered, washed with dilute sodium bicarbonate solution to remove benzoic acid if any and finally with water, dried and crystallised from petroleum ether (40-60), colourless needles, m.p. 105°C. Yield: 0.42 gm.

Analysis:

Found: N, 2.63%

\[ C_{32}H_{25}O_{9}N \] requires N, 2.52%

CYCLO-ISOMERISATION OF 2′-4 DIHYDROXY-3-METHOXY-4′-ETHOXY-5′-NITROCHALCONE:

7-ETHOXY-6-NITRO-3′-METHOXY-4′-HYDROXYFLAVANONE:

To the mixture of chalcone (0.5 gm) in hot ethanol (40 ml) dilute sulphuric acid (20 ml; 10 per cent) was added and the reaction mixture was refluxed on a boiling water bath for 30 hours. It was then filtered hot and left at the room temperature, ethanol was removed by evaporation. The brown colour product obtained was filtered, washed with water, dried and crystallised from ethanol, brown needles, m.p. 122°C. Yield: 0.28 gm.

Analysis:

Found: N, 3.78%

\[ C_{18}H_{17}O_{7}N \] requires N, 3.89%
BROMINATION OF 2'-4-DIHYDROXY-3-METHOXY-4'-ETHOXY-5'-NITROCHALCONE:

2'-4-DIHYDROXY-3-METHOXY-4'-ETHOXY-5'-NITRO-\( \alpha \):\( \beta \)

DIBROMOCHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and the bromine in acetic acid (5 ml: 10 per cent) was slowly added to it with constant stirring. The reaction mixture was kept cooled for 4 hours and then it was poured in ice water. The solid separated was filtered, washed with sodium thiosulphate solution, then again with water, dried and crystallised from acetone, yellow needles, m.p. 145°C. Yield: 0.39 gm.

Analysis:

Found: N, 2.59%; Br, 30.58%

\( \text{C}_{18}\text{H}_{17}\text{O}_{7}\text{NBr}_2 \) requires N, 2.69%; Br, 30.82%

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

A mixture of the above dibromochalcone (0.3 gm), potassium iodide (0.3 gm) and dry acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. Acetone was removed and the product obtained was washed with dilute sodium thiosulphate solution, then with water and crystallised from ethanol, brown needles, m.p. and mixed m.p. with original chalcone 142°C.
CYCLISATION OF 2β-DIHYDROXY-3-METHOXY-4β-ETHOXY-5β-
NITROCHALCONE; 7-ETHOXY-6-NITRO-3β-METHOXY-4β-HYDROXYFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate on the α:β Dibromochalcone:

A mixture of the dibromochalcone (0.5 gm), anhydrous potassium carbonate (0.5 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 4 hours. It was then filtered hot and acetone was removed. The product obtained was washed with dilute sodium thiosulphate solution, then with water and crystallised from ethanol, yellowish needles, m.p. 195°C. Yield: 0.28 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

A mixture of the chalcone (0.5 gm), selenium dioxide (0.5 gm) and dry n-amyl alcohol (20 ml) was refluxed on an oil bath at 150°C for 24 hours. It was then filtered hot to remove selenium. On cooling the filtrate a product precipitated was filtered, washed with petrol ether and crystallised from ethanol, yellowish needles, m.p. 195°C. Yield: 0.32 gm.

Analysis:

Found: N, 3.13%

C₁₈H₁₅O₇N requires N, 3.06%
OXIDATION OF 2'-4-DIHYDROXY-3-METHOXY-4'-ETHOXY-5'-NITROCHALCONS: 7-ETHOXY-6-NITRO-3'-METHOXY-4'-HYDROXYFLAVONOL:

(a) By Action of Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml: 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml: 20 vol) was added, and the reaction mixture was kept cool in the ice bath for 4 hours and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to yellow. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1). A pale yellow solid obtained was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 192°C. Yield: 0.29 gm.

(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of the chalcone (0.5 gm) and sodium peroxide (0.5 gm) in ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The solid separated was filtered, washed with water, dried, and crystallised from ethanol, pale yellow granules, m.p. 192°C. Yield: 0.31 gm.
Analysis:

Found : N, 3.37 %

C_{18}H_{15}O_{8}N requires N, 3.75 %

ACETYL DERIVATIVE OF FLAVONOL:

A mixture of the flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was refluxed on a boiling water bath for 4 hours. It was then treated with ice water and the solid separated was filtered, washed with water, dried and crystallised from ethanol; white needles, m.p. 198°C. Yield : 0.29 gm.

Analysis:

Found : N, 3.18 %

C_{22}H_{19}O_{10}N requires N, 3.37 %

CONDENSATION OF ETHYL ACETOACETATE WITH 2'-4'-DIHYDROXY-3'-METHOXY-4'-ETHOXY-5'-NITRO-N-ETHYLCYCLOHEXENE-6-ONE-1-CARBOXYLATE:

To a solution of sodium (0.2 gm) in absolute ethanol (15 ml), ethyl acetoacetate (1.0 ml) and the chalcone (0.5 gm) in ethanol (20 ml) were added. The reaction mixture was refluxed on a boiling water bath for 5 hours. It was then
cooled and diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The yellowish solid obtained was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 198°C.

Yield: 0.41 gm.

Analysis:

Found: N, 3.04%

C_{24}H_{25}O_7N requires N, 2.93%

HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE

ETHYL CYCLOHEXENONONE CARBOXYLATE: 2(3'-METHOXY-4'-HYDROXYPHENYL)-4-(2″-HYDROXY-4″-ETHOXY-5″-NITROPHENYL)-\(\Delta^1\)-CYCLOHEXENE-6-ONE:

To a solution of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml), sodium hydroxide (10 ml: 5 per cent) was added and the mixture was refluxed on a boiling water bath for 5 hours. It was then diluted with cold water, and acidified by dilute hydrochloric acid (1:1). A pale yellow solid separated was filtered washed with dilute sodium bicarbonate solution and then with water, dried and crystallised from ethanol, white needles, m.p. 338°C. Yield: 0.28 gm.

Analysis:

Found: N, 3.63%

C_{21}H_{21}O_7N requires N, 3.47%
ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-4 DIHYDROXY-3-METHOXY-4'-ETHOXY-5'-NITROCHalcone : 3-(2-HYDROXY-4-ETHOXY-5-NITROPHENYL)-5-(3-METHOXY-4-HYDROXYPHENYL)-ISOXAZOLINE :

2'-4 Dihydroxy-3-methoxy-4'-ethoxy-5'-nitrochalcone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added to it. The reaction mixture was refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A brown product obtained, was washed with water, dried and crystallised from ethanol, brown needles, m.p. 175°C. Yield : 0.61 gm.

Analysis:

Found : N, 7.21 %

C_{18}H_{18}O_{7}N_2 requires N, 7.49 %

IV CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE AND 4-CHLOROBENZALDEHYDE :

CONDENSATION OF 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE WITH 4-CHLOROBENZALDEHYDE : 2'-HYDROXY-4-CHLORO-4'-ETHOXY-5'-NITROCHalcone :

2-Hydroxy-4-ethoxy-5-nitroacetophenone (2.48 gm), 4-chlorobenzaldehyde (1.54 gm), ethanol (50 ml) and
potassium hydroxide (40 ml : 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture changed from a yellow to red. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). A yellow solid separated was filtered, washed with water, dried and crystallised from ethanol, yellow plates, m.p. 165°C. Yield : 3.6 gm.

Analysis:

\[
\text{Found : } C, 58.94\% ; H, 4.11\% ; N, 4.16\% ; Cl, 10.13\% \\
C_{17}H_{14}O_5NCl \text{ requires } C, 58.72\% ; H, 4.03\% ; N, 4.03\% ; Cl, 10.22\%
\]

**BENZOYL DERIVATIVE :**

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 5 hours. It was then cooled and treated with ice water containing dilute sulphuric acid. The white solid separated was filtered, washed with dilute sodium bicarbonate solution and water, dried and crystallised from petroleum ether (40-60), white needles, m.p. 108°C. Yield : 0.41 gm.

Analysis:

\[
\text{Found : } N, 3.08\% ; Cl, 7.79\% \\
C_{24}H_{18}O_6NCl \text{ requires } N, 3.10\% ; Cl, 7.86\%
\]
CYCLO-ISOMERISATION OF 2'-HYDROXY-4'-CHLORO-4'-ETHOXY-5'-NITROCHALCONE : 7-ETHOXY-6-NITRO-4'-CHLOROFLAVANONE :

To the hot solution of chalcone (0.5 gm) in ethanol (40 ml), dilute sulphuric acid (20 ml: 10 per cent) was added. The precipitated solid was dissolved in more ethanol (20 ml) and the clear solution was refluxed on a boiling water bath for 30 hours. Excess of ethanol was distilled off and the residual solution was then filtered hot and left at the room temperature. A brown solid separated was filtered, washed with water, dried and crystallised from ethanol, pale brown needles, m.p. 175°C. Yield: 0.26 gm.

Analysis:

Found: N, 4.04%; Cl, 10.41%

C$_{17}$H$_{14}$O$_5$NCl requires N, 4.03%; Cl, 10.22%

BROMINATION OF 2'-HYDROXY-4'-CHLORO-4'-ETHOXY-5'-NITROCHALCONE :

2'-HYDROXY-4'-CHLORO-4'-ETHOXY-5'-NITRO-α:β-DIBROMOCHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and bromine in acetic acid (5 ml: 10 per cent) was added to it. The mixture was kept cool for 4 hours, then poured in ice water, a yellow solid obtained was filtered washed with dilute sodium thiosulphate solution and finally with water, dried and crystallised from acetone, yellow needles, m.p. 120°C. Yield: 0.36 gm.
Analysis:

Found: N, 2.81%; Halogen, 38.31%

C_{17}H_{14}O_5NBr_2Cl requires N, 2.75%; Halogen, 38.52%

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

To the solution of the above dibromochalcone (0.3 gm) in dry acetone (20 ml), potassium iodide (0.3 gm) was added and the reaction mixture was refluxed on a water bath at 70°C for 3 hours. The solution was then filtered hot and acetone was removed. The yellow solid obtained was washed with dilute sodium thiosulphate solution and then with water, dried and crystallised from ethanol, m.p. and mixed m.p. with original chalcone 165°C.

CYCLISATION OF 2'-HYDROXY-4'-CHLORO-5'-ETHOXY-6'-NITROCHALCONE:

7'-ETHOXY-6'-NITRO-4'-CHLOROFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate on the \( \alpha : \beta \) Dibromochalcone:

The dibromochalcone (0.5 gm) in acetone (20 ml) was treated with anhydrous potassium carbonate (0.5 gm) and the reaction mixture was then refluxed on a water bath at 70°C for 4 hours. The solution was then filtered hot and acetone was removed. A pale brown solid obtained was washed with
water, dried and crystallised from ethanol, pale brown granules, m.p. 198°C. Yield: 0.21 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

To a solution of chalcone (0.5 gm) in n-amyl alcohol (20 ml), selenium dioxide (0.5 gm) was added and the reaction mixture was refluxed on an oil bath at 150°C for 24 hours. Selenium was then filtered off from the hot reaction mixture, and n-amyl alcohol was removed by steam distillation. The brown solid obtained was washed with petroleum ether (40-60) to remove traces of alcohol and crystallised from ethanol, pale brown granules, m.p. 198°C. Yield: 0.23 gm.

Analysis:

Found: N, 4.21%; Cl. 10.58%

C₁₇H₁₂O₅NCl requires N, 4.05%; Cl. 10.29%

Oxidation of 7'-Ethoxy-4'-Chloro-5'-Nitrochalcone:

7'-Ethoxy-6-Nitro-4'-Chloroflavonol:

(a) By Action of Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml: 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml: 20 vol) was added to it and the reaction mixture was kept in the ice bath for 4 hours, and then left over night at the
room temperature. The colour of the reaction mixture changed from an orange to yellow. It was then treated with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 212°C. Yield : 0.31 gm.

(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of the chalcone (0.5 gm), sodium peroxide (0.5 gm) and ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The pale yellow solid separated was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 212°C. Yield : 0.28 gm.

Analysis:

Found : N, 3.61 %; Cl. 9.72 %

C_{17}H_{12}O_6NCl requires N, 3.87 %; Cl, 9.82 %

Acetyl Derivative of Flavonol:

A mixture of the flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine, was heated on a boiling water bath for 4 hours. It was then diluted with ice water. The white solid separated was filtered, washed with water, and crystallised from ethanol, white needles, m.p. 158°C. Yield : 0.21 gm.
Analysis:

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<tr>
<th>Found</th>
<th>N, 3.71%</th>
<th>Cl, 8.51%</th>
</tr>
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<tr>
<td>C_{19}H_{14}O_{7}NCl requires</td>
<td>N, 3.43%</td>
<td>Cl, 8.77%</td>
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</tbody>
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CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-4'-CHLORO-4'-ETHOXY-5'-NITROCHALCONE : ETHYL-2-(4'-CHLOROPHENYL)-4-
(2''-HYDROXY-4''-ETHOXY-5''-NITROPHENYL)-Δ^4-CYCLOHEXENE-6-
ONE-1-CARBOXYLATE :

Sodium metal (0.2 gm) was dissolved in absolute ethanol (15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml). To this solution, ethyl acetoacetate (1.0 ml) was added and the mixture was refluxed on a boiling water bath for 4 hours. Then solution was poured in ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was filtered, washed with water, dried and crystallised from ethanol, yellow needles, m.p. 185°C.

Yield : 0.32 gm.

Analysis:

<table>
<thead>
<tr>
<th>Found</th>
<th>N, 3.18%</th>
<th>Cl, 7.29%</th>
</tr>
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<tbody>
<tr>
<td>C_{23}H_{22}O_{7}NCl requires</td>
<td>N, 3.04%</td>
<td>Cl, 7.74%</td>
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</table>
HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL CYCLOHEXENONE CARBOXYLATE : 2- (4'-CHLOROPHENYL)-4-(2''-HYDROXY-4''-ETHOXY-5''-NITROPHENYL)-Δ^4-CYCLOHEXENE-6-ONE :

A mixture of the above diphenyl cyclohexenone derivative (0.5 gm), ethanol (20 ml), and sodium hydroxide (10 ml : 5 per cent) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). A yellow solid separated was filtered, washed with dilute sodium bicarbonate solution and then with water, dried and crystallised from ethanol, pale yellow granules, m.p. 198°C. Yield: 0.21 gm.

Analysis:

Found: N, 3.31%; Cl, 9.29%
C_{20}H_{18}O_{5}NCl requires N, 3.58%; Cl, 9.16%

ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-4'-CHLORO-4'-ETHOXY-5'-NITROCHALCONE : 3-(2'-HYDROXY-4'-ETHOXY-5'-NITROPHENYL)-5-(4'-CHLOROPHENYL)-ISOXAZOLINE :

2'-Hydroxy-4'-chloro-4'-ethoxy-5'-nitrochalcone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added to it. The reaction mixture was refluxed on a boiling water bath
for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A colourless product obtained, was washed with water, dried and crystallised from ethanol, white needles, m.p. 168°C. Yield: 0.41 gm.

Analysis:

\[
\text{Found: N, 7.50 \% ; Cl, 9.99 \%} \\
\text{C}_{17} \text{H}_{15} \text{O}_{5} \text{N}_2 \text{Cl requires N, 7.72 \%; Cl, 9.79 \%}
\]

V CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE AND 4-NITROBENZALDEHYDE:

CONDENSATION OF 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE WITH 4-NITROBENZALDEHYDE: 2'-HYDROXY-4'-ETHOXY-4,5'-DINITROCHALCONE:

2-Hydroxy-4-ethoxy-5-nitroacetophenone (2.48 gm), 4-nitrobenzaldehyde (1.66 gm), ethanol (50 ml) and potassium hydroxide (40 ml : 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture changed from a yellow to red. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). A brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown needles, m.p. 242°C. Yield: 3.6 gm.
Analysis:

Found: C, 56.81%; H, 3.80%; N, 7.80%

C\textsubscript{17}H\textsubscript{11}O\textsubscript{7}N\textsubscript{2} requires C, 56.98%; H, 3.91%; N, 7.82%

BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 5 hours. It was then treated with ice water containing dilute sulphuric acid. The solid separated was filtered, washed with dilute sodium bicarbonate solution, then with water, dried and crystallised from petroleum ether (40-60), white needles, m.p. 89°C. Yield: 0.38 gm.

Analysis:

Found: N, 6.29%

C\textsubscript{24}H\textsubscript{18}O\textsubscript{8}N\textsubscript{2} requires N, 6.06%

CYCLO-ISOMERISATION OF 2'-HYDROXY-4'-ETHOXY-5'-DINITRO-CHALCONE : 7-ETHOXY-6-4' DINITROFLAVANONE:

To the hot solution of chalcone (0.5 gm) in ethanol (40 ml), dilute sulphuric acid (20 ml : 10 per cent) was added and the reaction mixture was refluxed on a boiling water bath for 30 hours. Excess of ethanol was distilled off and the residual solution was then filtered hot and left
at the room temperature, a pale brown solid separated, was filtered, washed with water, dried and crystallised from ethanol, pale brown needles, m.p. 198°C. Yield: 0.21 gm. Analysis:

Found: N, 7.58%

C₁₇H₁₄O₂N₂ requires N, 7.82%

BROMINATION OF 2'-HYDROXY-4'-ETHOXY-5'-DINITROCHALCONE:

2'-HYDROXY-4'-ETHOXY-5'-DINITRO-α : β DIBROMOCHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30.0 ml) and the bromine in acetic acid (5 ml: 10 per cent) was added to it. The reaction mixture was kept in an ice bath for 4 hours and then poured in ice water. The yellow solid separated was filtered washed with sodium thiosulphate solution, then with water, dried and crystallised from acetone, yellow needles, m.p. 190°C. Yield: 0.31 gm. Analysis:

Found: N, 5.61%; Br, 30.69%

C₁₇H₁₄O₂N₂Br₂ requires N, 5.40%; Br, 30.89%

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

The mixture of the above dibromochalcone (0.3 gm), dry acetone (20 ml) and potassium iodide (0.3 gm) was
refluxed on a water bath at 70°C for 3 hours. Acetone was removed. The brown solid obtained was filtered, washed with dilute sodium thiosulphate solution, then with water, dried and crystallised from ethanol, brown needles, m.p. 242°C.

**CYCLISATION OF 2'-HYDROXY-4'-ETHOXY-4'-5'-DINITROCHALCONE:**

7'-ETHOXY-6'-DINITROFLAVONE:

(a) **By Action of Acetone and Anhydrous Potassium Carbonate**

on the \( \alpha: \beta \) Dibromochalcone:

The dibromochalcone (0.5 gm) in acetone (20 ml) was mixed with anhydrous potassium carbonate (0.5 gm). The reaction mixture was then refluxed on a water bath at 70°C for 4 hours. The solution was then filtered hot, and acetone was removed, a pale brown solid was obtained, was washed with water, dried and crystallised from ethanol, brown needles, m.p. 180°C. Yield: 0.29 gm.

(b) **By Selenium Dioxide Oxidation of the Chalcone:**

To a solution of chalcone (0.5 gm) in n-amyl alcohol (20 ml), selenium dioxide (0.5 gm) was added and the reaction mixture was refluxed on an oil bath at 150°C for 24 hours. Selenium was then filtered off from the hot reaction mixture. On cooling a brown solid obtained was washed with petroleum
ether to remove alcohol and crystallised from ethanol, brown needles, m.p. 180°C. Yield: 0.18 gm.

Analysis:

Found: N, 7.56%  
C_{17}H_{12}O_7N_2 requires N, 7.86%  

OXIDATION OF 2'-HYDROXY-4'-ETHOXY-4'-5'-DINITROCHALCONE:  
7'-ETHOXY-6'-4'-DINITROFLAVONOL:

(a) By Action of Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml: 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml: 20 vol) was added, and the reaction mixture kept cool in the ice bath for 4 hours, and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to yellowish. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid obtained was filtered, washed with water, dried and crystallised from ethanol, yellowish brown needles, m.p. 198°C. Yield: 0.31 gm.

(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of chalcone (0.5 gm) and sodium peroxide (0.5 gm) in ethanol (20 ml) was refluxed on a boiling water
bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was filtered, washed with water and crystallised from ethanol, yellow needles, m.p. 198°C. Yield: 0.32 gm.

Analysis:

Found: N, 7.62%

C₁₇H₁₂O₈N₂ requires N, 7.53%

ACETYL DERIVATIVE OF FLAVONOL:

A mixture of flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was refluxed on a boiling water bath for 4 hours. It was then treated with ice water, and the white solid separated was filtered washed with water, dried and crystallised from ethanol, white granules, m.p. 118°C. Yield: 0.28 gm.

Analysis:

Found: N, 6.89%

C₁₉H₁₄O₉N₂ requires N, 6.75%
CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-4'-ETHOXY-4'-5'-DINITROCHALCONE : ETHYL-2-(4'-NITROPHENYL)-4-(2''-HYDROXY-4''ETHOXY-5''-NITROPHENYL)-Δ^4-CYCLOHEXENE-6-ONE-1-CARBOXYLATE:

Sodium metal (0.2 gm) was dissolved in absolute ethanol (0.5 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml). To this solution ethyl acetoacetate (1 ml) was added and the mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and diluted with ice water (100 ml), then acidified with dilute hydrochloric acid (1:1). The yellow solid separated was filtered, washed with water, dried and crystallized from ethanol, pale yellow granules, m.p. 245°C. Yield: 0.36 gm.

Analysis:

Found: N, 5.78 %

C_{23}H_{22}O_{9}N_2 requires N, 5.96 %

HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL CYCLOHEXENONE CARBOXYLATE : 2-(4'-NITROPHENYL)-4-(2''-HYDROXY-4''ETHOXY-5''-NITROPHENYL)-Δ^4-CYCLOHEXENE-6-ONE:

A solution of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml) was mixed with sodium hydroxide (10 ml : 5 per cent) and the mixture was refluxed on a boiling water bath for 5 hours. It was then
diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). A pale brown solid separated was filtered, washed with dilute sodium bicarbonate solution and then with water, dried and crystallised from ethanol, brown needles, m.p. 298°C. Yield: 0.28 gm.

Analysis:

Found: N, 7.12%

C_{20}H_{18}O_{7}N_{2} requires N, 7.04%

ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-4'-ETHOXY-4-5'-DINITROCHALCONE: 3-(2-HYDROXY-4-ETHOXY-5-NITROPHENYL)-5-(4-NITROPHENYL)-ISOXAZOLINE:

2'-Hydroxy-4'-ethoxy-4-5'-dinitrochalcone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added to it. The reaction mixture was refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A brown product obtained was washed with water, dried and crystallised from ethanol, brown needles, m.p. 195°C. Yield: 0.61 gm.

Analysis:

Found: N, 7.21%

C_{17}H_{15}O_{7}N_{3} requires N, 7.51%
VI CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-
ETHOXY-5-NITROACETOPHENONE AND 4-METHOXYBENZALDEHYDE:

CONDENSATION OF 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE
WITH 4-METHOXYBENZALDEHYDE: 2'-HYDROXY-4-METHOXY-5-
ETHOXY-5'-NITROCHALCONE:

2-Hydroxy-4-ethoxy-5-nitroacetophenone (2.48 gm),
4-methoxybenzaldehyde (1.49 gm), ethanol (50 ml) and potassium
hydroxide (40 ml : 40 per cent) were mixed in a tightly
corked flask. The reaction mixture was kept at the room
temperature for 24 hours. The colour of the reaction mixture
changed from a yellow to red. It was then diluted with ice
water and acidified with dilute hydrochloric acid (1:1).
The solid separated was filtered, washed with water and
crystallised from ethanol, yellow plates, m.p. 144°C.
Yield: 3.2 gm.

Analysis:

Found: C, 63.23 %; H, 4.78 %; N, 4.02 %

C_{10}H_{17}O_{4}N requires C, 62.98 %; H, 4.96 %; N, 4.08 %

BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm) a drop of pyridine
and benzoyl chloride (1.0 ml) was heated on a boiling water
bath for 5 hours. It was then cooled and treated with ice
water containing dilute sulphuric acid. The white solid separated was filtered, washed with dilute sodium bicarbonate solution, to remove benzoic acid if any, and finally with water, dried and crystallised from petroleum ether (40-60), white needles, m.p. 126°C. Yield: 0.33 gm.

Analysis:

Found: N, 3.34 %
\[ C_{25}H_{21}O_7N \] requires N, 3.13 %

CYCLO-ISOMERISATION OF 2'-HYDROXY-4'-METHOXY-4'-ETHOXY-5'-NITROCHALCONE: 7'-ETHOXY-6-NITRO-4'-METHOXYFLAVANONE:

To the mixture of chalcone (0.5 gm) in hot ethanol (40 ml) dilute sulphuric acid (20 ml: 10 per cent) was added and the reaction mixture was refluxed on a boiling water bath for 30 hours. It was then filtered hot and ethanol was removed. The brown colour product obtained was filtered, washed with water, dried and crystallised from ethanol, brown needles, m.p. 115°C. Yield: 0.21 gm.

Analysis:

Found: N, 4.17 %
\[ C_{18}H_{17}O_6N \] requires N, 4.08 %
BROMINATION OF 2'-HYDROXY-1'-METHOXY-4'-ETHOXY-5'-NITROCHALCONE:

2'-HYDROXY-1'-METHOXY-4'-ETHOXY-5'-NITRO-α : β-DIBROMOCHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and the bromine in acetic acid (5 ml: 10 per cent) was added to it. The reaction mixture was kept in an ice bath for 4 hours. Then it was treated with ice water. The yellow solid separated was filtered, washed with dilute sodium thiosulphate solution, then again with water, dried and crystallised from acetone, yellow needles, m.p. 124°C. Yield: 0.36 mg.

Analysis:

Found: N, 2.89%; Br, 31.59%

C_{18}H_{17}O_{6}NBr_{2} requires N, 2.78%; Br, 31.81%

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

A mixture of the above dibromochalcone (0.3 gm), potassium iodide (0.3 gm) and dry acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. Acetone was removed by evaporation and the product obtained was washed with dilute sodium thiosulphate solution, then with water and crystallised from ethanol, yellow plates m.p. and mixed m.p. with original chalcone 144°C.
CYCLISATION OF 2'-HYDROXY-5-METHOXY-5'-ETHOXY-5'-NITROCHALCONE:

7-ETHOXY-6-NITRO-4'-METHOXYFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate

on the α:β Dibromochalcone:

A mixture of dibromochalcone (0.5 gm), anhydrous potassium carbonate (0.5 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 4 hours. It was then filtered hot. Acetone was removed and the product obtained was washed with water and crystallised from ethanol, pale brown plates, m.p. 210°C. Yield: 0.25 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

A mixture of the chalcone (0.5 gm), selenium dioxide (0.5 gm) and n-amyl alcohol (20 ml) was refluxed on an oil bath at 150°C for 24 hours. It was then filtered hot to remove selenium. On cooling the filtrate, a product precipitated was filtered, washed with petroleum ether (40-60) and crystallised from ethanol, pale brown plates, m.p. 210°C. Yield: 0.21 gm.

Analysis:

Found: N, 4.36 %
C_{18}H_{15}O_6N requires N, 4.10 %
OXIDATION OF 2'-HYDROXY-4'-METHOXY-4'-ETHOXY-5'-NITROCHALCONE:
7'-ETHOXY-6'-NITRO-4'-METHOXYFLAVONOL:

(a) By Action of Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml : 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml : 20 vol) was added to it and the reaction mixture was kept cool in the ice bath for 4 hours and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to yellow. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1) a pale yellow solid obtained was filtered washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 210°C. Yield: 0.28 gm.

(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of the chalcone (0.5 gm) and sodium peroxide (0.5 gm) in ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The solid separated was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 210°C. Yield: 0.18 gm.

Analysis:

Found: N, 3.68 %
C_{18}H_{15}O_{7}N requires N, 3.92 %
ACETYL DERIVATIVE OF FLAVONOL :

A mixture of the flavonol (0.5 gtm), acetic anhydride (1.0 ml) and a drop of pyridine was refluxed on a boiling water bath for 4 hours. It was then treated with ice water and solid separated was filtered, washed with water, dried and crystallised from ethanol, yellowish needles, m.p. 133°C. Yield : 0.18 gm.

Analysis:

Found : N, 3.29 %
C<sub>20</sub>H<sub>17</sub>O<sub>8</sub>N requires N, 3.50 %

CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-4'-METHOXY-4'-ETHOXY-5'-NITROCHALCONE : ETHYL-2(4'-METHOXYPHENYL)-4-(2'-HYDROXY-4''-ETHOXY-5''-NITROPHENYL)-Δ³'-CYCLOHEXENE-6-ONE-1-CARBOXYLATE :

To a solution of sodium (0.2 gm) in ethanol (15 ml), ethyl acetoacetate (1.0 ml) and the chalcone (0.5 gm) in ethanol (20 ml) were added. The reaction mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The pale yellow solid obtained was filtered, washed with water, dried and crystallised from ethanol, pale brown granules, m.p. 149°C. Yield : 0.21 gm.
HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL CYCLOHEXENONE CARBOXYLATE : 2(4'-METHOXYPHENYL)-4-
(2''-HYDROXY-4''-ETHOXY-5''-NITROPHENYL)-Δ4-CYCLOHEXENE-6-ONE:

A solution of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml) was mixed with sodium hydroxide (10 ml : 5 per cent) and the mixture was refluxed on a boiling water bath for 5 hours. It was then diluted with cold water (100 ml) and acidified with dilute hydrochloric acid (1:1). A brown solid separated was filtered, washed with dilute sodium bicarbonate solution and then with water, dried and crystallised from ethanol, brown plates, m.p. 165°C. Yield : 0.18 gm.

Analysis:

Found : N, 3.51 %
C21H21O6N requires N, 3.66 %

ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2''-HYDROXY-4''-METHOXY-
4'-ETHOXY-5''-NITROCHALCONE : 3-(2-HYDROXY-4''-ETHOXY-5''-NITROPHENYL)-5 (4'-METHOXYPHENYL)-ISOXAZOLE:

2''-Hydroxy-4''-methoxy-4'-ethoxy-5''-nitrochalcone (1.0 gm)
was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added to it. The reaction mixture was refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A colourless product obtained was washed with water, dried and crystallised from ethanol, colourless plates, m.p. 136°C. Yield: 0.39 gm.

Analysis:

Found: N, 7.39 %

C₁₈H₁₈O₆N₂ requires N, 7.28 %

VII CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-5 NITROACETOPHENONE AND 2-4 DICHLOROBENZALDEHYDE:

CONDENSATION OF 2-HYDROXY-4-ETHOXY-5 NITROACETOPHENONE WITH 2-4 DICHLOROBENZALDEHYDE:

2-HYDROXY-2-4 DICHLORO-4'-ETHOXY-5'-NITROCHALCONE:

2-Hydroxy-4-ethoxy-5-nitroacetophenone (2.48 gm), 2-4-dichlorobenzaldehyde (1.93 gm), ethanol (50 ml) and potassium hydroxide (40 ml: 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture changed from a yellow to red. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1).
The yellow solid separated was filtered, washed with water, dried and crystallised from ethanol, yellow needles, m.p. 195°C. Yield: 4.0 gm.

Analysis:

\[
\text{Found: } C, 53.18\% ; H, 3.53\% ; N, 3.38\% ; Cl, 18.49\%
\]

\[
C_{17}H_{13}O_5NCl_2 \text{ requires } C, 53.39\% ; H, 3.40\% ; N, 3.66\% ; Cl, 18.59\%
\]

**BENZOYL DERIVATIVE**:

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 5 hours. It was then cooled and poured into ice water containing dilute sulphuric acid. The yellowish white solid separated was filtered, washed with dilute sodium bicarbonate solution, then with water, dried and crystallised from petrolleum ether (40-60), yellowish white needles, m.p. 96°C. Yield: 0.38 gm.

Analysis:

\[
\text{Found: } N, 2.59\% ; Cl, 14.48\%
\]

\[
C_{21}H_{17}O_6NCl_2 \text{ requires } N, 2.88\% ; Cl, 14.61\%
\]
CYCLO-ISOMERISATION OF 2'-HYDROXY-2-4-DICHLORO-4'-ETHOXY-5'-NITROCHALCOME : 7-ETHOXY-6-NITRO-2'-4'-DICHLOROFLAVANONE :

To a solution of chalcone (0.5 gm) in hot ethanol (40 ml) dilute sulphuric acid (20 ml : 10 per cent) was added and the reaction mixture was refluxed on a boiling water bath for 30 hours. Excess of ethanol was distilled off and the residual solution was then filtered hot and left at the room temperature. The yellow solid separated was filtered washed with water, dried and crystallised from ethanol, yellow needles, m.p. 122°C. Yield : 0.28 gm.

Analysis:

    Found : N, 3.51 %; Cl, 18.63 %

C_{17}H_{13}O_{2}NCl_{2} requires N, 3.66 %; Cl, 18.59 %

BROMINATION OF 2'-HYDROXY-2-4-DICHLORO-4'-ETHOXY-5'-NITROCHALCOME : 2'-HYDROXY-2-4-DICHLORO-4'-ETHOXY-5'-NITRODI-BROMOCHALCOME :

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and the bromine in acetic acid (5 ml : 10 per cent) was added to it. It was kept cool in an ice bath for 4 hours. Then the mixture was diluted with ice water, the yellow solid separated was filtered, washed with dilute sodium thiosulphate solution, then again with water, dried and
crystallised from acetone, yellow needles, m.p. 158°C.
Yield: 0.29 gm.

Analysis:

Found: N, 2.29%; Halogen, 42.31%

C_{17}H_{13}O_{2}NBr_{2}Cl_{2} requires N, 2.58%; Halogen, 42.62%

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

A mixture of the above dibromochalcone (0.3 gm), potassium iodide (0.3 gm) and dry acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. Acetone was removed and the product obtained was washed with dilute sodium thiosulphate solution and finally with water, dried and crystallised from ethanol, yellow needles, m.p. and mixed m.p. with original chalcone 195°C.

CYCLISATION OF 2'-HYDROXY-2'-DICHLORO-1'-ETHOXY-5'-NITROCHALCONE: 7-ETHOXY-6-NITRO-2'-4'-DICHLOROFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate on the α:β Dibromochalcone:

A mixture of the dibromochalcone (0.5 gm), anhydrous potassium carbonate (0.5 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 4 hours. The solution was then filtered hot and acetone was removed by evaporation and
brown solid obtained was washed with water, dried and crystallised from ethanol, brown granules, m.p. 210°C. yield : 0.23 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

A mixture of the chalcone (0.5 gm), selenium dioxide (0.5 gm) and n-amyl alcohol (20 ml) was refluxed on an oil bath at 150°C for 24 hours. It was then filtered hot to remove selenium and steam distilled to remove excess of n-amyl alcohol. The product obtained was washed with petroleum ether (40-60) to remove traces of n-amyl alcohol and crystallised from ethanol, brown granules, m.p. 210°C. Yield : 0.18 gm.

Analysis:

Found : N, 3.61 %; Cl, 18.23 %

C₁₁H₁₁O₂NCl₂ requires N, 3.68 %; Cl, 18.68 %

OXIDATION OF 2'-HYDROXY-2'-4'-DICHLOORO-4'-ETHOXY-5'-NITROCHALCONE:

7'-ETHOXY-6'-NITRO-2'-4'-DICHLOOROFLAVONOL:

(a) By Action of Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml : 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml : 20 vol) was added to it and the reaction mixture kept cool in the ice
bath for 4 hours, and then left overnight at the room temperature. The colour of the reaction mixture changed from a red to orange. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was filtered, washed with water, dried and crystallised from ethanol yellow granules, m.p. 210°C. 
Yield : 0.23 gm.

(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of the chalcone (0.5 gm) and sodium peroxide (0.5 gm) in ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was filtered, washed with water and crystallised from ethanol, yellow granules, m.p. 210°C. 
Yield : 0.21 gm.

Analysis:

Found : N, 3.38 %; Cl, 17.62 %

*C_{17}H_{11}O_{6}NCl_{2} requires N, 3.54 %; Cl, 17.93 %

Acetyl Derivative of Flavonol:

A mixture of flavonol (0.5 gm) acetic anhydride (1.0 ml) and a drop of pyridine was refluxed on a boiling water bath for 4 hours. It was then treated with ice water and the yellow solid separated was filtered, washed with water, dried
and crystallised from ethanol, yellow needles, m.p. 192°C.
Yield: 0.29 gm.

Analysis:

Found: N, 3.31%; Cl, 16.28%

C₁₉H₁₃O₇NCl₂ requires N, 3.19%; Cl, 16.17%

Condensation of Ethyl Acetoacetate with 2'-hydroxy-2-4-
Dichloro-4'-ethoxy-5'-nitrochalcone: Ethyl-2-(2'-4'-
Dichlorophenyl)-4-(2''-hydroxy-4''-ethoxy-5''-nitrophenyl)-Δ₄-
Cyclohexene-6-one-1-carboxylate:

Sodium metal (0.2 gm) was dissolved in absolute ethanol
(15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml).
To this solution ethyl acetoacetate (1.0 ml) was added and
the mixture was refluxed on a boiling water bath for 5 hours.
It was then cooled and diluted with ice water (100 ml), then
acidified with dilute hydrochloric acid (1:1). The yellow
solid separated was filtered, washed with water, dried and
crystallised from ethanol, yellow needles, m.p. 192°C.
Yield: 0.28 gm.

Analysis:

Found: N, 2.61%; Cl, 14.61%

C₂₃H₂₁O₇NCl₂ requires N, 2.83%; Cl, 14.37%
HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE
ETHYL CYCLOHEXENONE CARBOXYLATE : 2-(2'-4'-DICHLOOROPHENYL)-4-
(2''-HYDROXY-4''-ETHOXY-5''-NITROPHENYL)-Δ4-CYCLOHEXENE-6-ONE;

A solution of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml) was mixed
with sodium hydroxide (10 ml : 5 per cent) and the mixture
was refluxed on a boiling water bath for 5 hours. It was
then diluted with ice water (100 ml) and acidified with dilute
hydrochloric acid (1:1). A brown solid separated was filtered,
washed with water, dilute sodium bicarbonate solution and
finally with water, dried and crystallised from ethanol,
brown needles, m.p. 265°C. Yield : 0.21 gm.
Analysis:

Found : N, 3.21 % ; Cl, 16.61 %
C_{20}H_{17}O_5Cl_2 requires N, 3.32 % ; Cl, 16.83 %

ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-2,4-
DICHLOOR-4'-ETHOXY-5'-NITROCHALCONE : 3(2-HYDROXY-4-ETHOXY-
5-NITROPHENYL)-5-(2,4, DICHLOORPHENYL)-ISOXAZOLINE :

2'-Hydroxy-2,4-dichloro-4'-ethoxy-5'-nitrochalcone
(1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine
hydrochloride (1.0 gm) in water (5.0 ml) was added to it.
The reaction mixture was then refluxed on a boiling water
bath for 4 hours. It was then cooled and acidified with dilute
acetic acid (1:1). A colourless product obtained, was washed with water, dried and crystallised from ethanol white plates, m.p. 189°C. Yield: 0.49 gm.

Analysis:

Found: N, 7.28%; Cl, 17.68%

C_{17}H_{14}O_{5}N_{2}Cl_{2} requires: N, 7.06%; Cl, 17.88%

VIII CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE AND 3-NITROBENZALDEHYDE:

CONDENSATION OF 2-HYDROXY-4-ETHOXY-5-NITROACETOPHENONE WITH 3-NITROBENZALDEHYDE:

2'-HYDROXY-4'-ETHOXY-3-5 DINITROCHALCONE:

2-Hydroxy-4-ethoxy-5-nitroacetophenone (2.48 gm), 3-nitrobenzaldehyde (1.66 gm), ethanol (50 ml) and potassium hydroxide (40 ml: 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture was changed from a yellow to red. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). A brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown needles, m.p. 198°C. Yield: 3.7 gm.
Analysis:

Found : C, 56.91 %; H, 3.68 %; N, 7.40 %

C_{17}H_{14}O_{7}N_{2} requires C, 56.98 %; H, 3.91 %; N, 7.82 %

BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 5 hours. It was then cooled and treated with dilute sulphuric acid to remove excess of pyridine. The yellowish solid separated was filtered, washed with dilute sodium bicarbonate solution, and finally with water, dried and crystallised from petroleum ether (40-60), yellowish needles, m.p. 115°C. Yield : 0.32 gm.

Analysis:

Found : N, 6.32 %

C_{24}H_{18}O_{5}N_{2} requires N, 6.06 %

CYCLO-ISOMERISATION OF 2'-HYDROXY-4'-ETHOXY-3'-5'-DINITROCHALCONE : 7'-ETHOXY-6-3' DINITROFLAVANONE:

To the hot solution of chalcone (0.5 gm) in ethanol (40 ml) dilute sulphuric acid (20 ml; 10 per cent) was added. The precipitated solid was dissolved in more ethanol (20 ml) and the clear solution was refluxed on a boiling water bath for 30 hours. Excess of ethanol was distilled off,
and the residual solution was then filtered hot and left at
the room temperature when a brown solid separated. It was
filtered, washed with water and crystallised from ethanol,
brown granules, m.p. 122°C. Yield: 0.18 gm.
Analysis:

\[
\text{Found: } N, 7.61\% \\
\text{C}_{17}H_{14}O_7N_2 \text{ requires } N, 7.82\%
\]

**Bromination of 2'-Hydroxy-4'-ethoxy-3-5'-Dinitrochalcone:**

\[
2'-\text{Hydroxy-4'-ethoxy-3-5'-Dinitrochalcone} \rightarrow \beta \text{ Dibromochalcone}
\]

The chalcone (0.5 gm) was dissolved in acetic acid
(30 ml) and was treated with bromine in acetic acid (5 ml: 10 per cent). The mixture was kept cool for 4 hours and then
diluted with ice water. The yellow solid obtained was filtered,
washed with dilute sodium thiosulphate solution and then with
water, dried and crystallised from acetone, yellow needles,
m.p. 178°C. Yield: 0.34 gm.
Analysis:

\[
\text{Found: } N, 5.18\% ; \text{Br, 30.51}\% \\
\text{C}_{17}H_{14}O_7N_2Br_2 \text{ requires } N, 5.40\% ; \text{Br, 30.89}\%
\]

**Debromination of the Above Dibromochalcone:**

To the solution of dibromochalcone (0.3 gm) in dry
acetone (20 ml), potassium iodide (0.3 gm) was added and the
reaction mixture was refluxed on a water bath at 70°C for 3 hours. Acetone was removed and a brown solid obtained was washed with dilute sodium thiosulphate solution, then with water and crystallised from ethanol, brown needles, m.p. and mixed m.p. with original chalcone 198°C.

CYCLISATION OF 2'-HYDROXY-4'-ETHOXY-3,5'-DINITROCHALCONE:

7'-ETHOXY-6,3'-DINITROFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate

The dibromochalcone (0.5 gm) in acetone (20 ml) was treated with anhydrous potassium carbonate (0.5 gm). The reaction mixture was then refluxed on a water bath at 70°C for 4 hours. The solution was filtered when hot, and acetone was removed. The pale brown solid obtained, was filtered, washed with water, dried and crystallised from ethanol pale brown needles, m.p. 260°C. Yield: 0.28 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

A mixture of chalcone (0.5 gm), n-amyl alcohol (20 ml), and selenium dioxide (0.5 gm) was refluxed on an oil bath at 150°C for 24 hours. Selenium was then filtered off from the hot reaction mixture and the clear filtrate was subjected to steam distillation to remove n-amyl alcohol,
the brown solid obtained was washed with petroleum ether (40-60), dried and crystallised from ethanol, brown needles, m.p. 260°C. Yield: 0.28 gm.

Analysis:

Found: N, 7.61%

C_{17}H_{12}O_{7}N_{2} requires N, 7.36%

OXIDATION OF 2'-HYDROXY-4'-ETHOXY-3'-5'-DINITROCHALCONE:

7-ETHOXY-6-3'-DINITROFLAVONOL:

(a) By Action of Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml: 10 per cent) and the mixture was added to it and the reaction mixture was kept cool in the ice bath for 4 hours and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to yellowish green. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1). A brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown needles, m.p. 282°C. Yield: 0.28 gm.

(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of chalcone (0.5 gm), sodium peroxide (0.5 gm) and ethanol (20 ml) was refluxed on a boiling water bath
for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). A brown solid separated was filtered, washed with water and crystallised from ethanol, brown needles, m.p. 282°C. Yield: 0.23 gm.

Analysis:

Found: N, 7.68%

C\textsubscript{17}H\textsubscript{12}O\textsubscript{8}N\textsubscript{2} requires N, 7.53%

ACETYL DERIVATIVE OF FLAVONOL:

A mixture of flavonol (0.5 gm) acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water, a brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 295°C. Yield: 0.23 gm.

Analysis:

Found: N, 6.33%

C\textsubscript{19}H\textsubscript{14}O\textsubscript{9}N\textsubscript{2} requires N, 6.75%

CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-4'-ETHOXY-3,5-DINITROCHALCONE:

Sodium metal (0.2 gm) was dissolved in ethanol (15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml). To this
solution ethyl acetoacetate (1.0 ml) was added and the mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and poured in ice water, then acidified with dilute hydrochloric acid (1:1). A brown solid separated was filtered, washed with water dried and crystallised from ethanol, brown granules, m.p. 178°C. Yield : 0.17 gm.

Analysis:

Found : N, 5.88 %  
C_{23}H_{22}O_9N_2 requires N, 5.96 %

HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL CYCLOHEXENONE CARBOXYLATE : 2-(3'-NITROPHENYL)-5-(2''-HYDROXY-4''-ETHOXY-5''-NITROPHENYL)-4''-CYCLOHEXENE-6-ONE:

A mixture of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm), ethanol (20 ml) and sodium hydroxide (10 ml : 5 per cent) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). A brown solid separated, was filtered, washed with dilute sodium bicarbonate solution and then with water, dried and crystallised from ethanol brown needles, m.p. 290°C. Yield : 0.31 gm.
ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-4'-ETHOXY-3-5'-DINITROCHALCONE: 3(2-HYDROXY-4'-ETHOXY-5-NITROPHENYL)-5(3-NITROPHENYL)-ISOXAZOLINE:

2'-Hydroxy-4'-ethoxy-3-5'-dinitrochalcone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added to it. The reaction mixture was then refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A brown solid obtained was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 280°C. Yield: 0.61 gm.

Analysis:

Found: N, 7.69 %

C_{17}H_{15}C_{7}N_{3} requires N, 7.51 %
DIAGRAMATIC REPRESENTATION OF CHALCONE AND RELATED COMPOUNDS DERIVED FROM
2-HYDROXY-4-ETHOXY-5-BROMOACETOGENONE

(II)

C₂H₅O\(\text{Br}\) + CH₂CO₂Et → C₂H₅O\(\text{COCH}_{2}\text{CH} = \text{CH})_n + \text{Br}_n

KOH

(III)

C₂H₅O\(\text{Br}\) + CHO₂ → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

Bromine in acetic acid

(IV)

C₂H₅O\(\text{Br}\) + SeO₂ → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

KI and acetone

(II)

C₂H₅O\(\text{Br}\) + K₂CO₃ → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

Anhydrous

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

CH₃CO₂H₂O

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(IV)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

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C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

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C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

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C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(III)

C₂H₅O\(\text{Br}\) + \text{Pyridine} → C₂H₅O\(\text{COCH} = \text{CH})_n + \text{Br}_n

(II)
In this section, chalcones from 2-hydroxy-4-ethoxy-5-bromoacetophenone obtained by condensation with (1) benzaldehyde (2) 2-methoxybenzaldehyde (3) vanillin (4) 4-chlorobenzaldehyde (5) 4-methoxybenzaldehyde (6) 2,4 dichlorobenzaldehyde and (7) 3-nitrobenzaldehyde, using alkali as a condensing agent are described.

2-Hydroxy-4-ethoxy-5-bromoacetophenone required for the present work was prepared from 2-hydroxy-4-ethoxyacetophenone.

Condensations were carried out using different concentrations of potassium hydroxide. It was found after some trials, that 40 per cent potassium hydroxide was the best to get the maximum yield of the chalcones. The reaction period used was about 24 hours.
In these condensations also, only chalcones were isolated, all attempts to isolate a flavanone or other compounds have failed.

I  CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE AND BENZALDEHYDE:

The condensation was studied using different condensing agents:
(a) Potassium hydroxide solution of different concentrations, and
(b) Phosphorus oxychloride.

(a) Potassium Hydroxide:

The condensation has been investigated using different concentrations of alkali and for different reaction periods. The important conditions are tabulated below:
TABLE I

2-Hydroxy-4-ethoxy-5-bromoacetophenone : 2.85 gm.
Benzaldehyde : 1.17 gm.
Ethanol (Solvent) : 50 ml.

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium Hydroxide per cent ml</th>
<th>Temperature °C</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>25-30</td>
<td>24</td>
<td>2.6</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>100</td>
<td>4</td>
<td>1.8</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>25-30</td>
<td>24</td>
<td>3.1</td>
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<tr>
<td>4</td>
<td>40</td>
<td>100</td>
<td>4</td>
<td>1.9</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>25-30</td>
<td>24</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Optimum yield of the chalcone was obtained with 40 per cent alkali as a condensing agent and by keeping the reaction mixture for 24 hours at the room temperature (25-30°C).

The product was crystallised from ethanol, ethyl acetate or benzene. No other product could be isolated.

(b) Phosphorus oxychloride:

In the case of this condensing agent (1.0 ml) the mixture of ketone (2.85 gm) and aldehyde (1.17 gm) was kept at the room temperature for 24 hours. The chalcone was obtained in a yield of 2.1 gm.
The product obtained in all the above condensations has been assigned the structure, 2'-hydroxy-4'-ethoxy-5'-bromochalcone (I, \( R = H \)) on the following basis:

1. (a) The product is yellow in colour, and gives a characteristic red colour with concentrated sulphuric acid.
   (b) It gives a deep brown colour with ethanolic ferric chloride indicating -OH and -CO groups in ortho positions.
   (c) It is sparingly soluble in alkali but dissolves in ethanolic alkali with an orange colour.
   (d) It gives a benzoyl derivative (II, \( R = H \)).

2. (a) The probable flavanone structure has been ruled out as the product could be isomerised to the corresponding flavanone (III, \( R = H \)) with dilute ethanolic sulphuric acid (1) which gives the following tests:
   (b) It is insoluble in alkali as well as in ethanolic alkali,
   (c) It does not give any colour with ethanolic ferric chloride

3. (a) The product on bromination gives the corresponding dibromochalcone (IV, \( R = H \)) which on treatment with acetone and potassium iodide regenerates the original chalcone. The dibromide was also converted into the corresponding flavone (V, \( R = H \)) by treatment of acetone and anhydrous potassium carbonate.
The flavone gives a bluish fluorescence in ethanol, with concentrated sulphuric acid an orange colour with a bluish fluorescence is obtained.

(b) The chalcone (I, R = H) was oxidised by selenium dioxide in n-amyl alcohol to the corresponding flavone (V, R = H) which was identical with the flavone, obtained as above(2).

(4) The chalcone on treatment with alkaline hydrogen peroxide gave corresponding flavonol (VI, R = H)(3,4).

(a) It is soluble in alkali and gives a brown colour with ethanolic ferric chloride.

(b) It gives an orange colour with a greenish fluorescence with concentrated sulphuric acid.

(c) It gives an acetyl derivative (VII, R = H) with acetic anhydride.

(5) With ethyl acetooacetate in presence of sodium ethoxide it forms a cyclohexenone carboxylate derivative (VII, R = H). This gives an orange colour with concentrated sulphuric acid(5,6). It has been hydrolysed and simultaneously decarboxylated in presence of ethanolic sodium hydroxide to the corresponding cyclohexenone (IX, R = H).

(6) With hydroxylamine hydrochloride the chalcone forms corresponding isoxazoline derivative (X, R = H). It gives an orange colour with concentrated sulphuric acid.
It does not give any colour with ethanolic ferric chloride.

II CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE AND 2-METHOXYBENZALDEHYDE:

The condensation has been investigated using different concentrations of potassium hydroxide and the results obtained are as under:

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium Hydroxide per cent</th>
<th>Potassium Hydroxide ml</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>24</td>
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<tr>
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<td>60</td>
<td>40</td>
<td>24</td>
<td>3.2</td>
</tr>
</tbody>
</table>

It is quite obvious from the above results that the maximum yield of the chalcone was obtained when 40 per cent 40 ml potassium hydroxide was used.
Phosphorus oxychloride was used as a condensing agent but the yield was poor.

The structure, 2'-hydroxy-2-methoxy-4'-ethoxy-5'-bromochalcone (I, \( R = 2\text{-OCH}_3 \)) has been assined on the following basis:

(1)(a) The product is pale brown in colour, gives a brown colour with ethanolic ferric chloride and a red colour with concentrated sulphuric acid.

(b) It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali with an orange colour.

(c) It gives a benzoyl derivative (II, \( R = 2\text{-OCH}_3 \)) with benzoyl chloride.

(2) By treatment with dilute ethanolic sulphuric acid, it has been cyclised to flavanone (III, \( R = 2\text{-OCH}_3 \)), insoluble in alkali, not giving a ferric chloride test.

(3)(a) On treatment with bromine it forms \( \alpha:\beta \) dibromochalcone (IV, \( R = 2\text{-OCH}_3 \)) which can be debrominated into the original chalcone by acetone and potassium iodide treatment. It is also converted into the corresponding flavone (V, \( R = 2\text{-OCH}_3 \)), with acetone and anhydrous potassium carbonate method.

(b) On oxidation by selenium dioxide it gives a flavone (V, \( R = 2\text{-OCH}_3 \)) identical with the flavone, obtained as above. It gives a bluish fluorescence with concentrated sulphuric acid.
On oxidation by alkaline hydrogen peroxide, it isomerised to flavonol (VI, \( R = \text{P-OCH}_3 \)) characterised by its solubility in alkali, a brown colour with ethanolic ferric chloride, a greenish fluorescence with concentrated sulphuric acid and gives an acetyl derivative (VII, \( R = \text{2-OCH}_3 \)) with acetic anhydride and pyridine.

The chalcone forms corresponding ethyl cyclohexenone carboxylate derivative (VIII, \( R = \text{2-OCH}_3 \)) with ethyl acetooacetate and sodium ethoxide. It gives an orange colour with concentrated sulphuric acid. This carboxylate ester has been hydrolysed and simultaneously decarboxylated by ethanolic alkali to the corresponding cyclohexenone (IX, \( R = \text{2-OCH}_3 \)).

With hydroxylamine hydrochloride the chalcone forms isoxazoline derivative (X, \( R = \text{2-OCH}_3 \)). It gives an orange colour with concentrated sulphuric acid.

III CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE AND VANILLIN:

The condensation has been investigated using potassium hydroxide solution of different concentrations. The results obtained are as under:
TABLE-III

2-Hydroxy-1'-ethoxy-5'-bromoacetophenone : 2.85 gm.
Vanillin : 1.67 gm.
Ethanol (Solvent) : 50 ml.
Temperature (Room temperature) : 25-30°C

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium Hydroxide per cent</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>20</td>
<td>2.5</td>
</tr>
<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>3.6</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>2.9</td>
</tr>
</tbody>
</table>

It is clear from the above table that maximum yield of the chalcone was obtained when 40 per cent 40 ml potassium hydroxide was used.

Phosphorus oxychloride was used as a condensing agent, but the yield was poor.

The product obtained in all the above condensations has been assigned the structure, 2'-dihydroxy-3-methoxy-4'-ethoxy-5'-bromochalcone (I, R = 3-OCH₃, 4'-OH) on the following basis:


(1) (a) The product is brown in colour. It gives a brown colour with ethanolic ferric chloride and a red colour with concentrated sulphuric acid.

(b) It is sparingly soluble in aqueous alkali, but dissolves in ethanolic alkali with an orange colour.

(c) It gives a dibenzoyl derivative (II, \( R = 3-\text{OCH}_3, 4\text{-OOC}_6\text{H}_5 \)) with benzoyl chloride.

(2) By treatment with dilute ethanolic sulphuric acid, it has been cyclised to flavanone (III, \( R = 3-\text{OCH}_3, 4\text{-OH} \)) insoluble in alkali, not giving a ferric chloride test.

(3) (a) On treatment with bromine it forms \( \alpha : \beta \) dibromo-chalcone (IV, \( R = 3-\text{OCH}_3, 4\text{-OH} \)) which can be debrominated by treatment with potassium iodide and acetone. It is also converted to flavone (V, \( R = 3-\text{OCH}_3, 4\text{-OH} \)) by treatment with acetone and anhydrous potassium carbonate.

(b) It is oxidised by selenium dioxide in \( n \)-amyl alcohol to the flavone (V, \( R = 3-\text{OCH}_3, 4\text{-OH} \)) which is identical with the flavone obtained as above. It gives a bluish fluorescence with concentrated sulphuric acid.

(4) It is also oxidised to the corresponding flavonol (VI, \( R = 3-\text{OCH}_3, 4\text{-OH} \)) by treatment with alkali and hydrogen peroxide. It is soluble in alkali. It gives a brown colour with ethanolic ferric chloride solution,
and a greenish fluorescence with concentrated sulphuric acid. It gives a diacetyl derivative \((VII, R = 3-\text{OCH}_3, 4-\text{O.COCH}_3)\) with acetic anhydride and pyridine.

(5) The chalcone forms corresponding ethyl cyclohexenone carboxylate \((VII, R = 3-\text{OCH}_3, 4-\text{OH})\) with ethyl acetoacetate and sodium ethoxide. It gives an orange colour with concentrated sulphuric acid. This carboxylate ester has been hydrolysed and simultaneously decarboxylated by ethanolic alkali to the corresponding cyclohexenone \((IX, R = 3-\text{OCH}_3, 4-\text{OH})\).

(6) With hydroxylamine hydrochloride the chalcone forms isoxazoline derivative \((X, R = 3-\text{OCH}_3, 4-\text{OH})\). It gives an orange colour with concentrated sulphuric acid.

IV CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXY-5-BROMOAETOPHENONE AND

4-CHLOROBENZALDEHYDE:

The condensation has been investigated using different concentrations of potassium hydroxide and the results obtained are as under:
It is quite obvious from the above results that the maximum yield of the chalcone was obtained when 40 per cent 40 ml potassium hydroxide was used.

Phosphorus oxychloride was used as a condensing agent but the yield was poor.

The structure, 2'-hydroxy-4-chloro-4'-ethoxy-5'-bromo-chalcone (I, R = 4-Cl) has been assigned on the following basis:

(1)(a) The product is yellow in colour, gives a brown colour with ethanolic ferric chloride and a red colour with concentrated sulphuric acid.
(b) It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali with an orange colour.

(c) It gives a benzoyl derivative (II, R = 4-Cl) with benzoyl chloride.

(2) By treatment with dilute ethanolic sulphuric acid, it has been cyclised to flavanone (III, R = 4-Cl), insoluble in alkali, not giving a ferric chloride test.

(3)(a) On treatment with bromine it forms $\alpha : \beta$ dibromochalcone (IV, R = 4-Cl) which could be debrominated into the original chalcone by acetone and potassium iodide treatment. It is also converted into the corresponding flavone (V, R = 4-Cl) with acetone and anhydrous potassium carbonate.

(b) On oxidation by selenium dioxide, it gives a flavone (V, R = 4-Cl) identical with the flavone obtained as above. It gives a bluish fluorescence with concentrated sulphuric acid.

(4) On oxidation by alkaline hydrogen peroxide, it isomerised to flavonol (VI, R = 4-Cl) characterised by its solubility in alkali, a brown colour with ethanolic ferric chloride, a greenish fluorescence with concentrated sulphuric acid and gives an acetyl derivative (VII, R = 4-Cl) with acetic anhydride and pyridine.

(5) The chalcone forms corresponding ethylcyclohexenone carboxylate (VIII, R = 4-Cl) with ethyl acetoacetate
and sodium ethoxide. It gives an orange colour with concentrated sulphuric acid. This carboxylate ester has been hydrolysed and simultaneously decarboxylated by ethanoic alkali to the corresponding cyclohexenone (IX, R = \( \text{C}_6\text{H}_4\text{Cl} \)).

(6) With hydroxylamine hydrochloride the chalcone forms corresponding isoxazoline derivative (X, R = \( \text{C}_6\text{H}_4\text{Cl} \)), which gives an orange colour with concentrated sulphuric acid.

### Table V

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium Hydroxide per cent</th>
<th>Hydroxide ml</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>24</td>
<td>2.4</td>
</tr>
<tr>
<td>2</td>
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<td>24</td>
<td>2.7</td>
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<tr>
<td>3</td>
<td>40</td>
<td>40</td>
<td>24</td>
<td>3.7</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>24</td>
<td>3.1</td>
</tr>
</tbody>
</table>

The condensation has been investigated using different concentrations of potassium hydroxide and the results obtained are shown below.
It is quite obvious from the above result that the maximum yield of the chalcone was obtained when 40 per cent 40 ml potassium hydroxide was used.

Phosphorus oxychloride was used as a condensing agent but the yield was poor.

The structure, 2'-hydroxy-4'-methoxy-4'-ethoxy-5'-bromochalcone \((I, R = 4'-OCH_3)\) has been assigned on the following basis:

(1)(a) The product is yellow in colour, gives a brown colour with ethanolic ferric chloride and a red colour with concentrated sulphuric acid.

(b) It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali with an orange colour.

(c) It gives a benzoyl derivative \((II, R = 4'-OCH_3)\) with benzoyl chloride.

(2) By treatment with dilute ethanolic sulphuric acid, it has been cyclised to flavanone \((III, R = 4'-OCH_3)\), insoluble in alkali, not giving a ferric chloride test.

(3)(a) On treatment with bromine it forms \(\alpha : \beta\) dibromochalcone \((IV, R = 4'-OCH_3)\) which was debrominated into the original chalcone by acetone and potassium iodide treatment. It is also converted into the corresponding flavone \((V, R = 4'-OCH_3)\), with acetone and anhydrous potassium carbonate.
(b) On oxidation by selenium dioxide, it gives a flavone \((V, R = 4'-OCH_3)\) identical with the flavone, obtained as above. It gives a bluish fluorescence with concentrated sulphuric acid.

(4) On oxidation by alkaline hydrogen peroxide, it isomerised to flavonol \((VI, R = 4'-OCH_3)\) characterised by its solubility in alkali, a brown colour with ethanolic ferric chloride, a greenish fluorescence with concentrated sulphuric acid and gives an acetyl derivative \((VII, R = 4'-OCH_3)\) with acetic anhydride.

(5) The chalcone forms corresponding ethyl cyclohexenone carboxylate derivative \((VIII, R = 4'-OCH_3)\) with ethyl acetoacetate and sodium ethoxide. It gives an orange colour with concentrated sulphuric acid. This carboxylate ester has been hydrolysed and simultaneously decarboxylated by ethanolic alkali to the corresponding cyclohexenone \((IX, R = 4'-OCH_3)\).

(6) With hydroxylamine hydrochloride the chalcone forms corresponding isoxazoline derivative \((X, R = 4'-OCH_3)\). It gives an orange colour with concentrated sulphuric acid.
VI CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE AND

2-4 DICHLOROBENZALDEHYDE :

The condensation has been investigated under different conditions and the results obtained are as under:

<table>
<thead>
<tr>
<th>TABLE VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Hydroxy-4-ethoxy-5-bromoacetophenone : 2.85 gm.</td>
</tr>
<tr>
<td>2-4 Dichlorobenzaldehyde : 1.93 gm.</td>
</tr>
<tr>
<td>Ethanol (Solvent) : 50 ml.</td>
</tr>
<tr>
<td>Temperature (Room temperature) : 25-30°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium Hydroxide per cent</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20 40</td>
<td>24</td>
<td>2.6</td>
</tr>
<tr>
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<td>3.9</td>
</tr>
<tr>
<td>4</td>
<td>60 40</td>
<td>24</td>
<td>3.6</td>
</tr>
</tbody>
</table>

It is clear from the above table that maximum yield of the chalcone was obtained when 40 per cent 40 ml potassium hydroxide was used.
Phosphorus oxychloride was used as a condensing agent but the yield was poor.

The structure, 2'-hydroxy-2,4'-dichloro-4'-ethoxy-5'-bromochalcone (I, \( R = 2,4^-{(\text{Cl})_2} \)) has been assigned on the following basis:

1. (a) The product is yellow in colour and gives a brown colour with ethanolic ferric chloride while a red colour with concentrated sulphuric acid.
   (b) It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali with an orange colour.
   (c) It gives a benzoyl derivative (II, \( R = 2,4^-{(\text{Cl})_2} \)) with benzoyl chloride.

2. By treatment with dilute ethanolic sulphuric acid it has been cyclised to flavanone (III, \( R = 2,4^-{(\text{Cl})_2} \)) which is insoluble in alkali, not giving a ferric chloride test.

3. (a) The product on bromination forms \( \alpha : \beta \) dibromochalcone (IV, \( R = 2,4^-{(\text{Cl})_2} \)) which was debrominated by acetone and potassium iodide. It is also converted into the corresponding flavone (V, \( R = 2,4^-{(\text{Cl})_2} \)) with acetone and anhydrous potassium carbonate.
   (b) On oxidation by selenium dioxides it gives flavone (V, \( R = 2,4^-{(\text{Cl})_2} \)) identical with the flavone, obtained as above. It gives a bluish fluorescence with concentrated sulphuric acid.
The chalcone is also oxidised by alkaline hydrogen peroxide, to the corresponding flavonol (VI, \(2,4'-(\text{Cl})_2\)). It is soluble in alkali, a brown colour with ethanolic ferric chloride, a greenish fluorescence with concentrated sulphuric acid and gives an acetyl derivative (VII, \(2,4'-(\text{Cl})_2\)) with acetic anhydride and pyridine.

The chalcone forms corresponding ethyl cyclohexenone carboxylate derivative (VIII, \(R = 2,4'-(\text{Cl})_2\)) with ethyl acetoacetate and sodium ethoxide. It gives an orange colour with concentrated sulphuric acid. This carboxylate ester has been hydrolysed and simultaneously decarboxylated by ethanolic alkali to the corresponding cyclohexenone (IX, \(R = 2,4'-(\text{Cl})_2\)).

With hydroxylamine hydrochloride the chalcone forms isoxazoline derivative (X, \(R = 2,4'-(\text{Cl})_2\)). It gives an orange colour with concentrated sulphuric acid.

VII CHALCONE AND RELATED COMPOUNDS DERIVED FROM

2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE AND

3-NITROBENZALDEHYDE:

The condensation has been investigated under different conditions and the results obtained are as under:
<table>
<thead>
<tr>
<th>No.</th>
<th>Potassium Hydroxide per cent</th>
<th>ml</th>
<th>Reaction period (hrs)</th>
<th>Yield of chalcone (gm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20</td>
<td>40</td>
<td>24</td>
<td>2.2</td>
</tr>
<tr>
<td>2</td>
<td>40</td>
<td>20</td>
<td>24</td>
<td>2.9</td>
</tr>
<tr>
<td>3</td>
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<td>40</td>
<td>24</td>
<td>3.8</td>
</tr>
<tr>
<td>4</td>
<td>60</td>
<td>40</td>
<td>24</td>
<td>3.2</td>
</tr>
</tbody>
</table>

It is clear from the above table that the maximum yield of the chalcone was obtained when 40 per cent 40 ml potassium hydroxide was used.

Phosphorus oxychloride was used as a condensing agent but the yield was poor.

The structure, 2'-hydroxy-3-nitro-4'-ethoxy-5'-bromo-chalcone (I, R = 3-NO₂) has been assigned on the following basis:

(1)(a) The product is brown in colour and gives a brown colour with ethanolic ferric chloride while a red colour with concentrated sulphuric acid.
(b) It is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali with an orange colour.

(c) It gives a benzoyl derivative (II, \( R = 3\text{-NO}_2 \)) with benzoyl chloride.

(2) By treatment with dilute ethanolic sulphuric acid it has been cyclised to flavanone (III, \( R = 3\text{-NO}_2 \)), insoluble in alkali, not giving a ferric chloride test.

(3) (a) The product on bromination gives \( \alpha : \beta \) dibromochalcone (IV, \( R = 3\text{-NO}_2 \)) which was debrominated by acetone and potassium iodide. It is also converted into the corresponding flavone (V, \( R = 3\text{-NO}_2 \)) by acetone and anhydrous potassium carbonate.

(b) On Venkatraman oxidation by selenium dioxide in \( \eta \)-amyl alcohol, it is converted into the corresponding flavone (V, \( R = 3\text{-NO}_2 \)) which was identical with the flavone obtained as above. It gives an orange colour with a bluish fluorescence with concentrated sulphuric acid.

(4) It is also oxidised to a flavonol (VI, \( R = 3\text{-NO}_2 \)) by treatment with alkaline hydrogen peroxide. The flavonol gives following reactions:

(a) It is soluble in alkali.

(b) It gives a brown colour with ethanolic ferric chloride and a greenish fluorescence with concentrated sulphuric acid.
(c) It gives an acetyl derivative (VII, R = 3-NO₂) with acetic anhydride and pyridine.

(5) The chalcone forms corresponding ethyl cyclohexenone carboxylate derivative (VIII, R = 3-NO₂) with ethyl acetoacetate and sodium ethoxide which gives an yellow colour with concentrated sulphuric acid. This carboxylate ester has been hydrolysed and simultaneously decarboxylated by dilute ethanolic alkali to the corresponding cyclohexone (IX, R = 3-NO₂).

(6) With hydroxylamine hydrochloride the chalcone forms corresponding isoxazoline (X, R = 3-NO₂) which gives an orange colour with concentrated sulphuric acid.
SECTION III

EXPERIMENTAL
CHALCONEs AND RELATED COMPOUNDS DERIVED FROM
2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE:

2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE:

2-Hydroxy-4-ethoxyacetophenone (4 gm) was dissolved in acetic acid (40 ml). To this solution bromine in acetic acid (12 ml: 10 per cent) was added drop by drop with constant stirring. It was then left overnight at the room temperature, and then poured into ice water. The pale brown solid separated was filtered, washed with water, dilute sodium bisulphite solution (5 per cent) and again with water, dried and crystallised from ethanol, pale brown granules. m.p. 92°C. Yield: 4.1 gm.

Analysis:

Found: C, 46.61%; H, 4.21%; Br, 30.78%

C_{10}H_{11}O_{3}Br requires C, 46.34%; H, 4.25%; Br, 30.39%
CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE AND BENZALDEHYDE:

CONDENSATION OF 2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE WITH BENZALDEHYDE:

2'-HYDROXY-4'-ETHOXY-5'-BROMOCHALCONE:

2-Hydroxy-4-ethoxy-5-bromoacetophenone (2.35 gm), benzaldehyde (1.17 gm), ethanol (50 ml) and potassium hydroxide (40 ml : 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture changed from a yellow to orange. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was filtered, washed with water, dried and crystallised from ethanol, yellow granules, m.p. 140°C. Yield : 3.1 gm.

The product is sparingly soluble in dilute alkali but dissolves in ethanolic alkali giving an orange colour. It gives a brown colour with ethanolic ferric chloride solution and characteristic red colour with concentrated sulphuric acid.

Analysis:

Found : C, 58.69 % ; H, 4.18 % ; Br, 23.19 %

C<sub>17</sub>H<sub>15</sub>O<sub>3</sub>Br requires C, 58.79 % ; H, 4.32 % ; Br, 23.05 %

BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water
bath for 5 hours. Then it was cooled and treated with ice water containing dilute sulphuric acid. The yellow solid separated was filtered, washed with water, then with dilute sodium bicarbonate solution and finally with water, dried and crystallised from petroleum ether (40-60), yellow plates, m.p. 111°C. Yield: 0.36 gm.

Analysis:

Found: Br, 17.66%

C_{24}H_{19}O_{4}Br requires Br, 17.74%

CYCLO-ISOMERISATION OF 2'-HYDROXY-4'-ETHOXY-5'-BROMOCHALCONE:

7-ETHOXY-6-BROMOFLAVANONE:

To the hot solution of the chalcone (0.5 gm) in ethanol (40 ml) dilute sulphuric acid (20 ml: 10 per cent) was added, and the reaction mixture was refluxed on a boiling water bath for 30 hours. It was then filtered hot and left at the room temperature. The pale brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 112°C. Yield: 0.18 gm.

Analysis:

Found: Br, 23.11%

C_{17}H_{15}O_{3}Br requires Br, 23.05%
BROMINATION OF 2'-HYDROXY-4'-ETHOXY-5'-BROMOCHALCONE :

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and the bromine in acetic acid (5 ml : 10 per cent) was added slowly with constant stirring. The mixture was kept in an ice bath for 4 hours, and then diluted with ice water when the pale yellow solid separated was filtered, washed with water, dilute sodium thiosulphate solution and again with water, dried and crystallised from acetone, yellow needles, m.p. 162°C. Yield : 0.23 gm.

Analysis:

Found : Br, 47.69 %
C_{17}H_{15}O_{3}Br_{3} requires Br, 47.34 %

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE :

A mixture of the above dibromochalcone (0.3 gm) and potassium iodide (0.3 gm) in dry acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. Acetone was removed and the yellow solid obtained was filtered, washed with water, dilute sodium thiosulphate solution and again with water, dried and crystallised from ethanol, yellow granules. m.p. and mixed m.p. with original chalcone 140°C.

It gives a brown colour with ethanolic ferric chloride solution and a red colour with concentrated sulphuric acid.
CYCLISATION OF 2'-HYDROXY-4'-ETHOXY-5'-BROMOCHALCONE:

7'-ETHOXY-6-BROMOFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate

on the α:β Dibromochalcone:

The dibromochalcone (0.5 gm) in acetone (20 ml) was mixed with anhydrous potassium carbonate (0.5 gm). The reaction mixture was refluxed on a water bath at 70°C for 4 hours. The solution was then filtered hot and acetone was removed. The yellowish brown solid obtained was washed with water, dilute sodium thiosulphate solution and again with water, dried and crystallised from ethanol pale brown granules, m.p. 157°C. Yield: 0.26 gm.

The product gives a bluish fluorescence with concentrated sulphuric acid.

(b) By Selenium Dioxide Oxidation of the Chalcone:

A mixture of the chalcone (0.5 gm) in α-amyl alcohol (20 ml) and selenium dioxide (0.5 gm) was refluxed on an oil bath at 150°C for 24 hours. It was then filtered hot to remove selenium and steam distilled to remove α-amyl alcohol. The brown solid obtained was washed with petroleum ether (40-60) to remove traces of α-amyl alcohol, and crystallised from ethanol, pale brown granules, m.p. 157°C. Yield: 0.31 gm.
Analysis:

Found: Br, 23.61%
C_{17}H_{13}O_3Br requires Br, 23.19%

OXIDATION OF 2'-HYDROXY-4'-ETHOXY-5'-BROMOCHALCONE: 7'-ETHOXY-6-BROMOFLAVONOL:

(a) By Action of Alkaline Hydrogen Peroxide:

Chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml: 10 per cent) and the mixture was kept in an ice bath, hydrogen peroxide (20 ml: 20 vol) was added to it and the reaction mixture was kept cool in the ice bath for 4 hours and left overnight at the room temperature. The colour of the reaction mixture changed from an orange to yellowish green. It was then treated with ice water and acidified with dilute hydrochloric acid (1:1). The brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 134°C. Yield: 0.28 gm.

(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of the chalcone (0.5 gm) in ethanol (20 ml) and sodium peroxide (0.5 gm) was refluxed on a boiling water bath for 5 hours. It was then cooled and treated with ice water and acidified with dilute hydrochloric acid (1:1). The brown solid separated was filtered, washed with water, dried and
Crystallised from ethanol, brown granules, m.p. 134°C.
Yield: 0.38 gm.
Analysis:
Found: Br, 22.38%
C\textsubscript{17}H\textsubscript{13}O\textsubscript{4}Br requires Br, 22.16%

ACETYL DERIVATIVE OF FLAVONOL:
A mixture of the flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then cooled and treated with ice water. The brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 232°C. Yield: 0.21 gm.
Analysis:
Found: Br, 19.91%
C\textsubscript{19}H\textsubscript{15}O\textsubscript{5}Br requires Br, 19.86%

CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-4'-ETHOXY-5'-BROMOCHALCONE: ETHYL-2-PHENYL-4-(2''-HYDROXY-4''-ETHOXY-5''-BROMOPHENYL)- \Delta^1-CYCLOHEXENE-6-ONE-1-CARBOXYLATE:
To a solution of sodium (0.2 gm) in absolute ethanol (15 ml), ethyl acetoacetate (1 ml) and the chalcone (0.5 gm) in ethanol (20 ml) were added. The reaction mixture was then refluxed on a boiling water bath for 5 hours. It was cooled
and diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The brown solid obtained was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 166°C. Yield: 0.28 gm.

It gives an orange colour with concentrated sulphuric acid.

Analysis:

Found: Br, 17.69%

C_{23}H_{23}Br requires Br, 17.43%

**HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL CYCLOHEXENONE CARBOXYLATE: 2-PHENYL-4-(2''-HYDROXY-4''-ETHOXY-5''-BROMOPHENYL)-Δ^4-CYCLOHEXENE-6-ONE:**

A solution of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml) was mixed with sodium hydroxide (10 ml: 5 per cent) and the mixture was refluxed on a boiling water bath for 5 hours. It was then treated with ice water and acidified with dilute hydrochloric acid (1:1). The brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 122°C. Yield: 0.18 gm.

Analysis:

Found: Br, 20.73%

C_{20}H_{19}O_3Br requires Br, 20.67%
ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-4'-ETHOXY-5'-BROMOCHALCONE:

3-(2-HYDROXY-4'-ETHOXY-5 BROMOPHENYL)-5-PHENYLISOXAZOline:

2'-Hydroxy-4'-ethoxy-5'-bromochalcone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5 ml) was added to it. The reaction mixture was refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A brown coloured product obtained was washed with water, dried and crystallised from ethanol, brown granules. m.p. 211°C.

Yield: 0.22 gm.

Analysis:

Found: Br, 22.21%; N, 3.71%

C_{17}H_{16}O_{3}NBr requires Br, 22.10%; N, 3.86%

II: CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4'-ETHOXY-5'-BROMOACETOPHENONE AND 2-METHOXYBENZALDEHYDE:

CONDENSATION OF 2-HYDROXY-4'-ETHOXY-5'-BROMOACETOPHENONE WITH 2-METHOXYBENZALDEHYDE:

2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE:

2-Hydroxy-4'-ethoxy-5'-bromoacetophenone (2.85 gm), 2-methoxybenzaldehyde (1.49 gm), ethanol (50 ml) and potassium hydroxide (40 ml; 40 per cent) were mixed in a tightly corked
flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture changed from a yellow to orange. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 86°C. Yield: 3.7 gm.

The product is sparingly soluble in dilute alkali but dissolves in ethanolic alkali giving an orange colour. It gives a brown colour with ethanolic ferric chloride solution and characteristic red colour with concentrated sulphuric acid.

Analysis:

- Found: C, 57.68%; H, 4.31%; Br, 21.18%
- C₁₈H₁₇O₄Br requires C, 57.31%; H, 4.50%; Br, 21.22%

**BENZOYL DERIVATIVE:**

A mixture of the chalcone (0.5 gm), a drop of pyridine and benzoyl chloride (1.0 ml) was heated on a boiling water bath for 5 hours. Then it was cooled and treated with ice water containing dilute sulphuric acid. The yellow solid separated was filtered, washed with water, then with dilute sodium bicarbonate solution and again with water, dried and crystallised from petroleum ether (40-60), yellow needles, m.p. 112°C. Yield: 0.39 gm.
Analysis:

*Found: Br, 16.38%*

\[ C_{25}H_{21}O_5Br \text{ requires Br, 16.63%} \]

**CYCLO-ISOMERISATION OF 2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE:**

7-ETHOXY-6-BROMO-2'-METHOXYFLAVANONE:

To the hot solution of chalcone (0.5 gm), in ethanol (40 ml) dilute sulphuric acid (20 ml: 10 per cent) was added and the reaction mixture was refluxed on a boiling water bath for about 30 hours. It was then filtered hot and left at the room temperature. The brown solid obtained was filtered washed with water, dried and crystallised from ethanol, brown granules, m.p. 102°C. Yield: 0.18 gm.

The product gives a negative test with ethanolic ferric chloride.

Analysis:

*Found: Br, 21.53%*

\[ C_{18}H_{17}O_4Br \text{ requires Br, 21.22%} \]
BROMINATION OF 2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE:
2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE: α : β

DIBROMOCHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and the bromine in acetic acid (5 ml : 10 per cent) was slowly added to it with constant stirring. It was then kept in an ice bath for 4 hours and then was treated with ice water. A yellow solid separated was filtered, washed with water, dilute sodium thiosulphate solution and again with water, dried and crystallised from acetone, yellow needles, m.p. 81°C. Yield: 0.21 gm.

Analysis:

Found: Br, 44.38 %
C₁₈H₂₇O₄Br₃ requires Br, 44.69 %

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

The mixture of above dibromochalcone (0.3 gm) and potassium iodide (0.3 gm) in dry acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. Acetone was then removed and brown solid obtained was washed with water, dilute sodium thiosulphate solution and again with water, dried and crystallised from ethanol, brown granules, m.p. and mixed m.p. with original chalcone 86°C.
It gives a brown colour with ethanolic ferric chloride solution and a red colour with concentrated sulphuric acid.

CYCLISATION OF 2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE

7'-ETHOXY-6-BRMO-2'-METHOXYFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate

On the \[\alpha:\beta\] Dibromochalcone:

A mixture of the dibromochalcone (0.5 gm), anhydrous potassium carbonate (0.5 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 4 hours. It was then filtered when hot. Acetone was removed and the product obtained was washed with dilute sodium thiosulphate solution, then with water and crystallised from ethanol, brown granules, m.p. 139°C. Yield: 0.23 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

A mixture of the chalcone (0.5 gm), selenium dioxide (0.5 gm) and dry n-amyl alcohol (20 ml) was refluxed on an oil bath at 150°C for 24 hours. It was then filtered hot to remove selenium. On cooling the filtrate, a product precipitated was filtered, washed with petroleum ether (40-60) and crystallised from ethanol, brown granules, m.p. 139°C. Yield: 0.18 gm.
Analysis:

Found: Br, 21.61%

C\textsubscript{18}H\textsubscript{15}O\textsubscript{4}Br requires Br, 21.33%

OXIDATION OF 2'-HYDROXY-2-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE:

7'-ETHOXY-6-BROMO-2'-METHOXYFLAVONOL:

(a) By Action of Alkaline Hydrogen Peroxide:

The chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml: 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml: 20 vol) was added, and the reaction mixture was kept cool in the ice bath for 4 hours and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to yellowish green. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1). A pale yellow solid obtained was filtered, washed with water dried and crystallised from ethanol, pale yellow granules, m.p. 112°C. Yield: 0.23 gm.

(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of the chalcone (0.5 gm) and sodium peroxide (0.5 gm) in ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The solid
separated was filtered, washed with water, dried, and crystallised from ethanol, pale yellow granules, m.p. 112°C.

Yield: 0.31 gm.

Analysis:

Found: Br, 20.31%

C₁₈H₁₅O₅Br requires Br, 20.46%

**Acetyl Derivative of Flavonol:**

A mixture of the flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water and the solid separated was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 105°C.

Yield: 0.32 gm.

Analysis:

Found: Br, 18.32%

C₂₀H₁₇O₆Br requires Br, 18.48%

**Condensation of Ethyl Acetoacetate with 2'-Hydroxy-2-Methoxy-4'-Ethoxy-5'-Bromochalcone:** Ethyl-2(2'-Methoxyphenyl)-4-(2''-Hydroxy-4''-Ethoxy-5''-Bromophenyl)-Δ⁴-cyclohexene-6-one-1-carboxylate:

To a solution of sodium (0.2 gm) in absolute ethanol (20 ml), ethyl acetoacetate (1.0 ml) and the chalcone (0.5 gm)
in ethanol (20 ml) were added. The reaction mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The brown solid obtained was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 105°C. Yield: 0.31 gm.

Analysis:

**Found**: Br, 16.38 %

**C_{24}H_{25}O_{6}Br** requires Br, 16.36 %

**HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL CYCLOHEXENONE CARBOXYLATE**: 2(2'-METHOXYPHENYL)-4-(2"-HYDROXY-4"-ETHOXY-5"-BROMOPHENYL)-Δ^4^-CYCLOHEXENE-6-ONE:

A solution of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml) was mixed with sodium hydroxide (10 ml : 5 per cent) and the mixture was refluxed on a boiling water bath for 5 hours. It was then diluted with cold water (100 ml) and acidified with dilute hydrochloric acid (1:1). A pale yellow solid separated was filtered, washed with dilute sodium bicarbonate solution and then with water, dried and crystallised from ethanol, pale yellow needles, m.p. 99°C. Yield: 0.28 gm.

Analysis:

**Found**: Br, 19.28 %

**C_{21}H_{21}O_{4}Br** requires Br, 19.19 %
ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-2-
METHOXY-4'-ETHOXY-5'-BROMOCHALCONE; 3(2-HYDROXY-4-ETHOXY-
5-BROMOPHENYL)-5-(2-METHOXYPHENYL)-ISOXAZOLINE:

2'-Hydroxy-2-methoxy-4'-ethoxy-5'-bromochalcone (1.0 gm)
was dissolved in pyridine (5.0 ml) and hydroxylamine
hydrochloride (1.0 gm) in water (5.0 ml) was added to it. The
reaction mixture was refluxed on a boiling water bath for
4 hours. It was then cooled and acidified with dilute acetic
acid (1:1). A colourless product obtained was filtered, washed
with water, dried and crystallised from ethanol, white
granules, m.p. 142°C. Yield: 0.28 gm.
Analysis:

Found: Br, 20.23 %; N, 3.41 %

C₁₈H₁₈O₄N Br requires Br, 20.41 %; N, 3.57 %

III CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-
ETHOXY-5-BROMOACETOPHENONE AND VANillin: CONDENSATION OF
2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE WITH VANillin:
2'-4'-DIHYDROXY-3-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE:

2-Hydroxy-4-ethoxy-5-bromoacetophenone (2.85 gm),
vanillin (1.67 gm), ethanol (50 ml), and potassium hydroxide
(40 ml: 40 per cent) were mixed in a tightly corked flask.
The reaction mixture was left at the room temperature for about 24 hours. The colour of the reaction mixture changed from a yellow to orange. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The brown solid separated was filtered, washed with water, dried and crystallized from ethanol, brown needles, m.p. 100°C. Yield: 3.6 gm.

The chalcone is sparingly soluble in aqueous alkali but dissolves in ethanolic alkali giving an orange colour. It gives a brown colour with ethanolic ferric chloride while a red colour with concentrated sulphuric acid.

Analysis:

Found: C, 54.61%; H, 4.32%; Br, 20.61%

C_{18}H_{17}O_{5}Br requires C, 54.96%; H, 4.32%; Br, 20.35%

BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), a drop of pyridine and benzoyl chloride (1.0 ml) was refluxed on a boiling water bath for 5 hours. It was then cooled and treated with ice water containing dilute sulphuric acid. The pale brown solid separated was filtered, washed with water, dilute sodium bicarbonate solution and again with water, dried and crystallized from petroleum ether (40-60) brown needles, m.p. 110°C. Yield: 0.38 gm.

Analysis:

Found: Br, 13.39%

C_{32}H_{25}O_{7}Br requires Br, 13.30%
CYCLO-ISOMERISATION OF 2'-4 DIHYDROXY-3-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE : 7-ETHOXY-6-BROMO-3'-METHOXY-4'-HYDROXY-FLAVANONE :

To a solution of chalcone (0.5 gm) in hot ethanol (40 ml) sulphuric acid was added (20 ml : 10 per cent). The reaction mixture was refluxed on a boiling water bath for 30 hours. Excess of ethanol was distilled off and the residual solution was then filtered hot and left at the room temperature. The yellow solid separated was filtered, washed with water, dried and crystallised from ethanol, yellow granules, m.p. 108° C.

Yield : 0.29 gm.

Analysis :

Found : 20.61 %
C_{18}H_{17}O_{5}Br requires 20.35 %

BROMINATION OF 2'-4 DIHYDROXY-3-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE:

2'-4 DIHYDROXY-3-METHOXY-4'-ETHOXY-5'-BROMO - \alpha : \beta

DIBROMOCHALCONE :

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and the bromine in acetic acid (5 ml : 10 per cent) was slowly added to it with constant stirring. It was then kept in an ice bath for 4 hours. The reaction mixture was poured in ice water. The solid separated was filtered, washed with sodium thiosulphate solution, then with water, dried and
crystallised from acetone, yellow needles, m.p. 83°C.

Yield : 0.39 gm.

Analysis:

\[
\text{Found : Br, } 43.58\% \\
\text{C}_{18}H_{17}O_5Br_3 \text{ requires Br, } 43.40\%
\]

(b) DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

A mixture of the above dibromochalcone (0.3 gm) and potassium iodide (0.3 gm) in dry acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. Acetone was removed and the product obtained was washed with dilute sodium thiosulphate solution, then with water and crystallised from ethanol, brown needles, m.p. and mixed m.p. with original chalcone 100°C.

CYCLISATION OF 2'-4 DIHYDROXY-3-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE: 7-ETHOXY-6-BROMO-3'-METHOXY-4'-HYDROXYFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate on the \( \alpha : \beta \) Dibromochalcone:

A mixture of the dibromochalcone (0.5 gm) and anhydrous potassium carbonate (0.5 gm) in acetone (20 ml) was refluxed on a water bath at 70°C for 4 hours. It was filtered when hot. Acetone was removed and the product obtained was washed with
dilute sodium thiosulphate solution, then with water and crystallised from ethanol yellow granules m.p. 210°C.
Yield : 0.31 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

A mixture of the chalcone (0.5 gm), selenium dioxide (0.5 gm) and dry n-amyl alcohol (20 ml) was refluxed on an oil bath at 150°C for 2½ hours. It was then filtered hot to remove selenium. On cooling the filtrate, a product precipitated was filtered, washed with petroleum ether (40-60) and crystallised from ethanol, yellow granules, m.p. 210°C.
Yield : 0.29 gm.

Analysis:

Found : Br, 20.29 %
C_{18}H_{17}O_{5}Br requires Br, 20.46 %

OXIDATION OF 2'-4' DIHYDROXY-3-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE:

7-ETHOXY-6-BROMO-3'-METHOXY-4'-HYDROXYFLAVONOL:

(a) By Action of Alkaline Hydrogen Peroxide:

The chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml : 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml :20 vol) was added and the reaction mixture was kept in the ice bath for 4 hours and then left overnight at the room temperature.
The colour of the reaction mixture changed from an orange to yellow. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1), a pale yellow solid obtained was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 107°C. Yield : 0.37 gm.

(b) Using Sodium Peroxide in Ethanol Solution:

A mixture of the chalcone (0.5 gm) and sodium peroxide (0.5 gm) in ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The solid separated was filtered, washed with water, dried, and crystallised from ethanol, pale yellow granules, m.p. 107°C. Yield : 0.28 gm.

Analysis:

Found : Br, 19.39 %

C_{18}H_{19}O_{6}Br requires Br, 19.65 %

Acetyl Derivative of Flavonol:

A mixture of the flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water and the solid separated was filtered, washed with water, dried and crystallised from ethanol, white needles, m.p. 310°C. Yield : 0.18 gm.
Analysis:

Found : Br, 16.39 %

C_{22}H_{19}O_8Br requires Br, 16.29 %

CONDENSATION OF ETHYL ACETO ACETATE WITH 2'-4' DIOHYDROXY-3-
METHOXY-4'-ETHOXY-5'-BROMOCHELONE : ETHYL-2(3'-METHOXY-4'-
HYDROXYPHENYL)-4'-(2''-HYDROXY-4''-ETHOXY-5''-BROMOPHENYL)- Δ^4-
CYCLOHEXENE-6-ONE-1-CARBOXYLATE :

To a solution of sodium (0.2 gm) in absolute ethanol (15 ml), ethyl acetoacetate (1.0 ml) and the chalcone (0.5 gm) in ethanol (20 ml) were added. The reaction mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The yellow solid obtained was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 98°C. Yield : 0.29 gm.

Analysis:

Found : Br, 15.61 %

C_{24}H_{25}O_7Br requires Br, 15.84 %
HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL 
CYCLOHEXENONE CARBOXYLATE : 2(3'-METHOXY-4'-HYDROXYPHENYL)-4- 
(2''-HYDROXY-4''-ETHOXY-5''-BROMOPHENYL)-\Delta^4-CYCLOHEXENE-6-ONE :

To a solution of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml) and sodium hydroxide (10 ml : 5 per cent) was added and the mixture was refluxed on a boiling water bath for 5 hours. It was then diluted with cold water and acidified with dilute hydrochloric acid (1:1). A colourless solid separated was filtered, washed with dilute sodium bicarbonate solution and again with water, dried and crystallised from ethanol, white needles, m.p. 108°C. Yield : 0.28 gm.

Analysis:

Found : Br, 18.31 %

C_{21}H_{21}O_{5}Br requires Br, 18.48 %

ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-4 DIHYDROXY-3-
METHOXY-4'-ETHOXY-5'-BROMOCHALCONE : 3(2-HYDROXY-4'-ETHOXY-
5-BROMOPHENYL)-5-(4-HYDROXY-3-METHOXYPHENYL)-ISOXAZOLINE :

2'-4-Dihydroxy-3-methoxy-4'-ethoxy-5'-bromochalcone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added to it. The reaction mixture was refluxed on a boiling water bath for 4
hours. It was then cooled and acidified with dilute acetic acid (1:1). A colourless product obtained was filtered, washed with water, dried and crystallised from ethanol, white granules, m.p. 165°C. Yield: 0.81 gm.

Analysis:

Found: Br, 19.38%; N, 3.21%

C_{18}H_{18}O_{5}Br requires Br, 19.61%; N, 3.43%

IV CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE AND 4-CHLOROBENZALDEHYDE:

CONDENSATION OF 2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE WITH 4-CHLOROBENZALDEHYDE:

2'-HYDROXY-4'-CHLORO-4'-ETHOXY-5'-BROMOCHALCONE:

2-Hydroxy-4-ethoxy-5-bromoaceto phenone (2.85 gm), 4-chlorobenzaldehyde (1.54 gm), ethanol (50 ml) and potassium hydroxide (1.0 ml: 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture changed from a yellow to orange. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). A yellow solid separated was filtered, washed with water, dried and crystallised from ethanol, yellow plates, m.p. 180°C. Yield: 3.6 gm.
Analysis:

\[ C_{17}H_{14}O_3BrCl \] requires \ C, 53.47 \% ; \ H, 3.66 \% ; \ Halogen, 30.28 \%

\[ \text{Found: C, 53.29 \%; H, 3.61 \%; Halogen, 30.38\%} \]

BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 5 hours. It was then cooled and treated with ice water containing dilute sulphuric acid. The yellowish white solid separated was filtered, washed with dilute sodium bicarbonate solution and water, dried and crystallised from petroleum ether (40-60), yellowish needle, m.p. 108°C. Yield: 0.41 gm.

Analysis:

\[ C_{24}H_{18}O_4BrCl \] requires \ Halogen, 23.79 \%

\[ \text{Found: Halogen, 23.48 \%} \]

CYCLO-ISOMERISATION OF 2'-HYDROXY-4-CHLORO-5'-ETHOXY-6'-BROMOCHALCONE:

5-ETHOXY-6-BROMO-4'-CHLOROFLAVANONE:

To the hot solution of the chalcone (0.5 gm) in ethanol (40 ml) dilute sulphuric acid (20 ml : 10 per cent) was added. The precipitated solid was redissolved in more ethanol (20 ml) and the clear solution was then refluxed on a water bath for 30 hours. Excess of ethanol was distilled off and the residual
was then filtered hot and left at the room temperature. A pale yellow solid separated, was filtered, washed with water, dried and crystallised from ethanol, pale yellow granules, m.p. 108°C. Yield: 0.31 gm.

Analysis:

Found: Halogen, 30.39%  
C_{17}H_{14}O_3BrCl requires Halogen, 30.28% 

BROMINATION OF 2'-HYDROXY-4'-CHLORO-4'-ETHOXY-5'-BROMOCHALCONE:

2'-HYDROXY-4'-CHLORO-4'-ETHOXY-5'-BROMOCHALCONE:  

DIBROMOCHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and the bromine in acetic acid (5 ml: 10 per cent) was slowly added to it with constant stirring. The mixture was kept in an ice bath for 4 hours, then poured in ice water when the yellow solid was separated. It was filtered, washed with dilute sodium thiosulphate solution and finally with water, dried and crystallised from acetone, yellow needles, m.p. 78°C. Yield: 0.31 gm.

Analysis:

Found: Halogen, 50.48%  
C_{17}H_{14}O_3Br_2Cl requires Halogen, 50.87%
DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

The mixture of the above dibromochalcone (0.3 gm), dry acetone (20 ml) and potassium iodide (0.3 gm) was refluxed on a water bath at 70°C for 3 hours. The solution was then filtered hot, and acetone was removed. The yellow solid obtained was washed with dilute sodium thiosulphate solution and then with water, dried and crystallised from ethanol, m.p. and mixed m.p. with original chalcone 180°C.

CYCLISATION OF 2'-HYDROXY-4'-CHLORO-4'-ETHOXY-5'-BROMOCHALCONE:

7-ETHOXY-6-BROMO-4'-CHLOROFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate on the α : β Dibromochalcone:

The dibromochalcone (0.5 gm) in acetone (20 ml) was treated with anhydrous potassium carbonate (0.5 gm) and the reaction mixture was then refluxed on a water bath at 70°C for 4 hours. The solution was then filtered hot, and acetone was removed. A brown solid obtained was washed with water, dried and crystallised from ethanol, brown granules, m.p. 242°C. Yield: 0.31 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

To a solution of the chalcone (0.5 gm) in n-amyl alcohol (20 ml), selenium dioxide (0.5 gm) was added and the reaction
mixture was refluxed on an oil bath at 150°C for 24 hours. Selenium was then filtered off from the hot reaction mixture and the clear filtrate was subjected to steam distillation to remove n-amyl alcohol. The brown solid obtained was washed with petroleum ether (40-60) to remove traces of alcohol, and crystallised from ethanol, brown granules, m.p. 242°C.

Yield: 0.31 gm.

Analysis:

Found: Halogen, 30.53%

C_{17}H_{12}O_3BrCl requires Halogen, 30.44%

**OXIDATION OF 2'-HYDROXY-4'-CHLORO-4'-ETHOXY-5'-BROMOCHALCONE:**

**7-ETHOXY-6-BROMO-4'-CHLOROFLAVONOL:**

(a) By Action of Alkaline Hydrogen Peroxide:

The chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml: 10 per cent) and the mixture was kept in an ice bath, hydrogen peroxide (20 ml: 20 vol) was added and the reaction mixture was kept cool in the ice bath for 4 hours. The colour of the reaction mixture changed from an orange to greenish yellow. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1). The pale brown solid separated was filtered, washed with water, dried and crystallised from ethanol, pale brown granules, m.p. 138°C. Yield: 0.33 gm.
(b) Using Sodium Peroxide in Ethanoic Solution:

A mixture of the chalcone (0.5 gm), sodium peroxide (0.5 gm) and ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1). The pale brown solid separated was filtered, washed with water dried and crystallised from ethanol, pale brown granules, m.p. 138°C. Yield: 0.29 gm.

Analysis:

Found: Halogen, 29.28 %
C_{17}H_{12}C_{4}BrCl requires Halogen, 29.20 %

Acetyl Derivative of Flavonol:

A mixture of the flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then poured into ice water. The pale brown solid separated was filtered, washed with water, dried and crystallised from ethanol, pale brown granules, m.p. 80°C. Yield: 0.29 gm.

Analysis:

Found: Halogen, 26.51 %
C_{19}H_{14}O_{5}BrCl requires Halogen, 26.39 %
CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-4'-CHLORO-
4'-ETHOXY-5'-BROMOCHalcone ETHYL-2-(4'-CHLOROPHENYL)-4-(2''-
HYDROXY-4''-ETHOXY-5''-BROMOPHENYL) - \( \Delta^4 \)-CYCLOHEXENE-6-ONE-1-
CARBOXYLATE:

Sodium metal (0.2 gm) was dissolved in absolute ethanol
(15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml).
To this solution, ethyl acetoacetate (1 ml) was added and the
mixture was refluxed on a boiling water bath for 5 hours. The
solution was then poured in ice water (100 ml) and acidified
with dilute hydrochloric acid (1:1). The brown solid separated
was filtered, washed with water, dried and crystallised from
ethanol, brown granules, m.p. 142°C. Yield: 0.36 gm.
Analysis:

Found: Halogen, 23.51 %

\( C_{23}H_{22}O_5BrCl \) requires Halogen, 23.41 %

HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL
CYCLOHEXENONE CARBOXYLATE: 2-(4'-CHLOROPHENYL)-4-(2''-HYDROXY-
4''-ETHOXY-5''-BROMOPHENYL) - \( \Delta^4 \)-CYCLOHEXENE-6-ONE:

A mixture of above ethyl diphenyl cyclohexenone
carboxylate derivative (0.5 gm), in ethanol (20 ml) and sodium
hydroxide (10 ml: 5 per cent) was refluxed on a boiling
water bath for 5 hours. It was then poured in ice water (100 ml)
and acidified with dilute hydrochloric acid (1:1). A brown solid separated was filtered, washed with dilute sodium bicarbonate solution and then with water, dried and crystallised from ethanol, brown granules, m.p. 105°C. Yield: 0.29 gm.

Analysis:

Found: Halogen, 27.41 %

C_{20}H_{16}O_3BrCl requires Halogen, 27.34 %

ACTION OF HYDROXILAMINE HYDROCHLORIDE ON 2'-HYDROXY-4'-CHLORO-4'-ETHOXY-5'-BROMOCHALCONE : 3-(2-HYDROXY-4'-ETHOXY-5'-BROMOPHENYL)-5-(4-CHLOROPHENYL)-ISOXAZOLINE :

2'-Hydroxy-4-Chloro-4'-ethoxy-5'-bromochalcone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added to it. The reaction mixture was refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A colourless product obtained was washed with water, dried and crystallised from ethanol, white needles, m.p. 159°C. Yield: 0.81 gm.

Analysis:

Found: Halogen, 29.31 %; N, 3.43 %

C_{17}H_{15}O_3NBrCl requires Halogen, 29.13 %; N, 3.53 %
5-BROMOACETOPHENONE AND 4-METHOXYBENZALDEHYDE:

CONDENSATION OF 2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE WITH
4-METHOXYBENZALDEHYDE:

2'-HYDROXY-4'-ETHOXY-5'-BROMOCHELONE:

2-Hydroxy-4-ethoxy-5-bromoacetophenone (2.85 gm),
4-methoxybenzaldehyde (1.49 gm), ethanol (50 ml) and potassium
hydroxide (40 ml: 40 per cent) were mixed in a tightly
corked flask and kept at the room temperature for 24 hours.
The colour of the reaction mixture changed from a yellow to
orange. It was then diluted with ice water and acidified with
dilute hydrochloric acid (1:1). The yellow solid separated
was filtered, washed with water, dried and crystallised from
ethanol, yellow granules, m.p. 165°C. Yield: 3.70 gm.

The product is sparingly soluble in dilute alkali but
dissolves in ethanolic alkali giving an orange colour. It
gives a brown colour with ethanolic ferric chloride solution
and a characteristic red colour with concentrated sulphuric
acid.

Analysis:

Found: C, 57.39%; H, 4.38%; Br, 21.18%

C_{18}H_{17}O_{4}Br requires C, 57.31%; H, 4.50%; Br, 21.22%
BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 5 hours. Then it was cooled and treated with ice water containing dilute sulphuric acid. The yellow solid separated was filtered, washed with water, then with dilute sodium bicarbonate solution and again with water, dried and crystallised from petroleum ether (40-60), yellow needles, m.p. 115°C. Yield: 0.41 gm.

Analysis:

Found: Br, 16.51%

C_{25}H_{21}O_5Br requires Br, 16.63%

CYCLO-ISOMERISATION OF 2'-HYDROXY-4'-METHOXY-4'-ETHOXY-5'-

BROMOCHALCONE: 7-ETHOXY-6-BROMO-4'-METHOXYFLAVANONE:

To the hot solution of the chalcone (0.5 gm) in ethanol (40 ml) dilute sulphuric acid (20 ml: 10 per cent) was added and the reaction mixture was refluxed on a boiling water bath for about 30 hours. It was then filtered hot and left at the room temperature. The brown solid obtained was filtered, washed with water, dried and crystallised from ethanol, pale brown granules, m.p. 98°C. Yield: 0.28 gm.

The product gives a negative test with ethanolic ferric chloride.
Analysis:

Found : Br, 21.34 %

C_{16}H_{17}O_{4}Br requires Br, 21.22 %

BROMINATION OF 2'-HYDROXY-4-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE:

2'-HYDROXY-4-METHOXY-4'-ETHOXY-5'-BROMO-\alpha:\beta-DIBROMOCHALCONE:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and the bromine in acetic acid (5 ml : 10 per cent) was slowly added to it with constant stirring. It was kept in an ice bath for 4 hours and then treated with ice water. A yellow solid separated was filtered, washed with dilute sodium thiosulphate solution and with water, dried and crystallised from acetone, yellow needles, m.p. 98°C.

Yield : 0.32 gm.

Analysis:

Found : Br, 44.26 %

C_{16}H_{17}O_{4}Br requires Br, 44.69 %

DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

A mixture of the above dibromochalcone (0.3 gm), potassium iodide (0.3 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. Acetone was removed and a yellow solid obtained was washed with water, dilute sodium thiosulphate solution and again with water, dried and crystallised from ethanol, yellow granules, m.p. and mixed m.p. with original chalcone 165°C.
CYCLISATION OF 2'-HYDROXY-4'-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE:

7'-ETHOXY-6-BROMO-4'-METHOXYFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate on the \( \alpha : \beta \) Dibromochalcone:

A mixture of the dibromochalcone (0.5 gm), anhydrous potassium carbonate (0.5 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 4 hours. It was then filtered when hot. Acetone was removed and the product obtained was washed with dilute sodium thiosulphate solution, then with water and crystallised from ethanol, brown granules, m.p. 138°C. Yield: 0.31 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

A mixture of the chalcone (0.5 gm), selenium dioxide (0.5 gm) and dry \( \eta \)-amyl alcohol (20 ml) was refluxed on an oil bath at 150°C for 24 hours. It was then filtered hot to remove selenium. On cooling the filtrate, a product precipitated was filtered, washed with petroleum ether (40-60) and crystallised from ethanol, brown granules, m.p. 138°C. Yield: 0.24 gm.

Analysis:

Found: Br, 21.22 %

\( \text{C}_{18} \text{H}_{15} \text{O}_4 \text{Br} \) requires: Br, 21.33 %
OXIDATION OF 2'R-HYDROXY-4-METHOXY-4'R-ETHOXY-5'R-BROMOCHELALCONE :

7'-ETHOXY-6-BROMO-4'R-METHOXYFLAVONOL :

(a) By Action of Alkaline Hydrogen Peroxide :

The chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml : 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml : 20 vol) was added to it and the reaction mixture was kept cool in the ice bath for 4 hours and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to yellowish green. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1). A pale brown solid obtained was filtered, washed with water, dried and crystallised from ethanol, pale brown granules, m.p. 210°C. Yield : 0.28 gm.

(b) Using Sodium Peroxide in Ethanolic Solution :

A mixture of the chalcone (0.5 gm), sodium peroxide (0.5 gm) and ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The solid separated was filtered, washed with water, dried and crystallised from ethanol, pale brown granules, m.p. 210°C. Yield : 0.28 gm.

Analysis:

Found : Br, 20.61 %

C_{18}H_{15}O_7Br requires Br, 20.46 %
ACETYL DERIVATIVE OF FLAVONOL:

A mixture of the flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water and the solid separated was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 106°C. Yield: 0.22 gm.

Analysis:

Found: Br, 18.69%
C_{20}H_{17}O_{6}Br requires Br, 18.48%

CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-4'-METHOXY
4'-ETHOXY-5'-BROMOCHALCONE : ETHYL-2-(4'-METHOXYPHENYL)-4-
(2''-HYDROXY-4''-ETHOXY-5''-BROMOPHENYL)-\(\Delta^4\)-CYCLOHEXENE-6-
ONE-1-CARBOXYLATE:

To a solution of sodium (0.2 gm) in absolute ethanol (15 ml), ethyl acetoacetate (1.0 ml) and the chalcone (0.5 gm) in ethanol (20 ml) were added. The reaction mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). The brown solid obtained was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 160°C. Yield: 0.36 gm.

Analysis:

Found: Br, 16.21%
C_{24}H_{25}O_{6}Br requires Br, 16.36%
HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL CYCLOHEXENONE CARBOXYLATE: 2-{(4'-METHOXYPHENYL)-4-(2''-HYDROXY-4''-ETHOXY-5''-BROMOPHENYL)-Δ4-CYCLOHEXENE-6-ONE:

A mixture of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm), in ethanol (20 ml) and sodium hydroxide (10 ml : 5 per cent) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). A pale brown solid separated was filtered, washed with dilute sodium bicarbonate solution and then with water, dried and crystallised from ethanol, pale brown granules, m.p. 169°C. Yield: 0.28 gm.

Analysis:

Found: Br, 19.41 %

C_{2}H_{21}O_{4}Br requires Br, 19.19 %

ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-4'-METHOXY-4'-ETHOXY-5'-BROMOCHALCONE: 3-(2'-HYDROXY-4'-ETHOXY-5'-BROMOPHENYL)-5-(4'-METHOXYPHENYL)-ISOXAZOLINE:

2'-Hydroxy-4'-methoxy-4'-ethoxy-5'-bromoalchalone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added to it. The reaction mixture was refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid
A colourless product obtained was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 198°C. Yield: 0.26 gm.

Analysis:

Found: Br, 20.19%; N, 3.43%

C₁₉H₁₈O₄NBr requires Br, 20.41%; N, 3.57%

VI. CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-
ETHOXY-5-BROMOACETOPHENONE AND 2-4 DICHLOROBENZALDEHYDE:

CONDENSATION OF 2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE
WITH 2-4 DICHLOROBENZALDEHYDE: 2'-HYDROXY-2-4-DICHLORO-
4'-ETHOXY-5'-BROMOCHALCONE:

2-Hydroxy-4-ethoxy-5-bromoacetophenone (2.85 gm), 2,4-dichlorobenzaldehyde (1.93 gm), ethanol (50 ml), and potassium hydroxide (40 ml: 40 per cent) were mixed in a tightly corked flask. The reaction mixture was kept at the room temperature for 24 hours. The colour of the reaction mixture changed from a yellow to orange. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellow solid separated was filtered, washed with water, dried and crystallised from ethanol, yellow granules, m.p. 142°C. Yield: 3.90 gm.

The chalcone is sparingly soluble in aqueous alkali, but dissolves in ethanolic alkali giving an orange colour. It
gives a brown colour with ethanolic ferric chloride solution and a red colour with concentrated sulphuric acid.

Analysis:

Found : C, 49.21 %; H, 3.18 %; Halogen, 36.23 %

C_{17}H_{13}O_{3}BrCl_2 requires C, 49.04 %; H, 3.12 %; Halogen, 36.29 %

BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 5 hours. It was then cooled and poured in ice water containing dilute sulphuric acid. The yellowish white solid separated was filtered, washed with dilute sodium bicarbonate solution, then with water, dried and crystallised from petroleum ether (40-60) yellowish white needles, m.p. 112°C.

Yield : 0.39 gm.

Analysis:

Found : Halogen, 29.18 %

C_{24}H_{17}O_{4}BrCl_2 requires Halogen, 29.04 %

CYCLO-ISOMERISATION OF 2'-HYDROXY-2,4-DICHLORO-4'-ETHOXY-5'-BROMOCHALCONE : 7-ETHOXY-6-BROMO-2,4'-DICHLOROFLAVANONE:

To a solution of the chalcone (0.5 gm) in hot ethanol (40 ml), dilute sulphuric acid (20 ml : 10 per cent) was added and the reaction mixture was refluxed on a boiling water
bath for about 30 hours. Excess of ethanol was distilled off and the residual solution was then filtered hot and left at the room temperature. The yellow solid separated was filtered, washed with water dried and crystallised from ethanol, yellow granules, m.p. 146°C. Yield: 0.32 gm.

Analysis:

Found: Halogen, 36.53 %

C_{17}H_{13}OBrCl_2 requires Halogen, 36.29 %

**BROMINATION OF 2'-HYDROXY-2-4-DICHLORO-4'-ETHOXY-5'-BROMOCHALCONE :**

**BROMOCHALCONE :** 2'-HYDROXY-2-4-DICHLORO-4'-ETHOXY-5'-BROMOCHALCONE :

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml) and the bromine in acetic acid (5 ml: 10 per cent) was slowly added to it with constant stirring. The mixture was kept in an ice bath for 4 hours and then poured into ice water. The yellow solid separated was filtered, washed with dilute sodium thiosulphate solution to remove excess of bromine, then with water, dried and crystallised from acetone, yellow needles, m.p. 108°C. Yield: 0.36 gm.

Analysis:

Found: Halogen, 53.41 %

C_{17}H_{13}O_3Br_3Cl_2 requires Halogen, 53.96 %
DEBROMINATION OF THE ABOVE DIBROMOCHALCONE:

A mixture of the above dibromochalcone (0.3 gm), potassium iodide (0.3 gm) and dry acetone (20 ml) was refluxed on a water bath at 70°C for 3 hours. Acetone was removed and the product obtained was washed with dilute sodium thiosulphate solution and finally with water, dried and crystallised from ethanol, yellow granules, m.p. and mixed m.p. with original chalcone 142°C.

CYCLISATION OF 2'-HYDROXY-2,4-DICHLORO-4'-ETHOXY-5'-BROMOCHALCONE: 7-ETHOXY-6-BROMO-4'-DICHLOROFLAVONE:

(a) By Action of Acetone and Anhydrous Potassium Carbonate on the α:β Dibromochalcone:

A mixture of the dibromochalcone (0.5 gm), anhydrous potassium carbonate (0.5 gm) and acetone (20 ml) was refluxed on a water bath at 70°C for 4 hours. The solution was then filtered hot and acetone was removed. The yellowish solid obtained was filtered, washed with water, dried and crystallised from ethanol, yellowish needles, m.p. 134°C. Yield: 0.31 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone:

A mixture of the chalcone (0.5 gm) selenium dioxide (0.5 gm) and n-amyl alcohol (20 ml) was refluxed on an oil bath at 150°C for 24 hours. It was then filtered hot to remove
selenium and steam distilled to remove excess of n-amyl alcohol. The product obtained was washed with petroleum ether (40-60) to remove traces of n-amyl alcohol and crystallised from ethanol, yellowish brown granules, m.p. 134°C. Yield: 0.21 gm.

Analysis:

Found: Halogen, 36.29 %
C_{17}H_{11}OBrCl_2 requires Halogen, 36.48 %

OXIDATION OF 2'-HYDROXY-2'-DICHLORO-4'-ETHOXY-5'-BROMOFLAVONOL:

(a) By Action of Alkaline Hydrogen Peroxide:

The chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml: 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml: 20 vol) was added, and the reaction mixture was kept in the ice bath for 4 hours, and then left overnight at the room temperature. The colour of the reaction mixture changed from a red to orange. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1). The yellowish solid separated was filtered, washed with water, dried and crystallised from ethanol, yellow granules, m.p. 138°C. Yield: 0.26 gm.
(b) Using Sodium Peroxide in Ethanolic Solution:

A mixture of the chalcone (0.5 gm) and sodium peroxide (0.5 mM) in ethanol (20 ml) was refluxed on a boiling water bath for 1/2 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The yellowish solid separated was filtered, washed with water, dried and crystallised from ethanol, yellowish granules, m.p. 138°C. Yield: 0.32 gm.

Analysis:

Found: Halogen, 35.09%

C_{17}H_{11}O_{4}BrCl_2 requires Halogen, 35.12% 

Acetyl Derivative of Flavonol:

A mixture of flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water and the yellowish white solid separated was filtered, washed with water, dried and crystallised from ethanol, yellowish white needles, m.p. 131°C. Yield: 0.23 gm.

Analysis:

Found: Halogen, 32.08%

C_{19}H_{13}O_{5}BrCl_2 requires Halogen, 32.00%
CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-2-4-
DICHLOOR-4'-ETHOXY-5'-BROMOCHALCONE ; ETHYL-2-(2'-4-
DICHLOORPHENYL)-4-(2''-HYDROXY-4''-ETHOXY-5''-BROMOPHENYL)- 
\[ \Delta^4 \text{-CYCLOHEXENE-6-ONE-1-CARBOXYLATE :} \]

Sodium metal (0.2 gm) was dissolved in absolute ethanol (15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml). To this solution ethyl acetoacetate (1.0 ml) was added and the mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and diluted with ice water, then acidified with dilute hydrochloric acid (1:1). The yellowish white solid separated was filtered, washed with water, dried and crystallised from ethanol, yellowish white wooly needles, m.p. 181°C. Yield : 0.18 gm.

Analysis:

Found : Halogen, 28.38 %  
C_{23}H_{21}O_{5}BrCl_{2} requires Halogen, 28.61 %

HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE ETHYL CYCLOHEXENONE CARBOXYLATE: 2(2'-4'-DICHLOORPHENYL)-4-(2''-HYDROXY-4''-ETHOXY-5''-BROMOPHENYL)- \[ \Delta^4 \text{-CYCLOHEXENE-6-ONE :} \]

A solution of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml) was mixed with sodium hydroxide (10 ml : 5 per cent) and the mixture was
refluxed on a boiling water bath for 5 hours. It was then
diluted with ice water and acidified with dilute hydrochloric
acid (1:1). A brown solid separated was filtered, washed
with water, dilute sodium bicarbonate solution and finally
with water. It was then crystallised from ethanol, brown
granule m.p. 128°C. Yield: 0.21 gm.
Analysis:

Found: Halogen, 33.18%

C_{20}H_{17}O_3BrCl_2 requires Halogen, 33.11%

ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-2,4-
DICHLOOR-4'-ETHOXY-5'-BROMOCHALCONE: 3-(2-HYDROXY-4'-ETHOXY-
5-BROMOPHENYL)-5-(2,4-DICHLOROPHENYL) ISOXAZOLINE:

2'-Hydroxy-2,4-dichloro-4'-ethoxy-5'-bromochalcone
(1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine
hydrochloride (1.0 gm) in water (5.0 ml) was added to it.
The reaction mixture was refluxed on a boiling water bath
for 4 hours. It was then cooled and acidified with dilute
acetic acid (1:1). A dark brown solid obtained, washed with
water, dried and crystallised from ethanol, brown granules, m.p.
178°C. Yield: 0.29 gm.
Analysis:

Found: Halogen, 35.14% ; N, 3.12%

C_{17}H_{14}O_3NBrCl_2 requires Halogen, 35.04% ; N, 3.25%
VII CHALCONE AND RELATED COMPOUNDS DERIVED FROM 2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE AND 3-NITROBENZALDEHYDE:

CONDENSATION OF 2-HYDROXY-4-ETHOXY-5-BROMOACETOPHENONE WITH 3-NITROBENZALDEHYDE: 2'-HYDROXY-3-NITRO-4'-ETHOXY-5'-BROMOCHALCONE:

2-Hydroxy-4-ethoxy-5-bromoacetophenone (2.85 gm), 3-nitrobenzaldehyde (1.66 gm), ethanol (50 ml) and potassium hydroxide (40 ml: 40 per cent) were mixed in a tightly corked flask and kept at the room temperature for 24 hours. The colour of the reaction mixture changed from a yellow to orange. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). A brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 105°C. Yield: 3.8 gm.

Analysis:

Found: C, 52.31%; H, 3.28%; N, 3.44%; Br, 20.61%

C\textsubscript{17}H\textsubscript{14}O\textsubscript{5}NBr requires C, 52.04%; H, 3.57%; N, 3.57%; Br, 20.41%

BENZOYL DERIVATIVE:

A mixture of the chalcone (0.5 gm), benzoyl chloride (1.0 ml) and a drop of pyridine was heated on a boiling water
bath for 5 hours. It was then cooled, and treated with water containing dilute sulphuric acid. The yellow solid separated was filtered, washed with dilute sodium bicarbonate solution and finally with water, dried and crystallised from petroleum ether (40-60) yellow needles, m.p. 110°C. Yield: 0.38 gm.

Analysis:

Found: N, 2.59%; Br, 16.21%

C_{24}H_{18}O_6NBr requires N, 2.82%; Br, 16.13%

CYCLO-ISOMERISATION OF 2'-HYDROXY-3-NITRO-4'-ETHOXY-5'-BROMOCHALCONE:

To the hot solution of the chalcone (0.5 gm) in ethanol (40 ml) dilute sulphuric acid (20 ml: 10 per cent) was added. The precipitated solid was dissolved in more ethanol (20 ml) and the clear solution was refluxed on a boiling water bath for 30 hours. Excess of ethanol was distilled off and the residual solution was then filtered hot and left at the room temperature when a pale yellow solid separated. It was filtered, washed with water and crystallised from ethanol, pale yellow needles, m.p. 158°C. Yield: 0.28 gm.

Analysis:

Found: N, 3.39%; Br, 20.61%

C_{17}H_{14}O_5NBr requires N, 3.57%; Br, 20.41%
BROMINATION OF 2'-HYDROXY-3-NITRO-4'-ETHOXY-5'-BROMOCHALCOME:

The chalcone (0.5 gm) was dissolved in acetic acid (30 ml). The bromine in acetic acid (5 ml; 10 per cent) was added to it with constant stirring. It was then kept in an ice bath for 4 hours. Then the mixture was treated with ice water. The yellow solid obtained was filtered, washed with dilute sodium thiosulphate solution and then with water, dried and crystallised from acetone, yellow needles, m.p. 98°C. Yield: 0.38 gm.

Analysis:

Found: N, 2.36 %; Br, 43.59 %

C_{17}H_{14}O_{5}NBr_{3} requires N, 2.54 %; Br, 43.48 %

(b) DEBROMINATION OF THE ABOVE DIBROMOCHALCOME:

The mixture of the above dibromochalcone (0.3 gm), in dry acetone (20 ml) and potassium iodide (0.3 gm) was refluxed on a water bath at 70°C for 3 hours. Acetone was removed and a brown solid obtained was washed with dilute sodium thiosulphate solution, then with water and crystallised from ethanol, brown granules, m.p. and mixed m.p. with original chalcone 105°C.
CYCLISATION OF 2'-HYDROXY-3-NITRO-4'-ETHOXY-5'-BROMOCHALCONE :

7'-ETHOXY-6-BROMO-3'-NITROFLAVONE :

(a) By Action of Acetone and Anhydrous Potassium Carbonate

on the α : β Dibromochalcone :

The dibromochalcone (0.5 gm) in acetone (20 ml) was treated with anhydrous potassium carbonate (0.5 gm). The reaction mixture was then refluxed on a water bath at 70°C for 4 hours. The solution was then filtered hot and acetone was removed. The brown solid obtained, was washed with water, dried and crystallised from ethanol, brown granules, m.p. 240°C. Yield : 0.26 gm.

(b) By Selenium Dioxide Oxidation of the Chalcone :

To a solution of chalcone (0.5 gm) in n-amyl alcohol (20 ml), selenium dioxide (0.5 gm) was added and the reaction mixture was refluxed on an oil bath at 150°C for 24 hours. Selenium was then filtered off from the hot reaction mixture and the clear filtrate was subjected to steam distillation to remove n-amyl alcohol and the solid separated was crystallised from ethanol, brown granules, m.p. 240°C. Yield : 0.21 gm.

Analysis:

Found : N, 3.69 % ; Br, 20.38 %

C_{17}H_{12}O_{2}NBr requires N, 3.58 % ; Br, 20.51 %
OXIDATION OF 2'-HYDROXY-3-NITRO-4'-ETHOXY-5'-BROMOCHALCONE : 7-ETHOXY-6-BROMO-3'-NITROFLAVONOL :

(a) By Action of Alkaline Hydrogen Peroxide :

The chalcone (0.5 gm) in methanol (60 ml) was treated with sodium hydroxide (20 ml : 10 per cent) and the mixture was kept in an ice bath. Hydrogen peroxide (20 ml : 20 vol) was added, and the reaction mixture was kept cool in the ice bath for 4 hours and then left overnight at the room temperature. The colour of the reaction mixture changed from an orange to yellowish green. It was then poured into ice water and acidified with dilute hydrochloric acid (1:1). The brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 292°C. Yield : 0.21 gm.

(b) Using Sodium Peroxide in Ethanolic Solution :

A mixture of the chalcone (0.5 gm), sodium peroxide (0.5 gm) and ethanol (20 ml) was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water and acidified with dilute hydrochloric acid (1:1). The brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 292°C. Yield : 0.31 gm.
ACETYL DERIVATIVE OF FLAVONOL:

A mixture of the flavonol (0.5 gm), acetic anhydride (1.0 ml) and a drop of pyridine was heated on a boiling water bath for 4 hours. It was then treated with ice water and the pale brown solid separated was filtered, washed with water, dried and crystallised from ethanol, pale brown granules, m.p. 102°C. Yield: 0.20 gm.

Analysis:

Found: N, 3.61%; Br, 19.51%

C_{17}H_{12}O_{6}NBr requires N, 3.45%; Br, 19.71%

CONDENSATION OF ETHYL ACETOACETATE WITH 2'-HYDROXY-3-NITRO-
4'-ETHOXY-5'-BROMOCHALCONE: ETHYL-2-(3'-NITROPHENYL)-4-
(2''-HYDROXY-4''-ETHOXY-5''-BROMOPHENYL)-\Delta^4-CYClOHEXENE-6-ONE-
1-CARBOXYLATE:

Sodium metal (0.2 gm) was dissolved in ethanol (15 ml) and mixed with chalcone (0.5 gm) in ethanol (20 ml). To this solution ethyl acetoacetate (1.0 ml) was added and the
mixture was refluxed on a boiling water bath for 5 hours. It was then cooled and poured in ice water, and acidified with dilute hydrochloric acid (1:1). The brown solid separated was filtered, washed with water, dried and crystallised from ethanol, brown granules, m.p. 78°C. Yield: 0.31 gm.

Analysis:

\[
\text{Found: } N, 2.88\% ; \text{ Br, } 15.63\% \\
C_{23}H_{22}O_7NBr \text{ requires } N, 2.78\% ; \text{ Br, } 15.88\%
\]

HYDROLYSIS AND SIMULTANEOUS DECARBOXYLATION OF THE ABOVE

ETHYL CYCLOHEXENONE CARBOXYLATE : 2-(3'-NITROPHENYL)-4-(2"-HYDROXY-4"-ETHOXY-5"-BROMOPHENYL)-\[\Delta^4\]-CYCLOHEXENE-6-ONE:

A solution of the above ethyl diphenyl cyclohexenone carboxylate derivative (0.5 gm) in ethanol (20 ml) was mixed with sodium hydroxide (10 ml: 5 per cent) and the mixture was refluxed on a boiling water bath for 5 hours. It was then diluted with ice water (100 ml) and acidified with dilute hydrochloric acid (1:1). A brown solid separated was filtered, washed with dilute sodium bicarbonate solution and then with water, dried and crystallised from ethanol, brown granules, m.p. 220°C. Yield: 0.32 gm.

Analysis:

\[
\text{Found: } N, 3.36\% ; \text{ Br, } 18.63\% \\
C_{20}H_{18}O_5NBr \text{ requires } N, 3.24\% ; \text{ Br, } 18.52\%
\]
ACTION OF HYDROXYLAMINE HYDROCHLORIDE ON 2'-HYDROXY-3-NITRO-
 4'-ETHOXY-5'-BROMOCHalcone : 3(2-HYDROXY-4-ETHOXY-5-
BROMOPHENYL)-5-(3-NITROPHENYL)-ISOKAZONINE :

2'-Hydroxy-3-nitro-4'-ethoxy-5'-bromochalcone (1.0 gm) was dissolved in pyridine (5.0 ml) and hydroxylamine hydrochloride (1.0 gm) in water (5.0 ml) was added to it. The reaction mixture was refluxed on a boiling water bath for 4 hours. It was then cooled and acidified with dilute acetic acid (1:1). A colourless product obtained was filtered, washed with water, dried and crystallised from ethanol, white granules, m.p. 182°C. Yield: 0.47 gm.

Analysis:

Found: N, 3.61%; Br, 19.43%  
C_{17}H_{15}O_{5}N_{2}Br requires N, 3.44%; Br, 19.65%
REFERENCES

10. Sven Bodforss, Ber., 49, 2795 (1916).