CHAPTER - 3

SYNTHESIS OF ACETYL HYDROXYFLAVONES AND 3,4-DIHYDRO-2,2-DIMETHYL-2H-PYRANOFLAVONES

The flavonoid compounds occupy a prominent position among the plant phenols. They are important to man not only because they contribute to plant colour but also because many members are physiologically active. Among the recent developments, the discovery and expanded study of their synthesis are prominent. Flavones possessing prenyl substituents occur quite frequently in nature, so do those with 2,2-dimethylpyran ring system\textsuperscript{140,141}. Some typical examples\textsuperscript{142-168} of such compounds are given in Table 3.1 (Page Nos. 75 & 76).

A health food, designed to prevent diseases, consisted of extracts of Morbus bombycis or related plants (containing morusin (III g) and/or its hydrate)\textsuperscript{169}. Topazolin [5,7,4'-trihydroxy-3-methoxy-6-(3,3-dimethylallyl) flavone] showed very weak fungitoxic activity\textsuperscript{170}. Isopongaflavone (III d) was very much active against Maruca testulalis and Eldana saccharina and hence was effective as an antifeedant\textsuperscript{171}. Atalantoflavone dimethylether displayed significant insecticidal activity\textsuperscript{172}.

The emergence of this class of flavonoid compounds has given an impetus to devising methods for their synthesis.

3.1. Synthesis of 2,2-dimethyl -2H-pyranoflavones

Synthetic Methods

Jain \textit{et al}\textsuperscript{173} propargylated 5,7-dihydroxy -3-methylflavone (1) with 2-chloro-2-methyl -3-butyn in the presence of potassium carbonate and potassium iodide in acetone when the 7-propargyl ether (2) resulted. The angular and linear pyranoflavones 3 and 4 were formed in the ratio of 2:1 when the ether 2 was heated with N,N- dimethylaniline. On treatment with dilute alcoholic potash, the angular compound 3 underwent Wessely - Moser rearrangement to give the linear derivative 4. Propargylation with DMF as solvent yielded a 1:3:1 mixture of 7-propargylic ether 2, angular and linear pyranoflavones 3 and 4 respectively (Chart 3.1, Page No.78).
Table 3.1. Flavones with Isoprenoid Substituents

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Trivial Name</th>
<th>Substituents</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>8-Prenyl luteolin (Ia)</td>
<td>H OH H OH a H OH OH</td>
<td>142</td>
</tr>
<tr>
<td>2.</td>
<td>Artocarpesin (Ib)</td>
<td>H OH a OH H OH H OH</td>
<td>143</td>
</tr>
<tr>
<td>3.</td>
<td>Oxydihydroartocarpesin (Ic)</td>
<td>H OH b OH H OH H OH</td>
<td>143</td>
</tr>
<tr>
<td>4.</td>
<td>Artocarpin (Id)</td>
<td>a OH c OH H OH H OH</td>
<td>143</td>
</tr>
<tr>
<td>5.</td>
<td>Norartocarpin (Ie)</td>
<td>a OH c OMe H OH H OH</td>
<td>143</td>
</tr>
<tr>
<td>6.</td>
<td>Mulberrin (If)</td>
<td>a OH a OH H OH H OH</td>
<td>144</td>
</tr>
<tr>
<td>7.</td>
<td>Kuwanone C (Ig)</td>
<td>a OH H OH a OH H OH</td>
<td>145</td>
</tr>
<tr>
<td>8.</td>
<td>Integrin (Ih)</td>
<td>a OH H OMe H OH H OH</td>
<td>146</td>
</tr>
<tr>
<td>9.</td>
<td>Lanceolatin A(Ii)</td>
<td>H H H OMe d H H H</td>
<td>147</td>
</tr>
<tr>
<td>10.</td>
<td>cis-Tephrostachin (Ij)</td>
<td>H OMe H OMe e H H H</td>
<td>148</td>
</tr>
<tr>
<td>11.</td>
<td>trans-Tephrostachin (Ik)</td>
<td>H OMe H OMe d H H H</td>
<td>149</td>
</tr>
<tr>
<td>12.</td>
<td>trans-Anhydro</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>tephrostachin (Ik)</td>
<td>H OMe H OMe f H H H</td>
<td>149</td>
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<tr>
<td>13.</td>
<td>Carpachromene (Ila)</td>
<td>H OH H H H OH H H</td>
<td>150,151</td>
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</table>

Table 3.1. (Contd.)
<table>
<thead>
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<th>S.No.</th>
<th>Trivial Name</th>
<th>Substituents</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.</td>
<td>- (II b)</td>
<td>R, H r2 OMe r2 H</td>
<td>152</td>
</tr>
<tr>
<td>15.</td>
<td>Cycloartocarpesin (II c)</td>
<td>H OH H OH H OH H H</td>
<td>153,154</td>
</tr>
<tr>
<td>16.</td>
<td>Mulberrochromene (or)</td>
<td>a OH H OH H OH H H</td>
<td>144,155</td>
</tr>
<tr>
<td></td>
<td>Cudraflavone B (II d)</td>
<td></td>
<td></td>
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<tr>
<td>17.</td>
<td>Artobilochromene (II e)</td>
<td>H OH H H OH a OH H</td>
<td>156</td>
</tr>
<tr>
<td>18.</td>
<td>- (III a)</td>
<td>H H H H H H H H H</td>
<td>157</td>
</tr>
<tr>
<td>19.</td>
<td>- (III b)</td>
<td>H H H H -O-CH₂-O-H H</td>
<td>157</td>
</tr>
<tr>
<td>20.</td>
<td>- (III c)</td>
<td>H OH H H H H H H H</td>
<td>158</td>
</tr>
<tr>
<td>21.</td>
<td>Isopongaflavone (or)</td>
<td>H OMe H H H H H H H</td>
<td>149,152,159,160</td>
</tr>
<tr>
<td></td>
<td>Candidin (III d)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.</td>
<td>- (III e)</td>
<td>H OMe H H -O-CH₂-O-H H</td>
<td>157</td>
</tr>
<tr>
<td>23.</td>
<td>Desmodol (III f)</td>
<td>H OH Me H OH OH H H</td>
<td>161</td>
</tr>
<tr>
<td>24.</td>
<td>Morusin (III g)</td>
<td>a OH H OH H OH H H</td>
<td>162,163</td>
</tr>
<tr>
<td>25.</td>
<td>Racemoflavone (III h)</td>
<td>H OH H H OMe OH H H</td>
<td>164</td>
</tr>
<tr>
<td>26.</td>
<td>Atalantoflavone (or)</td>
<td>H OH H H H OH H H H</td>
<td>164,165</td>
</tr>
<tr>
<td></td>
<td>Limonianin (III i)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27.</td>
<td>Artonius - E (III j)</td>
<td>a OH H OH H OH H H</td>
<td>166</td>
</tr>
<tr>
<td>28.</td>
<td>Fulvinervin -B (III k)</td>
<td>H OH f H H H H H H</td>
<td>167</td>
</tr>
<tr>
<td>29.</td>
<td>Fulvinervin-C (III l)</td>
<td>H OH d H H H H H H</td>
<td>168</td>
</tr>
</tbody>
</table>

Key: a: -CH₂-CH=CH(CH₃)₂  
b: -CH₂-CH₂-C(OH) (CH₃)₂  
c: -CH=CH-CH(CH₃)₂  
d: -CH=CH-C(OH) (CH₃)₂ (trans)  
e: -CH=CH-C(OH) (CH₃)₂ (cis)  
f: -CH=CH-C(CH₃)=CH₂
Ahluwalia et al. obtained the angular product IIIa by the cyclisation of 7-(1',1'-dimethyl prop-2-ynyloxy)-2-phenyl-4H-benzopyran-4-one (6) by heating in N,N-dimethylaniline. When the eighth position of the flavone 5 was blocked by iodine and propynylation product 8 of the iodinated flavone 7 rearranged, the product was the linear flavone II (Chart 3.1, Page No.78).

When the flavone chrysin (9) was treated with 2-chloro-2-methyl-but-3-yne in dimethylformamide in the presence of potassium carbonate and potassium iodide for 16 hours at 65°C, the major product isolated was the linear pyranoflavone 10, the expected ether 11 and the angular pyranoflavone (IIIc) were formed in minor amounts. The 7-O-propargyl ether 11 afforded on partial hydrogenation with 10% Pd-BaSO₄ poisoned with quinoline, the α,α-dimethylallyl ether 12. In refluxing N,N-dimethylaniline, this ether rearranged in excellent yield to 13. The latter was cyclodehydrogenated to the dimethyl pyranoflavone IIIc (Chart 3.2, Page No.79).

Roy et al. prenylated chrysin (9) with 2-methyl but-3-ene-2-ol and BF₃-etherate to give 8-C-prenylchrysin (14), 6,8-di C, C-prenylchrysin (15) and 6-C-prenylchrysin (16). Oxidative cyclisation of 14 with DDQ furnished the pyranoflavone IIIc which was methylated to isopongaflavone (IIId) (Chart 3.2).

Apigenin (17) was prenylated under milder conditions (at 30-40°C) with 2-methyl-but-3-ene-2-ol in dioxane to give two main products, namely 7-O-prenylapigenin (18) and 6-C-prenylapigenin (19). The latter was oxidatively cyclised with DDQ to carpachromene (IIa) (Chart 3.3, Page No.80).

When prenylation was attempted at 45-50°C, apigenin (17) gave two major and four minor products, 6-C-prenylapigenin (19) and the angular dihydropyranoflavone 20, were formed in major amounts. The minor products isolated were 7-O-prenyl ether 18, the prenylated angular dihydropyranoflavone 21 and the linear dihydropyranoflavone 22 and its prenyl analogue 23 (Chart 3.3).
CHART 3.1

Jain et al.\textsuperscript{173} synthesis of pyranoflavones

\begin{align*}
\text{(ii) }C_6H_5N(CH_3)_2 & \\
\text{(iii) Propynylation} & \\
\text{(iii) }I_2/HIO_4 & \\
\end{align*}

Ahluwalia et al.\textsuperscript{173a} method

\begin{align*}
\text{(i) } & \\
\text{(i) } & \\
\text{(ii) } & \\
\text{(iii) } & \\
\text{(iv) } & \\
\end{align*}

(i) $\text{Cl}, K_2CO_3, KI \text{ & acetone}$

(ii) $C_6H_5N(CH_3)_2$

(iii) Propynylation

(iv) $I_2/HIO_4$
Synthesis of dimethylpyranoflavone IIIc from chrysin(9)

Roy et al\textsuperscript{159} method

\[
\begin{align*}
9 & \xrightarrow{\text{Cl}} \xrightarrow{\text{K}_2\text{CO}_3, \text{DMF}} 10 \\
11 & + \xrightarrow{10\% \text{Pd-BaSO}_4} 13 \\
12 & \xrightarrow{\text{C}_6\text{H}_5\text{NMe}_2} 13
\end{align*}
\]

14: 
R\textsubscript{1} = H, R\textsubscript{2} = \text{CH}_2-\text{CH} = \text{C(CH}_3\text{)}_2

15: 
R\textsubscript{1} = R\textsubscript{2} = \text{CH}_2\text{CH} = \text{C(CH}_3\text{)}_2

16: 
R\textsubscript{1} = -\text{CH}_2\text{CH} = \text{C(CH}_3\text{)}_2, R\textsubscript{2} = H

17: 
DDQ

\[
\begin{align*}
14 & \xrightarrow{\text{DDQ}} \xrightarrow{\text{OR}} \text{IIIc} R = H \\
\text{IIIId} R = \text{CH}_3
\end{align*}
\]
Aiming to prepare carpachromene (IIa) and related compounds Jain et al. studied the prenylation of acacetin 24 and apigenin 17. Acacetin 24 when refluxed with prenyl bromide in the presence of methanolic sodium methoxide for 4 hours gave 6,8-di-C-prenyl-25 and 6-C-prenyl-acacetin 26. Acid-catalysed cyclisation of 25 furnished the bis dihydropyran 27 whereas the mono methylether was cyclised to 28. Mono methylether of 6-C-prenylacacetin 26 was methylated followed by cyclisation with an acid to the corresponding chroman 29. 6-C-Prenylacacetin 26 with DDQ gave 30 which was methylated to yield carpachromene dimethylether 31 (Chart 3.3a, Page No.82).

Apigenin (17) was prenylated in the same manner to yield 6,8-di-C,C-prenyl (32), 7-O-prenyl (18) and 6-C-prenyl (19) derivatives. DDQ reaction of 19 provided natural carpachromene (IIa). The diprenyl derivative 32 was cyclodehydrogenated to result in the two possible pyranoflavones 33 and 34 (Chart 3.4, Page No.83).

Glabrachromene-I (35) isolated from pongamia glabra was converted into 5-methoxy-2-(3',4'-methylenedioxyphenyl) -8,8-dimethylpyrano (2,3-h) chrom-4-one (IIIe) by refluxing with selenium dioxide in amyl alcohol solution. DDQ in boiling benzene was also useful in the conversion of pyranochalcones to pyranoflavones.

Some pyranoflavanones 36,36a and 38 were transformed into the corresponding pyranoflavones IIIa, 37 and 39 when refluxed with DDQ in dry dioxane, for 3 hours (Chart 3.4).

6-Acetyl-5-hydroxy-2,2-dimethylchromene (40) and 6-acetyl-5-hydroxy-7-methoxy-2,2-dimethylchromene (41) were aroylated with aroyl chloride (42) using pyridine. The esters 43 formed underwent rearrangement under Baker-Venkataraman conditions (potassium hydroxide-pyridine) to give the diketones 44 which were
CHART 3.3a

Jain et al Method 151

\[ \text{24} \]

\[ \text{Br, NaOMe, MeOH} \]

\[ \text{25} \]

\[ \text{26} \]

\[ \text{27} \]

\[ \text{28} \]

\[ \text{29} \]

(i) \( \text{Me}_2\text{SO}_4 \)  (ii) \( \text{H}^+ \)  (iii) \( \text{DDQ} \)

\[ \text{30} \text{ R=H} \]

\[ \text{31} \text{ R=CH}_3 \]
CHART 3.4

Prenylation & DDQ reaction of Apigenin (17)

Conversion of pyranoflavanones into pyranoflavones

(i) DDQ / C₆H₆
**CHART 3.5**

2,2-Dimethyl pyranoflavone from acetylhydroxychromene

![Chemical Structures](image)

---

**Prasad et al.**

---

**CHART 3.5**

2,2-Dimethyl pyranoflavone from acetylhydroxychromene

![Chemical Structures](image)
CHART 3.6
Banerji and Goomer \textsuperscript{180} method

\[
\begin{align*}
&\text{51} \\
&\text{52} \\
&\text{53} \\
&\text{54} \quad R = \text{OCH}_3 \\
&\text{55} \quad R = \text{H} \\
&\text{56} \quad R = \text{H} \\
&\text{57} \quad R = \text{OCH}_3
\end{align*}
\]
cyclised to the pyranoflavones IIIa and IIIe respectively in boiling acetic acid containing a drop of concentrated hydrochloric acid 178 (Chart 3.5, Page No.84).

Applying a similar series of reactions to suitable o-hydroxy acetylchromans 45 and 46, Prasad et al 179a synthesised several dihydropyranoflavones like 38 and 29. The aroyl esters 47 and 48, and β-diketones 49 and 50 were the intermediates in the process (Chart 3.5).

Banerji and Goomer180 prepared the lithium enolate of evodionol (51) with lithium diisopropyl amide (LDA) at -25°C in THF. It was then aroylated at -78°C using 2,4-dimethoxy-benzoyl chloride to afford the β-diketone (52) in good yield, which was cyclised with p-toluencesulphonic acid to afford the cycloartocarpesin-trimethylether (53). A similar procedure was adopted to synthesise the pyranoflavones 54, 56, 57 and carpachromene dimethylether 55172 (Chart 3.6, Page No.85).

3.2. Present Work and Discussion

Synthesis of new acetylhydroxyflavones and pyranoflavones

Many methods reported for the synthesis of pyranoflavones starting from simple flavone moiety and the pyrano ring was the one which was then latter developed.

(i) Flavones can be prepared from chalcones and flavanones. α,β-Dibromochalcones when boiled in methanol followed by thermal cyclisation, gave the corresponding flavones181. Flavanones were dehydrogenated to flavones by the use of SeO₂182, NBS/pyridine183, a mixture of iodine and potassium acetate in acetic acid 184 and chloranil 185.

(ii) By Baker-Venkataraman rearrangement 186-188 of o-aroyloxyacetophenones which gave the β-diketones with potassium hydroxide/pyridine or sodium hydride. Ring closure was finally performed in ethanol - sulfurous acid, glacial acetic acid - sodium acetate or simply by heating the β-diketone in vacuum.

(iii) o-Hydroxy acetophenones when treated with aroyl chlorides in the presence of Li N (C₃H₇-i)₂ were transformed to flavones through β-diketones 189.
(iv) Allan-Robinson condensation\textsuperscript{122,190,191} flavones were obtained in one step by the condensation of an o-hydroxyacetophenone with the anhydride of an aromatic acid in the presence of the salt of the same acid or in the presence of triethylamine or pyridine as catalyst.

(v) Phenyl epoxy cinnamate was converted to o-hydroxy benzoyl acetophenone when irradiated with UV light under nitrogen atmosphere through the intermediacy of 2'-hydroxyepoxychalcone. The diketone formed was then cyclised to flavone by treatment with sodium acetate, acetic acid mixture\textsuperscript{192}.

(vi) Flavenes on treatment with potassium permanganate in acetone gave flavones\textsuperscript{193}.

(vii) Vijayalakshmi and Prasad\textsuperscript{74b} also synthesised several dihydro- pyranoflavones by Claisen condensation\textsuperscript{194} as a tool and using sodium hydride as an agent in acylation of certain ketones.

(viii) Prasad \textit{et al}\textsuperscript{75} synthesised dihydropyranoflavones and aurones from the corresponding dihydropyranochalcones by oxidative cyclisation using DDQ\textsuperscript{195-197}.

\textbf{3.2.1. Synthesis of new acetyl hydroxyflavones}

The dianisoyl and diveratroyl dioxy derivatives, 59 and 63, obtained from 5-acetyl-2,4-dihydroxyacetophenone 58 on Baker-Venkataraman rearrangement with pyridine and KOH yielded the corresponding \(\beta\)-diketones 60 and 64, which on acid-catalysed cyclisation with anhydrous sodium acetate and glacial acetic acid afforded the new acetyl hydroxyflavone derivatives 61, 62 and 65, 66 respectively (Scheme 3.1, Page No.88), (Scheme 3.5, Page No. 94).

\textbf{3.2.1.1. 6-Acetyl-7-hydroxy-3', 4'-dimethoxyflavone (62) (Scheme 3.1, Page No.88)}

\textbf{(a) Veratroylation of 5-Acetyl-2,4-dihydroxy acetophenone (58)}

The reaction of 5-acetyl-2,4-dihydroxy acetophenone, (58)\textsuperscript{198} with 3,4-dimethoxy benzoyl chloride (67) in presence of pyridine yielded the ester, 5-acetyl-2,4-[3',4',3",4"-tetramethoxy] dibenzoyloxy acetophenone (59). The ester was
SCHEME 3.1

SYNTHESIS OF 6-ACETYL-7-HYDROXY-3', 4'-DIMETHOXY FLAVONE (62)

58 \rightarrow 59 \rightarrow 60 \rightarrow 61

(i) \[ \text{H}_3\text{CO} - \text{y-c-0} - \text{COCH}_3 \]

(ii) KOH, Pyridine

(iii) NaOAc, AcOH

(iv) Ethanol, aq. Na$_2$CO$_3$

(i) \[ \text{H}_3\text{CO} - \text{Cl} \]

(ii) KOH, Pyridine

(iii) NaOAc, AcOH

(iv) Ethanol, aq. Na$_2$CO$_3$
crystallised from ethanol as colourless prisms, m.p. 132°C. Its IR spectrum (Fig.No. 3.1) showed an absorption band at 1720 cm\(^{-1}\) characteristic of ester carbonyl group and 1670 cm\(^{-1}\) characteristic of ketone carbonyl group. It did not give alcoholic ferric chloride test indicating the absence of phenolic -OH group. On this basis, the structure of the compound has been assigned as 5-acetyl-2,4-[(3',4',3'',4''-tetramethoxy) dibenzoyloxy] acetophenone (59).

(b) 2,4-Dihydroxy-5-[(3',4',-dimethoxy) benzoyleacyl] acetophenone (60)

The ester (59) obtained from 5-acetyl-2,4-dihydroxy acetophenone (58) and 3,4-dimethoxy benzoylchloride (67) (Veratroyl chloride) on Baker-Venkataraman rearrangement gave two products. The compound eluted with 2% ethyl acetate-petroleum ether mixture was found to be 5-acetyl-2,4-dihydroxy acetophenone (58) and the product obtained from 5% ethyl acetate-petroleum ether mixture was found to be 2,4-dihydroxy-5-[(3',4'-dimethoxy) benzoyleacyl] acetophenone (60), and it was crystallised from petroleum ether - ethyl acetate mixture as yellow needles, m.p. 185°C. It gave violet colour with alcoholic ferric chloride, indicating the presence of phenolic -OH group. Its IR spectrum (Fig.No. 3.2) showed absorption bands at 1630 and 1680 cm\(^{-1}\) characteristic of \(\beta\)-diketone. The 'H-NMR (Fig.No. 3.3) spectrum showed the following peaks. The methyl proton (C\(_5\)-COCH\(_3\)) appeared as a singlet at 2.60 \(\delta\), the peak at 3.90 \(\delta\) was due to the presence of two - OCH\(_3\) groups. Methylene protons appeared as a singlet at 4.45 \(\delta\). The olefinic proton of the enolic form appeared as a singlet at 6.30 \(\delta\), the doublet at 6.85 \(\delta\) due to the proton at C\(_5\)' position. The aromatic protons (3H, C\(_2\)'-H, C\(_6\)'-H and C\(_6\)-H) appeared as multiplet at 7.85\(\delta\). The phenolic protons, C\(_2\)-OH and C\(_4\)-OH appeared as two singlets at 8.10 and 8.50 \(\delta\). From proton NMR integration the ratio of the keto and enol forms was found to be 1:1.

On the basis of mass spectrum (Fig.No.3.4) the molecular ion peak was found to be at 358; (M\(^+\) C\(_{19}\)H\(_{18}\)O\(_7\)). The fragmentation pattern of 2,4-dihydroxy-5-[(3',4' -dimethoxy)benzoyleacyl] acetophenone (60) was shown in Scheme 3.2 (Page No.90).
Fig. 3.1: IR spectrum of 5-Acetyl-2,4-[1(3',4',3''-tetramethoxy) dibenzoxyloxy] acetophenone (59)
Fig. 3.2. IR spectrum of 2,4-Dihydroxy-5-[(3',4'-dimethoxy) benzoylacetyl] acetophenone (60)
Fig. 3.3. Proton NMR spectrum of 2,4-Dihydroxy-5-[3',4'-dimethoxy] benzoylacetyl] acetophenone (60)
Fig. 3.4. Mass spectrum of 2,4-Dihydroxy-5-[(3',4'-dimethoxy) benzoylacetyl] acetophenone (60)

<table>
<thead>
<tr>
<th>m/e</th>
<th>Relative Intensity (%)</th>
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<tr>
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<td>2.85</td>
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<tr>
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<td>2.71</td>
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<td>161.0</td>
<td>5.87</td>
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<td>359.0</td>
<td>16.18</td>
</tr>
<tr>
<td>360.0</td>
<td>3.21</td>
</tr>
</tbody>
</table>
SCHEME 3.2

CgH6O3 m/e 150 (2.85%)  
\(-\text{CH}_2=\text{C}=0\)  

C9H10O3 m/e 166 (19.5%)  
C8H7O3 m/e 151 (2.71%)  

C9H10O6 m/e 179 (20.34%)  
C10H12O3 m/e 180 (14.49%)  

C11H10O4 m/e 206 (4.01%)  

C19H18O7 m/e 358 (66.2%)  
MOLECULAR ION PEAK

C16H16O3 m/e 179 (20.34%)  
CgH13O4 m/e 163 (3.20%)  

FRAGMENTATION PATTERN FOR 2, 4 - DIHYDROXY - 5 - [(3', 4'-DIMETHOXY) BENZOYL ACETYL] ACETOPHENONE(60)
On the basis of above spectral data the structure of the compound was assigned as 2,4-dihydroxy-5-[(3',4'-dimethoxy)benzoylacetyl] acetophenone (60).

\[
\begin{align*}
\text{HO} & \quad \text{OH} \\
\text{H}_3\text{CO} & \quad \text{COCH}_2\text{CO} \\
\end{align*}
\]

\[
\begin{align*}
\text{OCH}_3 & \quad \text{OCH}_3 \\
\text{HO} & \quad \text{OH} \\
\text{H}_3\text{CO} & \quad \text{CH}=\text{C} \\
\text{OCH}_3 & \quad \text{OCH}_3 \\
\end{align*}
\]

(c) 6-Acetyl-7-hydroxy-3',4'-dimethoxyflavone (62)

Acid catalysed cyclisation of the \(\beta\)-diketone (60) gave a product which was purified by column chromatography over silica gel using petroleum ether -ethyl acetate (95:5) as a solvent system. Removal of solvent gave a product, m.p. 215°C. Its IR spectrum (Fig.No.3.5) showed two bands at 1740 and 1620 cm\(^{-1}\), characteristic of \(\alpha,\beta\)-unsaturated carbonyl group. The \(^1\)H-NMR spectrum (Fig.No.3.6) showed the following peaks. The two singlets at 2.25 and 2.65 \(\delta\) were due to the protons of two acetyl groups at \(C_3\) and \(C_6\) respectively. The two methoxyl protons at \(C_3'\) and \(C_4'\) appeared as two singlets at 3.88 and 3.99 \(\delta\) respectively. The doublet at 6.85 \(\delta\) was due to the presence of proton at \(C_5'\) position with \(J=9\) Hz. The proton at \(C_8\)-position appeared as a singlet at 6.80 \(\delta\) overlapped with \(C_5\) - H. The doublet at 7.30\(\delta\) was due to the proton at \(C_6'\) position with \(J=9\) Hz. The singlet at 7.53 \(\delta\) was due to \(C_2'\) position. The singlet at 8.55 \(\delta\) was due to the proton at \(C_7\)-position. The phenolic proton (\(C_7\)-OH) appeared as a singlet at 12.55 \(\delta\).

It gave violet colour with alcoholic ferric chloride indicating the presence of phenolic - OH group. From the above data, the structure of the compound has been assigned as 3,6-diacetyl-7-hydroxy-3',4'-dimethoxyflavone (61).

In mass analysis (Fig.No.3.7) the molecular ion peak was found to be at m/e 382 (M\(^+\) C\(_{21}\) H\(_{18}\) O\(_7\)). The fragmentation pattern of 3,6-diacetyl-7-hydroxy-3',4'-dimethoxyflavone (61) is shown in Scheme 3.3 (Page No.92).
Fig. 3.5. IR spectrum of 3,6-diacetyl-7-hydroxy-3',4'-dimethoxyflavone (61)
Fig. 3.6. Proton NMR spectrum of 3,6-diacetyl-7-hydroxy-3',4'-'dimethoxyflavone (61)
Fig. 3.7. Mass spectrum of 3,6-Diacetyl-7-hydroxy-3',4'-dimethoxyflavone (61)
SCHEME 3.3

FRAGMENTATION PATTERN OF 3,6-DIACETYL-7-HYDROXY-3',4'-DIMETHOXY FLAVONE

(61)
SCHEME 3.4

\[
\begin{align*}
\text{C}_{10}H_{10}O_{2} & \quad \text{m/e 162} \\
\text{C}_{18}H_{12}O_{6} & \quad \text{m/e 324} \\
\text{C}_{17}H_{14}O_{5} & \quad \text{m/e 298} \\
\text{C}_{18}H_{16}O_{5} & \quad \text{m/e 312 (6.34%)} \\
\text{C}_{19}H_{16}O_{6} & \quad \text{m/e 340} \\
\text{C}_{9}H_{6}O_{4} & \quad \text{m/e 178}
\end{align*}
\]

FRAGMENTATION PATTERN FOR 6-ACETYL-7-HYDROXY-3',4'-DIMETHOXY FLAVONE (62)
SCHEME 3.5
SYNTHESIS OF 6 - ACETYL - 7 - HYDROXY - 4' - METHOXY FLAVONE (66)

(i) H_3CO-COCl

(ii) KOH, Pyridine

(iii) NaOAc, AcOH

(iv) Ethanol, aq. Na_2CO_3
The product obtained from the de-C-acetylation of 3,6-diacetyl-7-hydroxy-3',4'-dimethoxyflavone (61) showed the IR bands (Fig No. 3.8) at 1640 and 1620 cm⁻¹ indicating the presence of α,β-unsaturated carbonyl group, and melting at 240°C.

The ¹H-NMR spectrum (Fig No.3.9) showed the following peaks. The methyl proton of C₆-COCH₃ appeared as a singlet at 2.65 δ. The singlet at 3.88 δ was due to the protons of two-OCH₃ groups (at C₃' and C₄' position). The peak at 6.55 δ was due to the C₃ proton. The proton at C₃' position appeared as a doublet at 6.85 δ with J=9 Hz. The aromatic protons at C₆ and C₅ positions appeared as two singlets at 6.90 and 8.55 δ respectively. The singlet at 7.25 δ was due to the proton at C₂' position. The C₆'-H appeared as a doublet at 7.40 δ with J=9 Hz. The phenolic proton at C₇ position (C₇-OH) appeared as a singlet at 12.55 δ.

In mass analysis (Fig.No.3.10) the molecular ion peak was found to be at m/e 340 (M⁺ C₁₉H₁₆O₆). The fragmentation pattern of 6-acetyl-7-hydroxy-3',4'-dimethoxyflavone (62) is shown in Scheme 3.4 (Page No.93).

From the above data the structure of the compound has been assigned as 6-acetyl-7-hydroxy-3',4'-dimethoxyflavone (62).

Adopting the same procedure, other new acetyl hydroxyflavone 6-acetyl-7-hydroxy-4'-methoxyflavone (66) was obtained through the intermediate 3,6-diacetyl-7-hydroxy-4'-methoxyflavone (65) (Scheme 3.5, Page.No.94).

3.2.2. Synthesis of 2,2-dimethyl-2H- pyranoflavones

The present work was undertaken with the view to synthesise several dihydropyranoflavones as mentioned earlier in the objective. The earlier methods ¹²²,¹⁷³,¹⁷⁵,¹⁹⁹, for the synthesis of such compounds gave rather poor yields and afforded a number of other compounds, which are difficult to separate. We described herein a facile method for the preparation of 3,4-dihydropyranoflavones 70. The readily accessible 2-benzylidene derivatives 69 were used as the starting materials in our study (Scheme 3.6, Page.No.96).
Fig. 3.8. IR spectrum of 6-acetyl-7-hydroxy-3',4'-dimethoxyflavone (62)
Fig. 3.9. Proton NMR spectrum of 6-Acetyl-7-hydroxy-3',4'-dimethoxyflavone (62)
Fig. 3.10. Mass spectrum of 6-Acetyl-7-hydroxy-3'-dimethoxyflavone (62)
SCHEME 3.6

69 a-d

R, R, R, KCN/
-------------*
EtOH
OCH3
69 e-h

Mechanism

69 a, g & 70 a, g, i; R1 = R2 = OCH3
69 b, f, j & 70 b, f, j; R1 = OCH3 = R2 = H
69 c, e, k & 70 c, e, k; R1, R2 = -O - CH2 - O -
69 d, h & 70 d, h; R1 = R2 = H

70 a-d

70 e-h

70 i-k

69 i-k

70
In our new method, 5,6-dihydro 2-(3',4'-dimethoxy) benzylidene-7,7-dimethylpyrano (2,3-f) benzo furan-3-one (69 a) was treated with potassium cyanide in ethanol to give a single product as evidenced by TLC. The compound showed an absorption band at 1630 cm\(^{-1}\) in its IR spectrum due to the presence of an \(\alpha,\beta\)-unsaturated carbonyl function. The \(^1H\)-NMR spectrum (Fig No. 3.11) revealed a six proton singlet at 1.40 δ and two triplets at 1.88 and 2.90 δ characteristic of a 2,2-dimethyl chroman system. A six proton singlet at 3.96 δ showed the presence of two methoxy groups. The aromatic region of the spectrum consisted of three singlets at 6.64, 6.90 and 7.90 δ ascribable to C₃-H, C₁₀-H and C₅-H protons respectively. A three proton multiplet centering around 7.30 δ was assigned to the protons of ring B of the flavone part. The molecular ion peak at m/e 366 agrees to the molecular formula C₂₂H₂₂O₅. The compound showed satisfactory micro analysis also, consistent with this formula.

From these evidences, the structure of this compound has been assigned as 6,7-dihydro-2-(3',4'-dimethoxy)phenyl-8,8-dimethylpyrano (2,3-g)chrom-4-one (70a). \(^{13}\)C-NMR spectrum provided an additional proof for the formation of the flavone 70a.

Similarly derived were the dihydropyranoflavones 70 b-d from 69 b-d respectively (Scheme 36, Page No.96).

Treatment with potassium cyanide in ethanol, 4-methoxy-8,9-dihydro-2-[3',4'-methylenedioxy] benzylidene -7,7-dimethylpyrano (2,3-g) benzofuran -3-one (69e)
Fig. 3.11. Proton NMR spectrum of 6,7-Dihydro-2-(3',4'-dimethoxy)phenyl-8,8-dimethylpyran (70a)
gave 70e as colorless needles from petroleum ether-ethyl acetate. The IR absorption at 1635 cm\(^{-1}\) revealed the presence of \(\alpha,\beta\)-unsaturated carbonyl functionality. The \(^1H\)-NMR spectrum showed a six proton singlet and two triplets in the aliphatic region with J=7Hz (1.50, 1.93 and 2.95 \(\delta\) respectively) which were assigned of the gem-dimethyl, the C\(_9\)-2H and the C\(_{10}\)-2H respectively. Three signals indicated the presence of a dimethylchroman system. A two proton singlet appeared at 6.10 \(\delta\) was due to the methylenedioxy protons. Three singlets and two doublets appeared (6.35 s, 6.60 s, 6.90 d, 7.35 s and 7.50 d, ppm) amounting to five aromatic protons. The mass spectrum showed the molecular ion peak at m/e 380 (C\(_{22}\)H\(_{20}\)O\(_6\)). All these put together attested the structure of 5-methoxy-9,10-dihydro-2-(3',4'-methylenedioxy) phenyl -8,8-dimethylpyrano (2,3-h) chrom -4-one (70e) for the compound synthesised.

On treatment with potassium cyanide in ethanol, 8-methoxy-6,7-dihydro-2-(3',4'-dimethoxy) benzylidene -5,5-dimethylpyrano (2,3-e) benzofuran -3-one (69i) furnished a compound with m.p. 210-212°C. The IR spectrum (Fig.No.3.12) revealed an \(\alpha,\beta\)-unsaturated carbonyl absorption at 1630 cm\(^{-1}\). The \(^1H\)-NMR spectrum indicated the presence of a gem-dimethyl group by a six proton singlet at 1.40 \(\delta\). The methylene protons were assigned to the two triplets that appeared at 1.78 and 2.60 \(\delta\) integrating to two protons each. A singlet at 3.88 \(\delta\) was assigned to the nine protons of the 3-methoxy groups. Singlet proton signals at 6.38,6.40 and 7.24 \(\delta\) were due to C\(_{2}\)-H, C\(_3\)-H and C\(_4\)'-H respectively. The aromatic protons, C\(_5\)'-H and C\(_7\)-H showed two doublets at 6.82 and 7.40 \(\delta\) with \(J=10\text{Hz}\). The \(^{13}\text{C}\)-NMR (Fig.No.3.13) also attested the compound to be a flavone. The emergence of molecular ion peak at m/e 396 and the elemental analysis were consistent with the molecular formula C\(_{23}\)H\(_{24}\)O\(_6\). Thus the structure of the compound synthesised was assigned as, 9 methoxy -7,8-dihydro-2-(3',4'-dimethoxy) phenyl -6,6-dimethylpyrano (2,3-f) chrom -4-one (70i).

The dihydropyranoflavones 70f-h and 70j and k were similarly synthesised from the 2-benzylidene derivatives (Scheme 3.7, Page No.96) 69f-h, 69j and k.
Fig. 3.12. IR spectrum of 9-Methoxy-7,8-dihydro-2-(3',4'-dimethoxy)phenyl-6,6-dimethylpyrano (2,3-f) chrom-4-one (70i)
Fig. 3.13. $^{13}$C-NMR spectrum of 9-Methoxy-7,8-dihydro-2-(3',4'-dimethoxy)phenyl-6,6-dimethyl pyrano (2,3-f) chrom-4-one (70i)
respectively. All these compounds were characterised by spectral means. The mechanism of the formation of compound 70 from 69 is also explained (Scheme 3.6, Page No.96).

Thus we have developed a facile method for the preparation of new acetyl hydroxyflavones and 3,4-dihydro-2,2-dimethyl-2H-pyranoflavones from easily accessible 5-acetyl resacetophenone and 2-benzylidene derivatives respectively.

3.3. Experimental

3.3.1. Synthesis of 6-acetyl-7-hydroxy-3',4'-dimethoxyflavone (62)

(a) 5-Acetyl-2,4-[(3',4',3'',4''-)tetramethoxy] dibenzoyloxyacetopheneone (59)

A mixture of 5-acetyl-2,4-dihydroxyacetophenone\(^\text{198}\) (58, 1.94 g, 0.01 mole) and 3,4-dimethoxybenzoyl chloride (67, 4g, 0.02 mole) was heated in the presence of pyridine (6 mL) on a boiling water bath for 6 hours. It was poured into ice-water and acidified with 1:1 HCl. The product obtained was filtered and dried. It was crystallised from ethanol as colourless prisms. It did not give colouration with alcoholic ferric chloride.

\[
\begin{align*}
\text{m.p.} & : 132^\circ\text{C} \\
\text{Yield} & : 2.5\text{g (69.83\%)} \\
\text{IR (KBr)} & : \nu_{\text{max}} \text{ cm}^{-1} \\
\text{(Fig. 3.1)} & : 1720, 1670, 1580, 1500, 1435, 1400, 1320, 1260, 1240, 1200, 1180, 1140, 1120, 1060, 1010, 920, 900, 860, 820, 740.
\end{align*}
\]

(b) 2,4-Dihydroxy-5-[(3',4'-dimethoxy) benzoylacetyl]acetopheneone (60)

A mixture of 5-acetyl-2,4-[(3',4',3'',4''-)tetramethoxy]-dibenzoyloxy]acetophenone (59, 1.3g, 0.004 mole) and powdered potassium hydroxide (4.2 gm) was stirred in the presence of pyridine (18 mL) at 70°C for 6 hours. The reaction mixture was poured into ice-water and acidified with 1:1 HCl and extracted with ethyl acetate. The residue showed two spots on TLC. The first compound was
eluted with 2% ethyl acetate-petroleum ether as colourless needles. It was identified as 5-acetyl-2,4-dihydroxyacetophenone (m.m.p and super imposable IR spectra).

The second compound (60) was eluted with 5% ethyl acetate-petroleum ether mixture as yellow prisms. It gave violet colour with alcoholic ferric chloride.

\[
\begin{align*}
\text{m.p.} & : 185^\circ \text{C} \\
\text{Yield} & : 0.500 \text{ g (}55.86\%\text{)} \\
\text{IR (KBr)} & : \nu_{\text{max}} \text{ cm}^{-1} \\
(\text{Fig. 3.2}) & : 1680, 1630, 1590, 1560, 1500, 1440, 1300, 1250, 1160, 1120, 1000 \text{ and } 840. \\
\text{'H-NMR (CDCl}_3) & : \delta \text{ values} \\
(\text{Fig. 3.3}) & : 2.60 (s, 3H, C_5'-\text{COCH}_3), 3.90 (s, 6H, C_3'-\text{OCH}_3 \text{ & C}_4'-\text{OCH}_3), 4.45 (s, 2H, \text{CH}_2), 6.30 (s, 1H, \text{CH} = \text{C}-), 6.85 (d, 1H, C_5'-\text{H}, J=9Hz); 7.85 (m, 3H, C_2'-\text{H}, C_6'-\text{H} \text{ & C}_6'-\text{H}), 8.10(s, 1H, C_2'-\text{OH or C}_4'-\text{OH}); 8.50 (s, 1H, C_4'-\text{OH or C}_2'-\text{OH}) \\
\text{Mass analysis} & : \text{Molecular ion peak (M^+):} 358 (C_{19}H_{18}O_6^+; 66.2\%) \\
(\text{Fig. 3.4.}) & : \text{Base peak :} 165 (C_9H_9O_3^+; 100\%) \\
(\text{Scheme 3.2, Page No.90}) & : \text{Other fragmented ion peak (}) \% \text{) } 341 (5.65), 206 (4.01), 180 (14.49), 179 (20.34), 166 (19.5), 163 (3.20), 151 (2.71), 150 (2.85). \\
\end{align*}
\]

(c) 3,6-Diacetyl-7-hydroxy-3',4'-dimethoxyflavone (61)

A mixture of 2,4-dihydroxy 5-[(3',4'-dimethoxy)- benzoylacetetyl] acetophenone (60, 0.358 gm, 0.001 mole) fused sodium acetate (0.99 gms) and glacial acetic acid (10.2 mL) was refluxed on an oil bath for 4 hours, cooled and poured into ice-cold water. The product was purified by passing through a silica gel column and eluting with petroleum ether - ethyl acetate (95:5, 400 mL) as a solvent system. The product
obtained on removal of solvent was found to be 3,6-diacetyl-7-hydroxy-3',4'-dimethoxy flavone (61) and it was crystallised from petroleum ether as colourless crystals.

| m.p.     | 215°C |
| Yield    | 0.32g (15.35%) |
| IR (KBr) | $\nu_{\text{max}}$ cm$^{-1}$ |

(Fig. 3.5) 1740, 1620, 1595, 1500, 1420, 1400, 1340, 1300, 1250, 1220, 1180, 1120, 1000, 940, 900, 830, 780 and 720.

'H-NMR (CDCl$_3$) : δ values

(Fig. 3.6) 2.25 (s, 3H, C$_3$-COCH$_3$), 2.65 (s, 3H, C$_6$-OCH$_3$)

3.88 and 3.99 (2 s, 6H, C$_3'$-OCH$_3$ & C$_4'$-OCH$_3$),

6.80 (s, 1H, C$_8$-H), 6.85 (d, 1H, C$_3'$-H, J=9Hz);

7.30 (d, 1H, C$_6'$ H, J = 9 Hz); 7.53 (s, 1H, C$_2'$ - H);

8.55 (s, 1H, C$_5$-H ) 12.55 (s, 1H, C$_7$-OH)

Mass analysis : Molecular ion peak (M$^+$):382 (C$_{21}$H$_{18}$O$_7^+$, 81.85%)

(Fig. 3.7.) Base peak : 165 (C$_9$H$_9$O$_3^+$, 100%)

(Scheme 3.3, Page.No.92) Other fragmented ion peak (%)

381 (C$_{21}$ H$_{17}$ O$_7^+$); 368 (9.1), 367 (35.13)
366 (4.91), 353 (15.86), 351 (25.99),
340 (10.15), 339 (10.35), 336 (4.40),
335 (12.47), 325 (9.03), 323 (4.35).

(d) 6-Acetyl-7-hydroxy-3',4'-dimethoxyflavone (62)

A mixture of 3,6-diacetyl-7-hydroxy-3',4'-dimethoxyflavone (61, 1.9g 0.005 mole) and aqueous sodium carbonate solution (2 N, 10 mL) in ethanol (10mL) was refluxed for about 3 hours on a water bath. It was cooled and excess ethanol was removed. The residue was poured into ice-water and acidified with 1:1 dilute hydrochloric acid. The product, 6-acetyl-7-hydroxy-3',4'-dimethoxy-flavone (62) was crystallised from petroleum ether - ethyl acetate
(90:10) as colourless needles.

<table>
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<th>Value</th>
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<td>m.p.</td>
<td>240°C</td>
</tr>
<tr>
<td>Yield</td>
<td>1.27g (75%)</td>
</tr>
<tr>
<td>IR (KBr)</td>
<td>$v_{\text{max}}$ cm$^{-1}$</td>
</tr>
<tr>
<td>(Fig. 3.8)</td>
<td>1640, 1620, 1580, 1500, 1470, 1440, 1400, 1390, 1340, 1320, 1280, 1260, 1240, 1200, 1160, 1100, 1000, 1080, 940, 900, 800 and 790.</td>
</tr>
<tr>
<td>$^1$H-NMR (CDCl$_3$)</td>
<td>$\delta$ values</td>
</tr>
<tr>
<td>(Fig. 3.9)</td>
<td>2.65 (s, 3H, C$_6$-COCH$_3$), 3.88 (s, 6H, C$_5$'-OCH$_3$ &amp; C$_4$'-OCH$_3$), 6.55 (s, 1H, C$_3$-H), 6.85 (d, 1H, C$_5$'-H J=9 Hz), 6.90 (s, 1H, C$_8$ - H), 7.25 (s, 1H, C$_2$'-H), 7.40 (d, 1H, C$_6$'-H J=9 Hz), 8.55 (s, 1H, C$_5$ - H), 12.55 (s, 1H, C$_7$ - OH).</td>
</tr>
<tr>
<td>Mass analysis</td>
<td>Molecular ion peak (M$^+$): 340 (C$<em>{19}$H$</em>{16}$O$_6$)</td>
</tr>
<tr>
<td>(Fig. 3.10.)</td>
<td>Other fragmented ion peak (%)</td>
</tr>
<tr>
<td>(Scheme 3.4, Page No.93)</td>
<td>325 (39.2), 324, 312 (6.34) 298, 178, 162.</td>
</tr>
<tr>
<td>Analysis</td>
<td>Found C, 66.96, H, 4.23% C$<em>{19}$H$</em>{16}$O$_6$ (340) requires C, 67.05, H, 4.36%</td>
</tr>
</tbody>
</table>

3.3.2. Synthesis of 6-acetyl-7-hydroxy-4'-methoxy flavone (66)

(a) 5-Acetyl-2,4-((4',4,6''-dimethoxy) dibenzoyloxy) acetophenone (63)

A mixture of 5-acetyl-2,4-dihydroxyacetophenone (58, 1.94 g, 0.01 mole) and 4-methoxybenzoyl chloride (68, 3.4 mL, 0.02 mole) was heated in presence of pyridine (8 mL) on a boiling water bath for 6 hours. The contents were poured into ice-water and acidified with 1:1 hydrochloric acid. The colourless solid obtained was purified by crystallisation from alcohol. It did not give colouration with alcoholic ferric chloride.

<table>
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<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p.</td>
<td>142°C</td>
</tr>
</tbody>
</table>
(b) 2,4-Dihydroxy-5-[(4'-methoxy) benzoyl]acetophenone (64)

A mixture of 5-acetyl-2,4-[(4',4'"-dimethoxy)-dibenzoyloxy]acetophenone (63, 1.5 g, 0.0032 mole) and powdered potassium hydroxide (4.2 gm) was stirred in presence of pyridine (18 mL) at 70°C for 6 hours. The reaction mixture was poured into ice-water and acidified with 1:1 hydrochloric acid. It was extracted with ethyl acetate and found to be a mixture of two compounds (TLC) which were separated by passing through a silica gel column and eluting with 2% and 5% ethylacetate-petroleum ether mixture respectively. The first compound was found to be identical with 5-acetyl-2,4-dihydroxyacetophenone (58) by m.m.p. and superimposable IR spectra. The second compound (64) which was eluted with 5% ethyl acetate - petroleum ether mixture crystallised as yellow needles. It gave violet colour with alcoholic ferric chloride.

\[ \text{m.p.} \quad 145 - 146 \degree C \]
\[ \text{Yield} \quad 0.390 g (37.17\%) \]
\[ \text{IR (CHCl}_3) \quad \nu_{\text{max}} \text{ cm}^{-1} \]
\[ (\text{Fig. 3.15}) \quad 1680, 1620, 1600, 1540, 1380, 1340, 1240, 1210, 1100, 1060, 940 \text{ and } 870. \]
\[ \text{\textsuperscript{1}H- NMR (CDCl}_3) \quad \delta \text{ values} \]
\[ (\text{Fig. 3.16}) \quad 2.55 (d,3H, C_5\text{-COCH}_3, J= 10Hz ), 3.75(s, 3H, C_4\text{',-OCH}_3), 4.40(s,2H, COCH}_2\text{CO), 6.30 (s, 1H,-CH=C-) 6.50 (s,1H, C_5\text{-H}), \]
Fig. 3.14. IR spectrum of 5-Acetyl-2,4-(4',4''-dimethoxy) dibenzoyloxy acetophenone (63)
Fig. 3.15. IR spectrum of 2,4-Dihydroxy-5-(4'-methoxy) benzoylactetyl acetophenone (64)
Fig. 3.16. Proton NMR spectrum of 2,4-Dihydroxy-5-[(4'-methoxy) benzoylacetyl] acetophenone (64)
6.80 (d, 2H, C\textsubscript{3}'-H \& C\textsubscript{5}-H, J= 10Hz)  
7.10 (b s, 1H,C\textsubscript{4}-OH), 7.70,8.12 (m, 3H, C\textsubscript{2}'-H, C\textsubscript{6}'-H, C\textsubscript{6}-H) 12.80 (s,1H, C\textsubscript{2}-OH); 15.30 (s, 1H, -CH=\text{C-OH})

Mass analysis : Molecular ion peak (M\textsuperscript{+}):328 (C\textsubscript{18}H\textsubscript{16}O\textsubscript{6})  
(Fig. 3.17.) Base peak : 135 (C\textsubscript{8}H\textsubscript{7}O\textsubscript{2}, 100%)  
(Scheme 3.7, Page No.105) Other fragmented ion peak (%)  
179(11.9), 150(4.66), 136(9.47) 108(3.1), 107(5.76).

(c) 3,6-Diacetyl-7-hydroxy-4'-methoxyflavone (65)

A mixture of 2,4-dihydroxy-5-[(4'-methoxy)-benzoylacetyl] acetophenone (64, 0.328g, 0.001 mole), fused sodium acetate (0.8 gm) and glacial acetic acid (9.6 mL) was refluxed on an oil bath for 6 hours, cooled and poured into ice-cold water, extracted with ethyl acetate and dried over anhydrous sodium sulfate. The residue obtained on removal of solvent was purified by passing through a silica gel column and eluting with petroleum ether - ethyl acetate (95:5, 400 mL) as a solvent system. The product obtained by removal of solvent was found to be 3,6-diacetyl-7-hydroxy-4'-methoxyflavone (65), and it was crystallised as colourless prisms.

m.p. : 227°C  
Yield : 0.30g (8.06%)  
IR (CHCl\textsubscript{3}) : $v\text{_{max}}$ cm\textsuperscript{-1}  
(Fig. 3.18) 1645, 1630, 1600, 1590, 1470, 1410, 1380, 1340, 1320, 1280, 1250, 1150, 1120, 1020, 940, 850, 720 and 600.  
'H -NMR (CDCl\textsubscript{3}) : $\delta$ values  
(Fig. 3.19) 2.55 (s,3H, C\textsubscript{3}-COCH\textsubscript{3}), 2.73(s, 3H, C\textsubscript{6}-COCH\textsubscript{3}), 3.85(s,3H, C\textsubscript{4}'- OCH\textsubscript{3}), 6.95(s,1H, C\textsubscript{6}'-H),6.80(d, 2H, C\textsubscript{3}'-H, C\textsubscript{5}'-H, J=10Hz), 7.80(d, 2H, C\textsubscript{3}'-H \& C\textsubscript{5}'-H, J=10Hz), 8.66 (s, 1H, C\textsubscript{5}-H), 12.70 (s, 1H, C\textsubscript{5}-OH).
Fig. 3.17 Mass spectrum of 2,4-Dihydroxy-5-[(4'-methoxy) benzoylacetyl] acetophenone (64)
SCHEME 3.7

FRAGMENTATION PATTERN OF 2,4-DIHYDROXY-5-(4'-METHOXY) BENZOYL ACETYL ACETOPHENONE (64)
Fig. 3.18. IR spectrum of 3,6-Diacetyl-7-hydroxy-4'-methoxyflavone (65)
Fig. 3.19. Proton NMR spectrum of 3,6-Diacetyl-7-hydroxy-4'-methoxyflavone (65)
(d) 6-Acetyl-7-hydroxy-4'-methoxyflavone (66)

A mixture of 3,6-diacetyl-7-hydroxy-4'-methoxyflavone (65, 1.76 g, 0.005 mole) in ethanol (10 mL) and aqueous sodium carbonate solution (2N, 10 mL) was refluxed for about 3 hours on a water bath. It was cooled and excess ethanol was removed. The residue was poured into ice-water and acidified with 1:1 dilute hydrochloric acid to give 66 and it was crystallised as colourless crystals.

m.p. : 248 - 249°C
Yield : 1.16 g (75%)
IR (CHCl₃) : υ max cm⁻¹
(Fig. 3.20) 1640, 1620, 1600, 1590, 1500, 1460, 1440, 1400, 1340, 1320, 1270, 1240, 1220, 1160, 1140, 1070, 1010, 940 and 820
'H-NMR (CDCl₃) : δ values
: 2.72 (s, 3H, C₆-COCH₃), 3.90 (s, 3H, C₄-OCH₃), 6.50 (s, 1H, C₃-H), 7.05 (s, 1H, C₄-H), 7.10 (d, 2H, C₃'-H & C₅'-H, J=10 Hz), 7.90 (d, 2H, C₄'-H & C₆'-H, J=10 Hz), 8.70 (s, 1H, C₅-H), 12.65 (s, 1H, -C₅-OH).
Analysis : Found C, 69.56; H, 4.37% C₁₈H₁₄O₅ (310) requires C, 69.67; H, 4.50%

3.3.3. Synthesis of dihydropyranoflavones (70a-k)

General Procedure

A mixture of 2-benzylidene-benzofuran-3-one (69, 0.002 mole) and potassium cyanide (0.130 g, 0.02 mole) in absolute ethanol (5 mL) was refluxed for 6 hours. The completion of the reaction was followed by TLC analysis on
Fig. 3.20: IR spectrum of 6-Acetyl-7-hydroxy-4'-methoxyflavone (66)
silica gel with petroleum ether (60 - 80°C) - ethyl acetate (3:1) as a solvent system. After 6 hours, the reaction mixture was cooled, diluted with water and acidified with dilute hydrochloric acid. It was then extracted with ethyl acetate (3X15 mL) and dried over anhydrous sodium sulfate and concentrated to get a crude product. The product 70 was purified by passing through a column of silica gel (Acme's, 62-120 mesh (25 cm column) and eluting with petroleum ether - ethyl acetate (24:1, 2X100 mL) mixture.

(a) 6,7-Dihydro-2-[3',4'-dimethoxy] phenyl 8,8-dimethyl pyrano (2,3-g) chrom-4-one (70 a)

5,6-Dihydro -2-[3',4'-dimethoxy] benzylidene-7,7-dimethylpyrano (2,3-f) benzo-furan -3-one (69a, 0.732 g)

Colorless needles

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p.</td>
<td>165 - 166°C (PE-EA)</td>
</tr>
<tr>
<td>Yield</td>
<td>0.41 g (56%)</td>
</tr>
<tr>
<td>IR (KBr)</td>
<td>( \nu_{\text{max}} ) cm(^{-1})</td>
</tr>
<tr>
<td></td>
<td>1630, 1610, 1600, 1550, 1455, 1350, 1320, 1260, 1205, 1170, 1155, 1100, 1060, 930 and 875.</td>
</tr>
<tr>
<td>'H-NMR (CDCl(_3))</td>
<td>( \delta ) values (Table 3.2, Page No.114)</td>
</tr>
<tr>
<td>(Fig. 3.11)</td>
<td></td>
</tr>
<tr>
<td>(^{13})C-NMR (CDCl(_3))</td>
<td>( \delta ) values</td>
</tr>
<tr>
<td></td>
<td>22.434 (C-6), 27.353 (C(_6)- CH(_3))(_2)),</td>
</tr>
<tr>
<td></td>
<td>32.849(C-7), 56.400 &amp; 56.452 (2X-OCH(_3)),</td>
</tr>
<tr>
<td></td>
<td>76.387 (C-8), 104.751 (C-5a) 106.306 (C-3),</td>
</tr>
<tr>
<td></td>
<td>109.085 (C-5'), 111.501 (C-2'), 117.472 (C-4a),</td>
</tr>
<tr>
<td></td>
<td>120.115 (C-6'), 120.568 (C-10), 124.967(C-1'),</td>
</tr>
<tr>
<td></td>
<td>126.615 (C-5), 149.571 (C-3'), 152.169 (C-4'),</td>
</tr>
<tr>
<td></td>
<td>156.500 (C-2), 159.608 (C-10a),</td>
</tr>
</tbody>
</table>
163.263 (C-9a) & 178.465 (C=O).

Mass analysis : m/e :366 (M+)
Analysis : Found C, 72.04; H, 5.97% C_{22}H_{22}O_{5} (366.42)
requires C, 72.12; H, 6.05%

(b) 6,7-Dihydro-2-[4'-methoxy]phenyl - 8,8-dimethylpyrano (2,3-g) chrom-4-one (70b)

5,6-Dihydro - 2-[4'-methoxy] benzylidene-7,7-dimethylpyrano (2,3-f) benzofuran -3-one (69b, 0.672 g)

Colorless prisms
m.p. : 160 - 161°C (PE-EA)
Yield : 0.47 g (70%)
IR (KBr) : \nu_{\text{max}} \text{ cm}^{-1}
1630, 1605, 1555, 1455, 1365, 1310, 1270,
1175, 1115, 1070, 1025, 910, and 860
'H -NMR (CDCl_{3}) : \delta \text{ values} (Table 3.2, Page No.114)
Mass analysis : m/e : 336 (M+)
Analysis : Found C, 74.82; H, 5.87% C_{21}H_{20}O_{4} (336.41)
requires C, 74.98; H, 5.99%

(c) 6,7-Dihydro -2-[3',4'-methylenedioxy]phenyl-8,8-dimethyl pyrano (2,3-g) chrom-4-one (70c)

5,6-Dihydro -2-[3',4'-methylenedioxy] benzylidene-7,7-dimethylpyrano (2,3-f) benzofuran -3-one (69c, 0.700 g)

Colorless prisms
m.p. : 223- 234°C (PE-EA)
Yield : 0.46 g (65%)
IR (KBr) : \nu_{\text{max}} \text{ cm}^{-1}
1640, 1620, 1595, 1500, 1445, 1370, 1345, 1285, 1175, 1150, 1065, 1025, 920 and 845

'H -NMR (CDCl₃) : δ values (Table 3.2, Page No.114)
Mass analysis : m/e : 350(M⁺)
Analysis : Found C, 71.87; H,5.21% C₂₁H₁₈O₅ (350)
requires C, 71.99; H, 5.18%

(d) 6,7-Dihydro - 2- phenyl -8,8-dimethyl pyrano (2,3-g) chrom-4-one (70d)
5,6-Dihydro-2- benzylidene-7,7-dimethylpyrano (2,3-f) benzo furan -3-one (69d, 0.612 g)

Colorless needles
m.p. : 145- 146°C (PE-EA)
Yield : 0.29 g (49%)
IR (KBr) : v max cm⁻¹
1635, 1600, 1580, 1550, 1440, 1380, 1360, 1280, 1170, 1120, 890 and 800
'H -NMR (CDCl₃) : δ values (Table 3.2, Page No.114)
Mass analysis : m/e : 306 (M⁺)
Analysis : Found C, 78.20; H,5.92% C₂₀H₁₈O₃ (305.38)
requires C, 78.41; H, 5.92%

(e) 5-Methoxy -9,10-dihydro-2-[3',4'-methylenedioxy]phenyl - 8,8-dimethyl pyrano (2,3-h) chrom-4-one (70e)
4-Methoxy -8,9-dihydro-2-[3',4'-methylenedioxy] benzylidene-7,7-dimethylpyrano (2,3-g) - benzo furan -3-one (69e, 0.760 g)

Colorless needles
m.p. : 277- 278°C (PE-EA)
Yield : 0.49 g (65%)
IR (KBr) : v max cm⁻¹
\( \text{1635, 1610, 1580, 1440, 1380, 1360, 1240,} \\
\text{1200, 1150, 1100, 1020, 950 and 840} \)

\[ 'H\text{-NMR (CDCl}_{3}\text{)} : \delta \text{ values (Table 3.2, Page No.115)} \]

\[ \text{Mass analysis : m/e : 380 (M*)} \]

\[ \text{Analysis : Found C, 69.26; H,5.19\% C}_{22}\text{H}_{20}\text{O}_{6} (380.40) \]

\[ \text{requires C,69.46; H, 5.30\%} \]

\( (f) \text{ 5-Methoxy -9,10- dihydro-2-[4'-methoxy] phenyl -8,8- dimethyl pyrano (2,3-h) chrom-4-one (70f)} \)

4-Methoxy -8,9-dihydro-2-[4'-methoxy] benzylidene-7,7-dimethylpyrano (2,3-g) - benzofuran -3-one (69f, 0.732 g)

\text{Colorless needles}

\[ \text{m.p. : 220- 221^\circ C (PE-EA)} \]

\[ \text{Yield : 0.46g (63\%)} \]

\[ \text{IR (KBr) : } \nu_{\text{max}} \text{ cm}^{-1} \]

\[ \text{1635, 1620, 1580, 1485, 1450, 1380, 1365,} \\
\text{1250, 1175, 1150, 1110, 1020, 960 and 880} \]

\[ 'H\text{- NMR (CDCl}_{3}\text{)} : \delta \text{ values (Table 3.2, Page No.115)} \]

\( (g) \text{ 5-Methoxy -9,10- dihydro -2-[3',4'-dimethoxy] phenyl - 8,8-dimethyl pyrano (2,3-h) chrom-4-one (70g)} \)

4-Methoxy -8,9-dihydro -2-[3',4'-dimethoxy] benzylidene-7,7-dimethylpyrano (2,3-g) - benzofuran -3-one (69g, 0.792 g)
Fig. 3.22. Proton NMR spectrum of 5-Methoxy-9,10-dihydro-2-(4'-methoxy)phenyl-8,8-dimethylpyrano (2,3-h) chrom-4-one (70f)
Colorless needles

m.p. : 255-256°C (PE-EA)
Yield : 0.51 g (64%)
IR (KBr) : $\nu_{\text{max}}$ cm$^{-1}$
1630, 1590, 1470, 1440, 1360, 1340, 1180,
1160, 1040, 950 and 860
'H- NMR (CDCl$_3$) : $\delta$ values (Table 3.2, Page No.115)
Mass analysis : m/e : 396 (M$^+$)
Analysis : Found C, 69.48; H, 5.96% C$_{23}$H$_{24}$O$_6$ (396.32)
requires C, 69.68; H, 6.10%

(h) 5-Methoxy -9,10- dihydro -2- phenyl - 8,8-dimethyl pyrano (2,3-h) chrom-4-one (70h)

4-Methoxy -8,9-dihydro-2-benzylidene-7,7-dimethylpyrano (2,3-g) -
benzofuran -3-one (69h, 0.672 g)

Colorless needles

m.p. : 205-206°C (PE-EA)
Yield : 0.34 g (50%)
IR (KBr) : $\nu_{\text{max}}$ cm$^{-1}$
(Fig. 3.23) 1640, 1600, 1430, 1380, 1350, 1290, 1180,
1140, 1100, 1080, 950 and 870
'H- NMR (CDCl$_3$) : $\delta$ values (Table 3.2, Page No.115)
$^{13}$C-NMR (CDCl$_3$) : $\delta$ values
 : 16.686(C-10), 26.639 (C$_8$-CH$_3$)$_2$),
31.873 (C-9), 56.259(OCH$_3$),
75.993 (C-8), 96.982 (C-6) 101.380(C-4a),
108.833(C-3 & C-10a), 125.781(C-2' & C-6'),
128.951(C-3' & C-5'),131.071(C-4'),
Fig. 3.23. IR spectrum of 5-Methoxy-9,10-dihydro-2-Phenyl-8,8-dimethylpyrano (2,3-h) chrom-4-one (70h)
131.824(C-1'), 159.300(C-2), 159.125(C-6a),
159.996(C-5, C-10b) and 177.947 (C4=O)

Mass analysis : m/e : 336 (M*)
Analysis : Found C, 74.92; H, 6.12% C21H20O4 (336.43)
requires C, 74.98; H, 5.98%

(i) 9-Methoxy -7,8- dihydro-2- (3',4'-dimethoxy) phenyl -6,6-dimethyl pyrano (2,3-f)
chrom-4-one (70i)

8-Methoxy -6,7-dihydro -2-(3',4'-dimethoxy) benzylidene -5,5-
dimethylpyrano (2,3-e) - benzofuran -3-one (69i, 0.792 g)

Colorless needles
m.p. : 210-212°C (PE-EA)
Yield : 0.49g (63%)

IR (KBr) :
υmax cm⁻¹
(Fig.3.12 )
1630, 1590, 1500, 1440, 1390, 1350, 1280,
1260, 1190, 1140, 1045, 980 and 860

' H- NMR (CDCl₃) : δ values (Table 3.2, Page No.116)

' C-NMR (CDCl₃) : δ values
(Fig.3.13 )
16.644(C-8), 26.018 (C₆-(CH₃)₂),
30.833 (C-7), 55.329, 55.555,
55.644 (C9- OCH₃), C₃'-OCH₃ & C₄'-OCH₃,
74.928(C-6), 89.838 (C-10) 106.236(C-3),
107.660 (C-2), 108.085(C-5'), 108.663 (C-4a),
110.526 (C-8a), 118.893 (C-6'), 123.955 (C-1'),
148.643 (C-3'), 150.940 (C-4'), 154.271 (C-2),
157.603 (C-4b), 159.608 (C-10a),
160.805 (C-9) & 177.042 (C₄=0).

Mass analysis : m/e : 396 (M²)
Analysis : Found C, 69.68; H, 6.10% C₂₃H₂₄O₆ (396.44)
requires C, 69.68; H, 6.10%
(j) 9-Methoxy-7,8-dihydro-2-(4'-methoxy) phenyl-6,6-dimethyl pyrano (2,3-f) chrom-4-one (70j)

8-Methoxy-6,7-dihydro-2-(4'-methoxy) benzylidene-5,5-dimethyl pyrano (2,3-e) - benzofuran -3-one (69j, 0.732 g)

Colorless needles

m.p. : 203- 204°C (PE-EA)
Yield : 0.49g (68%)
IR (KBr) : \( \nu_{\text{max}} \text{ cm}^{-1} \)
1640, 1605, 1575, 1515, 1460, 1375, 1310, 1275, 1175, 1100, 1020, and 825

'H-NMR (CDCl₃) : \( \delta \) values (Table 3.2, Page No.116)
Mass analysis : m/e: 366 (M*)
Analysis : Found C, 72.08; H, 6.08% C₂₂H₂₂O₅ (366.51)
requires C,72.12; H, 6.05%

(k) 9-Methoxy-7,8-dihydro-2-(3',4'-methylenedioxy) phenyl-6,6-dimethylpyrano (2,3-f) chrom-4-one (70k)

8-Methoxy-6,7-dihydro-2-(3',4'-methylenedioxy) benzylidene-5,5-dimethylpyrano (2,3-e) - benzofuran -3-one (69k, 0.760 g)

Colorless needles

m.p. : 222- 224°C (PE-EA)
Yield : 0.51 g (67%)
IR (KBr) : \( \nu_{\text{max}} \text{ cm}^{-1} \)
1630, 1590, 1545, 1415, 1375, 1360, 1250, 1190, 1160, 1100, 1090, 940 and 840

'H-NMR (CDCl₃) : \( \delta \) values (Table 3.2, Page No.116)
Mass analysis : m/e: 380 (M*)
Analysis : Found C, 69.40; H, 5.39% C₂₂H₂₀O₆ (380.32)
requires C,69.46; H, 5.30%
<table>
<thead>
<tr>
<th>Compound</th>
<th>C(CH$_2$)$_2$ (s)</th>
<th>Methylen protons (2t, J=7Hz)</th>
<th>Aromatic Protons</th>
<th>Other Protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>70a</td>
<td>1.40</td>
<td>1.88, 2.90</td>
<td>6.90 (s, 1H, C$_6$-H), 7.30 (m, 3H, C$_3$-H, C$_4$-H, C$_5$-H)</td>
<td>3.96 (s, 6H, C$_1$-OCH$_3$ &amp; C$_2$-OCH$_3$)</td>
</tr>
<tr>
<td>70b</td>
<td>1.40</td>
<td>1.86, 2.90</td>
<td>6.84 (s, 1H, C$_1$-H), 6.96 (d, 2H, C$_2$-H, 7.82 (d, 2H, C$_2$-H, C$_6$-H, 7.90 (s, 1H, C$_3$-H)</td>
<td>3.88 (s, 3H, C$_4$'-OCH$_3$)</td>
</tr>
<tr>
<td>70c</td>
<td>1.42</td>
<td>1.92, 2.94</td>
<td>6.92 (s, 1H, C$_1$-H), 7.42 (s, 1H, C$_1$-H), 7.86 (d, 1H, C$_2$-H, 7.98 (s, 1H, C$_3$-H)</td>
<td>6.12 (s, 2H, C$_1$-C$_4$' &amp; C$_4$' OCH$_3$)</td>
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<tr>
<td>70d</td>
<td>1.37</td>
<td>1.85, 2.90</td>
<td>6.90 (s, 1H, C$_1$-H), 7.52 (s, 1H, C$_1$-H), C$_4$-H, 7.90 (m, 3H, C$_3$-H, C$_4$-H, C$_5$-H)</td>
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</table>

Table 3.2

'H-NMR Data of the Dihydropyranoflavones (δ values)
<table>
<thead>
<tr>
<th>Compound</th>
<th>C(CH₃)₂ (s)</th>
<th>Methylene protons (2t, J=7Hz)</th>
<th>H-3(s)</th>
<th>Aromatic Protons</th>
<th>Other protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 e</td>
<td>1.50</td>
<td>1.93, 2.95</td>
<td>6.60</td>
<td>6.35 (s, 1H, C₆'-H), 6.90 (d, 1H, C₅'-H, J=10Hz), 7.35 (s, 1H, C₂'-H), 7.50 (d, 1H, C₆'-H, J=10Hz)</td>
<td>3.95 (s, 3H, C₅'-OCH₃), 6.10 (s, 2H, C₃' &amp; C₄'-OCH₂-O)</td>
</tr>
<tr>
<td>70 f</td>
<td>1.35</td>
<td>1.85, 2.90</td>
<td>6.54</td>
<td>6.23 (s, 1H, C₆'-H), 6.93 (d, 2H, C₃'-H, C₅'-H, J=9Hz), 7.75 (d, 2H, C₂'-H &amp; C₆'-H, J=9Hz)</td>
<td>3.82, 3.88(2 s,6H, C₅'-OCH₃ &amp; C₄'-OCH₃)</td>
</tr>
<tr>
<td>70 g</td>
<td>1.30</td>
<td>1.80, 2.82</td>
<td>6.50</td>
<td>6.20 (s, 1H, C₆'-H), 6.85 (d, 1H, C₅'-H, J=10Hz), 7.25 (s, 1H, C₂'-H), 7.40 (d, 1H, C₆'-H J=10Hz)</td>
<td>3.85(s,9H,C₅'-OCH₃, C₃'-OCH₃&amp;C₄'-OCH₃)</td>
</tr>
<tr>
<td>70 h</td>
<td>1.43</td>
<td>1.94, 2.97</td>
<td>6.73</td>
<td>6.33 (s, 1H, C₆'-H), 7.53 (m, 3H, C₃'-H, C₄'-H and C₅'-H), 7.90 (m, 2H, C₂'-H &amp; C₆'-H)</td>
<td>3.95(s,3H,C₅'-OCH₃)</td>
</tr>
</tbody>
</table>

Table Contd...
<table>
<thead>
<tr>
<th>Compound</th>
<th>C(CH₃)₂ (s)</th>
<th>Methylene protons (2 t, J=7Hz)</th>
<th>H-3(s)</th>
<th>Aromatic Protons</th>
<th>Other protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>70 i</td>
<td>1.40</td>
<td>1.78, 2.60</td>
<td>6.40</td>
<td>6.38 (s, 1H, C₁₀⁻H), 6.82 (d, 1H, C₅⁺⁻H, J=10Hz), 7.24 (s, 1H, C₂⁺⁻H) 7.40 (d, 1H, C₆⁻H, J=10Hz)</td>
<td>3.88(s,9H,C₅⁻OCH₃, C₃⁻OCH₃&amp;C₄⁺⁻OCH₃)</td>
</tr>
<tr>
<td>70 j</td>
<td>1.40</td>
<td>1.80, 2.66</td>
<td>6.45</td>
<td>6.40 (s, 1H, C₁₀⁻H), 6.92 (d, 2H, C₂⁻⁻H, and C₅⁻⁻H, J=9Hz), 7.90 (d, 2H, C₂⁺⁻H &amp; C₆⁻⁻H, J=9Hz)</td>
<td>3.83,3.90 (2 s,6H, C₉⁻OCH₃&amp; C₄⁺⁻OCH₃)</td>
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<tr>
<td>70 k</td>
<td>1.40</td>
<td>1.78, 2.58</td>
<td>6.40</td>
<td>6.65-7.03 (m, 4H, C₁₀⁻⁻H, C₂⁻⁻H, C₅⁺⁻H and C₆⁻⁻H)</td>
<td>3.82,(s,3H,C₉⁻OCH₃), 5.98 (s, 2H, C₃⁻ &amp; C₄⁺⁻OCH₂O⁻)</td>
</tr>
</tbody>
</table>