CHAPTER II

SECTION A

Synthesis of naturally occurring 7-methoxy, 5,7-dimethoxy and 7,8-dimethoxy substituted isoflavones
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2.2.1. Introduction

Isoflavones are very distinctive subclass of the flavonoids having a 3-phenylchroman skeleton. They display an exceedingly diverse range of biological properties and often serve as an important intermediates for the synthesis of other subclass of isoflavonoids such as isoflavanones, coumestanes, isoflavonols, 3-phen>icoumarins, pterocarpanoids, rotenoids etc.

From the perusal of literature described in the 'General Introduction' it is observed that although there are numerous reported methods available for the synthesis of isoflavones, many of them have certain disadvantages such as starting materials are not easily available, unwanted side reactions, lengthy reaction period and very often low yields. Besides, not much attention has been given to synthesize these compounds from flavanone, which is a proven biosynthetic precursor.

Recently Singh et ah developed a new reagent namely thallium(III) p-tosylate and utilized for the quantitative conversion of flavanone to isoflavone. We felt that this methodology may well offer an excellent synthetic route, if it is found to be applicable to isoflavones with typical natural substitution pattern. As a demonstration of the potential of this methodology, we decided to synthesize naturally occurring/derived isoflavones having typical natural substitution patterns like 7-methoxy, 5,7-dimethoxy and 7,8-dimefhoxy on ring A and alkoxy substituents at 2,3,4 & 5 positions of ring B.

2.2.2. Present work

The structures of isoflavones (4a-n) synthesized during the present study are presented in Chart 1 and their trivial/ chemical name and natural sources are presented in Table 1. The key step for the synthesis of all isoflavones is oxidative 2,3-aryl rearrangement of respective flavanones using thallium(III) p-tosylate. 7,8,3\4,.5’-Pentamethoxyisoflavone (4n), which has been recently isolated from

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Chart 1: Structures of naturally occurring 7-alkoxy 1,8-dialkoxy......
Table 1: Naturally Occurring Isoflavones and their Natural Sources

<table>
<thead>
<tr>
<th>Compd.</th>
<th>Trivial / Chemical name</th>
<th>Natural/ Derivative</th>
<th>Source</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 a</td>
<td>Di-O-methylaidzein</td>
<td>Natural</td>
<td>Dalbergia violacea</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Maackia tenifolia</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Glycyrrhiza pallidiflora</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Calopogonium mucunoides</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Myrocarpus perciferum</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>M. fastigiatus, M. balsamum</td>
<td>8</td>
</tr>
<tr>
<td>4 b</td>
<td>Cabreuvin</td>
<td>Natural</td>
<td>Calopogonium mucunoides</td>
<td>6</td>
</tr>
<tr>
<td>4 c</td>
<td>7,2',4'-Trimethoxyisoflavone</td>
<td>Natural derivative</td>
<td>Arachis hypogaea</td>
<td>9</td>
</tr>
<tr>
<td>4 d</td>
<td>Pseudobambigenin methyl ether</td>
<td>Natural derivative</td>
<td>Arachis hypogaea</td>
<td>9</td>
</tr>
<tr>
<td>4 e</td>
<td>Babtigenin trimethylether</td>
<td>Natural derivative</td>
<td>Ouratea hexasperma</td>
<td>10</td>
</tr>
<tr>
<td>4 f</td>
<td>5,7-Dimethoxyisoflavone</td>
<td>Natural derivative</td>
<td>Ouratea hexasperma</td>
<td>10</td>
</tr>
<tr>
<td>4 g</td>
<td>5,7,4'-Trimethoxyisoflavone</td>
<td>Natural derivative</td>
<td>Derris robusta</td>
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<tr>
<td>4 h</td>
<td>5,7,3',4'-Tetramethoxyisoflavone</td>
<td>Natural derivative</td>
<td>Tephrosia maxima</td>
<td>12</td>
</tr>
<tr>
<td>4 i</td>
<td>Derrstone</td>
<td>Natural</td>
<td>Tephrosia maxima</td>
<td>12</td>
</tr>
<tr>
<td>4 j</td>
<td>7,8-Dimethoxyisoflavone</td>
<td>Natural derivative</td>
<td>Tephrosia maxima</td>
<td>12</td>
</tr>
<tr>
<td>4 k</td>
<td>Retuline dimethylether</td>
<td>Natural derivative</td>
<td>Tephrosia maxima</td>
<td>12</td>
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<td>4 l</td>
<td>7,8,3',4'-Tetramethoxyisoflavone</td>
<td>Natural derivative</td>
<td>Tephrosia maxima</td>
<td>12</td>
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<tr>
<td>4 m</td>
<td>Purpuranin-A</td>
<td>Natural</td>
<td>Petalostemon purpureus</td>
<td>2</td>
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<tr>
<td>4 n</td>
<td>7,8,3',4',5'-Pentamethoxyisoflavone</td>
<td>Natural derivative</td>
<td>Petalostemon purpureus</td>
<td>2</td>
</tr>
</tbody>
</table>
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*Petalostemon purpureum* but no synthesis is reported till now, is selected as the representative example for the synthesis of all isolavones.

It was achieved in three consecutive steps starting from 3,4-dimethoxy-2-hydroxyacetophenone (1 c) (Scheme-1) which was prepared by well known literature method and was explained in experimental section.

Synthesis of 2'-Hydroxyl-3',4', 3, 4, 5-pentamethoxychalcone (2 n)

The Claisen-Schmidt condensation of the 3,4-dimethoxy-2-hydroxyacetophenone (1 c) with 3, 4, 5-trimethoxybenzaldehyde in presence of potassium hydroxide in methanol afforded 2'-hydroxyl-3\', 4', 3, 4, 5-pentamethoxychalcone (2 n) in 84% yield.

The IR spectrum of 2 n showed bands at 1635 and 3390 cm⁻¹ due to chelated \( \alpha,\beta \)-unsaturated ketone and hydroxyl groups, respectively. The \(^1\)H-NMR (CDCl₃, 200MHz) spectrum of 2 n showed four singlets of 5 methoxy groups at 5 3.864, 3.922, 3.959 (3 \( H \) each) and 3.935 (6H), two AB doublets at 5 7.412 and 7.822 (\( J=15.34 \) Hz) of \( \alpha \)- and \( \beta \)-protons of chalcone, respectively. A singlet of two protons at 8 6.871, two doublets of one proton each at 8 6.533 & 7.673 (\( J=9.16 \) Hz) and one proton singlet at 5 13.269 were also appeared and assigned to \( H-2 \) & \( H-6 \), 77-5' & 77-6' and OH group, respectively.

Similarly the Chalcones (2 a-m) were obtained by Claisen-Schmidt condensation of substituted 2-hydroxyacetophenones (1 a-c) with substituted aromatic aldehydes as described above in good yields and their characterization data are presented in Table 2.

Synthesis of 7, 8, 3', 4\'-pentamethoxyflavanone (3 n)

Flavanones are isomeric with chalcones, which are found to be the precursors of former synthetically as well as biosynthetically. The more frequently 2'}
hydroxychalcones are isomerized to respective flavanones by heating in acidic solution such as hydrochloric acid in acetic acid, sulfuric acid in ethanol etc but yields are moderate to low and longer reaction time is required especially when alkoxy substituents are present at the aromatic rings. This may be due to dealkylation during the reaction. During the present study we found that 2'-hydroxychalcones are easily cyclized to respective flavanones by refluxing in pyridine-methanol-water (1: 1: 1) in high yield. Hence 2 n was isomerized to 7,8,3',4',5'-pentamethoxyflavanone (3 n) by refluxing in pyridine-methanol-water (1: 1: 1) for 12 hrs in 85% yields.

\[ \text{Reagents and Conditions} \]
\[ \text{i) Aromatic aldehyde, KOH-MeOH, rt, 24 hrs;} \]
\[ \text{ii) Pyridine: MeOH: H2O (1: 1: 1), reflux, 12 hrs;} \]
\[ \text{iii) Thallium(III) p-tosylate, MeCN, reflux, 2 hrs;} \]

The IR spectrum of 7,8,3',4',5'-pentamethoxyflavanone (3n) was recorded in KBr pellet and showed absorption at 1685 cm\(^{-1}\) which was assigned to carbonyl group of flavanone. The \(^1\)H-NMR (CDCl\(_3\), 200 MHz) of 3 n showed characteristic H-2 proton of flavanone ring as a doublet of doublets which appeared at \(\delta\) 5.394 (J=13.36 & 2.79 Hz) and two double doublets of H-3 centered at \(\delta\) 2.82 (J=16.86 & 2.86 Hz) and \(\delta\) 3.045 (J=16.82 & 13.36 Hz) were assigned to H-3a and H-3e,
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respectively, forming MI ABX system. Signals for five methoxyls appeared at 5 3.845, 3.865, 3.933 (3 tfeach) and 3.899 (6 H) as singlets. The aromatic protons appeared in three sets as a two-proton singlet at 5 6.694 (H-T & H-6') and two doublets at 5 6.662 (J=8.94 Hz) & 6 7.703 (7=8.90 Hz) of one proton each and assigned to H-6 & #-5, respectively.

Similarly, other 2'-hydroxychalcones (2 a-m) were isomerized to the respective flavanones (3 a-m) by refluxing the former in pyridine: methanol: water (1: 1: 1) for 12 hrs in 80-84% yields and their characterization data are presented in Table 3.

Oxidative 1,2-aryl migration of flavanone to isoflavoiie using thallium (III) p-tosylate

Even though, there are numerous methods available in the literature for the synthesis of isoflavones from different precursors but less attention has been paid to flavanones as precursors. According to detailed enzymatic studies, the isoflavonoids share a common bioj.ynthetic pathway with flavonoids with intermediacy of flavanones, then a 2,3-füryl migration occurs to afford isoflavonoids and mechanism for the enzyme induced flavanone — iso flavone conversion has been proposed. The first chemical analogy of this rearrangement had been observed by lead tetraacetate oxidation of flavanone which afforded a mixture of 3-acetoxy flavanone, flavone along with trace of isoflavone (<10%) while thallium(III) nitrate (TTN) in methanol, thallium(III) acetate in acetic acid yielded exclusively flavones.

Recently, our group has introduced a new thallium(III) salt i.e. thallium(III) p-tosylate which converts flavanones to isoflavones by oxidative 1,2 aryl migration in almost quantitative yield. It was felt that this methodology would provide an alternative and convenient access to the natural as well as synthetic isoflavones, if we studied the general applicability of this new reagent in details and it would be
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more expedient and widely applicable.

Thus 7,8,3',4',5'-pentamethoxyflavanone (3 n) on treatment with thallium(III) jC-tosylate in refluxing acetonitrile for 2 hours afforded 7,8,3',4',5'-pentamethoxyisoflavone (4 n) in 96% yield. The IR spectrum of 7,8,3',4',5'-pentamethoxy isoflavone (4n) showed absorption at 1648 cm$^{-1}$ due to carbonyl group of isoflavone. The $^1$H NMR spectrum was recorded in CDC1$_3$ (200 MHz). The appearance of characteristic H-2 proton of isoflavone at 8 8.039 as singlet and disappearance of flavanone signals in aliphatic region confirms the formation of isoflavone nucleus. A :wo-proton singlet at 5 6.792 was attributable to both H-T and H-6\ The five methoxy groups appeared at 8 3.902, 4.013 (6 H each) and 3.844 (3 H) as singlets. The H-5 and H-6 protons appeared as ort/zo-coupled doublet at 8 8.044 (7=9.01 Hz) and ii 7.08 (J= 9.06 Hz), respectively.

Mass spectral analysis of 7, 8, 3', 4', 5'-pentamethoxy isoflavone (4n)

The EI mass spectrum fragmentation of 7, 8, 3', 4', 5'-pentamethoxy isoflavone is presented in Chart 2. The molecular ion was appeared at m/z 372 and other characteristic Retio-Diels -Alder (RDA) fragments found at m/z 181 and 192. The other characteristic ions found in the spectrum are 357, 329 and 186. The probable fragmentation pattern is summarized in Chart 2.
Similarly, the above oxidative 2,3-aryl migration induced by thallium(III) p-tosylate was extended successfully for the synthesis of D-O-methyl Daidzein (4a), Cabreuvin (4b), 7,2',4'-Trimethoxyisoflavone (4c), Pseudobartigenin methylether (4d), Bartigenin trimethylether (4e), 5,7-Dimethoxy isoflavone (4f), 5, 7, 4'-Trimethoxyisoflavone (4g), 5,7,3',4'-tetramethoxy isoflavone (4h), Derrustone (4i), 7,8-Dimethoxyisoflavone (4j), Retusine dimethylether (4k), 7,8,3',4'-Tetramethoxyisoflavone (4l) and Purpurinin-A (4m). The spectral data of all these compounds are presented in the experimental section.
Plausible mechanism of flavanonc to isoflavone induced by thallium (III) p-tosySaie

A probable mechanism for the transformation of flavanone to isoflavone is depicted in Scheme 2.

**SCHEME 2**

Initial enolisation of flavanone (3) followed by electrophilic attack by the thallium (III) p-tosylate reagent at the face of the molecule anti to C2-Ar gives intermediates thallium adduct which undergo subsequent dehassilation assisted by the neighbouring C2-Ar ring to form a bridged carbocation (5). This carbocation (5) loses 3-H accompanied by the migration of C2-Ar ring to afford isoflavone (4). Here the 2, 3-aryl shift is a favoured path because of anchimeric assistance from the 2-Ar group.

Conclusion

In conclusion, it is found that thallium(III) p-tosylate mediated oxidative conversion of flavanone to isoflavone constitutes a simple and convenient procedure
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for synthesizing the later. As a demonstration of the potential of this methodology, we synthesized fourteen naturally occurring / derived isoflavones such as Di-<9-methyl Daidzein (4 a), Cabreuvin (4 b), 7,2\4'-Trimethoxyisoflavone (4 c), Pseudobabtigenin methyl ether (4 d), Babtigenin trimethyl ether (4 e), 5,7-Dimethoxyisoflavone (4 f), 5,7,4'-Trimefhoxy-isoflavone (4 g), 5,7,3',4'-Tetramethoxyisoflavone (4 h), Derrustone (4 i), 7,8-Dimethoxyisoflavone (4 j), Retusine dimethyl ether (4 k), 7,8,3',4'-Tetramethoxyisoflavone (4 I), Purpuranin-A (4 in) and 7,8,3',4',5'-Pentamethoxyisoflavone (4 n). This methodology may find considerable use in the synthesis of isoflavones and related systems in the future.
2.2.3. Experimental

Resacetophenone

Zinc chloride (82.5 g; 600 mmoles) was dissolved with the aid of heat in glacial acetic acid (80 mL) in a 1-L beaker. To this hot mixture (~140°C) resorcinol (55 g; 500 mmoles) was added with constant stirring. The solution was heated on a sand bath until it just begins to boil. The flame was removed and the reaction was allowed to complete by itself at a temperature not exceeding of 159°C. After standing on the sand bath without further heating for 20 min, the solution was diluted with a mixture of 125 mL of concentrated hydrochloric acid and 125 mL of water. The resulting dark red solution was placed in the cooling bath maintaining temperature below 5°C and the solid, so obtained, was filtered, washed with 500 mL of dilute hydrochloric acid (1:3) in 100-mL portions till filtrate free from zinc salt. The orange red product was dried and distilled under reduced pressure to get light yellow solid; yield 52 g (67%); mp 143-144°C (Lit\textsuperscript{17} mp 142-44°C).

2-Hydroxy-4-methoxyacetophenone (1 a)

A mixture of resacetophenone (15.2 g, 100 mmoles), dimethyl sulfate (12.6 g, 100 mmoles) and anhydrous potassium carbonate (20 g) in dry acetone (70 mL) was heated under reflux for 4 hrs. The reaction mixture was filtered when hot and inorganic salts were washed with dry acetone (2 x 25 mL). The combined filtrates were distilled under reduced pressure and gummy mass, so obtained, was purified by column chromatography using hexane: ethyl acetate (20: 1) as eluent to afford 2-hydroxy-4-methoxyacetophenone (1a), yield 13 g (80%), mp 51°C (Lit\textsuperscript{18} 52-53°C).

2, 4, 6-Trihydroxyacetophenone (Phloroacetophenone)

A mixture of dry phloroglucinol (12.6 g; 100 mmoles), anhydrous acetonitrile (8.2 g; 200 mmoles), sodium-dried ether (100 mL) and finely powdered
fused zinc chloride (5 g) was added to a 500 mL Buckner flask fitted with a side inlet tube having calcium chloride guard tube. The flask was cooled in ice-salt mixture and a rapid stream of hydrogen chloride was passed through the solution for 2 hrs. The flask was stoppered and kept in refrigerator for 3 days. A bulky orange-yellow precipitate of k-famine hydrochloride was formed, ether was decanted and the precipitate was washed with anhydrous ether (2 x 25 mL). The orange-yellow precipitates were transferred with the help of hot water (500 mL) to 1-L flask and the solution was refluxed for 2 hrs. The solution was cooled to 80°C, decolorizing carbon (3 g) was added, boiled for further 5 minutes and filtered while hot with suction through a predated Buckner funnel and washed with hot water (2 x 100 mL). The filtrate was allowed to stand overnight, off-white needles were filtered at the pump and dried at 120°C to afford phloroacetophenone, yield 14.5 g (85%), mp 217-219°C (Lit mp 217°C).

4, 6-Dimethoxy -2-hydroxyacetophenone (1 b)

A mixture of 2, 4, 6-Trihydroxyacetophenone (3.36 g, 0.02 mole) dimethyl sulfate (5.29 g, 0.042 mole) and anhydrous potassium carbonate (6 g) in dry acetone (50 mL) was heated under reflux for 12 hrs. The reaction mixture was filtered when hot. The resultant solid was washed with dry acetone and the solvent evaporated under reduced pressure. The gummy mass was purified by column chromatography and elution with 100% hexane afforded 2-hydroxy-4, 6-dimethoxyacetophenone (1 b), yield 2.55 g (65%), mp 80-81°C (Lit mp 80-82°C).

2,3, 4-Trihydroxyacetophenone (Gallacetophenone)

In a 250 mL round bottom flask, fitted with a reflux condenser to which was attached a calcium chloride tube, 28 g (210 mmoles) of freshly fused and finally powdered zinc chloride was dissolved in 38 mL of glacial acetic acid by heating in an oil bath at 135-40°C. Acetic anhydride (95%; 40 g; 370 mmoles) was then added.
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to the clear pale brown liquid followed by the addition in one lot of distilled
pyrogallol (50 g; 400 mmoles). The mixture was heated at 140-45° for 45 minutes
with frequent and vigorous shaking. The unused acetic acid and acetic anhydride
were removed by distilling under reduced pressure and the red brown cake, so
obtained, was broken by the addition of 300 mL of water with mechanical stirring
for a few minutes. The resultant mixture was cooled in an ice bath, filtered with
suction and washed with cold water. The crude material (40 g) was
chromatographed over silica gel column and crystallized to yield straw colored
needles of 2, 3, 4-trihydroxyacetophenone (Gallacetophenone), yield 36 g (54%),
mp 170-172°C (Lit\textsuperscript{21} mp 171-172°C);

3, 4-Dimethoxy-2-hydroxyacetophenone (1 c)

A mixture of gallacetophenone (8.4 g, 50 mmoles), dimethyl sulfate (15.14 g,
120 mmoles) and anhydrous potassium carbonate (20 g) in dry acetone (200 mL)
was heated under reflux for 4 hrs. The reaction mixture was filtered when hot and
inorganic salts were wished with dry acetone. The combined organic solvent was
concentrated under reduced pressure and the resultant gummy mass was purified by
column chromatography to afford 2-hydroxy-3, 4-dimethoxyacetophenone (1 c); mp
82-83°C (Lit\textsuperscript{22} 83°C); yield 7.83 g (80%).

Substituted 2'-Hydroxychalcones (2 a-n): General procedure

To a solution of potassium hydroxide (1.23 g; 22 mmoles) in methanol was
added substituted 2-hydroxyacetophenone (1 a-c; 10 mmoles) followed by aromatic
aldehyde (11 mmoles) and the resulting mixture was stirred at room temperature for
24 hrs. After completion of reaction, the reaction mixture was poured in ice-cold
water and resulting solution was neutralized with dilute hydrochloric acid. The
yellow precipitates so obtained, were filtered off, dried and crystallized from
alcohol to afford substituted 2'-hydroxychalcones (2 a-n) and their characterization
data are given in Table 2.

A typical procedure is as follows:

2'-Hydroxy-3', 4', 3, 4, 5-pentamethoxychalcone (2 n): Compound 2 n was prepared by condensation of 3, 4-dimethoxy-2-hydroxyacetophenone (1 c; 1.96 g; 10 mmoles) and 3,4,5-trimethoxybenzaldehyde (1.96 g; 10 mmoles) in presence of potassium hydroxide (1.23 g; 22 mmoles) according to the procedure described above. The product, after usual work up, crystallized from ethanol to afford 2'-hydroxy-3',4',3,4,5-pentamethoxychalcone (2 n) as yellow crystalline solid, yield 3.14 g (84%), mp 129-30°C, IR (KBr) cm⁻¹: 3390, 1635; ¹H-NMR (CDCl₃, 200MHz) δ: 3.864 (s, 3H, C₄-OCH₃), 3.922 (s, 3H, C₈-OCH₃), 3.935 (s, 6H, C₅ & C₇-OCH₃), 3.959 (s, 3H, C₇-OCH₃), 6.533 (d, 1H, J=9.09 Hz, C₆-H), 6.871 (s, 2H, C₂ & C₆-H), 7.412 (d, 1H, J=15.34 Hz, C₅α-H), 7.673 (d, 1H, J=9.16 Hz, C₅-H), 7.822 (d, 1H, J=15.30 Hz, C₈-H), 13.269 (s, 1H, D₂O exchangeable, C₂-OH).

The ¹H-NMR data of other unknown 2'-hydroxychalones is given below:

2'-Hydroxy-4'-methoxy-3', 4-methylenedioxychalcone (2 d): 3.866 (s, 3H, OCH₃), 6.043 (s, 2H, -OCH₂O-), 6.430 – 6.453 (2H, m, H-3' & H-5'), 6.861 (d, 1H, J = 7.96 Hz, H-5), 7.144 (dd, 1H, J = 1.59 & 8.08 Hz, H-6), 7.177 (d, 1H, J = 1.58 Hz, H-2), 7.458 (d, 1H, J = 15.37 Hz, H-α), 7.814 (d, 1H, J = 9.62 Hz, H-6'), 7.858 (d, 1H, J = 15.44 Hz, H-β), 13.523 (s, 1H, OH).

2'-Hydroxy-4', 3, 4, 5-tetramethoxychalcone (2 e): ¹H-NMR (CDCl₃, 200MHz): δ 3.872 (s, 3H, OCH₃), 3.908 (s, 3H, OCH₃), 3.934 (s, 6H, 2 X OCH₃), 6.480 – 6.514 (2H, m, H-3' & H-5'), 6.871 (s, 2H, C₂ & C₆-H), 7.452 (d, 1H, J = 15.36 Hz, H-α), 7.808 (d, 1H, J=15.34 Hz, H-β), 7.837 (d, 1H, J = 8.28 Hz, H-6'), 13.269 (s, 1H, O-H).

2'-Hydroxy-3', 4'-dimethoxy-3, 4-methylenedioxychalcone (2 m): ¹H-NMR (CDCl₃, 200MHz): δ 3.922 (s, 3H, OCH₃), 3.959 (s, 3H, OCH₃), 6.043 (s, 2H, OCH₂O), 6.533 (d, 1H, J = 9.09 Hz, H-5'), 6.861 (d, 1H, J = 7.96 Hz, H-5), 7.144
Isomerization of substituted 2'-hydroxychalcones (2 a-n) to substituted flavanones (3 a-n): General procedure

Substituted 2'-hydroxychalcones (2 a-n; 300 mg) was dissolved in pyridine: methanol: water (1: 1: 1; 30 mL) and the reaction mixture was refluxed for 12 hrs on a hot plate. After completion of the reaction, it was cooled to room temperature and the solvent was concentrated to 5 mL under reduced pressure. Water (50 mL) was added to the concentrated reaction mixture and extracted with chloroform (2 x 25 mL). The organic phase was washed with dilute hydrochloric acid, saturated sodium bicarbonate solution followed by water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was passed through a small bed of basic alumina using ethyl acetate-hexane (1: 10) as eluent to give respective substituted flavanones (3 a-n) in 80-90% yield and their characterization data are given in Table 3.

A typical procedure is given below:

7,8,3',4',5'-Pentamethoxyflavanone (3 n): The compound 3 n was prepared by refluxing 2'-hydroxy-3',4',3,4,5-pentamethoxychalcone (2 n, 300 mg) in pyridine, methanol, water (1: 1: 1; 30 mL) for 12 hrs on a hot plate. The reaction mixture on usual work up as above afforded crude 7,8,3',4',5'-pentamethoxyflavanone (3 n) which was further purified passing through basic alumina using ethyl acetate: hexane as eluent, yield 255 mg (85%) mp 154-55°C, IR (KBr) cm⁻¹: 1685; 'H-NMR (CDCl₃, 200MHz) 8: 2.820 (dd, 1H, J=2.86 & 16.86 Hz, C₂-77), 3.045 (dd, 1H, J=13.36 & 16.82 Hz, C₂-77), 3.845 (s, 3H, C₅-OC₇₃), 3.865 (s, 3H, C₇-OC₇₃), 3.899 (s, 6H, C₃. & C₄-OC₇₃), 3.933 (s, 3H, C₅-OC₇₃), 5.394 (dd, 1H, J=13.36 &
2.79 Hz, C₃-H), 6.662 (d, 1H, J=8.94 Hz, C₆-H), 6.694 (s 2H, C₂- & C₆-H), 7.703 (d, 1H, J=8.90 Hz, C₅-H).

The ¹H-NMR data of other unknown flavanones are given below:

7-Methoxy-3',4'-methylenedioxyflavanone (3 d): δ 2.784 (dd, 1H, J=2.88 & 16.84 Hz, H₅-3), 3.056 (dd, 1H, J= 13.28 & 16.82 Hz, H₆-3), 3.886 (s, 3H, OCH₃), 5.423 (dd, 1H, J= 2.86 & 13.26 Hz, H-2), 5.997 (s, 2H, OCH₂O), 6.436 (d, 1H, J = 2.31 Hz, H-8), 6.569 (dd, 1H, J = 8.82 & 2.35 Hz, H-6), 6.832 (d, 1H, J = 7.99 Hz, H-5'), 6.918 (dd, 1H, J = 8.16 & 1.66 Hz, H-6'), 7.006 (d, 1H, J = 1.63 Hz, H-2'), 7.848 (d, 1H, J = 8.86 Hz, H-5).

7,3',4',5'-Tetramethoxyflavanone (3 e): δ 2.820 (dd, 1H, J =2.84 & 16.86 Hz, H₅-3), 3.045 (dd, 1H, J = 13.36 & 16.82 Hz, H₆-3), 3.845 (s, 3H, OCH₃), 3.866 (s, 3H, OCH₃), 3.899 (s, 6H, 2 X OCH₃), 5.394 (dd, 1H, J = 2.78 & 13.34 Hz, H-2), 6.519 (d, 1H, J =2.32 Hz, H-4), 6.632 (dd, 1H, J = 8.82 & 2.34 Hz, H-6), 6.694 (s, 2H, H-2' & H-6'), 7.877 (d, 1H, J = 8.81 Hz, H-5).

7,8-Dimethoxy-3',4'-methylenedioxyflavanone (3 m): δ 2.846 (dd, 1H, J = 3.12 & 16.92 Hz, H₅-3), 3.013 (dd, 1H, J = 12.50 & 16.9 Hz, H₆-3), 3.865 (s, 3H, OCH₃), 3.933 (s, 3H, OCH₃), 5.414 (dd, 1H, J = 12.96 & 3.11 Hz, H-2), 5.995 (s, 2H, OCH₂O), 6.666 (d, 1H, J = 8.94 Hz, H-6), 6.832 (d, 1H, J =7.99 Hz, H-2'), 6.918 (dd, 1H, J = 1.69 & 8.16 Hz, H-6'), 7.006 (d, 1H, J = 1.63 Hz, H-5'), 7.703 (d, 1H, J= 8.90 Hz, C₅-H).

Oxidation of substituted flavanones (3 a-n) to isoflavones (4 a-n) using thallium(III) p-tosylate (TTS): General Procedure

To a solution of substituted flavanones (3 a-n; 1 mmole) in acetonitrile (15 mL) was added thallium (III) p-tosylate (800 mg; 1.1 mmoles) and the resulting mixture was refluxed for 2 hrs on a hot plate. The reaction mixture was cooled to room temperature, diluted with dichloromethane (50 mL) and the separated
thallium(I) \( p \)-tosylate was filtered off and washed with dichloromethane (20 mL). The filtrate was washed with saturated aqueous solution of sodium hydrogen carbonate (2 x 50 mL) followed by water and dried over anhydrous sodium sulfate. The solvent was then distilled off under reduced pressure and the residue was passed over small bed of basic alumina and recrystallised from ethyl acetate-hexane to afford substituted isoflavones (4 a-n) and their characterization data are listed in Table 4.

A typical procedure is given below:

7,8,3',4',5'-Pentamethoxyisoflavone (4 n): Compound 4 n was prepared by oxidative rearrangement of 7,8,3',4',5'-pentamethoxyflavanone (4 n; 312 mg; 1 mmole) using thallium(III) \( p \)-tosylate (800 mg; 1.1 mmole) as described above. The product after usual workup was purified by passing through a small bed of basic alumina using ethyl acetate-hexane (1: 10) as eluent to afford 7,8,3',4',5'-pentamethoxyisoflavone (4 n), yield 291 mg (94%), mp 143-44°C (Lit\(^2\) mp 144°C), IR (KBr) cm\(^{-1}\): 1648; \(^1\)H-NMR (CDCl\(_3\), 200 MHz) \( \delta \): 3.844 (s, 3H, C\(_4\)-OCH\(_3\)), 3.902 (s, 6H, C\(_3\)- & C\(_5\)-OCH\(_3\)), 4.013 (s, 6H, C\(_7\) & C\(_8\)-OCH\(_3\)), 6.792 (s, 2H, C\(_2\)- & C\(_6\)-H), 7.080 (d, 1H, J=9.06 Hz, C\(_6\)-H), 8.039 (s, 1H, C\(_7\)-H), 8.044 (d, 1H, J=9.01 Hz, C\(_5\)-H).

The \(^1\)H-NMR data of other isoflavones (4 a-m) are given below:

7,4'-Dimethoxyisoflavone (4a): \(^1\)H-NMR (CDCl\(_3\), 200 MHz): \( \delta \) 3.912 (s, 3H, C\(_7\)-OCH\(_3\)), 6.852 (d, 1H, J= 2.32 Hz, C\(_8\)-H), 6.916 - 7.002 (m, 3H, C\(_6\), C\(_7\)- & C\(_5\)-H), 7.512 (brd, 2H, J= 8.92 Hz, C\(_2\)- & C\(_6\)-H), 7.942 (s, 1H, C\(_7\)-H), 8.212 (d, 1H, J= 8.96 Hz, C\(_5\)-H).

7,3',4'-Trimethoxyisoflavone (4b): \(^1\)H-NMR (CDCl\(_3\), 200 MHz): \( \delta \) 3.917 (s, 3H, C\(_4\)-OCH\(_3\)), 3.923 (s, 3H, C\(_7\)-OCH\(_3\)), 3.932 (s, 3H, C\(_3\)-OCH\(_3\)), 6.865 (d, 1H, J= 2.34 Hz, C\(_8\)-H), 6.928 (d, 1H, J= 8.34 Hz, C\(_5\)-H), 7.004 (dd, 1H, J= 2.34 & 9.01 Hz, C\(_6\)-H), 7.059 (dd, 1H, J= 1.92 & 8.34 Hz, C\(_6\)-H), 7.216 (d, 1H, J= 1.90 Hz, C\(_2\)-H),
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7.952 (s, 1H, C₂-H), 8.218 (d, 1H, J= 8.94 Hz, C₅-H).

7,2',4'-Trimethoxyisoflavone (4c): ¹H-NMR (CDCl₃, 200 MHz): δ 3.779 (s, 3H, OCH₃), 3.843 (s, 3H, OCH₃), 3.913 (s, 3H, OCH₃), 6.508 (m, 2H, C₇ & C₅-H), 6.852 (d, 1H, J= 2.30 Hz, C₅'-H), 6.969 (dd, 1H, J= 2.30 & 8.89 Hz, C₆'-H), 7.254 (d, 1H, J= 8.94 Hz, C₆'-H), 7.890 (s, 1H, C₂'-H), 8.191 (d, 1H, J= 8.91 Hz, C₅-H).

7-Methoxy-3',4'-methylenedioxyisoflavone (4d): ¹H-NMR (CDCl₃, 200 MHz): δ 3.924 (s, 3H, C₇-OCH₃), 5.972 (s, 2H, -OCH₂O-), 6.832 – 6.862 (m, 2H, C₈ & C₅-H), 7.008 (dd, 1H, J= 2.28 & 8.96 Hz, C₆'-H), 7.061 (dd, 1H, J= 1.96 & 8.32 Hz, C₆'-H), 7.218 (d, 1H, J= 1.92 Hz, C₂'-H), 7.968 (s, 1H, C₂'-H), 8.216 (d, 1H, J= 8.92 Hz, C₅-H).

7,3',4',5'-Tetramethoxyisoflavone (4e): ¹H-NMR (CDCl₃, 200 MHz): δ 3.838 (s, 3H, OCH₃), 3.901 (s, 6H, 2 x OCH₃), 3.924 (s, 3H, OCH₃), 6.789 (s, 2H, C₂ & C₆-H), 6.872 (d, 1H, J= 2.32 Hz, C₆-H), 7.011 (dd, 1H, J= 2.34 & 8.98 Hz, C₆-H), 7.962 (s, 1H, C₂-H), 8.224 (d, 1H, J= 8.94 Hz, C₅-H).

5,7-Dimethoxyisoflavone (4f): ¹H-NMR (CDCl₃, 200 MHz): δ 3.896 (s, 3H, OCH₃), 3.946 (s, 3H, OCH₃), 6.384 (d, 1H, J= 2.12 Hz, C₂-H), 6.492 (d, 1H, J= 2.08 Hz, C₆-H), 7.324 – 7.484 (m, 3H, C₃', C₄', & C₅'-H), 7.524 – 7.598 (m, 2H, C₂ & C₆-H), 7.782 (s, 1H, C₂-H).

5,7,4'-Trimethoxyisoflavone (4g): ¹H-NMR (CDCl₃, 200 MHz): δ 3.832 (s, 3H, C₄-OCH₃), 3.893 (s, 3H, C₇-OCH₃), 3.939 (s, 3H, C₅-OCH₃), 6.372 (d, 1H, J= 2.18 Hz, C₆-H), 6.446 (d, 1H, J= 2.18 Hz, C₆-H), 6.935 (brd, 2H, J= 8.64 Hz, C₃ & C₅-H), 7.484 (brd, 2H, J= 8.64 Hz, C₂ & C₆-H), 7.763 (s, 1H, C₂-H).

5,7,3',4'-Dimethoxyisoflavone (4h): ¹H-NMR (CDCl₃, 200 MHz): δ 3.892 (s, 3H, OCH₃), 3.912 (s, 3H, OCH₃), 3.934 (s, 3H, OCH₃), 3.944 (s, 3H, OCH₃), 6.388 (d, 1H, J= 2.14 Hz, C₆-H), 6.490 (d, 1H, J= 2.10 Hz, C₆-H), 6.930 (d, 1H, J= 8.20 Hz, C₅-H), 7.028 (dd, 1H, J= 1.98 & 8.32 Hz, C₆-H), 7.216 (d, 1H, J= 2.02 Hz, C₂-H), 7.782 (s, 1H, C₂-H).

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5,7-Dimethoxy-3',4'-methylenedioxyisoflavone (4i): $^1$H-NMR (CDCl$_3$, 200 MHz): δ 3.893 (s, 3H, C$_7$-OCH$_3$), 3.940 (s, 3H, C$_5$-OCH$_3$), 5.978 (s, 2H, -OCH$_2$O-), 6.373 (d, 1H, J = 2.10 Hz, C$_8$-H), 6.445 (d, 1H, J = 2.12 Hz, C$_6$-H), 6.835 (d, 1H, J = 8.01 Hz, C$_5$-H), 6.940 (dd, 1H, J = 1.58 & 7.99 Hz, C$_6$-H), 7.099 (d, 1H, J = 1.66 Hz, C$_2$-H), 7.756 (s, 1H, C$_2$-H).

7,8-Dimethoxyisoflavone (4j): $^1$H-NMR (CDCl$_3$, 200 MHz): δ 4.012 (s, 6H, 2x OCH$_3$), 7.068 (d, 1H, J = 9.02 Hz, C$_6$-H), 7.336 – 7.482 (m, 3H, C$_3'$, C$_4'$ & C$_5'$-H), 7.528 – 7.602 (m, 2H, C$_2'$ & C$_6$-H), 7.992 (s, 1H, C$_2$-H), 8.042 (d, 1H, J = 8.98 Hz, C$_5$-H).

7,8,4'-Trimethoxyisoflavone (4k): $^1$H-NMR (CDCl$_3$, 200 MHz): δ 3.848 (s, 3H, C$_4$-OCH$_3$), 4.010 (s, 6H, C$_7$ & C$_8$-OCH$_3$), 6.980 (brd, 2H, J = 8.68 Hz, C$_3'$ & C$_5'$-H), 7.065 (d, 1H, J = 9.05 Hz, C$_6$-H), 7.504 (brd, 2H, J = 8.68 Hz, C$_2'$ & C$_6$-H), 7.997 (s, 1H, C$_2$-H), 8.045 (d, 1H, J = 9.05 Hz, C$_5$-H).

7,8,3',4'-Tetramethoxyisoflavone (4l): $^1$H-NMR (CDCl$_3$, 200 MHz): δ 3.919 (s, 3H, C$_4$-OCH$_3$), 3.933 (s, 3H, C$_3'$-OCH$_3$), 4.013 (s, 6H, C$_7$ & C$_8$-OCH$_3$), 6.935 (d, 1H, J = 8.30 Hz, C$_5'$-H), 7.034 – 7.097 (m, 2H, C$_6$ & C$_6'$-H), 7.214 (d, 1H, J = 1.71 Hz, C$_2$-H), 8.026 (s, 1H, C$_2$-H), 8.048 (d, 1H, J = 8.85 Hz, C$_5$-H).

7,8-Dimethoxy-3',4'-methylenedioxyisoflavone (4m): $^1$H-NMR (CDCl$_3$, 200 MHz): δ 4.008 (s, 6H, C$_7$ & C$_8$-OCH$_3$), 5.997 (s, 2H, -OCH$_2$O-), 6.873 (d, 1H, J = 8.09 Hz, C$_5$-H), 6.986 (dd, 1H, J = 1.60 & 8.08 Hz, C$_6$-H), 7.043 – 7.091 (m, 2H, C$_6$ & C$_2$-H), 7.984 (s, 1H, C$_2$-H), 8.038 (d, 1H, J = 9.17 Hz, C$_5$-H).
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Table 2: Characterization data of 2'-hydroxychalcones (2a-n)

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CHAPTER II, Section A: Synthesis of naturally occurring 7-alkoxy, 7,8-dialkoxy

Table 3: Characterization data of substituted flavanones (3a-n)

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<th>R₅</th>
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| 3b        | H | OMe| H | H | OMe | OMe | H | 82 | 120-21 (120-21)
| 3c        | II | OMe| H | OMe | H | OMe | H | 80 | 118-20 |
| 3d        | 11 | OMe| H | II | -OCM₂O- | H | 85 | 116-18 |
| 3e        | H | OMe| H | H | OMe | OMe | OMe | 82 | 149-50 |
| 3f        | H | OMe| OMe| H | H | H | H | 84 | 123-24 (140)
| 3g        | H | OMe| OMe| H | H | OMe | H | 80 | 120-21 (123)
| 3fa       | H | OMe| OMe| H | OMe | OMe | H | 82 | 159-60 (161)
| 3i        | H | OMe| OMe| H | -OCH₂O- | H | 84 | 159-60 (164-66)
| 3j        | OMe| OMe| H | H | H | H | H | 82 | 116-17 (120)
| 3k        | OMe| OMe| H | H | H | OMe | H | 80 | 112-13 (115)
| 3l        | OMe| OMe| H | H | OMe | OMe | H | 84 | 140-42 (143-44)
| 3m        | OMe| OMe| H | H | -OCH₂O- | H | 84 | 151-52 |
| 3n        | OMe| OMe| H | H | OMe | OMe | OMe | 85 | 154-55 |
CHAPTER II, Section A: Synthesis of naturally occurring 7-alkoxy, 7,8-dialkoxy.

Rafale 4: Characterization data of substituted isoflavoncs (4a-n)

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CHAPTER II, Section A: Synthesis of naturally occurring 7-alkoxy, 7,8-dialkoxy

2.2.4. References


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$^1$H NMR spectrum of 7,8,3',4',5'-pentamethoxy isoflavone (4n)

Mass spectrum of 7,8,3',4',5'-pentamethoxy isoflavone (4n)
$^1$H NMR spectrum of Derrustone (4i)

$^1$H NMR spectrum of Retusine dimethylether (4k)