CHAPTER II

SECTION B

Synthesis of Erythrinin-A and analogues
2.3.1. Introduction

Isoflavonoids possessing prenyl substituents and those with a 2,2-dimethylpyran ring system occur frequently, they are generally known as complex isoflavonoids (Chart 1). These pyranoisoflavonoids are plant secondary metabolites exhibiting insecticidal, antifungal and antibacterial properties. The biological activities associated with pyranoisoflavonoids have aroused a renewed interest in the synthesis of these compounds.

![Chart 1](image)

Biosynthesis of pyranoisoflavones in plants are same as that of simple isoflavones, except the formation of an additional carbons involving cyclic side structure is believed to be formed via a putative intermediate (A) (Scheme 1)
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These pyranoid flavones generally occurs either in linear or angular form. Erythrinin-A (1a) is linearly fused pyrano derivative of 7-oxygenated isoflavones. It was isolated from *Erythrina variegata*.

First total synthesis of Erythrinin-A was reported by suresh *et al* by Claisen-Schmidt condensation of 6-acetyl-7-hydroxy-2,2-dimethyl-3,4-dihydro-2/-/l-benzopyran (2a) with anisaldeliiyde followed by epoxidation of respective O-benzylated chalcone (4) using alkaline hydrogen peroxide which on further treatment with BF$_3$-Et$_2$O followed by hydrolysis, deprotection and dehydrogenation to afford Erythrinin-A (1a)(Scheme 2).
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Later, Jain et al. synthesized Erythinin-A methyl ether (1b) by formylating the deoxybenzoin 13 using ethylformate and sodium. The synthesis of deoxybenzoin 13 itself is cumbersome, multistep processes and was obtained from deoxybenzoin 8 in only 20% yield. (Scheme-3)
An alternative route was also developed by the same authors which involved the Claisen-Schmidt condensation of 6-acetyl-7-hydroxy-2,2-dimethyl chromene (14) with anisaldehyde followed by oxidative rearrangement with TTN in methanol to afford Erythrinin-A methyl ether (1b) in overall yield 5 %. (Scheme 4)
2.3.2. Present work

We have been examining the scope and limitations of thallium(III) reagents in heterocyclic synthesis. After achieving remarkable success in synthesizing simply substituted natural isoflavones mediated by thallium(III) p-tosylate through oxidative 1,2 aryl migration of respective flavanones, we just wondered whether this methodology will be applicable for synthesizing complex isoflavones like Erythrinin-A. Even though several methods has been reported in the literature for synthesizing these complex pyranoisoflavones, to best of our knowledge no report has ever utilized this thallium(III) salts mediated oxidative 1,2-aryl migration methodology for synthesizing pyranoisoflavone from flavanone precursor. in this section we demonstrated a short and simple route to Erythrinin-A & its analogues using a new reagent thallium(III) p-tosylate. Based on this a Retrosynthetic Scheme was developed for the synthesis of Erythrinin A as shown below.

![Retrosynthesis of Erythrinin-A](image)

The synthesis of Erythrinin-A and its analogues were achieved in four consecutive steps as outline in Scheme 5 starting from resacetophenone. Resacetophenone was prepared by well known literature methods and its preparation was explained in the experimental section of section A. Synthesis of Erythrinin-A has been selected as the representative example of the series.
Synthesis of 6-acetyl-7-hydroxy-2,2-dimethyl-3,4-dihydro-2H-1-benzopyran (2a)

Condensation of resacetophenone (2,4-Dihydroxy acetophenone) (16) with isoprene in presence of phosphoric acid as catalyst afforded a mixture of two major products 2a & 2b along with a minor product (2c) which were separated by column chromatography.

Major compounds 2a & 2b were identified by $^1$H NMR spectroscopy and comparing the inciting points reported in the literature.\(^6\)

Compound 2b which eluted first from the column showed positive ferric reaction and its $^1$H NMR (200MHz, CDCl\(_3\)) showed the characteristic protons of chroman ring, \(i.e\) two coupled triplets at \(\delta 1.783 \& 2.482 \ (J = 6.9 \text{ Hz})\) due to H-3 & H-4 and gem dimethyl protons at \(\delta 1.326\) as singlet. Appearance of two ortho coupled doublets at \(\delta 6.304 \ (J = 8.82 \text{ Hz})\) and \(\delta 7.476 \ (J = 8.91 \text{ Hz})\) for protons H-8 & H-7 and a singlet at \(\delta 13.64\) corresponding to one chelated hydroxy group attached at C-5 and the protons of-COCH\(_3\) appeared as a singlet at \(\delta 2.482\) indicated the compound 2b as 6-acetyl-5-hydroxy-2,2-dimethyl-3,4-dihydro-2H-1-benzopyran.

Compound 2a which eluted second from the column also showed positive ferric reaction and its $^1$H NMR (200MHz, CDCl\(_3\)) which is very similar to compound 2b except the appearance of two one proton singlets at \(\delta 6.240\) and \(\delta 7.352\) of aromatic protons H-5 & H-8, indicated the compound 2a as 6-acetyl-7-hydroxy-2,2-dimethyl-3,4-dihydro-2H-1-benzopyran.
Reagents and conditions

i) Isoprene, H₃PO₄, toluene, 30-35°C, 20 hrs

ii) Ar-CHO, Ba(OH)₂-MeOH, rt, 72 hrs, 70-75% or Ar-CHO, piperidine, benzene, reflux, 12 hrs, 83-85%.

iii) Pyridine-MeOH-H₂O (1:1:1), reflux, 12 hrs, 80-82%.

iv) Thallium(III) p-tosylate, MeCN, reflux, 2 hrs, 90-92%.

v) HBr, Ac₂O, reflux

vi) DDQ, benzene, reflux, 24 hrs.

SCHEME 5
The minor compound 2c showed negative ferric reaction indicating the absence of a hydroxyl group and comparing its mp 77-79°C with reported literature value, it was identified as dichroman 2c.

The compound 6-acetyl-7-hydroxy-2,2-dimethyl-3,4-dihydro-2H-1-benzopyran (2a) has been used for further step.

**Synthesis of 6-(4'-methoxy cinnamoyl)-7-hydroxy-2,2-dimethyl-3,4-dihydro-2i/-1-benzopyran (3b)**

The Claisen-Schmidt condensation of 6-acetyl-7-hydroxy-2,2-dimethyl-3,4-dihydro-2//-1-benzopyran (2a) with anisaldehyde in presence of barium hydroxide in methanol afforded 6-(4-methoxycinnamoyl)-7-hydroxy-2,2-dimethyl-2//-1-benzopyran (3b) in 75% yield. Alternatively, 2a was condensed with anisaldehyde in presence of catalytic amount of piperidine in dry benzene by continuously removing water formed during the reaction using Dean-Stark apparatus to afford 6-(4'-methoxycinnamoyl)-7-hydroxy-2s2-dimethyl-3,4-dihydro-2//-1-benzopyran (3b) in better yield (85%).

The IR spectrum of pyranochalcone showed a band at 1664 cm$^{-1}$ for compound 3b was ascribed to a,$\beta$-unsaturated carbonyl group and a band at 3200 cm$^{-1}$ was ascribed to phenolic hydroxyl group of chalcones. The *H NMR (200 MHz, CDCl$_3$) spectrum of 3b showed two doublets at 8 7.458 and 7.858 (J = 15.37 Hz) which revealed the AB system of a chalcone and a singlet at 5 13.365 corresponding to one chelated hydroxyl group attached at C-5. The *H NMR also showed the characteristic protons of chroman ring i.e. two coupled triplets at 5 1.811 and 2.804 (J = 6.78 Hz) due to H-3 and HA and gem dimethyl protons at 5 1.342 as a singlet. Two one proton singlets appeared at 5 6.390 and 7.680 due to H-8 & H-5 respectively and three protons singlet appeared at 8 3.864 was assigned to methoxy protons. The other four protons of an aromatic ring appeared as a doublet (2H each) at $\delta$ 6.945 (J = 8.69 Hz) and 5 7.613 (J=8.59 Hz) were assigned to H-3', H-5' & H-2',H-6' respectively.

Similarly the chalcones (3a,c,d) were obtained by Claisen-Schmidt condensation of 2a with aromatic aldehydes as described above in good yields.
and their characterization data are presented in the experimental section (Table 1).

Synthesis of 2-(4-methoxyphenyl)-8,8-dimethyl-2,3,6,7-tetrahydro-4H,8H-benzo[1,2-b;5,4-b']dipyran-4-one (17b)

Isomerisation-cyclisation of 6-(4'-methoxy cinnamoyl)-7-hydroxy-2,2-dimethyl-3,4-dihydro-2H-1-benzopyran (3b) to corresponding flavanone 2-(4-methoxy phenyl)-8,8-dimethyl-6,7-dihydro-8H-pyranoflavanone (17b) was achieved by refluxing the chalcone 3 b in pyridine, methanol, water (1:1:1) for 12 hrs.

The IR spectrum of 2-(4-methoxy phenyl)-8,8-dimethyl-6,7-dihydro-8H-pyranoflavanone (17b) showed the absorption band at 1660 cm\(^{-1}\) due to carbonyl group of a flavanone ring. The \(^1\)H NMR (200 MHz, CDCl\(_3\)) spectrum of compound 17b showed the disappearance of signals due to \(\alpha,\beta\)-unsaturated ketone of chalcones (\(\delta\) 7.458 & 7.858) and appearance of typical ABX pattern of flavanone at \(\delta\) 5.372 (J=12.73 & 3.03 Hz) of H-2 as a doublet of doublet, double doublets of \(H_{ax}\)-3 at \(\delta\) 3.029 (J = 12.73 & 16.84 Hz) and a overlaped multiplet of three protons at \(\delta\) 2.728-2.826 was assigned to \(H_{ax}\)-3 (1H) and H-6 (2H). The other protons of dihydrochromone ring appeared (H-7) as a triplet at \(\delta\) 1.816 (J = 6.78 Hz) and a singlet at \(\delta\) 1.349 (6H) of gem dimethyl group. The protons of C\(_2\)-aryl ring of flavanone appeared as two ortho-coupled doublets (2H each) at \(\delta\) 6.947 & 7.392 (J= 8.73 Hz) and assigned to H-3', H-5' & H-2', H-6' respectively. Similarly two singlets appeared at \(\delta\) 6.382 & 7.680 were assigned to H-10 & H-5 respectively.

Similarly, other pyranochalcones (3 a,c,d) were isomerized to respective flavanones (17 a,c,d) by refluxing the former in pyridine: methanol: water (1: 1: 1) for 12 hrs in 80-85% yields and their characterization data are presented in the experimental section (Table 2).
Synthesis of 6,7-dihydro-erythrinin-A methyl ether (18b)

It is important here to mention that there are numerous reports describing the conversion of these complex flavanones to flavones, but to best of our knowledge no method has been so far described to convert these pyranoflavanone to pyranoisoflavone by oxidative 1,2-aryl migration of the phenyl ring. Here, we first time applied this methodology of converting pyranoflavanone to pyrano isoflavone by oxidative 1,2-aryl migration induced by thallium(III) p-tosyikate. The treatment of 2-(4-methoxy phenyl)-8,8-dimethyl-6,7-dihydro-8H-pyranoflavanone (17b) with thallium(III) p-tosylate in refluxing acetonitrile for 2 hrs afforded 6,7-dihydro erythrinin-A methyl ether (18b) in high yield by oxidative rearrangement.

The II. spectrum of dihydro erythrinin-A methylether (18b) showed the absorption band at 1650cm⁻¹ due to carbonyl group of an isoflavone. The ¹H NMR (200 MHz, CDCl₃) spectrum of compound 18b showed the disappearance of characteristic flavanone signals and appearance of a singlet at δ 7.875, H-2 proton, a characteristic of an isoflavone. The two coupled triplets at δ 1.882 and 2.927 (2 H each, J=6.57 Hz) of H-6 & H-7 protons and a sharp singlet at δ 1.39 (6 H) of gem dimethyl groups confirm the chroman ring. A sharp singlet at δ 3.842 (3 H) of methoxy group and two AB broad doublets at δ 6.968 & 7.492 (2 H each, J = 8.75 Hz) confirmed the presence para methoxyphenyl ring at C3 position of isoflavone. The ¹H NMR spectrum also showed two singlets at δ 6.796 & 8.020 and were assigned to H-10 & H-5, respectively.

Similarly, the above oxidative 2,3-aryl migration induced by thallium(III) p-tosylate was extended to the synthesis of dihydro erythrinin-A analogues 3-(phenyl)-8,8-dimethyl-6,7-dihydro-4H,8H-benzo[1,2-b:5,4-b']dipyran-4-one (18a), 3-(4-benzyloxyphenyl)-8,8-dimethyl-6,7-dihydro-4H,8H-benzo[1,2-b:5,4-b']dipyran-4-one (18c), 3-(3',4'-methyleneoxyphenyl)-8,8-dimethyl-6,7-dihydro-4H,8H-benzo[1,2-b:5,4-b']dipyran-4-one (18d) successfully. The spectral data of all these compounds are presented in the experimental section.
Synthesis of Erythrinin-A (1a)

Dihydro erythrinin-A methylether (13b) can easily be demethylated by treating with HBr & Ac₂O followed by dehydrogenation with DDQ in dry benzene to afford Erythrinin-A as the method well documented in the literature.⁴

Plausible mechanism of pyranoflavanone to pyranoisoflavone

A probable mechanism for the transformation of pyrano flavanone to pyrano isoflavone is depicted in Scheme 6.
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Initial enolisation of pyrano flavanone (A) followed by electrophilic attack by the thallium(III) p-tosylate reagent at the face of the molecule anti to the 2-Ar gives intermediate (C), which undergo subsequent dethallation assisted by the neighbouring 2-Ar ring to form a bridged carbocation (D), this carbocation (D) loses 3-H accompanied by the migration of 2-Ar ring to yield isoflavone (E). Here the 2,3-aryl shift is a favoured path because of anchimeric assistance from the 2-Ar group.

Synthesis of substituted 8,8-diinethy1-10-methoxy-8H-6,7-dihydropyrano[2,3:7,6]isoflavones (18 e-h)

After demonstrating the utility of thallium(III) p-tosylate for the synthesis of complex isoflavones, particularly Erythrinin-A & its analogues, it was felt that it would be appropriate to include some more example to understand the general applicability of this new and versatile reagent. So gallacetophenone (20) was selected as the starting material for synthesizing the title compounds 18 e-h. The entire reaction sequence has been depicted in Scheme 7. All these compounds were characterized and explained in experimental section.
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Reagents and conditions:

i) ZnCl₂, AcOH-AC₂O, 140-145°C, 45 mins, 85%

ii) Isopropene, H₃PO₄, toluene, 30-35°C, 20 hrs, 80%

iii) CH₃I, K₂CO₃, acetone, 65°C, 5 hrs, 94%.

iv) Ar-CHO, Ba(OH)₂-MeOH, rt, 72 hrs, 70% or Ar-CHO, piperidine, toluene, reflux, 12 hrs, 82-85%.

v) Pyridine-methanol-water (1:1:1), reflux, 12 hrs, 80-85%.

vi) Thallium(III) p-tosylate, MeCN, reflux, 2 hrs, 90-92%.

SCHEME 7
Conclusion

From the results described above a new general method of synthesizing linearly oriented pyranoisoflavones has been developed using oxidative 1,2-aryl migration methodology induced by thallium(III) /?-tosylate. As a demonstration of this Erythrinin-A (1a) and similar pyranoisoflavones (18a-h) were synthesized successfully.
2.3.3. Experimental

**Reaction of Resacetophenone with Isoprene: Synthesis of 6-Acetyl-5-hydroxy-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (2a) and 6-Acetyl-7-hydroxy-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (2 b)**

A solution of isoprene (8.6 mL) in toluene (40 mL) was added to a mixture of 2, 4-dihydroxyacetophenone (10 g; 65.8 mmoles), orthophosphoric acid (90%, 7 mL) and toluene (40 mL) with constant stirring at 30-35°C during 8 hrs. Stirring was continued for further 12 hrs and then ethyl acetate (100 mL) was added to the reaction mixture. The reaction mixture was transferred in a separating funnel, washed with water (2 x 50 mL) followed by saturated aqueous sodium bicarbonate solution (2 x 50 mL) and dried over anhydrous sodium sulfate. The solvent was distilled off at reduced pressure to give reddish gummy mass. The reaction mixture showed three spots on TLC which were purified by column chromatography over silica gel (200 g; 100-200 mesh) and eluted with i) Petroleum ether ii) Benzene Petroleum ether (1: 19) and finally iii) Benzene Petroleum ether (1: 9) to afford three fractions:

**Fraction A**, crystallized from petroleum ether to afford 6-acetyl-5-hydroxy-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (2 b), 2.5 g; mp 69-70°C (lit 6 mp 69-70°C); $^1$H-NMR (CDCl$_3$) δ: 1.326 (s, 6H, 2 x CH$_3$), 1.783 (t, 2H, J=6.9 Hz, C$_3$-H) 2.482 (s, 3H, COCH$_3$), 2.688 (t, 2H, J=6.9 Hz, C$_4$-H), 6.304 (d, 1H, J=8.82 Hz, C$_8$-H), 7.476 (d, 1H, J=8.91 Hz, C$_7$-H), 13.164 (s, 1H, C$_3$-OH, D$_2$O exchangeable).

**Fraction B**, crystallized from petroleum ether to afford 6-acetyl-7-hydroxy-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (2 a), 3.0 g; mp 118-19°C (lit 6 mp 118-19°C); $^1$H-NMR (CDCl$_3$) δ: 1.323 (s, 6H, 2 x CH$_3$), 1.791 (t, 2H, J=7 Hz, C$_3$-H), 2.479 (s, 3H, COCH$_3$), 2.682 (t, 2H, J=6.9 Hz, C$_4$-H), 6.240 (s, 1H, C$_8$-H), 7.352 (s, 1H, C$_7$-H), 13.178 (s, 1H, C$_7$-OH, D$_2$O exchangeable).
**Fraction C**, crystallized from benzene-petroleum ether to afford 2 e, 1.0 g; mp 78-79°C (lit. mp 78-79°C); 

\[ ^1H-\text{NMR (CDCl}_3\text{) 8: 1.321 (s, 6H, 2 x CH}_3\text{), 1.364 (s, 6H, 2 x CH}_3\text{), 1.775 (t, 4H, J =6.9 Hz, C}_3\text{-H & C}_3\text{-H), 2.521-2.669 (m, 7H, C}_4\text{, C}_5\text{-H & COCH}_3\text{), 7.456 (s, 1H, C}_5\text{-H).} \]

6-Acetyl-7, 8-dihydroxy-2, 2-dimethyl-3, 4-dihydro-2\(H\)-1-benzopyran (21)

A solution of isoprene (8 mL) in toluene (25 mL) was added to a mixture of 2, 3, 4-trihydroxyacetophenone (10 g, 60 mmole), orthophosphoric acid (90%, 6 mL) and toluene (40 mL) with constant stirring at 30-35°C during 8 hrs. Stirring was continued for further 12 hrs, ethylacetate (50 mL) and water (50 mL) were added to the reaction mixture and it was shaken well and transferred to a seperating funnel. The organic layer was separated, washed with saturated aqueous sodium hydrogen carbonate (2 x 50 mL) followed by water and dried over orthophosphoric acid (90%, 6 mL) and toluene (40 mL) with constant stirring at 30-35°C during 8 hrs. Stirring was continued for further 12 hrs, ethyl acetate (50 mL) and water (50 mL) were added to the reaction mixture and it was shaken well and transferred to a separating funnel. The organic anhydrous sodium sulfate. The solvent was then distilled off under reduced pressure and the residue was purified by column chromatography using hexane: ethyl acetate (9: 1) to afford 6-acetyl-7, 8-dihydroxy-2, 2-dimethyl-3, 4-dihydro-2\(H\)-1-benzopyran (21), yield 11.3 g (80%), mp 124-25°C (Lit. mp 122-24°C).

6-Acetyl-7-hydroxy-8-methoxy-2, 2-dimethyl-3, 4-dihydro-2\(H\)-1-benzopyran (22)

A mixture of 6-acetyl-7, 8-dihydroxy-2, 2-dimethyl-3, 4-dihydro-2\(H\)-1-benzopyran (6 g, 25 mmoles), methyl iodide (5.68 g, 40 mmoles) and anhydrous potassium carbonate (10 g) in dry acetone (50 mL) was heated under reflux for 5 hrs. The reaction mixture was filtered when hot and inorganic salts were washed with dry acetone (25 mL). The solvent was distilled off at reduced pressure and the residue was purified by passing through a column of silica gel using hexane: ethyl acetate (19: 1) as eluent to afforded 6-acetyl-7-hydroxy-8-methoxy-2, 2-
dimethyl-3, 4-dihydro-2H-1-benzopyran (22), yield 6.0 g (94%), mp 98-99°C (Lit.6 mp 102-103°C).

6-Cinnamoyl-7-hydroxy-8-(unsubstituted or methoxy)-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (3a-h): General procedure

To a solution of 6-acetyl-7-hydroxy-8-(unsubstituted or methoxy)-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (2a, 22; 10 mmoles) and an aromatic aldehyde (10 mmoles) in methanol (50 mL) was added barium hydroxide (3.42 g; 20 mmoles) solution in water (20 mL) and the resulting mixture was stirred at room temperature for 72 hrs. The whole mixture was added with stirring to ice cold 1 N hydrochloric acid and the resulting yellow solid was filtered, washed with water, dried and recrystallized from alcohol to afford 6-Cinnamoyl-7-hydroxy-8-(unsubstituted or methoxy)-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (3a-h) and their characterization data are listed in Table 1. ..

A typical procedure is given below:

6-(4', Methoxycinnamoyl)-7-hydroxy-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (3b)

The compound 3b was synthesized by condensation of 6-acetyl-7-hydroxy-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (2a, 2.20 g, 10 mmoles) with 4-methoxybenzaldehyde (1.36 g, 10 mmoles) in presence of barium hydroxide (3.42 g; 20 mmoles) as described above. The product after usual workup was crystallized from ethanol to afford 6-(4', Methoxycinnamoyl)-7-hydroxy-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (3b) as yellow needles, yield 2.37 g (75%); mp 144-45°C (lit.² mp 146-47°C).

Alternate Method: General procedure

A mixture of 6-acetyl-7-hydroxy-8-methoxy-2, 2-dimethyl-3, 4-dihydro-277-1-benzopyran (2a, 10 mmoles), aromatic aldehyde (11 mmoles) and catalytic amount of piperidine (0.2 mL) in sodium dry benzene (60 mL) was refluxed in an oil bath and water was removed using Dean-Stark apparatus. After the completion of reaction (24 hrs.), the solvent was removed on water bath and
further concentrated under reduced pressure. The reaction mixture was taken up in ethyl acetate (100 mL) and an organic layer was washed with 10% hydrochloric acid (2 x 50 mL) followed by water and with aqueous sodium bicarbonate. The organic layer was dried over anhydrous sodium sulfate and solvent was removed under reduced pressure. The concentrated gummy mass was chromatographed over silica gel column using pet-ether-ethyl acetate as an eluent to afford 6-cinnamoyl-7-hydroxy-8-(unsubstituted or methoxy)-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (3 a-h) and their characterization data are given in Table 1.

A typical procedure is as follows:

6-(4'-Methoxy-cinnamoyl)-7-hydroxy-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (3b)

The compound 3b was synthesized by condensation of 6-acetyl-7-hydroxy-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (2 a, 1.10 g, 5 mmole) with anisaldehyde (0.75 g, 5.5 mmole) in presence of pyrrolidine (0.2 mL) as described above. The product after usual workup was purified by using column chromatography over silica gel using petrol ether-ethyl acetate (9:1) as an eluent to afford 6-(4'-methoxy-cinnamoyl)-7-hydroxy-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (3b) as yellow plates, yield 1.32 g (85%), mp 144-45°C (Lit4 mp 146-47°C); IR (KBr) cm⁻¹: 1664, 3200; 1H-NMR (CDCl₃, 200MHz) δ: 1.342 (s, 6H, 2 × CH₃), 1.811 (t, 2H, J = 6.78 Hz, C₃-H), 2.804 (t, 2H, J = 6.74 Hz, C₄-H), 3.864 (s, 3H, C₄-OCH₃), 6.390 (s, 1H, C₅-H), 6.945 (br, 2H, J = 8.69 Hz, C₂' & C₃'-H), 7.458 (d, 1H, J = 15.37 Hz, C₆'-H), 7.613 (brd, 2H, J = 8.39 Hz, C₂' & C₆'-H), 7.680 (s, 1H, C₅'-H), 7.858 (d, 1H, J = 15.37 Hz, C₇'-H), 13.365 (s, 1H, D₂O exchangeable, C₇-OH).

The 1H-NMR data of other unknown chalcones (3 a-h) are given below:

6-(3', 4'-Methylene-dioxycinnamoyl)-7-hydroxy-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (3 d): 1H-NMR (CDCl₃, 200MHz) δ: 1.342 (s, 6H, 2 × CH₃), 1.811 (t, 2H, J = 6.78 Hz, C₃-H), 2.804 (t, 2H, J = 6.74 Hz, C₄-H), 6.043 (s, 2H, -OCH₂O-), 6.390 (s, 1F, C₆'-H), 6.861 (d, 1H, J = 7.96 Hz, C₃'-H), 7.144 (dd, 1H, J = 8.08 & 1.62 Hz, C₆'-H), 7.177 (d, 1H, J = 15.59 Hz, C₂'-H), 7.458 (d, 1H, J
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=15.37 Hz, Cα-H), 7.680 (s, 1H, C5-H), 7.858 (d, 1H, J =15.37 Hz, C8-H),
13.365 (s, 1H, D2O exchangeable, C7-OH).

6-(4′-Methoxycinnamoyl)-7-hydroxy-8-methoxy-2, 2-dimethyl-3, 4-dihydro-
2H-1-benzopyran (3 f): 1H-NMR (CDCl3, 200MHz) δ: 1.340 (s, 6H, 2 x CH3),
1.814 (t, 2H, J =6.77 Hz, C3-H), 2.802 (t, 2H, J =6.74 Hz, C4-H), 3.864 (s, 3H,
C4-OCH3), 3.882 (s, 3H, C8-OCH3), 6.942 (brd, 2H, J =8.56 Hz, C3′ & C5-H),
7.456 (d, 1H, J =15.29 Hz, Cα-H), 7.610 (brd, 2H, J =8.58 Hz, C2′ & C6-H),
7.686 (s, 1H, C5-H), 7.858 (d, 1H, J =15.27 Hz, C8-H), 12.984 (s, 1H, D2O
exchangeable, C7-OH).

6-(3′, 4′-Dimethoxycinnamoyl)-7-hydroxy-8-methoxy-2, 2-dimethyl-3, 4-
dihydro-2H-1-benzopyran (3 g): 1H-NMR (CDCl3, 200MHz) δ: 1.342 (s, 6H, 2
x CH3), 1.814 (t, 2H, J =6.76 Hz, C3-H), 2.804 (t, 2H, J =6.74 Hz, C4-H), 3.824
(s, 3H, C3-OCH3), 3.866 (s, 6H, C8, C4-OCH3), 6.945 (bd, 1H, J =8.66 Hz, C7-
H), 7.458 (d, 1H, J =15.17 Hz, Cα-H), 7.613 (bd, 2H, J =8.59 Hz, C2′ & C6-H),
7.680 (s, 1H, C5-H), 7.358 (d, 1H, J =15.37 Hz, C8-H), 13.365 (s, 1H, D2O
exchangeable, C7-OH).

6-(3′, 4′-Methylenedioxyacinamoyl)-7-hydroxy-8-methoxy-2, 2-dimethyl-3,
4-dihydro-2H-1-benzopyran (3 h): 1H-NMR (CDCl3, 200MHz) δ: 1.344 (s,
6H, 2 x CH3), 1.811 (t, 2H, J =6.78 Hz, C3-H), 2.804 (t, 2H, J =6.74 Hz, C4-H),
3.862 (s, 3H, C8-OCH3), 6.022 (s, 2H,-OCH2O-), 6.842 (d, 1H, J =8.02 Hz, C5-
H), 7.142 (dd, 1H, J = 8.02 & 1.6 Hz, C6′-H), 7.169 (d, 1H, J =1.6Hz, C2′-H),
7.458 (d, 1H, J =15.37Hz, Cα-H), 7.668 (s, 1H, C5-H), 7.852 (d, 1H, J =15.37 Hz,
C8-H), 13.362 (s, 1H, D2O exchangeable, C7-OH).

123
Table 1: 6-Cinnainoyl-7-hydroxy-8-(unsubstituted or methoxy)-2, 2-dimethyl-3, 4-dihydro-2/?-l-benzopyraii (3 a-h)

<table>
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<th>Compel. No</th>
<th>R</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>mp (lit mp) (°C)</th>
<th>Yield(^a) %</th>
</tr>
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<tbody>
<tr>
<td>3a</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>188-89 (189)</td>
<td>70 (78)</td>
</tr>
<tr>
<td>3b</td>
<td>H</td>
<td>H</td>
<td>OMe</td>
<td>H</td>
<td>144-45 (146-47)</td>
<td>75 (85)</td>
</tr>
<tr>
<td>3c</td>
<td>H</td>
<td>H</td>
<td>OCH(_2)Ph</td>
<td>H</td>
<td>180-82</td>
<td>72 (80)</td>
</tr>
<tr>
<td>3d</td>
<td>H</td>
<td>H</td>
<td>-OCH(_2)0-</td>
<td>208-09 (201-02)</td>
<td>70 (75)</td>
<td></td>
</tr>
<tr>
<td>3e</td>
<td>OMe</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>140-41 (112-13)</td>
<td>72 (85)</td>
</tr>
<tr>
<td>3f</td>
<td>OMe</td>
<td>H</td>
<td>OMe</td>
<td>H</td>
<td>159-61</td>
<td>79 (85)</td>
</tr>
<tr>
<td>3g</td>
<td>OMe</td>
<td>H</td>
<td>OMe</td>
<td>OMe</td>
<td>172-73 (134-36)</td>
<td>69 (76)</td>
</tr>
<tr>
<td>3h</td>
<td>OMe</td>
<td>H</td>
<td>-OCH(_2)0-</td>
<td>160-61 (148-49)</td>
<td>70 (81)</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Yield in parenthesis is obtained by alternate method

Substituted 8, 8-Diniethyl-10-(unsubstituted or methoxy)-SH, 6, 7-dihydropyrano[2, 3: 7, 6]flavanone (17 a-h): General procedure

6-Cinnamoyl)-7-hydroxy-8-(unsubstituted or methoxy)-2, 2-dimethyl-3, 4-dihydro-2/1-benzopyran (3 a-h; 600 mg) was dissolved in pyridine: methanol: water (1: 1: 1; 60 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 15 mL under reduced pressure. To this water (50 mL) was added 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, the residue was passed through a small bed of basic alumina using ethyl acetate-hexane (1:10) as eluent to give respective 8, 8-dimethyl-10-(unsubstituted or methoxy)-8i7, 6, 7-
dihydropyrano[2, 3: 7, 6]flavanone (17 a-h) in 80-85% yield and their characterization data are given in Table 2.

A typical procedure is given below:

4'-Methoxy-8, 8-dimethyl-8H, 6, 7-dihydropyrano[2, 3: 7, 6]flavanone (17 b)

Compound 17 b was prepared by refluxing of 6-(4'-methoxycinnamoyl)-7-hydroxy-2, 2-dimethyl-3, 4-dihydro-2H-1-benzopyran (3 b; 600 mg) in a mixture of pyridine: methanol: water (1: 1: 1; 60 mL) 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 4'-methoxy-8, 8-dimethyl-8H, 6, 7-dihydropyrano[2, 3: 7, 6]flavanone (17 b) as white crystalline solid, mp 124-25°C; yield 510 mg (85%); IR (KBr) cm⁻¹: 1660; ¹H-NMR (CDCl₃, 200MHz) δ: 1.349 (s, 6H, 2 x CH₃), 1.816 (t, 2H, J=6.78 Hz, C₇-H), 2.728 – 2.826 (m, 3H, C₆'-H & C₃'-Hₖ), 3.029 (dd, 1H, J=12.73 & 16.84 Hz, C₃-Hₖ), 3.830 (s, 3H, C₄-OCH₃), 5.372 (dd, 1H, J=12.73 & 3.03 Hz, C₂'-H), 6.382 (s, 1H, C₁₀'-H), 6.947 (brd, 2H, J=8.73 Hz, C₇' & C₃'-H), 7.392 (brd, 2H, J=8.59 Hz, C₂' & C₆'-H), 7.680 (s, 1H, C₅-H).

The ¹H-NMR data of other compounds (17 a-h) are given below:

8, 8-Dimethyl-8H, 6, 7-dihydropyrano[2, 3: 7, 6]flavanone (17 a): 1.359 (s, 6H, 2 x CH₃), 1.830 (t, 2H, J=6.76 Hz, C₇-H), 2.747 – 2.922 (m, 3H, C₆'-H & C₃'-Hₖ), 3.023 (dd, 1H, J=11.73 & 16.91 Hz, C₃'-Hₖ), 3.842 (s, 3H, C₈-OCH₃), 5.491 (dd, 1H, J=11.65 & 3.83 Hz, C₂'-H), 6.398 (s, 1H, C₈-H), 7.354 – 7.509 (m, 5H, C₂-C₆H₃), 7.680 (s, 1H, C₅-H).

3', 4'-Methylenedioxy-8, 8-dimethyl-8H, 6, 7-dihydropyrano[2, 3: 7, 6]flavanone (17 d): 1.342 (s, 6H, 2 x CH₃), 1.796 (t, 2H, J=6.87 Hz, C₇-H), 2.678 – 2.826 (m, 3H, C₆'-H & C₃'-Hₖ), 2.994 (dd, 1H, J=12.83 & 16.74 Hz, C₃'-Hₖ), 5.368 (dd, 1H, J=12.78 & 3.33 Hz, C₂'-H), 5.974 (s, 2H, -OCH₂O-), 6.378 (s, 1H, C₈-H), 6.836 (d, 1H, J=8.24 Hz, C₅'-H), 6.918 (dd, 1H, J=1.82 & 8.24 Hz, C₆'-H), 7.000 (d, 1H, J=1.79 Hz, C₂'-H), 7.676 (s, 1H, C₅-H).

10-Methoxy-8, 8-dimethyl-8H, 6, 7-dihydropyrano[2, 3: 7, 6]flavanone (17 e): 1.359 (s, 6H, 2 x CH₃), 1.830 (t, 2H, J=6.76 Hz, C₇-H), 2.747 – 2.922 (m, 3H, C₆'-H & C₃'-Hₖ), 3.023 (dd, 1H, J=11.73 & 16.91 Hz, C₃'-Hₖ), 3.842 (s, 3H, C₈-
CHAPTER II, Section B: Synthesis of Erythrinin-A and analogues

OCH₃), 5.491 (dd, 1H, J=11.65 & 3.83 Hz, C₂-H), 7.354 – 7.509 (m, 6H, C₅-H & C₃-C₆-H₅).

4', 10-Dimethoxy-8, 8-dimethyl-8H, 6, 7-dihydropyranono[2, 3: 7, 6]flavanone (17 f): 1.398 (s, 6H, 2 x CH₃), 1.823 (t, 2H, J=6.70 Hz, C₇-H), 2.740 – 2.891 (m, 3H, C₆-H & C₃-Hₐ), 3.028 (dd, 1H, J=11.74 & 16.75 Hz, C₇-H₆), 3.823 (s, 6H, C₈-OCH₃ & C₄'-OCH₃), 5.437 (dd, 1H, J=11.62 & 3.36 Hz, C₂-H), 6.937 (brd, 2H, J=8.56 Hz, C₃' & C₅-H), 7.409 (brd, 2H, J=8.50 Hz, C₂' & C₆'-H), 7.461 (s, 1H, C₅-H).

3', 4', 10-Trimethoxy-8, 8-dimethyl-8H, 6, 7-dihydropyranono[2, 3: 7, 6]flavanone (17 g): 1.401 (s, 6H, 2 x CH₃), 1.827 (t, 2H, J=6.75 Hz, C₇-H), 2.743 – 2.921 (m, 3H, C₆-H & C₃-Hₐ), 3.042 (dd, 1H, J=11.45 & 16.91 Hz, C₃-H₈), 3.836 (s, 3H, C₈-OCH₃), 3.896 (s, 3H, C₄'-OCH₃), 3.904 (s, 3H, C₃'-OCH₃), 5.445 (dd, 1H, J=11.50 & 3.67 Hz, C₂-H), 6.885 (d, 1H, J=8.11 Hz, C₅-H), 6.993 – 7.038 (m, 2H, C₂' & C₆'-H), 7.460 (s, 1H, C₅-H).

3', 4'-Methylenedioxy-10-methoxy-8, 8-dimethyl-8H, 6, 7-dihydropyranono[2, 3: 7, 6]flavanone (17 h): 1.392 (s, 6H, 2 x CH₃), 1.826 (t, 2H, J=6.75 Hz, C₇-H), 2.743 – 2.921 (m, 3H, C₆-H & C₃-Hₐ), 3.032 (dd, 1H, J=11.53 & 16.91 Hz, C₃-H₈), 3.842 (s, 3H, C₈-OCH₃), 5.436 (dd, 1H, J=11.50 & 3.57 Hz, C₂-H), 5.974 (s, 2H, -OCH₂O-), 6.886 (d, 1H, J=8.04 Hz, C₃-H), 6.928 (dd, 1H, J=1.42 & 8.04 Hz, C₆-H), 7.002 (d, 1H, J=1.49 Hz, C₂-H), 7.460 (s, 1H, C₅-H).

Oxidative rearrangement of substituted 8, 8-Dimethyl-10-(unsubstituted or methoxy)-8H, 6, 7-dihydropyranono[2, 3: 7, 6]flavanones (17 a-h) using Thallium (III) p-tosylate (TTS): Synthesis of substituted 8, 8-Dimethyl-10 (unsubstituted or methoxy)-8H, 6, 7-dihydro-pyranono[2, 3: 7, 6]isoflavones (18 a-h): General procedure

To a solution of substituted 8, 8-dimethyl-10 (unsubstituted or methoxy)-8H, 6, 7-dihydropyranono[2, 3: 7, 6]flavanones (17 a-h; 1 mmole) in acetonitrile (15 mL) was added thallium (III) p-tosylate (800 mg; 1.1 mmole) and the resulting mixture was refluxed for 2 hrs. 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 8, 8-dimethyl-10 (unsubstituted or methoxy)-8H, 6, 7-dihydropyran[2, 3: 7, 6]isoflavone (18 a-h) and their characterization data are given in Table 3.

A typical procedure is given below:

4'-Methoxy-8, 8-dimethyl-8H, 6, 7-dihydropyran[2, 3: 7, 6]isoflavone (6, 7-dihydroerythrinin-A methyl ether (18 b)

Compound 18 b was prepared by oxidative rearrangement of 4'-methoxy-8, 8-dimethyl-8H, 6, 7-dihydropyran[2, 3: 7, 6]flavane (17 b; 338 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: 9) as eluent to afford 4'-methoxy-8, 8-dimethyl-8H, 6, 7-dihydropyran[2, 3: 7, 6]isoflavone (18 b), yield 302 mg (90%), mp 184-85°C (Litmp 183-84°C), IR (KBr) cm⁻¹: 1650; ¹H-NMR (CDCl₃, 200MHz) δ: 1.390 (s, 6H, 2 x CH₃), 1.882 (t, 2H, J=6.75 Hz, C₇-H), 2.927 (t, 2H, J=6.57 Hz, C₈-H), 3.842 (s, 3H, C₄-OC₃H₃), 6.796 (s, 1H, C₁₀-H), 6.968 (brd, 2H, J=8.75 Hz, C₃ & C₅-H), 7.492 (brd, 2H, J=8.71 Hz, C₂ & C₆-H), 7.875 (s, 1H, C₇-H), 8.020 (brs, 1H, C₈-H).

The ¹H-NMR data of other compounds (18 a-h) are given below;

8, 8-Dimethyl-8H, 6, 7-dihydropyran[2, 3: 7, 6]isoflavone (18 a): 1.396 (s, 6H, 2 x CH₃), 1.887 (t, 2H, J=6.75 Hz, C₇-H), 2.927 (t, 2H, J=6.67 Hz, C₈-H), 6.810 (s, 1H, C₉-H), 7.364 – 7.478 (m, 3H, C₃, C₄ & C₅-H), 7.515 – 7.583 (m, 2H, C₂ & C₆-H), 7.909 (s, 1H, C₇-H), 8.031 (brs, 1H, C₈-H).

3', 4'-Methylenedioxy-8, 8-dimethyl-8H, 6, 7-dihydropyran[2, 3: 7, 6]isoflavone (18 d): 1.386 (s, 6H, 2 x CH₃), 1.878 (t, 2H, J=6.78 Hz, C₇-H), 2.914 (t, 2H, J=6.77 Hz, C₈-H), 5.984 (s, 2H, -OC₃H₂O-), 6.791 (s, 1H, C₉-H), 6.917 (s, 1H, C₁₀-H), 7.364 – 7.478 (m, 3H, C₃, C₄ & C₅-H), 7.515 – 7.583 (m, 2H, C₂ & C₆-H), 7.901 (s, 1H, C₇-H), 8.021 (brs, 1H, C₈-H).
6.859 (d, 1H, J=7.91 Hz, C₅-H), 6.967 (dd, 1H, J=1.53 & 7.98 Hz, C₆-H), 7.089 (d, 1H, J=1.49 Hz, C₂-H), 7.861 (s, 1H, C₁-H), 8.012 (brs, 1H, C₅-H).

10-Methoxy-8, 8-dimethyl-8H, 6, 7-dihydropyran[2, 3: 7, 6]isoflavone (18 e): 1.449 (s, 6H, 2 x CH₃), 1.900 (t, 2H, J=6.75 Hz, C₇-H), 2.937 (t, 2H, J=6.71 Hz, C₆-H), 3.982 (s, 3H, C₈-OCH₃), 7.331 - 7.496 (m, 3H, C₃', C₄', & C₅'-H), 7.55 - 7.583 (m, 2H, C₁ & C₆'-H), 7.803 (brs, 1H, C₂-H), 7.994 (s, 1H, C₂-H).

4', 10-Dimethoxy-8, 8-dimethyl-8H, 6, 7-dihydropyran[2, 3: 7, 6]isoflavone (18 f): 1.446 (s, 6H, 2 x CH₃), 1.896 (t, 2H, J=6.73 Hz, C₇-H), 2.932 (t, 2H, J=6.79 Hz, C₆-H), 3.843 (s, 3H, C₄-OCH₃), 3.975 (s, 3H, C₈-OCH₃), 6.973 (brd, 2H, J=8.81 Hz, C₃' & C₅'-H), 7.409 (brd, 2H, J=8.82 Hz, C₁ & C₆'-H), 7.795 (brs, 1H, C₅-H), 7.962 (s, 1H, C₂-H).

3', 4', 10-Trimethoxy-8, 8-dimethyl-8H, 6, 7-dihydropyran[2, 3: 7, 6]isoflavone (18 g): 1.449 (s, 6H, 2 x CH₃), 1.900 (t, 2H, J=6.68 Hz, C₇-H), 2.936 (t, 2H, J=6.68 Hz, C₆-H), 3.914 (s, 3H, C₄-OCH₃), 3.929 (s, 3H, C₃-OCH₃), 3.977 (s, 3H, C₈-OCH₃), 6.928 (d, 1H, J=8.29 Hz, C₃-H), 7.050 (dd, 1H, J=1.95 & 8.22 Hz, C₆-H), 7.210 (d, 1H, J=1.81 Hz, C₂-H), 7.799 (brs, 1H, C₅-H), 7.994 (s, 1H, C₁-H).

3', 4'-Methylenedioxy-10-methoxy-8, 8-dimethyl-8H, 6, 7-dihydropyran[2, 3: 7, 6]isoflavone (18 h): 1.477 (s, 6H, 2 x CH₃), 1.936 (t, 2H, J=6.67 Hz, C₇-H), 2.751 (t, 2H, J=6.82 Hz, C₆-H), 4.014 (s, 3H, C₄-OCH₃), 6.198 (s, 2H, -OCH₂O-), 6.861 (d, 1H, J=8.34 Hz, C₃-H), 6.984 (dd, 1H, J=1.94 & 8.34 Hz, C₆-H), 7.104 (d, 1H, J=1.94 Hz, C₂-H), 7.794 (brs, 1H, C₅-H), 8.064 (s, 1H, C₁-H).
Table 2: Substituted 8,8-Dimethyl-10-(unsubstituted or methoxy)-8H-6,7-dihydro-pyano[2,3:7,6]flavanones (17 a-h)

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<tr>
<th>Compound</th>
<th>R</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>mp (lit mp)</th>
<th>Yield</th>
<th>Molecular formula</th>
<th>Analytical data (Calc.)</th>
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<tbody>
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<td>H</td>
<td>H</td>
<td>H</td>
<td>150-51</td>
<td>80</td>
<td>C_{26}H_{20}O_{3}</td>
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</tr>
<tr>
<td>17b</td>
<td>H</td>
<td>H</td>
<td>OMe</td>
<td>H</td>
<td>124-25</td>
<td>85</td>
<td>C_{21}H_{22}O_{4}</td>
<td>74.72(74.56) / 6.47(6.51)</td>
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<tr>
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<td>H</td>
<td>H</td>
<td>OMe</td>
<td>H</td>
<td>125-27</td>
<td>82</td>
<td>C_{27}H_{20}O_{4}</td>
<td>77.98(78.26) / 6.51(6.28)</td>
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<tr>
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<td>H</td>
<td>O-CH_{2}-O</td>
<td>127-128</td>
<td>83</td>
<td>C_{21}H_{20}O_{3}</td>
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</tr>
<tr>
<td>17e</td>
<td>OMe</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>105-07</td>
<td>85</td>
<td>C_{21}H_{22}O_{4}</td>
<td>74.53(74.56) / 6.75(6.51)</td>
</tr>
<tr>
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<td>H</td>
<td>OMe</td>
<td>H</td>
<td>124-26</td>
<td>82</td>
<td>C_{22}H_{22}O_{4}</td>
<td>71.89(71.74) / 6.47(6.52)</td>
</tr>
<tr>
<td>17g</td>
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<td>H</td>
<td>OMe</td>
<td>OMe</td>
<td>150-51</td>
<td>80</td>
<td>C_{23}H_{26}O_{6}</td>
<td>69.54(69.35) / 6.38(6.53)</td>
</tr>
<tr>
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<td>O-CH_{2}-O</td>
<td>151-53</td>
<td>80</td>
<td>C_{22}H_{22}O_{6}</td>
<td>68.95(69.11) / 5.92(5.76)</td>
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Table 3: Substituted 8,8-Dimethyl-10-(unsubstituted or methoxy)-8H-6,7-dihydro-pyran-2,3:7,6]isoflavones (18a-h)

<table>
<thead>
<tr>
<th>Compound</th>
<th>No</th>
<th>R</th>
<th>R1</th>
<th>R2</th>
<th>R3</th>
<th>mp(lit mp)</th>
<th>Yield %</th>
<th>Molecular formula</th>
<th>Analytical data (Calc.)</th>
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<tbody>
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<td>18a</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>215-17</td>
<td>92</td>
<td>C_{21}H_{18}O_{3}</td>
<td>78.21(78.43) 5.92(5.88)</td>
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<tr>
<td>18b</td>
<td>H</td>
<td>H</td>
<td>OMe</td>
<td>H</td>
<td>H</td>
<td>184-85 (183-84)</td>
<td>90</td>
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<tr>
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<td>H</td>
<td>OBz</td>
<td>H</td>
<td>H</td>
<td>202-04</td>
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<td>C_{22}H_{24}O_{4}</td>
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</tr>
<tr>
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<td>H</td>
<td>O-CH_{2}-O</td>
<td></td>
<td></td>
<td>189-90(191-92)</td>
<td>94</td>
<td>C_{21}H_{18}O_{3}</td>
<td>71.96(72.00) 5.29(5.14)</td>
</tr>
<tr>
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<td>OMe</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>173-75</td>
<td>92</td>
<td>C_{21}H_{20}O_{4}</td>
<td>74.86(75.00) 6.12(5.95)</td>
</tr>
<tr>
<td>18f</td>
<td>OMe</td>
<td>H</td>
<td>OMe</td>
<td>H</td>
<td>H</td>
<td>159-61</td>
<td>92</td>
<td>C_{23}H_{22}O_{5}</td>
<td>72.36(72.13) 5.89(6.01)</td>
</tr>
<tr>
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<td>OMe</td>
<td>OMe</td>
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<td>94</td>
<td>C_{23}H_{24}O_{6}</td>
<td>69.63(69.70) 6.14(6.06)</td>
</tr>
<tr>
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<td></td>
<td>&gt;220</td>
<td>90</td>
<td>C_{22}H_{26}O_{6}</td>
<td>69.58(69.47) 5.12(5.26)</td>
</tr>
</tbody>
</table>
CHAPTER II, Section B: Synthesis of Erythrinin-A and analogues

2.3.4. References

$^1$H NMR spectrum of 6,7-Dihydroerythrinin-A methylether (18b)

Mass spectrum of 6,7-Dihydroerythrinin-A methylether (18b)
$^1$H NMR spectrum of $3',4'$-Methylenedioxy-8,8-dimethyl-8$H,6,7$-dihydropyranol2,3':7,6$isoavone (18d)

$^1$H NMR spectrum of $3',4',10$-Trimethoxy-8,8-dimethyl-8$H,6,7$-dihydropyranol2,3':7,6$isoavone (18g)