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CINNAMYLATION STUDIES OF 5,7-DIHYDROXY-2-METHYLISOFLAVONE AND CHROMONE

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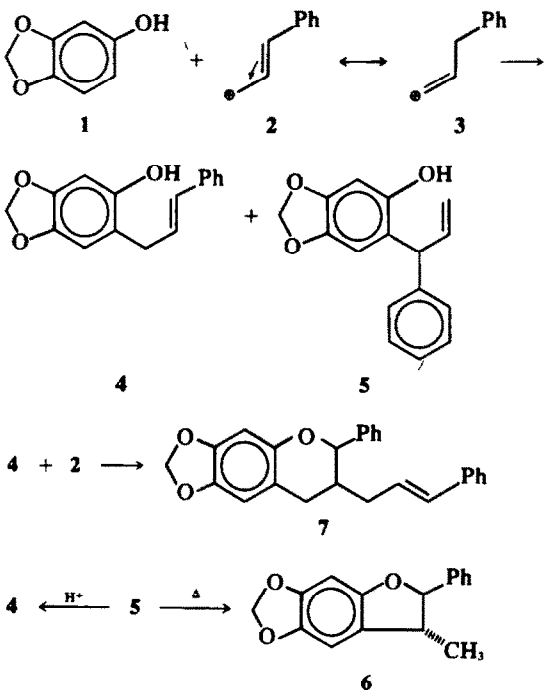
Abstract—Cinnamylation of 5,7-dihydroxy-2-methyl-isoflavone and chromone with cinnamyl alcohol in the presence of aqueous acetic acid yields 6,8-dicinnamyl- and 8-cinnamyl- derivatives, respectively. On the other hand, cinnamylation with cinnamyl bromide in the presence of methanolic sodium methoxide affords the corresponding 6-cinnamyl derivatives along with the same dicinnamyl derivatives. Cyclodehydrogenation of the monocinnamyl derivatives with DDQ is sluggish and gives the corresponding flavenes only in small yields.

Cinnamic acids and alcohols are important biogenetic units in the evolution of varied types of natural products such as coumarins, flavonoids, isoflavonoids, lignans and lignins.[1] Some polyphenols, like anthocyanins, are esterified with cinnamic acid.[2] In the group of flavanolignans,[3] a cinnamyl unit has reacted in the side phenyl of flavonoids, but in cinnamyl phenols (also called benzyl styrens[4]), simple phenols are cinnamylated in the benzene nucleus. Related to the latter compounds are flavenes and different types of neoflavonoids[5] such as dalbergins, dalbergiquinols, dalbergiquinones, quinomethides and neoflavenes, which have been isolated mainly from *Dalbergia* and *Machaerium* spp. In the biogenetic evolution of these compounds, the role of *C*-alkylation of phenols with cinnamyl pyrophosphate has been emphasized by Ollis *et al*[6] and by Jurd.[7] Since benzyl styrenes and some neoflavonoids have been found to possess pronounced microbiocidal properties,[8] and there is a possibility of the occurrence of more complicated cinnamylphenols in nature, cinnamylation of 5,7-dihydroxy-2-methylisoflavone and chromone have now been studied.

Earlier cinnamylation of simple phenols like resorcinol, pyrogallol, phloroglucinol, 2-methoxyquinol, 4-methoxyphenol and sesamol, have been carried out by reaction with cinnamyl alcohol in the presence of different acids.[9-11] Thus, depending on the strength of the organic acid, the nucleophilicity of phenols, and the stability of the potential cinnamyl cation, different types of products have been isolated. In the presence of mild acids like aqueous acetic, propionic and citric acids, phenols (e.g. sesamol **1**) have been found to react with cinnamyl **2** or 1-phenylallyl cation **3** to give a mixture of *o*-cinnamylphenols (e.g. **4**) and *o*-(1-phenylallyl) **5**). The occasional additional isolation of 2,3-dihydro-2-phenyl-3-methyl-benzofurans (like **6**) in the above mixture has recently been found to be due to thermal rearrangement of *o*-(1-phenylallyl) phenols during work-up.[11] In the presence of stronger acids like aqueous formic acid, the yield of *o*-cinnamyl phenols increases considerably and a new product identified as 3-cinnamyl flavan derivative (see **7**) is formed. This is because excess of cinnamyl cation combines further with *o*-cinnamylphenol **4** to give 2-phenyl-3-cinnamyl flavan **7** and strongly acidic conditions promote the conversion of 3,3-diaryl propene **5** into *o*-cinnamyl phenol **4**.



In the present work, cinnamylation has been carried out under both acidic and alkaline conditions. Cinnamylation under acidic conditions has been brought about with cinnamyl alcohol in the presence of 75 per cent aqueous acetic acid in order to avoid the formation of secondary products. The alkaline method uses cinnamyl bromide in

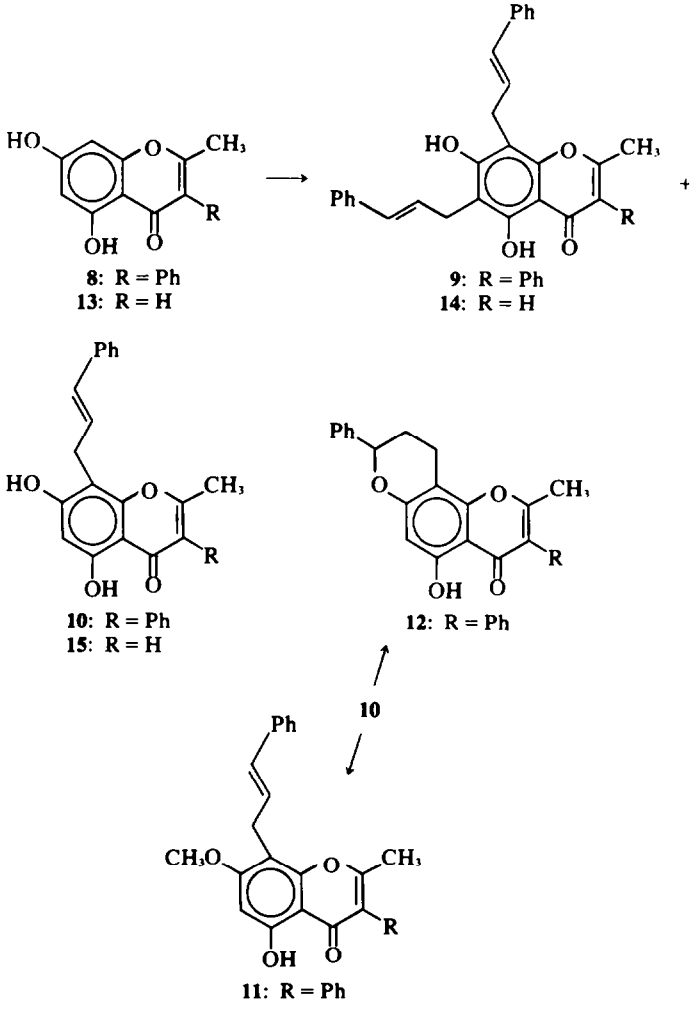
the presence of methanolic sodium methoxide. The latter method is akin to *C*-prenylation with prenyl bromide[12] and *C*-methylation with methyl iodide.[13]

Cinnamylation under acidic conditions

5,7-Dihydroxy-2-methylisoflavone[14] **8**, when heated with cinnamyl alcohol in 75 per cent aqueous acetic acid gave a mixture from which only two products (**A** and **B**) could be obtained crystalline after purification by column chromatography. The product **A** analysed for a dicinnamyl derivative and gave a diacetate (NMR* 2·22 and 2·28, 2s, $2CH_3CO_2$–) indicating both the hydroxyls to be free. Since the NMR spectra of the product **A** and its acetate showed signals of aromatic protons of only three phenyl groups and two $-CH_2-CH=CH-$ units, the product **A** is considered to be 5,7-dihydroxy-2-methyl-6,8-dicinnamylisoflavone **9**.

*Unless otherwise stated, NMR spectra were measured with 60 MHz spectrometer in $CDCl_3$ and chemical shifts reported in δ values.

The product **B** was found to be a mono *C*-cinnamyl derivative by its NMR spectrum and that of its acetate. Thus the spectrum of the diacetate showed two singlets of acetoxyl groups at 2·22 and 2·30 and both the spectra showed protons of one cinnamyl residue, intact phenyl ring and one aromatic proton of the ring **A**. The location of the cinnamyl residue was established in the 8 position because the 7-methyl ether (positive ferric reaction; NMR 3·90, 1s, 3H, OCH_3) formed with one mole of dimethyl sulphate, did not undergo reaction with formic acid. However, the dihydroxy compound itself underwent cyclisation, albeit on long heating, with formic acid due to stability of *o*-cinnamyl phenol under acidic conditions (see [11]). The cyclised product was identified as 4″,5″-dihydro-5-hydroxy-2-methyl-6″-phenyl pyrano (2″,3″:7,8) isoflavone **12** by NMR. Thus it showed five protons of dihydropyran ring as one triplet of a benzylic methylene group at 2·80, one triplet of a methine group at 5·88 and a broad doublet of a methylene group at 1·31. Had the product **B** been a 6-C-cinnamyl derivative, its partial methyl ether would not have undergone acid cyclisation

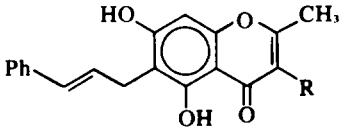


to give a flavan. Thus the product **B** is 5,7-dihydroxy-2-methyl-8-cinnamylisoflavone **10** and its partial methyl ether **11**. This was further confirmed by comparing the signals of aromatic protons of ring **A** in the hydroxy compound and its diacetate. The singlet at 6·36 in the hydroxy product undergoes a marked downfield shift to 7·24 in the diacetate.

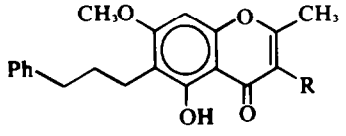
A parallel cinnamylation reaction of 5,7-dihydroxy-2-methyl chromone[15] (or noreugenin, **13**) under the same conditions gave also a similar mixture of two products which were identified in the same manner as 6,8-dicinnamyl noreugenin **14** and 8-cinnamyl noreugenin **15**.

Cinnamylation in the presence of alkali

Cinnamylation of 5,7-dihydroxy-2-methylisoflavone **8** when carried out with cinnamyl bromide in the presence of methanolic sodium methoxide also yielded a mixture of two compounds, one of which was found identical with 6,8-dicinnamyl derivative **9** formed in the first reaction. The other product was shown by analysis and NMR to be mono *C*-cinnamyl derivative, but different from **10**. Hence it was considered to be 5,7-dihydroxy-2-methyl-6-*C*-cinnamylisoflavone **16**. This was confirmed by the preparation of its diacetate and 7-methyl ether (using one mole of Me_2SO_4 in presence of K_2CO_3 and acetone) and a study of their NMR spectra. Thus the aromatic singlet at 6·40 in the hydroxy compound and that at 6·39 in the methoxy compound underwent no significant shift in the diacetate. A parallel reaction with noreugenin also gave a similar mixture of two products which were identified in the same manner as 6,8-dicinnamylnoreugenin **14** and 6-cinnamylnoreugenin **17**.



16: R = Ph
17: R = H

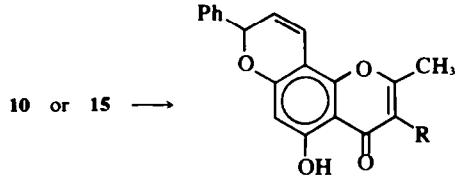


18: R = Ph
19: R = H

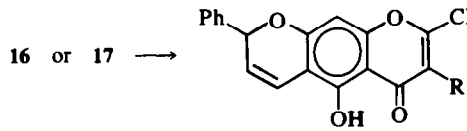
The above experiments of cinnamylation under acidic and alkaline conditions indicate that although the dicinnamyl derivative is a common product, different monocinnamyl derivatives are obtained. The alkaline method gives predominantly 6-cinnamyl derivative, whereas the acidic conditions affords 8-cinnamyl derivative. Thus the two methods are complimentary to each other and one can get 6 and 8 cinnamyl derivative of a chromone or an isoflavone by using alkaline and acid conditions respectively. The formation of 8-cinnamyl derivative under acidic conditions is analogous to the Friedel–Crafts alkylation of a phenol and the formation of 6-cinnamyl derivative is due to pronounced carbanion activity of 6 position under alkaline conditions as in acetoacetic ester. The formation of dicinnamyl derivative under both the conditions is due to the formation of a resonance-stabilised cation like 3-methylbut-2-enyl cation.

Synthesis of 2-phenyl pyrano derivatives from C-cinnamyl compounds **10**, **15**, **16** *and* **17**

Flav-3-enes have recently been considered to be precursors of flavans and flavylium salts[16] and since these can be obtained from *o*-cinnamyl phenols by a step of cyclodehydrogenation, the *C*-cinnamyl **16** and **17** and cinnamyl derivatives 8- **10** and **15** of 5,7-dihydroxy-2-



20: R = Ph
21: R = H



22: R = Ph
23: R = H

methyl isoflavone and noreugenin have now been reacted with DDQ. Although the reaction is sluggish, requiring continuous refluxing for 10–15 h, and there is a lot of darkening of the product, the corresponding flavenes **20–23** have been obtained in each case and their structures established by NMR. Thus, all of them showed signals of three aromatic protons of the pyran ring, one as a doublet in the neighbourhood of 6·95 and two as a multiplet in the region 5·6–6·2. The lesser yields of cyclodehydrogenation products in the above reaction than those formed from *ortho* 3-methylbut-2-enyl phenols with DDQ is due to the presence of free hydrogen in the 6″-position of the flavene which may promote further oxidation.

The insecticidal activity of the above prepared cinnamylated compounds and flavenes is under investigation.

EXPERIMENTAL

Unless otherwise stated, mps are uncorrected; light petroleum had boiling range 60–80°; silica gel was used for column chromatography and TLC; solvent systems for TLC were: (A) benzene:EtOAc (19:1) (B) benzene:EtOAc (9:1) (C) benzene:MeOH (19:1) (D) toluene:ethyl formate:formic acid (5:4:1) (E) benzene:MeOH (4:1); R_f values are those taken on TLC; UV data were recorded in methanol and figures within brackets refer to log ϵ values; IR spectra were measured on a Perkin–Elmer infracord machine using KBr disc.

Cinnamylation of 5,7-dihydroxy-2-methylisoflavone **8**

Method I (under acidic conditions). To a solution of 5,7-dihydroxy-2-methylisoflavone[14] **8** (5g) in warm aqueous acetic acid (acetic acid : water 75:25, 450 ml) was added cinnamyl alcohol (8·4 g, 3 moles equivalent) in one lot. The resulting mixture was heated on a boiling water-bath for 12 h, diluted with water and extracted with ether. The ethereal extract was washed thoroughly with water until almost free from acetic acid, and dried over Na_2SO_4. The ethereal residue was examined by TLC which showed three major compounds and hence subjected to column chromatography. The column was eluted successively with (i) benzene:light petroleum (1:1), (ii) benzene, and (iii) benzene:ethyl acetate (1:19), when three fractions A to C were obtained. *Fraction A*: crystallised from benzene-light petroleum mixture to yield 5,7-dihydroxy-2-methyl-6,8-dicinnamylisoflavone **9** (200 mg) as cream-coloured plates, mp. 200–201°; R_f 0·87 (Solvent B); green ferric reaction; λ_{max} 255 and 292 (shoulder) nm (4·07 and 4·65 respectively); NMR: 2·32 (1s, 3H, CH_3 at position 2), 3·70 (1d, J 5Hz, 4H, 2Ar–CH_2), 6·30–6·50 (1m, 4H, 2-CH=CH–), and 7·27–7·48 (m, 15H, $3C_6H_5$), 12·94 (1s, 1H, chelated OH) (Found: C, 81·5; H, 5·6. $C_{34}H_{28}O_4$ requires C, 81·6; H, 5·6%). The diacetate prepared by the Ac_2O-py method crystallised from ethyl acetate-light petroleum mixture as white needles, mp 230–31°; R_f 0·69 (Solvent D); λ_{max} 247 and 306 (shoulder) nm (3·89 and 4·64 respectively); ν_{max} 1780 (CO of OAc), and 1650 cm^{-1} (C=O); NMR: 2·22, 2·28, 2·32 (3s, 9H, $2CH_3CO_2$, and $1CH_3$ at 2 position), 3·46 and 3·66 (2d, J 5Hz, 4H, 2-Ar–CH_2), 6·22–6·62 (m, 4H, 2-CH=CH–), 7·26–7·47 (m, 15H, $3C_6H_5$–) (Found: C, 78·1; H, 5·6. $C_{38}H_{32}O_6$ requires C, 78·1; H, 5·5%). *Fraction B*: crystallised from ethyl acetate-like petroleum mixture giving 5,7-dihydroxy-2-methyl-8-cinnamylisoflavone **10** (400 mg) as cream-coloured needles, mp 207–208°; R_f 0·52 (Solvent A); green ferric reaction; λ_{max} 256 and 292 (shoulder) nm (3·76 and 4·35 respectively); NMR: 2·26 (1s, 3H, CH_3 in 2 position), 3·64 (1d, J 5Hz, 2H, Ar–CH_2), 6·38 (1s, 1H, ArH_6), 6·50–6·60 (1m, 2H, 1-CH=CH–), 7·27–7·47 (m, 10H, 2-C_6H_5–) and 13·30 (1s, 1H, chelated OH) (Found: C, 78·4; H, 5·5. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2%). The diacetate prepared by the Ac_2O–NaOAc method crystallised from benzene-light petroleum mixture as white shining needles, mp 164–65°; R_f 0·73 (Solvent D); λ_{max} 243 and 305 (shoulder) nm (3·69 and 4·51 respectively); ν_{max} 1770 (C=O, OAc), 1640 cm^{-1} (C=O); NMR: 2·22, 2·30, 2·37 (3s, 9H, $2CH_3CO_2$ and $1CH_3$ in position 2), 3·52 (1d, J 5Hz, 2H, Ar–CH_2), 7·24 (s, 1H, ArH_6), 6·16–6·34 (m, 1-CH=CH–), 7·26–7·44 (m, 10H, $2C_6H_5$–) (Found: C, 74·3; H, 5·3. $C_{29}H_{24}O_6$ requires C, 74·3; H, 5·2%). *Fraction C*: crystallised from ethyl acetate-light petroleum mixture and gave the unchanged compound (3·8 g).

Method II (Cinnamylation under alkaline conditions). To a solution of 5,7-dihydroxy-2-methylisoflavone **8** (5g) in anhydrous methanol (150 ml), a methanolic soln of sodium methoxide (7g Na in 100 ml methanol) was added. The mixture was cooled, treated with cinnamyl bromide (11 ml, 3 moles equivalent) in one lot and the resulting mixture was refluxed for 10 h. After removal of the solvent under reduced pressure, the residue was treated with ice, acidified and extracted with ether. The ethereal extract was washed thoroughly with water, dried (Na_2SO_4) and distilled. The residue on examination with TLC (Solvent B) was found to be a mixture of three major compounds which were separated by column chromatography, elution being done successively with (i) benzene:light petroleum (1:1), (ii) benzene alone, and (iii) benzene:ethyl acetate (19:1), when three fractions A, B and C were obtained. *Fraction A*: crystallised from benzene-light petroleum mixture affording 5,7-dihydroxy-2-methyl-6,8-dicinnamylisoflavone **9** (250 mg) identical with the one obtained above. *Fraction B*: crystallised from benzene-light petroleum mixture as yellow needles of 5,7-dihydroxy-2-methyl-6-cinnamylisoflavone **16** (300 mg), mp 182–83°; R_f 0·54 (Solvent B); green ferric reaction; λ_{max} 257, and 292 (shoulder) nm (4·19 and 4·56 respectively); NMR: 2·29 (1s, 3H, CH_3 in position 2), 3·66 (1d, J 5Hz, 2H, Ar-CH_2), 6·40 (1s, 1H, aromatic H in position 8), 6·46–6·62 (m, 2H, 1-CH=CH–), 7·30–7·41 (m, 10H, 2-C_6H_5–), 13·26 (1s, 1H, chelated OH) (Found: C, 77·6; H, 5·5. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2%). The diacetate prepared by Ac_2O–NaOAc method crystallised from methanol as a white fluffy solid, mp 180–81°; R_f 0·54 (Solvent E); λ_{max} 243, and 304 (shoulder) nm (4·45 and 4·17 respectively); ν_{max} 1770 (C=O, OAc), 1640 cm^{-1} (C=O); NMR: 2·20, 2·28, 2·36 (3s, 9H, $2CH_3CO_2$, and $1CH_3$ in position 2), 3·48 (1d, J 5Hz, 2H, Ar-CH_2), 6·30 (1s, 1H aromatic H in position 8), 6·08–6·38 (m, 2H, 1-CH=CH–) and 7·10–7·38 (m, 10H, $2C_6H_5$–) (Found: C, 74·00; H, 5·5. $C_{29}H_{24}O_6$ requires C, 74·3; H, 5·2%). *Fraction C*: crystallised from ethyl acetate-light petroleum mixture giving unchanged compound (3·7 g).

5-Hydroxy-7-methoxy-2-methyl-8-cinnamylisoflavone **11**

A soln of 5,7-dihydroxy-2-methyl-8-cinnamylisoflavone **10** (100 mg) in anhydrous acetone (30 ml) was refluxed with Me_2SO_4 (0·026 ml) and K_2CO_3 (0·5 g) for 3 h. After removal of the solvent, the residue was treated with water. The solid was filtered, dried and crystallised from methanol when 5-hydroxy-7-methoxy-2-methyl-8-cinnamylisoflavone **11** was obtained as white flakes (85 mg); mp 145–46°; R_f 0·75 (Solvent C); green ferric reaction; λ_{max} 252, and 292 (shoulder) nm (3·47 and 4·21 respectively); ν_{max} 1670, 1640 (–CO–C=C–); NMR: 2·26 (1s, 3H, $1CH_3$ in position 2), 3·52 (1d, J 5Hz, 2H, Ar-CH_2), 3·90 (1s, 3H, OCH_3), 6·24–6·45 (m, 2H, 1-CH=CH–), 6·39 (1s, 1H, aromatic H in position 6), 7·12–7·46 (m, 10H, 2-C_6H_5–), 13·14 (1s, 1H, chelated OH) (Found: C, 78·5; H, 5·9. $C_{26}H_{22}O_4$ requires C, 78·4; H, 5·5%). When this compound was heated with formic acid on steam bath for 100 h, the compound was recovered unchanged.

4″,5″-Dihydro-5-hydroxy-2-methyl-6″-phenyl pyrano (2″,3″:7,8) isoflavone **12**

5,7-Dihydroxy-2-methyl-8-cinnamylisoflavone **10** (100 mg) was heated with formic acid (50 ml) over a steam-bath for 50 h and then poured into ice-cold water. The solid thus obtained crystallised from benzene-light petroleum mixture when **12** was obtained as light yellow solid (50 mg), mp 144–45°; R_F 0·46 (Solvent A); green ferric reaction; λ_{max} 259 nm (4·55), ν_{max} 1640 cm^{-1} (C=O); NMR: 1·31 (br.d, J 6Hz, 2H, CH_2 at 5″ position), 2·32 (1s, 3H, CH_3 in 2 position), 2·80 (1t, J 5Hz, 2H, CH_2 in 4″ position), 5·88 (1t, J 5Hz, 1H at 6″ position), 6·26 (s, 1H, aromatic H in position 6), 7·18–7·26 (m, 10H, 2-C_6H_5–) (Found: C, 78·2; H, 5·4. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2%).

5-Hydroxy-7-methoxy-2-methyl-6-cinnamylisoflavone **18**

5,7-Dihydroxy-2-methyl-6-cinnamylisoflavone **16** (100 mg) was reacted with Me_2SO_4 (0·026 ml) in the presence of acetone (40 ml) and K_2CO_3 (0·5 g) and the product crystallised from methanol when 5-hydroxy-7-methoxy-2-methyl-6-cinnamylisoflavone **18** was obtained as light yellow needles (80 mg), mp 136–37°; R_f 0·48 (Solvent A); green ferric reaction; λ_{max} 256, and 292 (shoulder) nm (3·90 and 4·40 respectively); ν_{max} 1670, 1640 cm^{-1} (CO–C=C–); NMR: 2·27 (1s, 3H, CH_3 in position 2), 3·57 (1d, J 5Hz, 2H, Ar-CH_2), 3·91 (1s, 3H, OCH_3), 6·39 (1s, 1H aromatic proton in position 8), 6·28–6·71 (m, 2H, 1-CH=CH–), 7·21–7·35 (m, 10H, 2-C_6H_5–) and 12·87 (1s, 1H, chelated OH) (Found: C, 78·5; H, 5·8. $C_{26}H_{22}O_4$ requires C, 78·4; H, 5·6%).

Cinnamylation of 5,7-dihydroxy-2-methylchromone **13**

Method I (under acidic conditions)

5,7-Dihydroxy-2-methylchromone[15] **13** (5 g) was heated with cinnamyl alcohol (10·4 g, 3 mol equivalent) in aqueous acetic acid (acetic acid:water 75:25, 400 ml) on a water bath for 12 h. The product was subjected to column chromatography and the column

eluted successively with (i) benzene:light petroleum (1:1), (ii) benzene:ethylacetate (19:1), and (iii) benzene:ethylacetate (10:1) when three fractions A to C were obtained. *Fraction A*: crystallised from benzene-light petroleum mixture affording 5,7-dihydroxy-2-methyl-6,8-dicinnamylchromone **14** as cream-coloured solid (300 mg), mp 163–64°; green ferric reaction; R_f 0·71 (Solvent B); λ_{max} 252 and 292 (shoulder) nm (3·75 and 4·46 respectively); NMR: 2·45 (1s, 3H, CH_3 in position 2), 3·82 (1d, J 5Hz, 4H, 2Ar-CH_2-), 6·28 (1s, 1H, in position 3), 6·60–6·78 (m, 4H, 2-CH=CH-) and 7·58 (br.s, 10H, 2C_6H_5-) (Found: C, 78·9; H, 5·9. $C_{28}H_{24}O_4$ requires C, 79·2; H, 5·7%). The diacetate formed by Ac_2O-py method crystallised from ethyl acetate-light petroleum mixture as white needles, mp 179–80°; R_f 0·61 (Solvent D); λ_{max} 248, and 292 (shoulder) nm (3·70 and 4·51 respectively); ν_{max} 1760 (CO of AcO), 1650 cm^{-1} (C=O); NMR: 2·30, 2·32 (2s, 6H, 2CH_3CO_2), 2·41 (1s, 3H, CH_3 in position 2), 3·66, 3·48 (2d, J 5Hz, 4H, 2-Ar-CH_2-), 6·06 (1s, 1H in position 3), 6·1–6·45 (m, 4H, 2-CH=CH-) and 7·28 (1s, 10H, 2-C_6H_5-) (Found: C, 74·3; H, 5·3. $C_{32}H_{28}O_6$ requires C, 74·3; H, 5·2%). *Fraction B*: crystallised from ethyl acetate-light petroleum yielding 5,7-dihydroxy-2-methyl-8-cinnamylchromone **15** as light yellow needles (500 mg), mp 186–88°; R_f 0·54 (Solvent B); green ferric reaction; λ_{max} 255, and 292 (shoulder) nm (3·81 and 4·38 respectively); NMR: 2·34 (1s, 3H, CH_3 in position 2), 3·70 (1d, J 5Hz, 2H, Ar-CH_2-), 6·08 (1s, 1H, in position 3), 6·26–6·56 (m, 3H, 1-CH=CH- and an aromatic H in position 6), 7·28 (1s, 5H, 1C_6H_5-) and 12·72 (1s, 1H, chelated OH) (Found: C, 74·2; H, 5·5. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). The diacetate (Ac_2O-py) crystallised from benzene-light petroleum mixture as white needles, mp 149–50°; R_f 0·56 (Solvent D); λ_{max} 245, and 292 (shoulder) nm (4·30 and 4·52 respectively); ν_{max} 1775 (C=O, OAc), 1660 cm^{-1} (C=O); NMR: 2·32, 2·34 (2s, 6H, 2AcO), 2·42 (1s, 3H, CH_3 in position 2), 3·70 (1d, J 5Hz, 2H, Ar-CH_2-), 6·08 (1s, 1H in position 3), 6·21–6·42 (m, 2H, -CH=CH-), 6·88 (1s, 1H aromatic H in position 6) and 7·28 (1s, 5H, 1-C_6H_5-) (Found: C, 70·8; H, 5·4. $C_{23}H_{20}O_6$ requires C, 70·4; H, 5·1%). *Fraction C*: crystallised from acetone-light petroleum mixture giving the unchanged chromone (3·6 g).

Method II (under alkaline conditions). A soln of 5,7-dihydroxy-2-methylchromone **13** (4 g) in methanol (150 ml) and methanolic sodium methoxide (6 g Na in 100 ml methanol) was refluxed with cinnamyl bromide (12·8 ml, 3 moles) for 10 h. The product was subjected to column chromatography and the column eluted as above to give three fractions A, B and C. *Fraction A*: crystallised from benzene-light petroleum yielding 5,7-dihydroxy-2-methyl-6,8-dicinnamylchromone **14** (175 mg) identical in mp and mmp with the one obtained above. *Fraction B*: crystallised from benzene to give 5,7-dihydroxy-2-methyl 6-cinnamylchromone **19** as yellow needles (400 mg), mp 239–40°; R_f 0·51 (Solvent B); green ferric reaction; λ_{max} 253, and 292 (shoulder) nm (3·52 and 3·46 respectively); NMR (DMSO-d_6); 2·34 (1s, 3H, CH_3 in position 2), 3·46 (1d, J 5Hz, 2H, Ar-CH_2-), 6·16 (1s, 1H in position 3), 6·30–6·42 (m, 2H, -CH=CH-), 6·45 (1s, 1H aromatic H in position 8) and 7·30 (s, 5H, 1-C_6H_5-) (Found: C, 73·6; H, 5·2. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). *Fraction C* crystallised to give the unchanged chromone (2·8 g).

5-Hydroxy-7-methoxy-2-methyl-8-cinnamylchromone

A soln of 5,7-dihydroxy-2-methyl-8-cinnamylchromone **15** (100 mg) in acetone (25 ml) was refluxed with Me_2SO_4 (0·032 ml) in the presence of K_2CO_3 (0·5 g) for 3 h. The product crystallised from aqueous methanol when 5-hydroxy-7-methoxy-2-methyl-8-cinnamylchromone was obtained as a white solid (90 mg), mp 108–9°; R_f 0·57 (Solvent C); green ferric reaction; λ_{max} 251 and 292 (shoulder) nm (3·14 and 4·14 respectively); ν_{max} 1660 cm^{-1} (C=O); NMR: 2·38 (1s, 3H, CH_3 in position 2), 3·60 (1d, J 5Hz, 2H, Ar-CH_2-), 3·90 (1s, 3H, OCH_3), 6·00 (1s, 1H in position 3), 6·20 (1s, 1H, aromatic proton in position 6), 6·24–6·45 (m, 2H, -CH=CH-), 7·25 (1s, 5H, 1C_6H_5-) and 12·87 (1s, 1H, chelated OH) (Found: C, 74·5; H, 6·0. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%).

5-Hydroxy-7-methoxy-2-methyl-6-cinnamylchromone **19**

A soln of 5,7-dihydroxy-6-cinnamylchromone **17** (100 mg) in acetone (25 ml) was refluxed with Me_2SO_4 (0·032 ml) in the presence of K_2CO_3 and the product crystallised from methanol when **19** was obtained as light yellow needles (90 mg), mp 115–16°; R_f 0·64 (Solvent B); λ_{max} 255, and 292 (shoulder) nm (3·88 and 4·31 respectively); ν_{max} 1650 cm^{-1} (CO); NMR: 2·34 (1s, 3H, CH_3 in position 2), 3·52 (1d, J 5Hz, 2H, Ar-CH_2), 3·88 (1s, 3H, OCH_3), 6·00 (1s, 1H in position 3), 6·28–6·48 (m, 3H, 1-CH=CH- and one aromatic proton in position 8), 7·24 (1s, 5H, 1C_6H_5-) and 13·00 (1s, 1H, chelated OH) (Found: C, 74·9; H, 6·0. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%).

5-Hydroxy-2-methyl-6″-phenyl pyrano(2″,3″:7,8)isoflavone **20**

To a soln of 5,7-dihydroxy-2-methyl-8-cinnamylisoflavone **10** (100 mg) in dry benzene (50 ml) was added DDQ (60 mg) and the resulting soln refluxed for 12 h over a steam-bath when a lot of dark solid separated out. The soln was filtered hot and the filtrate evaporated to dryness. THe residue was purified by column chromatography. Elution with light petroleum-chloroform (1:1) gave the flavene **20** which crystallised from benzene-light petroleum as yellow needles (40 mg), mp 291–92°; R_f 0·66 (Solvent B); green ferric reaction; λ_{max} 267, and 304 (shoulder) nm (4·61 and 4·46 respectively); NMR: 2·29 (1s, 3H, CH_3 in position 2), 5·65–6·10 (m, 2H, 2 protons at 6″ and 5″ positions), 6·32 (1s, 1H, aromatic H at position 6), 6·98 (1d, J 10Hz, 1H, at 4″ position), 7·26–7·40 (m, 10H, 2C_6H_5-) and 13·19 (1s, 1H, chelated OH) (Found: C, 78·5; H, 5·2. $C_{25}H_{18}O_4$ requires C, 78·5; H, 4·7%).

5-Hydroxy-2-methyl-6″-phenyl pyrano(2″,3″:6,7)isoflavone **22**

5,7-Dihydroxy-2-methyl-6-cinnamylisoflavone **16** (100 mg) was reacted with DDQ (60 mg) for 10 h as above. The product was purified by column chromatography. Elution with chloroform:light petroleum (1:1) gave the flavene which crystallised from benzene-light petroleum mixture as light yellow flakes (30 mg), mp 123–24°; R_f 0·64 (Solvent B); green ferric reaction; λ_{max} 281 nm (4·47); NMR: 2·24 (1s, 3H, CH_3 in position 2), 5·65–6·00 (m, 2H protons at 6″ and 5″ positions), 6·28 (1s, 1H, aromatic H at position 8), 6·95 (1d, J 10Hz, 1H at 4″ position), 7·21–7·36 (m, 10H, 2C_6H_5-) and 13·12 (1s, 1H, chelated OH) (Found: C, 78·5; H, 5·2. $C_{25}H_{18}O_4$ requires C, 78·5; H, 4·7%).

5-Hydroxy-2-methyl-6″ phenyl-pyrano(2″,3″:7,8)chromone **21**

5,7-Dihydroxy-2-methyl-8-cinnamylchromone **15** (200 mg) was refluxed in benzene with DDQ (175 mg) for 10 h. The product was purified by column chromatography. Elution with chloroform-light petroleum (1:9) gave a fraction which crystallised from methanol yielding **21** as pale yellow needles (60 mg), mp 122–23°; R_f 0·32 (Solvent B); green ferric reaction; NMR: 2·32 (1s, 3H, CH_3 in position 2), 5·64–5·92 (m, 2H, protons at 6″ and 5″ positions), 6·02 (1s, 1H in position 3), 6·26 (1s, 1H aromatic H in position 6), 6·94 (2d, J 10Hz and 2Hz, 1H at 4″ position), 7·36 (1s, 5H, 1C_6H_5-) and 12·95 (1s, 1H, chelated OH) (Found: C, 74·9; H, 5·1. $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·6%).

5-Hydroxy-2-methyl-6″-phenyl-pyrano2″,3″:6,7)chromone **23**

5,7-Dihydroxy-2-methyl-6-cinnamylchromone **17** (200 mg) was reacted with DDQ (175 mg) as described earlier. The product was purified by column chromatography. Elution with benzene-light petroleum (1:3) gave a compound which crystallised from benzene-light petroleum mixture yielding flavene **23** as yellow shining needles (50 mg), mp 139–40°; R_f 0·54 (Solvent B); green ferric reaction; λ_{max} 279 nm (4·49); NMR: 2·32 (1s, 3H, 1CH_3 in

position 2), 5·88 (1s, 1H at position 3), 5·66–6·00 (m, 2H, protons at 6″ and 5″ positions), 6·26 (1s, 1H, aromatic H in position 8), 9·96 (2d, J 10Hz and 2Hz, 1H, at 4″ position), 7·40 (1s, 5H, 1-$C_6\underline{H}_5$–) and 12·95 (1s, 1H, chelated O$\underline{H}$) (Found: C, 74·9; H, 5·1. $C_{19}H_{14}O_4$ requires C, 74·5; H, 4·6%).

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