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CHALCONES OF *FLEMINGIA CHAPPAR* HAM
THE STRUCTURE AND SYNTHESIS OF FLEMICHAPPARIN

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Abstract—From the whole plant of *Flemingia chappar* Ham, two crystalline chalcones have been isolated. The major one has been characterised as 2′,4′-dihydroxychalcone (II) and the structure of the minor one, a new naturally occurring chalcone named flemichapparin, has been established as 2′,4′-dihydroxy-5′-methoxychalcone (VI) from spectral, chemical and synthetic evidence.

FLEMINGIA CHAPPAR Ham is a leguminous plant growing in the hilly parts of West Bengal and Bihar. The roots of this plant have been reported to possess medicinal properties.[1] A limited amount of chemical research has been carried out on this genus in the past. Only two species of this genus, *Flemingia macrophylla*,[2] and *Flemingia rhodocarpa*[3] were previously reported to contain colouring matters. Recently, the isolation and structure elucidation of a new group of chalcones from the seed pods of *F. rhodocarpa*[4] has been published by Cardillo *et al.* Since no chemical investigation on *Flemingia chappar* has been made, we have undertaken a systematic chemical examination of the flavonoid constituents occurring in *F. chappar*.

From the whole plant of *F. chappar* we have isolated two crystalline flavonoids and β-sitosterol. Part of this work dealing with the characterisation of the major coloured constituent as 2′,4′-dihydroxychalcone (II) has been published as a preliminary communication.[5] The minor colouring matter has now been found to be a new naturally occurring chalcone which we have designated as flemichapparin.† The details of our previous work and the isolation, structure-elucidation and synthesis of flemichapparin (VI) are elaborated in this communication.

Extraction of the dried and powdered whole plant of *F. chappar* with both light petroleum and chloroform followed by chromatography afforded two crystalline coloured constituents, compound-A (m.p. 149–150°, yield 0·1%) and compound-B (m.p. 158–160°, yield 0·03%). Difficulties were encountered in the separation of the major coloured constituent from the minor one as the two compounds appeared to be more or less of similar polar character.

Compound-A, $C_{15}H_{12}O_3$ (M^+ 240), m.p. 149–150°, produced a deep brown colour with ferric chloride indicating its phenolic nature. The UV absorption maxima at 260,

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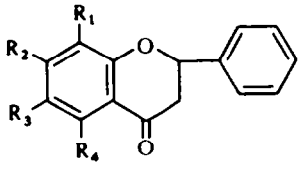
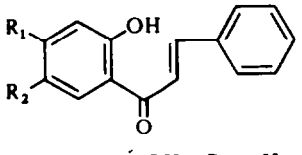
320 and 340 mμ suggested the presence of a chalcone system.[6] The IR bands at 1640 cm^{-1} and 3270 cm^{-1} were attributed to chelated carbonyl and phenolic hydroxyl groups respectively. The compound was a chalcone as it readily isomerized to the corresponding flavanone on treatment with sodium hydroxide followed by acidification. The transformation product exhibited a deep red colour in the Shinoda reaction[7] characteristic of flavanones. This compound was free from methoxyl (Zeisel) and produced a negative ferric reaction but was readily soluble in aqueous sodium carbonate,[8] thereby indicating the presence of a phenolic-OH group *para* to a carbonyl function. The IR spectrum disclosed the occurrence of a strong conjugated carbonyl band (1660 cm^{-1}), a weak phenolic peak (3200 cm^{-1}) and a complex aromatic substitution pattern. The UV spectrum, λ_{max}^{EtOH} 230 (log ε 3·70), 277 (log ε 4·76) and 312 mμ (log ε 3·56), appeared to be similar to that of 7,4′-dihydroxy liquiritigenin and the displacement of the 231 mμ band by 10 mμ on addition of sodium acetate suggested that the —OH group might be situated at 7-position of the flavanone skeleton.[9]



I: $R_1 = R_3 = R_4 = H$, $R_2 = OH$
IIIa: $R_1 = R_4 = H$, $R_2 = OH$, $R_3 = OCH_3$
IIIb: $R_1 = R_4 = H$, $R_2 = OCH_3$, $R_3 = OH$
IIIc: $R_1 = R_4 = H$, $R_2 = R_3 = OCH_3$
IVa: $R_1 = R_3 = H$, $R_2 = OH$, $R_4 = OCH_3$
IVb: $R_1 = R_3 = H$, $R_2 = OCH_3$, $R_4 = OH$
Va: $R_3 = R_4 = H$, $R_2 = OH$, $R_1 = OCH_3$
Vb: $R_3 = R_4 = H$, $R_2 = OCH_3$, $R_1 = OH$



II: $R_1 = OH$, $R_2 = H$
VI: $R_1 = OH$, $R_2 = OCH_3$

Final confirmation as to the location of the —OH group in the 7-position was secured by synthesis of 7-hydroxyflavanone (I) by the cyclization of resorcinol with cinnamic acid in presence of polyphosphoric acid following the method of Hassebe[10] and this compound was found to be identical in all respects (m.p., m.m.p., superimposable IR) with the flavanone (I) obtained by the isomerization of the natural chalcone, compound-A. These data settled the structure of the natural chalcone, compound-A, as II.

A synthetic sample of II, prepared by the condensation of resacetophenone with benzaldehyde in presence of strong alkali, was found to be identical with the natural chalcone (II) in all respects. There seems to be no report on the isolation of such a simple biogenetically important chalcone (II) from a plant source so far.

Compound-B, designated as flemichapparin, m.p. 158–160°, analysed for $C_{16}H_{14}O_4$ (M^+ 270). The colour reactions (negative Shinoda and a greenish brown ferric colour) and UV absorption maxima at 225 (log ε 4·07), 313 mμ (log ε 4·32) and minima at 252 (log ε 3·65), 355 mμ (log ε 3·99) with no appreciable change in alkali indicated the compound to be a chalcone. It contained a phenolic —OH (ν_{max}^{Nujol} 3200 cm^{-1}), chelated conjugated >C=O (ν_{max}^{KBr} 1640 cm^{-1}) and —OCH_3 (3H singlet at 3·95 δ) groups.

The NMR spectrum of flemichapparin showed two *trans*-olefinic protons at 7·9 δ (d, $J = 16$ c/s) and 7·35 δ (d, $J = 16$ c/s) providing evidence for the chalcone system.[4, 11] Two sharp singlets at 6·66 and 7·28 δ and five aromatic protons around 7·3–7·88 δ were also discernible in the spectrum.

The mass spectrum of flemichapparin exhibited, in addition to the molecular ion peak at *m/e* 270, a number of prominent peaks. The unsubstituted nature of the B ring of flemichapparin was indicated[12] by the presence of peaks at *m/e* 193 (M-77) and *m/e* 166 (M-104) corresponding to loss of a phenyl group and a neutral styrene molecule ($C_6H_5CH=CH_2$) respectively from the molecular ion. A medium intensity peak at *m/e* 151 (*m/e* 166-15) arising by loss of —CH_3 from a —OCH_3 suggested that the A ring of flemichapparin contained a —OCH_3 substituent.

From these spectral data it was inferred that flemichapparin might be the homologue of 2′,4′-dihydroxychalcone (II) having a —OMe substituent in the A ring. The correctness of a chalcone system as well as the nature of substitution pattern in ring A of flemichapparin were secured from chemical and spectral data of its transformation products discussed in the sequel.

Flemichapparin on treatment with aqueous sodium hydroxide and subsequent acidification gave a flavanone, $C_{16}H_{14}O_4$. The latter gave a deep red colour in the Shinoda reaction[7] characteristic of flavanones but the ferric reaction was negative. It was readily soluble in aqueous sodium carbonate. The IR spectrum (Nujol) showed a CO band (1642 cm^{-1}) and no —OH absorption. However, the similarity in properties of this flavanone with 7-hydroxyflavanone (negative ferric reaction, solubility in sodium carbonate, similarity in IR spectra), suggested the presence of a —OH group in the 7-position of this flavanone. The UV spectrum [λ_{max}^{EtOH} 240 (log ε 3·40), 280 (log ε 3·35) and 346 mμ (log ε 3·38); $\lambda_{max}^{EtOH/NaOH}$ 260, 280 and 350 mμ], on the other hand, resembled closely those of 6,7,3′,4′-tetrahydroxyflavanone derivatives.[9] The latter data indicated that a —OMe group might be present at 6 position of this flavanone. Supporting evidence for the presence of 2,4,5-substitution pattern in ring A of flemichapparin were secured from NMR and spectral data of the derived flavanone.

The NMR spectrum of the flavanone, $C_{16}H_{14}O_4$, signals at 7·49 δ (singlet, 5H aromatic), 7·40 and 6·62 δ (two ss, aromatic), 6·42 δ (s, disappeared on D_2O exchange, phenolic —OH), and 3·95 δ (s —OCH_3). The protons of the γ-pyrone ring constitute an ABX system[13, 14] whose AB part (H_A-3, H_B-3) appears around 2·9 δ as a triplet. The X part (H-2) appears as a double doublet at 5·46 δ*. The data suggested the substitution pattern III rather than IV and V for the flavanone on the basis of the following facts. In phloroglucinol type IV of flavanones the C-6 and C-8 protons appears as a general rule[11] at 5·8 and 6·1 δ respectively. The absence of a low field aromatic proton above 7·68 δ without *ortho* coupling ruled out the possibility of a substitution pattern of type V. In structure III the two aromatic singlets at 6·62 and 7·40 δ could reasonably be assigned to C-8 and C-5 protons respectively.

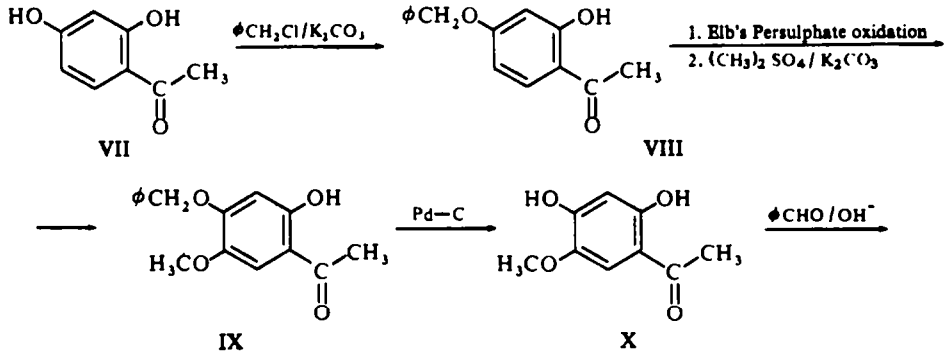
Moreover, methylation of this flavanone with diazomethane afforded the corresponding dimethyl ether, m.p. 170–171°, the physical properties[15] (m.p., IR and green colour in the Shinoda reaction) of which agreed with those reported for 6,7-dimethoxy flavanone (IIIc) thereby confirming that a 2,4,5-substitution pattern was present in flemichapparin.

On the basis of the data presented above, two alternative structures (IIIa and IIIb) could be assigned to the flavanone derived from flemichapparin. Of these, IIIa was considered to be the logical formulation for the flavanone since a direct comparison (m.p., m.m.p., IR) of the latter with authentic 7-methoxy-6-hydroxyflavanone[16] (IIIb)

* We thank the referee for his suggestion regarding the NMR spectrum of this region.

was proved to be different. The structure of flemichapparin should therefore be represented by VI.

CHART I



Finally, the structure of flemichapparin was confirmed by its unambiguous synthesis (Chart I). Resacetophenone in acetone was benzylated with benzyl chloride in presence of anhydrous potassium carbonate. The resulting benzyl derivative (VIII) on Elbs' persulphate oxidation and subsequent methylation with dimethyl sulphate and potassium carbonate afforded IX. The latter was debenzylated with Pd-C in ethyl acetate and the product[17] (X) on condensation with benzaldehyde in presence of strong alkali furnished the desired chalcone (VI), which was found to be identical with flemichapparin (VI) in all respects (m.p., m.m.p., and superimposable IR, Fig 1).

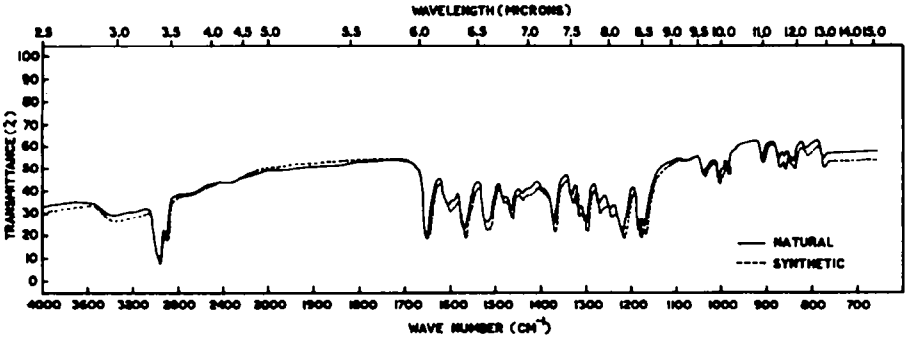


FIG 1.

The co-occurrence of the chalcones (II and VI) in the same plant is of biogenetic significance. It has been pointed out by Shinoda and Sato[18] that chalcones containing the 2,4,6-trihydroxybenzoyl nucleus isomerize readily to the corresponding flavanones while those containing the 2,4-dihydroxybenzoyl grouping are relatively more stable in the chalcone form. The smooth isolation of the chalcones (II and VI) from the whole plant of *Flemingia chappar* provides circumstantial evidence for the correctness of the above view. The biogenetic precursor of flemichapparin (VI) is undoubtedly the chalcone II, the former being derived from the latter by unexceptional steps.

EXPERIMENTAL

All m.ps are uncorrected. Light petroleum refers to b.p. 60–80°. The UV spectra were measured with a Carl Zeiss Universal Spectrophotometer (Model VSU-1) using 95% aldehyde free EtOH and IR spectra with Perkin–Elmer Spectrophotometer as mulls in Nujol or KBr disc. NMR spectra were determined with a Varian A-60 instrument in $CDCl_3$ with TMS as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). TLC experiments were carried out using silica gel-G as adsorbent and benzene-ethylacetate (3 : 1), unless otherwise stated, as the developer. The spots were detected with iodine vapour. The analytical samples were routinely dried at 80° over P_2O_5 for 24 hrs *in vacuo*.

Isolation of compound-A and compound-B

Air dried finely pulverized whole plant of *F. chappar* (1 kg) was successively extracted (24 hr) with light petroleum and $CHCl_3$ in a Soxhlet apparatus. Concentration of the petrol extract afforded a yellow solid, compound-A (0·8 g) which was filtered off. The filtrate was further concentrated (18 g) and directly chromatographed over silica gel (300 g). The chromatogram was washed with solvents of increasing polarity using light petroleum, benzene, chloroform and MeOH in different proportions. The early benzene eluates on evaporation gave an unidentified red solid (0·06 g). Compound-A (0·2 g) migrated out with benzene-$CHCl_3$ (4 : 1) followed by β-sitosterol (0·1 g). The benzene-$CHCl_3$ (1 : 3) eluates on evaporation afforded an orange solid (0·2 g), Compound-B.

Besides light petroleum extract, Compound-B could also be isolated by direct chromatography of the $CHCl_3$ extract (crude 20 g) over silica gel (400 g) in the same way as followed for the light petroleum extract. The eluates (benzene-$CHCl_3$, 1 : 3) on evaporation gave another crop of orange solid (0·1 g), Compound-B.

Compound-A (II). Crystallized from benzene as fine yellow needles, m.p. 149–150°. (Found: C, 75·21; H, 4·87. $C_{15}H_{12}O_3$ requires: C, 75·00: H, 5·00%); UV λ_{max}^{EtOH} 260, 320, 340 mμ: R_f 0·46; M⁺ 240.

Isomerization of compound-A (II) *to the corresponding flavanone* (I)

Compound-A (II; 1·00 g) was dissolved in alcohol (10 ml) and refluxed (140°) with 1·5% NaOH aq (15 ml) for 30 min and allowed to stand for 12hr. On acidification with 50% AcOH (aq) I (0·60 g) separated out and was crystallized from benzene as needles, m.p. 189–190°. (Found: C, 74·81; H, 4·82. Calc. for $C_{15}H_{12}O_3$: C, 75·00; H, 5·00%); R_f 0·40; UV λ_{max}^{EtOH} 231 (log ε 3·70), 277 (log ε 4·76), 312 mμ (log ε 3·56).

Synthesis of 7-hydroxyflavanone (I)

An intimate mixture of P_2O_5 (7·50 g) and ortho-phosphoric acid (89%, 12 ml) was heated (100°) for 3 hr. To this resorcinol (0·50 g) and cinnamic acid (0·70 g) were added and again heated (100°) for 25 min, kept for 2 hr, poured into water (100 ml) and extracted with ether (2 × 50 ml). The ether extract was chromatographed over silica gel (5 g) and the solid (0·20 g) afforded in the benzene-$CHCl_3$ (1 : 1) eluates was crystallized from benzene-light petroleum (3 : 1), m.p. 185–186°. It did not depress the melting point of the flavanone obtained by the isomerisation of compound—A (II).

Synthesis of 2′,4′-dihydroxy chalcone (II)

An intimate mixture of resacetophenone (0·25 g in EtOH 5 ml) and benzaldehyde (0·125 g) was treated with alkali (3·75 g NaOH in 5 ml of water) dropwise with shaking in the cold (0–5°) and kept for 8 days at room temp with occasional shaking, acidified with HCl 6N, an oil separated which solidified in the refrigerator after 3-days, extracted with ether (2 × 50 ml), ether evaporated and purified by preparative TLC using the solvent system, toluene-ethyl formate-formic acid (5 : 4 : 1). Crystallized from benzene as yellow needles (II), m.p. 147–149°; R_f 0·46. It did not depress the m.p. of the naturally occurring chalcone, compound—A (II), on admixture.

Compound-B, flemichapparin (VI)

It crystallized from benzene as orange prisms, m.p. 158–160°. (Found: C, 71·18; H, 5·11. $C_{16}H_{14}O_4$ requires: C, 71·11; H, 5·19%) R_f 0·32 UV λ_{max}^{MeOH} 225 (log ε 4·07), 313 (log ε 4·32) mμ; λ_{min}^{MeOH} 252 (log ε 3·65), 355 mμ (log ε 3·99), no appreciable change in the maxima with N/10 NaOH; NMR -OCH_3 (s, 3·95 δ), 2ArH (s, 6·66, 7·28 δ), 5 ArH (m, 7·3–7·8 δ), α and β H of chalcone (d, 7·35 δ, J = 16 c/s) and (d, 7·9 δ J = 16 c/s).

Isomerization of flemichapparin (VI) *to the corresponding flavanone* (IIIa)

Flemichapparin (0·5 g) was refluxed for 30 min with a mixture of alcohol (2 ml) and 1·5% NaOH aq (1·5

ml) at 140°. The reaction product was diluted (25 ml) and acidified with 50% AcOH (aq). The solid separated was crystallized from light petrol ether benzene (1:1), m.p. 180–181°. (Found: C, 71·30; H, 5·32. $C_{16}H_{14}O_4$ requires: C, 71·11; H, 5·19%). R_f 0·34. UV λ_{max}^{EtOH} 240 (log ε 3·40), 280 (log ε 3·55) and 346 mμ (log ε 3·38). $\lambda_{max}^{EtOH/N/10\ NaOH}$ 260, 280 and 350 mμ; NMR 2H, C—3H (t, 2·9 δ, J = 5 c/s), OCH_3 (s, 3·95 δ), 1H C—2H (doubled 5·46 δ, J = 5 c/s), phenolic OH (s, 6·42 δ disappeared on D_2O exchange), 2 ArH (s, 7·40, 6·62 δ), 5 ArH (s, 7·49 δ).

6,7-*Dimethoxyflavanone* (IIIc)

Compound flavanone IIIa (0·06 g) was methylated with diazomethane in ether and the product (0·04 g) was crystallized from light petroleum-benzene (1:1) m.p. 170–171°. R_f 0·58, UV λ_{max}^{EtOH} 237 (log ε 4·26), 274 (log ε 4·1), and 337 mμ (log ε 3·8); IR 1670 cm^{-1} (conjugated >C=O), 1610, 1582, 1500 (aromatic), no (-OH); green colour with $FeCl_3$.

Synthesis of flemichapparin

4-*Benzyloxy*-2-*hydroxy-acetophenone* (VIII). Resacetophenone (VI, 10 g) in anhyd acetone (50 ml) was refluxed with benzyl chloride (15 ml) and anhyd K_2CO_3 on a water bath for 3 hr. The mixture was cooled and after usual work up was chromatographed over silica gel (150 g). On elution with light petroleum-benzene (1:1), a colourless product (8 g) migrated out which was crystallized from light petroleum-benzene (3:2) as plates, m.p. 103–104°. (Found: C, 74·52; H, 5·93. Calc. for $C_{15}H_{14}O_3$: C, 74·38; H, 5·78%).

4-*Benzyloxy*-2,5-*dihydroxy acetophenone*

A stirred soln of VIII (5 g) in pyridine (100 ml) and NaOH aq (6 gm in 100 ml) was treated with aqueous potassium persulphate (10·5 g in 250 ml) for 3 hr, set aside for 24 hr, acidified with HCl 6N and the unchanged substituted acetophenone (2·9 g) was filtered off. The filtrate after extraction with ether was treated with $NaSO_3$ (10 g) and conc HCl (125 ml) and kept on a boiling water bath for 30 min when golden yellow needles began to separate. The mixture was cooled, filtered and the residue was washed with water and dried (1·2 gm). The filtrate, on ether extraction, provided more compound (0·15 g). Crystallization from aqueous EtOH gave pale yellow needles of the titled compund, m.p. 159–160°, giving a deep green ferric colour. (Found: C, 69·51; H, 5·59. Calc. for $C_{15}H_{14}O_4$: C, 69·76; H, 5·42%).

4-*Benzyloxy*-2-*hydroxy*-5-*methoxy-acetophenone* (IX)

4-Benzyloxy-2,5-dihydroxy acetophenone (0·5 g) was refluxed with Me_2SO_4 (1 mole), anhyd acetone (20 ml) and anhyd K_2CO_3 (1 g) for 8 hr. The mixture was cooled, filtered and the crude extract was chromatographed over silica gel. Elution with light petroleum-benzene (3:1) yielded a product which crystallized from EtOH as pale yellow needles (0·45 g), m.p. 128–129°, giving a green ferric reaction. (Found: C, 70·72; H, 5·75. Calc. for $C_{16}H_{16}O_4$: C, 70·58; H, 5·91%).

2,4-*Dihydroxy*-5-*methoxy-acetophenone* (X)

10% Pd-C (0·45 g) and dry EtOAc (50 ml) were saturated with H_2; IX (0·45 g) in EtOAc (50 ml) was added and the absorption stopped when 43 mol of H_2 had been absorbed at room temp. The soln was filtered and evaporated. Crystallization of the product from hot water gave colourless plates (0·3 g), m.p. 170–171°, showing a green ferric reaction. (Found: C, 60·05; H, 5·43. Calc. for $C_9H_{10}O_4$: C, 59·89; H, 5·55%).

2′,4′-*Dihydroxy*-5′-*methoxychalcone* (VI)

An intimate mixture of X (0·25 g) in EtOH (5 ml) and benzaldehyde (0·15 g) was treated with alkali (3·75 gm in 5 ml water) dropwise with constant shaking in the cold (2–5°) and kept for 8 days at room temp with occasional shaking, acidified with 6N HCl, a light orange solid separated, extracted with ether (2 × 25 ml) and concentrated. TLC showed it to be a mixture of two ketones. The two major ketonic compounds were separated on preparative silica gel chromato-plates (size, 20 × 20 cm and thickness of silica gel layer *ca* 1 mm) in the system toluene-ethylformate-formic acid (5:4:1). The bands at R_f 0·57 and 0·47 were scrapped off and the respective silica zones were eluted separately with $CHCl_3$. The bands having R_f 0·57 yielded VI while the bands having R_f 0·47 afforded the unreacted ketone. The chalcone crystallized from benzene as orange needles (0·06 g) m.p. 158–159°. The synthetic chalcone was found to be identical with the naturally occurring VI in all respects (m.p., m.m.p., TLC, and superimposable IR in Nujol).

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