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A NEW PTEROCARPAN AND COUMESTAN IN THE ROOTS OF *FLEMINGIA CHAPPAR**

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Abstract—Flemichapparin-B, a new naturally occurring pterocarpan, and flemichapparin-C, a new coumestan, isolated from the roots of *Flemingia chappar* (Leguminosae; Lotoideae) have been shown to be 6a,11a-dehydropterocarpan (IV) and 7-*O*-methylmedicagol (V) respectively.

INTRODUCTION

THE ISOLATION and structure elucidation of three new naturally occurring chalcones, flemichapparin, flemichapparin-A and 2′,4′-dihydroxychalcone from the whole plant of *Flemingia chappar* (Leguminosae; Lotoideae) was earlier reported.[1–4] The leaves or flowers of this plant have also been found to contain the same chalcones.[5] Since legume plants especially those belonging to the subfamily Lotoideae,[6] are known to elaborate isoflavones,, pterocarpans, coumestans and rotenoids, we became interested, from biogenetic consideration, to search for related isoflavonoids in the roots of *F. chappar*. The present communication discusses the isolation, structure elucidation and biogenetic significance of the occurrence of a new pterocarpan, flemichapparin-B and a new coumestan, flemichapparin-C in the roots of *F. chappar*.

RESULTS AND DISCUSSION

The chloroform extract of the dried roots of *F. chappar* on chromatography over either neutral alumina or silica gel furnished flemichapparin-B, m.p. 179–180°, $C_{17}H_{12}O_5$ (M^+ 296), $[\alpha]_D \pm 0°$, in poor yield (0·006%). Functional group analysis revealed the presence of –OMe (3H *s*, at 3·85 δ) and a methylenedioxy group (2H, *s*, at 6·08 δ; positive Labat test). The IR spectrum (KBr) indicated olefinic unsaturation (1650 cm^{-1}), aromatic system (1610, 1570, 1515, 1470 cm^{-1}), phenylether linkage (1232 cm^{-1}) and furan ring (1070 cm^{-1}). The intense absorption in the UV spectrum (λ_{max}^{EtOH} 232_{inf}, 250, 292, 339 and 358 nm) indicated a substituted stilbene type of structure.[7,8] The MS showed, besides the molecular ion peak at *m/e* 296 (base peak), another intense peak at *m/e* 281 ($M^+ - 15$; loss of –Me from –OMe), suggesting a highly stable aromatic skeleton. These data fit in well with a dehydroperocarpan structure for flemichapparin-B, which was eventually confirmed by correlating it with a known pterocarpan.

* Preliminary reports of this work appeared in *Chem. & Ind.* 745, 1113 (1970).

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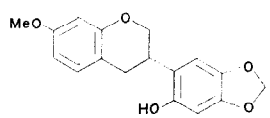
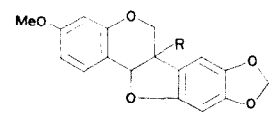
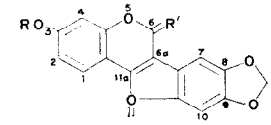
Hydrogenation of flemichapparin-B with Adam's catalyst in acetic acid afforded tetrahydroflemichapparin-B, $C_{17}H_{16}O_5$(M^+ 300), m.p. 139–140°. Pterocarpans under such conditions undergo hydrogenolysis to give dihydropterocarpans, which are isoflavan derivatives.[9,10] The uptake of 2 mol of hydrogen was due to reduction of an olefinic unsaturation followed by hydrogenolysis to yield tetrahydroflemichapparin-B. The properties of the latter are consistent with those reported for (—)-dihydropterocarpin[9] (I). The isoflavan structure of tetrahydroflemichapparin-B(I) is also in conformity with its MS data[11] [*m/e* 300(M^+); R.D.A. fragments at *m/e* 164 and 137].



(I)



(II) R = H
(III) R = OH



(IV) R = Me; R′ = H_2
(V) R = Me; R′ = O
(VI) R = H; R′ = O

Catalytic reduction of flemichapparin-B with 10% Pd–C in methanol, on the other hand, furnished dihydroflemichapparin-B, $C_{17}H_{14}O_5$, the physical constants [m.p. 185°; λ_{max}^{EtOH} 281 (log ε 3·62), 287 (log ε 3·67) and 313 nm (log ε 3·93); ν_{max}^{KBr} 1610, 1582, 1510, 1493, 1030, 938 cm^{-1}] of which compared excellently with those reported for (±)-pterocarpin[12] (II) [m.p. 185–186°; λ_{max}^{EtOH} 281 (log ε 3·60), 287 (log ε 3·66) and 311 nm (log ε 3·89); ν_{max}^{Nujol} 1614, 1585, 1503, 1493, 1027, 930 cm^{-1}].

On the basis of the structures of tetrahydroflemichapparin-B (I) and dihydroflemichapparin-B (II), flemichapparin-B is formulated as 6a,11a-dehydropterocarpan (IV). NMR spectral data also support this assignment.[7,8]

The structure of flemichapparin-B is identical with anhydropisatin (IV), a transformation product of pisatin (III), another naturally occurring pterocarpan.[13,14] This is for the first time that the dehydropterocarpan (IV) has been obtained from a natural source.

The $CHCl_3$ extract of the roots of this plant on chromatography over silica gel afforded yet another compound, flemichapparin-C, m.p. 272°, $C_{17}H_{12}O_6$ (M^+ 310), $[\alpha]_D \pm 0°$ ($CHCl_3$), in poor yield (0·0005%). The pure compound gives a brilliant deep blue to violet fluorescence in solution and this property was utilised for its isolation by column chromatography. Flemichapparin-C contains an OMe group (Zeisel) and a methylenedioxy function[15] (positive Labat test; ν_{max}^{KBr} 935 cm^{-1}).[16] The IR spectrum also indicated aromatic bands (1600, 1500, 1460 cm^{-1}) and a furan ring (1070 cm^{-1}). A band at 1740 cm^{-1}, characteristic of an $\alpha\beta$-unsaturated-δ-lactone, together with the blue fluorescence pointed to a coumarin structure.[7] This was further confirmed by the fact that flemichapparin-C, being non-acidic, dissolved in 0·1 (N) NaOH and was precipitated unchanged on acidification.

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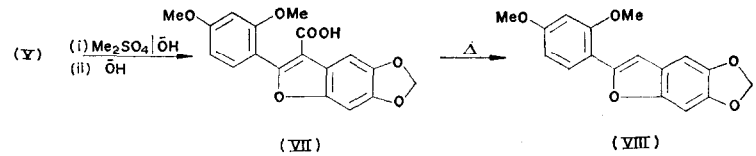
The UV spectrum (λ_{max}^{EtOH} 345, 308, 296 and 246 nm) showed a close resemblance with that of the coumestans.[17,18] The MS data [*m/e* 310 (M^+), *m/e* 295 ($M^+ - 15$; $M^+ - Me$), and *m/e* 267 ($M^+ - 15$–28; $M^+ - Me$–CO] were also in conformity with a coumestan structure[19,20] for flemichapparin-C. A degradative scheme, consistent with these data, was drawn (Scheme 1) on the basis of structure (V) for flemichapparin-C.



(VII) (VIII)

Accordingly, (V) was converted to the corresponding ester by methylative ring opening[17] with dimethyl sulphate and alkali, and the ester to the acid by hydrolysis. The acid (VII), m.p. 235°, $C_{18}H_{14}O_7$ (M^+ 342), showed no peak at 1740 cm^{-1} in its IR spectrum and instead exhibited a new peak at 1680 cm^{-1} showing that it was an $\alpha\beta$-unsaturated acid[21] as expected. Decarboxylation of (VII) furnished a compound, m.p. 165–166°, the properties of which agreed well with the expected benzofuran compound (VIII).[17]

The identity of flemichapparin-C as the 7-*O*-methyl ether of medicagol (V)[17,23] was finally established by comparing its physical and spectral data (m.p., m.m.p., TLC, identical IR) with a pure sample of 7-*O*-methylmedicagol prepared by methylating an authentic specimen of medicagol (VI). The occurrence of 7-*O*-methylmedicagol (V, flemichapparin-C) is reported for the first time.

The co-occurrence of 6a,11a-dehydropterocarpan (IV, flemichapparin-B) and a coumestan, 7-*O*-methylmedicagol (V, flemichapparin-C) in the same plant provides circumstantial evidence for the hypothesis[22,23] that dehydropterocarpan, formed from a suitably substituted 2′-hydroxyisoflavanone by unexceptional steps, is a key intermediate in the biosynthesis of pterocarpans and coumestans.

EXPERIMENTAL

M.ps were determined on a Kofler block and are uncorrected. For column chromatography Brockmann alumina and silica gel (BDH, 60–120 mesh) were used. Silica gel G was used for TLC and iodine was used for developing the plates. Light petrol. used had b.p. 60–80°.

Isolation of flemichapparin-B (IV). The air dried and powdered roots (2 kg) of *Flemingia chappar* were exhaustively extracted with $CHCl_3$ in a Soxhlet for 24 hr. The brownish gummy residue (15 g) obtained was chromatographed on a column of alumina (30 g). The fractions eluted with light petrol.–benzene (1 : 1) and containing a light yellow semi-solid were combined (500 mg) and rechromatographed on alumina (12 g). A colourless solid was obtained in the fractions eluted with light petrol.–benzene (1 : 1) which was crystallized from aq. EtOH to give needles (IV) (120 mg), m.p. 179–180°, $[\alpha]_D \pm 0°$ ($CHCl_3$). (Found: C, 69·40; H, 4·54. $C_{17}H_{12}O_5$ requires: C, 68·92; H, 4·05%.) NMR ($CDCl_3$): δ 7·45 (*d*, 1-H *J* 9·0 Hz); 6·6 (*d*, 2-H *J* 4·0 Hz); 6·52 (*s*, 4-H); 6·78 (*s*, 7-H); 7·08 (*s*, 10-H); 6·08 (*s*, OCH_2O); 5·59 (*s*, $-CH_2-$) and 3·85 (*s*, OMe).

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Tetrahydroflemichapparin-B (I). IV (40 mg) in HOAc (20 ml) was hydrogenated over 10% Pd–C (30 mg). After 4 hr, the catalyst was removed, the filtrate diluted with a large vol. H_2O (150 ml) and extracted with Et_2O (200 ml). The ethereal solution yielded a solid, which crystallized from aq. alcohol as shining plates (I, 16 mg) m.p. 139–140°, (M^+ 300), negative Gibbs test. (Found: C, 68·34; H, 5·46. $C_{17}H_{16}O_5$ requires: C, 68·00; H, 5·33%.)

Dihydroflemichapparin-B (II). IV (20 mg) dissolved in hot MeOH (80 ml) was hydrogenated over 10% Pd–C (20 mg). After consumption of 1 mol of H_2, the catalyst was filtered off, and the filtrate on concentration gave a residue which crystallized from MeOH to give (II), m.p. 185–186°, (12 mg). (Found: C, 68·69; H, 4·78. $C_{17}H_{14}O_5$ requires: C, 68·45; H, 4·69%.)

Isolation of flemichapparin-C (V). After elution of flemichapparin-B (IV) from the column, a greenish white semi-solid (100 mg) exhibiting fluorescence was obtained by washing the column with benzene–light petrol. (3:1). This was rechromatographed on a column of neutral alumina and the benzene eluates exhibiting a bluish fluorescence yielded an amorphous solid (40 mg), m.p. 258–265°, on evaporation of the solvent and repeated trituration with petrol. The solid was not homogeneous and showed the presence of sitosterol on TLC plates, and was rechromatographed over silica gel (2 g). The fractions showing intense blue fluorescence and giving a single spot on TLC plates yielded a colourless solid. The latter on crystallization from aq. EtOH by slow evaporation at room temp. furnished needles (V) (10 mg), m.p. 272°. (Found: C, 66·22; H, 3·49. $C_{17}H_{10}O_6$ requires: C, 65·80; H, 3·32%.)

Methylative ring opening to the corresponding ester. A mixture of V (25 mg), Me_2SO_4 (0·3 ml) and anh. K_2CO_3 (25 mg) was refluxed for 30 min in acetone (6 ml). Methanolic KOH (10%) was added dropwise until the solution did not turn yellow on further addition of alkali. The mixture was refluxed for another 30 min, filtered, concentrated to a small vol. (2 ml) and was directly used for the next step of the reaction.

Hydrolysis of the ester to the acid (VII). The above ester solution was hydrolysed by refluxing with methanolic KOH (10%; 3·4 ml) for 1 hr. The mixture was diluted and acidified with conc. HCl. The extract yielded a colourless residue which crystallized from Et_2O as needles, m.p. 235° (VII) (20 mg). IR: ν_{max}^{KBr} 1680 cm^{-1} ($\alpha\beta$-unsaturated acid); MS: *m/e* 342 (M^+). (Found: C, 63·46; H, 4·15. $C_{18}H_{14}O_7$ requires: 63·15: H, 4·09%.)

Decarboxylation of the acid (VII) *to the corresponding benzofuran compound* (VIII). The acid VII (20 mg) was decarboxylated by heating at 230–240° for 2 hr. The dark residue was dissolved in Et_2O (25 ml), extracted with 2 × 10% Na_2CO_3, washed and dried. The ethereal solution on evaporation gave a crystalline solid (VIII, 2 mg), m.p. 165–166°.

Methylation of medicagol (VI). A mixture of VI (20 mg), anh. K_2CO_3 (20 mg) and Me_2SO_4 (0·2 ml) was refluxed in acetone (5 ml) for 4 hr. The mixture was filtered and the filtrate evaporated to dryness. The residue, a colourless solid, gave 2 spots on TLC in Et_2O–petrol. (7:3) Co-TLC with an authentic sample showed that about 60% of (VI) was converted to its methyl ether and the rest was unchanged. The methyl ether was separated from (VI) by utilizing the difference in solubility of the two in acetone. The methyl ether, being more soluble, remained in the mother liquor while the unreacted (VI) readily crystallized out. After several such crystallization from acetone, the mother liquor, freed of (VI), was evaporated to dryness. The crude methyl ether was recrystallised from aq. EtOH as needles, m.p. 270° (V, 8 mg).

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