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Flavones of *Pajanelia multijuga* P.DC. and *Ligustrum neilgherense var. obovata* C.B.Cl.*

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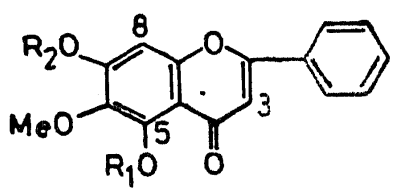
Abstract. From the hexane and methanol extracts of the bark of *Pajanelia multijuga* P.DC., oroxylin A and chrysin have been isolated. Methanol extract of the leaves of *Ligustrum neilgherense var. obovata* C.B.Cl. afforded d-mannitol and kaempferitrin. Structures of these compounds have been confirmed by shifts of the methoxyl groups on addition of benzene and $Eu(dpm)_3$ induced shifts in the NMR.

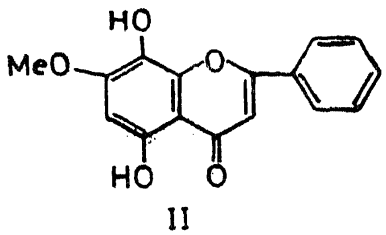
Keywords. Flavones; *Pajanelia multijuga*; *Ligustrum neilgherense var obovata*; lanthanide NMR shifts; oroxylin A; chrysin; kaempferitrin.

1. Introduction

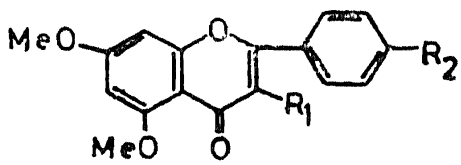
No chemical work appears to have been carried out previously on any part of *Pajanelia multijuga* P.DC. (family: Bignoniaceae). Hexane extract of the bark afforded a yellow crystalline compound $C_{16}H_{12}O_5$ (M^+, m/e 284), m.p. 201-2°, which gave a blue-green ferric colour, a positive Shinoda test and exhibited λ_{max} 271 and 320 nm. A bathochromic shift of Band I to 332 nm on addition of $AlCl_3$ indicated it to be a 3- or 5- hydroxyflavone. The presence of a 7-hydroxyl group was shown by the batho-



I $R_1 = R_2 = H$
III $R_1 = H$; $R_2 = Me$
IV $R_1 = R_2 = Me$
V $R_1 = R_2 = Ac$
VI $R_1 = Ac$; $R_2 = Me$



II



VII $R_1 = R_2 = H$
VIII $R_1 = R_2 = OMe$

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chromic shift of Band I on addition of sodium acetate. Methylation with dimethylsulphate gave the monomethylether m.p. 168-9° and the dimethylether m.p. 165-6°. NMR spectra of these compounds together with the other data indicated that the compound should be a monomethoxy 5, 7-dihydroxyflavone (Mabrry *et al* 1970) formule oroxylin A (I) or wogonin (II).

Oroxylin-A is reported to have m.p. 232° (Naylor and Dyer 1901) and later reports of the natural (Row *et al* 1948; Shah *et al* 1936; 1938) and synthetic material, (Simpson 1956; Murti and Seshadri 1949 a, b) quote m.p. 219-220°. M.p. of the flavone isolated by us and its dimethylether appeared to be closer to wogonin (Shibata *et al* 1923). Since authentic samples of wogonin and oroxylin-A were not available, we proposed to use the benzene induced shifts (Wilson *et al* 1968) and also the shift reagent $Eu(dpm)_3$ to make a choice between (I) and (II). The small shift of the methoxyl signal in the fully methylated compound on addition of benzene suggested that the methoxyl group should be situated at C-6 as in oroxylin-A (I). The mono- and dimethyl-ethers should therefore be (III) and (IV). Acetylation of (I) and (III) gave (V) and (VI) respectively. Addition of $Eu(dpm)_3$ to (IV) in $CDCl_3$ caused as expected a shift of 7.15 p.p.m. due to the 5- methoxyl group, 3.17 p.p.m. due to the 6-methoxyl group and 1·24 p.p.m. attributed to the 7-methoxyl group (Okigawa *et al* 1975). The structure of the natural product was also supported by its mass spectral fragments which indicated the presence of a 6-methoxyl group (Kingston 1971; Rodriguez *et al* 1972).

When our identification of the compound was completed, we came across a Japanese paper (Takido *et al* 1975) reporting the isolation of wogonin and oroxylin-A (m.p. 201-2°). A sample of oroxylin-A kindly supplied by M Takido confirmed the identity of our compound.

Chromatographic separation of the methanol extract gave chrysin, identified by comparison with an authentic sample (Geissman 1962). Addition of $Eu(dpm)_3$ to the dimethyl-ether (VII) induced expected shifts of the methoxyl groups.

The leaves of *Ligustrum neilgherense var. obovata* C.B.Cl. on methanol extraction gave on concentration a solid which on chromatographic separation on polyamide gave yellow crystals m.p. 195-6° identical with kaempferitrin (Geissman 1962). Acid hydrolysis gave kaempferol and rhamnose. The tetramethylether of kaempferol (VIII) showed $Eu(dpm)_3$ induced shift of 8·4 p.p.m. due to the 5-methoxyl, 0·88 p.p.m. due to the 7-methoxyl and 4′-methoxyl groups, and 0·08 p.p.m. attributed to the 3-methoxyl group. Further extraction of the leaves with hot methanol afforded d-mannitol.

2. Experimental

Ir spectra were recorded on Perkin-Elmer Infracord Spectrophotometer and nmr spectra on Varian A 60 spectrometer using TMS as an internal standard. The mass spectra were determined on Atlas CH-7 instrument. The melting points were determined by capillary method and are uncorrected.

2.1. *Isolation of oroxylin-A (I) and chrysin*

The powdered bark of *Pajanelia multijuga* (5 kg) was extracted by cold percolation

with hexane (3×20 l) and the extract concentrated under vacuum to 100 ml and left overnight. The solid separated was collected (450 mg) and crystallized from methanol to afford yellow needles (150 mg) m.p. 201-2°. M.m.p. with oroxylin A (Lit. m.p. 201-2°) (Takido *et al* 1975) was undepressed and their ir spectra were identical. m/e 284 (Takido *et al* 1975) (CM^+, 100%), 269 (70), 241 (80), 167 (12). δ (CD_3SOCD_3): 13·0 (1H, S, 5-OH), 8·0 (2 H, m, H-2′, 6′), 7·6 (3H, m, H-3′, 4′, 5′), 6·89 (1H, S, H-8), 6.63 (1H, S, H-3), 3·85 (3H, S, OMe). (Found: C, 67·6; H, 4·6. Calc. for $C_{16}H_{12}O_5$: C, 67·6; H, 4·3%).

The compound (I, 75 mg) on heating with sodium acetate (0·5 g) and acetic anhydride (3 ml) gave the diacetate (V; 60 mg), m.p. 144° (Lit. m.p. 131-2°) (Row *et al* 1948). δ ($CDCl_3$): 7·83 (2H, m, H-2′, 6′), 7·55 (3H, m, H-3′, 4′, 5′), 7·3 (1H, S, H-8), 6·62 (1H, S, H-3), 3·9 (3H, S, 6-OMe), 2·5 (3H, S, 5-OAc), 2·37 (3H, S, 7-OAc).

The bark was further extracted with methanol (2 × 20 l), the percolates concentrated under vacuum to 500 ml, left overnight and the yellow solid collected (12 g). A portion of this (2g) was chromatographed on silica gel (20g) in benzene, when the first eluted fractions contained oroxylin-A. Later fractions on crystallization gave chrysin, m.p. 286-7° identical in its m.m.p. and IR spectra with an authentic sample.

2.2. *Methylation of oroxylin-A to give (III) and (IV)*

Oroxylin-A (300 mg) in dry acetone (50 ml) was refluxed with K_2CO_3 (3 g) and dimethylsulphate (600 mg) for 4 hr. The reaction mixture on work up gave a gum (260 mg) which was chromatographed on silica gel (3 g) in benzene. Fractions (15 ml) were collected and the separation monitored by TLC. Fractions (1-12) (elution: benzene) gave on crystallization from hexane —CH_2Cl_2 (III), m.p. 168-9°. m/e 298 (M^+, 40%), 283 (50), 255 (45), 181 (15); δ ($CDCl_3$): 12·7 (1H, S, 5-OH), 7·83 (2H, m, H-2′, 6′), 7·5 (3H, m, H-3′, 4′, 5′), 6·61 (1H, S, H-8), 6·53 (1H, S, H-3), 3·9 (6H, S, OMe). ($CDCl_3$: C_6D_6 — 1:1), 3·87 (3H, S, 6-OMe); 3·55 (3H, S, 7-OMe). (Found: C, 68·8; H, 5·1. $C_{17}H_{14}O_5$ requires: C, 68·5; H, 4·7%. M^+, at m/e 298).

The monomethylether (III; 60 mg) was warmed at 70° with acetic anhydride (0·6 ml) and pyridine (0·6 ml) for 15 min and left overnight. Usual work up gave the acetate (VI; 15 mg) as colourless needles m.p. 130°, (Lit. m.p. 130-1° (Row *et al* 1948). δ ($CDCl_3$): 7·83 (2H, m, H-2′, 6′), 7·5 (3H, m, H-3′, 4′, 5′), 6·91 (IH, S, H-8), 6·6 (IH, S, H-3), 3·98 (3H, S, 6-OMe), 3·86 (3H, S, 7-OMe), 2·5 (3H, S, 5-OAc).

Fractions 15-16 (elution: $CHCl_3$+1%MeOH) gave on crystallization from hexane-CH_2Cl_2 colourless needles of (IV), m.p. 165-6°. m/e 312 (M^+, 12%), 297 (100), 269 (20), 195 (12). δ ($CDCl_3$); 7·85 (2H, m, H—2′, 6′), 7·5 (3H,m, H—3′, 4′, 5′) 6·79 (1H, S, H—8), 6·61 (1H, S, H—3), 4·01, 4·0, 3·9 (9H, S each, 5, 6, 7, OMe). (C_6D_6): 4·09 (3H, S, 6-OMe), 3·78 (3H, S, 5-OMe), 3.33 (3H, S, 6-OMe). (Found: C, 69·2; H, 5·5. $C_{18}H_{16}O_5$ requires: C, 69·2; H, 5·2%. M^+, at m/e 312).

2.3. *Isolation of kaempferitrin*

The powdered leaves of *Ligustrum neilgherense* (5 kg) were extracted in the cold with hexane (2×25 l) and then with methanol (20 l). The methanol extract on concentration under vacuum to 500 ml gave a solid which on chromatography over polyamide

in water afforded kaempferitrin (20 g), m.p. 195-6°. It was identical in its m.m.p. and IR spectra with an authentic sample.

Further extraction of the leaves with hot methanol (2×20 l) and concentration to 1·5 l gave colourless crystals (4 g), m.p. 165-7° identified as d-mannitol.

Acknowledgements

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