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*; lanthamide 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 C₁₆H₁₂O₅ (M⁺, m/e 284), m.p. 201-2º, 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 AlCl₃ indicated it to be a 3- or 5-hydroxyflavone. The presence of a 7-hydroxyl group was shown by the batho-
chromic shift of Band I on addition of sodium acetate. Methylation with dimethyl- 
sulphate gave the monomethyl ether m.p. 168-9° and the dimethyl ether 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 (Mabry et al 1970) 
formula 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, (Simp-
son 1956; Murti and Seshadri 1949 a, b) quote m.p. 219-220°. M.p. of the flavone 
isolated by us and its dimethyl ether 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 CDCl₃ 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 

When our identification of the compound was completed, we came across a Japa-
nese 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.C.I. on methanol extraction 
gave yellow crystals m.p. 195-6° identical with kaempferitrin (Geissman 1962). Acid 
hydrolysis gave kaempferol and rhamnose. The tetramethyl ether 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 deter-
mined 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. 201-20. M.m.p. with oroxylin A (Lit. m.p. 201-20) (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$_3$SOCD$_3$): 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. 144-6° (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). 3. 2. 2. Methylation of oroxylin-A to give (III) and (IV)

Oroxylin-A (300 mg) in dry acetone (50 ml) was refluxed with K$_2$CO$_3$ (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$_2$Cl$_2$ (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$_6$D$_6$—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 (1H, S, H-8), 6-6 (1H, 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$_2$Cl$_2$ 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$_6$D$_6$): 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$_8$ 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.

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