Heartwood Constituents of *Swartzia madagascariensis*

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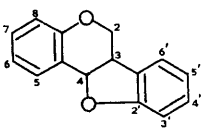
RECENTLY we reported the isolation and identification of three known coumaranochromans and a new constituent, 7-hydroxy-4′-methoxypterocarpan [named from pterocarpan as (I)], from the heartwood of *Swartzia madagascariensis* Desv. (subfamily: Caesalpinioideae).[1] We now report the isolation and identification of four more coumaranochromans and a coumaronochromen from the same heartwood.

Thin-layer chromatography of the ether extract of the heartwood revealed the presence of three minor components, apart from the two major components already described,[1] with R_f values 0·22, 0·55, and 0·69 (in $CHCl_3$ on SiO_2–$CaSO_4$). By elution of these bands from preparative-scale thin-layer chromatograms, three extracts were obtained. Extract 1 (R_f 0·22), which was soluble in aqueous sodium hydroxide, was shown by gas–liquid chromatography (g.l.c.) to contain two major components which were separated by conversion into their acetates and crystallisation from ethyl acetate–light petroleum. Hydrolysis of the acetates with ammonium hydroxide in ethanol gave the free phenols, 7-hydroxy-8-methoxy-4′,5′-methylenedioxypterocarpan (II), m.p. 159—161°, $[\alpha]_D$ −197° (all in $CHCl_3$), ν_{max} 3400 (OH), 1615, 1515 cm.$^{-1}$ (aryl), λ_{max} 308 mμ (log ε 4·11), and 7-hydroxy-4′,8-dimethoxypterocarpan (III), m.p. 158—160°, $[\alpha]_D$ −161°, ν_{max} 3390 (OH), 1620, 1600, 1500 cm.$^{-1}$ (aryl), λ_{max} 284 mμ (log ε 4·09). Extract 2 (R_f 0·55), which was insoluble in aqueous sodium hydroxide, was shown by g.l.c. to contain two major components, separable by crystallisation from benzene, 7,8-dimethoxy-4′,5′-methylenedioxypterocarpan (IV), m.p. 245—247°, $[\alpha]_D$ −202° ν_{max} 1619, 1515 cm.$^{-1}$ (aryl), λ_{max} 310 mμ (log ε 3·97), and 4′,7,8-trimethoxypterocarpan (V), m.p. 118—120°, $[\alpha]_D$ −158°, ν_{max} 1625, 1615, 1505 cm.$^{-1}$ (aryl), λ_{max} 284 mμ (log ε 3·84), 290 mμ (sh.). Extract 3 (R_f 0·69), which was insoluble in aqueous sodium hydroxide, was shown by g.l.c. to contain one major component, and this was isolated by column chromatography on silicic acid with chloroform–benzene as eluant, to give 4′,7-dimethoxypterocarp-3-en (VI), m.p. 110—112°, $[\alpha]_D \pm 0°$, ν_{max} 1658 (C=C), 1620, 1502 cm.$^{-1}$ (aryl), λ_{max} 230, 242, 335 and 352 mμ (log ε 4·23, 4·21, 4·48, and 4·42 respectively).

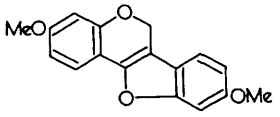
Comparison of the absorptions of the protons at C-2, C-3, and C-4 in the nuclear magnetic resonance (n.m.r.) spectra of 4′,7-dimethoxypterocarpan, 7-methoxy-4′,5′-methylenedioxypterocarpan, and

[1] S. H. Harper, A. D. Kemp, and W. G. E. Underwood, *Chem. and Ind.*, 1965, 562.

7-acetoxy-4′,5′-methylenedioxypterocarpan with the absorption pattern in the same regions of the spectra of (II)—(V) indicated the presence of the



(I)

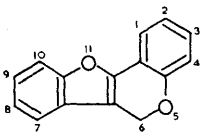


(VI)

coumaranochroman ring system. The aromatic region in the n.m.r. spectra of (II) and (IV) consisted of an AB quartet (J 8·5 c./sec.) and two singlets, whereas in (III) and (V) it consisted of an AB quartet (J 8·5 c./sec.) and an ABX system. The presence of the benzyl phenyl ether system was confirmed by reduction to dihydro-derivatives containing phenolic hydroxyl groups. The positions of the substituents in (II)—(V) were established by consideration of the above n.m.r. data and by oxidation, when the substituted 2-hydroxybenzoic acids were identified by paper chromatography.

Oxidation of (VI) gave only 2-hydroxy-4-methoxybenzoic acid, which together with the infrared, ultraviolet, and n.m.r. spectral data pointed to the coumaronochromen structure, and this was confirmed by synthesis of (VI) from 4′,7-dimethoxypterocarpan. (VI) has recently been synthesised from di-*O*-methylcoumestrol.[2]

[*Note added in proof*]—After discussion with the Editor, we have agreed that in future we will use the numbering system here indicated



for pterocarpen and for its 6a,11a-dihydro-derivative, pterocarpan.

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[2] W. J. Bowyer, J. N. Chatterjea, S. P. Dhoubadel, B. O. Handford, and W. B. Whalley, *J. Chem. Soc.*, 1964, 4212.