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ISO- AND NEO-FLAVONOIDS FROM *DALBERGIA INUNDATA**

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Key Word Index—*Dalbergia inundata*; Leguminosae; (*S*)-4-methoxydalbergione; formononetin; caviunin; 3′-O-methylorobol.

Plant. Dalbergia inundata Bth., "cipó de tucunaré", shrub, subfamily Leguminosae–Lotoideae.[2] *Source.* Flooded banks of the Amazon river and its tributaries.

Wood. The powdered wood (5 kg) was extracted with EtOH. The extract was chromatographed on silica, yielding, in order, lupenone (30 mg), stearic acid (30 mg), (*S*)-4-methoxydalbergione (20 mg),[3] lupeol (25 mg), a mixture of sitosterol and stigmasterol (40 mg), caviunin (800 mg), 3′-*O*-methylorobol (300 mg) and formononetin (180 mg). The structure of 5,7,4′-trihydroxy-3′-methoxyisoflavone (3′-*O*-methylorobol) was deduced by UV (spectral shifts in presence of NaOAc and $AlCl_3$), MS (retro-Diels–Alder fragments corresp. to diOH-ring A and OH.OMe-ring B) and PMR spectrometry (isoflavone H-2 *s*, 5 aromatic proton signals whose chemical shift and multiplicity indicate the 5,7,3′,4′-oxygenation pattern). The H-5′ signal suffers a strong shift (Δ −0·42 ppm) upon acetylation, relatively to the remaining ring B proton signals (H-2′ Δ +0·04 ppm, H-6′ Δ −0·18 ppm). The ring B hydroxyl can, thus, only be located at C-4′. Indeed, 5,7,3′-trihydroxy-4′-methoxyisoflavone (pratensein *ex Trifolium pratense*) has a different m.p. 272–274°.[4] 3′-*O*-Methylorobol has previously been isolated only as an unresolved mixture with pratensein from *Thermopsis* spp.[5]

3′-*O-Methylorobol.* m.p. 218–220° (MeOH) [Found, C, 64·1; H, 4·4, $C_{16}H_{12}O_6$ requires: C, 64·0; H, 4·5%]. λ_{max}^{etOH} (nm): 265, 295, 345 (ϵ 20400, 9300, 360), λ_{max}^{etOH} (nm): 280, 330 (ϵ 18600, 10500) (acidif. restores curve in EtOH), $\lambda_{max}^{etOH+naOAc}$ (nm): 274, 330 (ϵ 20700, 6000), $\lambda_{max}^{et\ OH+H_3Bo_3+NaOAc}$ (nm): 265, 295, 345 (ϵ 18000, 6600, 2000), $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 277, 315 (ϵ 21900, 6000). λ_{min}^{KBr} (cm^{-1}): 3320, 1660, 1625, 1582, 1518, 1455, 1380, 1280,

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1208. PMR [$(CD_3)_2CO$, τ]: −3·30 (*s*, O<u>H</u>-5), 1·84 (*s*, H-2), 2·74 (*d*, *J* 2 Hz, H-2'), 2·90 (*dd*, *J* 8 and 2 Hz, H-6'), 3·14 (*d*, *J* 2 Hz, H-5'), 3·57 (*d*, *J* 2 Hz, H-8), 3·70 (*J* 2 Hz, H-6), 6·10 (*s*, OC<u>H</u>$_3$). MS: M + 1 301 (16%), M 300 (100%), *m/e* (%) 299 (9), 285 (11), 284 (12), 271 (10), 268 (36), 257 (11), 229 (15), 179 (9), 177 (9), 163 (10), 153 (34), 149 (16), 148 (16), 137 (10), 135 (11), 134 (15), 133 (23), 132 (38), 124 (10), 123 (9), 120 (15), 117 (13), 105 (23). *Triacetate*, m.p. 184–186° (C_6H_6). λ_{min}^{KBr} (cm^{-1}): 1745, 1617, 1505, 1430, 1365, 1270, 1200, 1125, 1030, 910. PMR [$(CD_3)_2CO$, τ]: 1·58 (*s*, H-2), 2·53 (*d*, *J* 2 Hz, H-8), 2·72 (sec. split *d*, H 9 Hz, H-5', H-6'), 2·78 (*d*, superimp. on part of preceding, H-2'), 2·91 (*d*, *J* 2 Hz, H-6), 6·10 (*s*, OC<u>H</u>$_3$), 7·62 (*s*, two COC<u>H</u>$_3$), 7·70 (*s*, COC<u>H</u>$_3$).

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AZAFRIN FROM ROOTS OF *PEDILANTHUS TITHYMALOIDES*

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Plant. Pedilanthus tithymaloides, dried Roots. *Source.* Supplied by Dr. Steinmetz, Amsterdam, The Netherlands. *Previous work.* Epifriedelanol acetate, friedelin, epifriedelinol, 1-dotriacontanol and β-sitosterol.[1]

Dried roots. Within a programme to study the occurrence and distribution of irritants and cocarcinogens in plants 1 kg of roots were Soxhleted with diverse solvents of increasing polarity as follows, and the irritation units (IU) and irritation doses 50 (ID_{50}) on the mouse ear determined following the standard procedure:[2] EtOAc (35·1 g, IU: 1500 μg/ear, ID_{50}: 150 μg/ear), Et_2O (26 g, IU: >848 μg/ear, ID_{50}: 213 μg/ear), $CHCl_3$ (9·2 g, IU: >630 μg/ear) and *n*-PrOH (3·5 g, IU: >650 μg/ear). After treatment with perchloric acid in MeOH no increase in the irritation activity was observed in any extract. The ETOAc extract on silica gel column, deactivated with 13% H_2O, upon elution with Et_2O-light petrol, (1:1), gave a compound with MS and R_f value identical with that of azafrin.[4] MW: *m/e*, 426 (22·6%), 408 (7·6%), 393 (1·9%), 382 (3·8%), 375 (1·9%), 364 (1·89%), 349 (1·88%), 347 (1·9%), 328 (5·7%), 327 (15·4%), 316 (1·9%), 299 (1·9%), 133 (13%), 109 (100%), 91 (21·3%), 83 (5·45%), 73 (1·9%), 69 (39·2%), 59 (4·7%), 43 (53·5%). R_f = 0·05 (Et_2O-petrol., on Merck silica gel $60F_{254}$, TLC, pre-coated plate). It appears from this observation that the dried roots do not contain irritant principles such as 12,13-di- or 13-monoesters of phorbol and

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