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LEGUMINOSAE

THE ISOFLAVONES OF *PTERODON PUBESCENS**†

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Abstract—The trunk wood of *Pterodon pubescens* Benth. (Leguminosae-Lotoideae) contains 3′,4′,6,7-tetramethoxyisoflavone (Ia), 2′,6,7-trimethoxy-4′,5′-methylenedioxyisoflavone (Ib) and 2′,3′,4′,6,7-pentamethoxyisoflavone (Ic).

Pterodon pubescens Benth. (Leguminosae-Lotoideae) is native to the savannahs of Central and Southern Brazil. The fruits contain geranylgeraniol, all-*trans*-(—)-14,15-epoxygeranylgeraniol,[3] besides two additional diterpenes[4] and alkaloids.[5] The wood is suitable for joists and railroad ties.[6] Fractional crystallization of its benzene extract yielded a new compound, in addition to 3′,4′,6,7-tetramethoxyisoflavone (Ia), which was synthesized[7] prior to its isolation from the heartwood of *Cordyla africana*,[8] and 2′,6,7-trimethoxy-4′,5′-methylenedioxyisoflavone (Ib, milldurone), a constituent of *Cordyla africana*[8] and of *Millettia dura*.[9]

The IR and UV spectra showed that the new compound, $C_{20}H_{20}O_7$, was an isoflavone. This indication was reinforced by the NMR spectrum which contained the signal at 2·05 τ due to the isoflavonoid 2-H, and revealed the presence of 5 methoxyls and of 4 aromatic protons. The chemical shifts of two singlets (2·35, 3·10 τ) allocated two of these protons to the *para*-positions of ring A, while the chemical shifts and coupling constant of two doublets (3·25, 2·93 τ, J 9·1 Hz) allocated the remaining two protons to the 5′,6′-positions of ring B. Hydrogenation to the isoflavanone caused the following diamagnetic shifts of the aromatic

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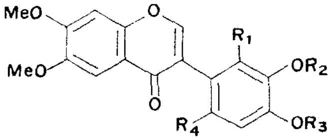

	R_1	R_2	R_3	R_4
Ia	H	Me	Me	H
b	H	$-OCH_2-$		OMe
c	OMe	Me	Me	H
d	H	Me	Me	OMe

proton signals: $\Delta_{5\text{-H}}$ 0·25 ppm, $\Delta_{8\text{-H}}$ 0·42 ppm, $\Delta_{5'\text{-H}}$ 0·11 ppm, $\Delta_{6'\text{-H}}$ 0·25 ppm. These values are comparable to reported data on other isoflavone–isoflavanone pairs,[8] and corroborate the analysis leading to constitution Ic. This is isomeric with the known 2′,4′,5′,6,7-pentamethoxyisoflavone (Id).[8] Indeed, the mass spectra of these compounds are very similar, both showing a strong M-31 peak which, in the case of isoflavones, is diagnostic of a methoxyl at C-2′.

EXPERIMENTAL

For experimental techniques see Ref. 10.

Isolation of Ia, b and c. The ground wood (5·0 kg) was extracted with hot benzene. The benzene solution was evaporated and the residue was fractionally crystallized from EtOH, appearing in order of increasing solubility Ib (205 mg), Ia (35 mg) and Ic (30 mg).

3′,4′,6′,7-*Tetramethoxyisoflavone* (Ia) and 2′,6,7-trimethoxy-4′,5′-*methylenedioxyisoflavone* (Ib). M.p., IR, UV, NMR and mass spectra of these compounds were identical to Ref. 8 values. Direct comparison with an authentic sample of milldurone[9] confirmed the identity of Ib.

2′,3′,4′,6,7-*Pentamethoxyisoflavone* (Ic), m.p. 170–172° was obtained as fine colourless crystals from EtOH. (Found: C, 64·3; H, 5·5. $C_{20}H_{20}O_7$ requires: C, 64·5; H, 5·4%.) $\nu_{\max}^{\text{KBr}}$ (cm^{-1}): 1626, 1600, 1500, 1260, 1174, 1143, 1026, 900. $\lambda_{\max}^{\text{EtOH}}$ 250, 315 nm (ϵ 33,300, 17,300). NMR ($CDCl_3$, τ): 2·05 (s, 2-H), 2·35 (s, 5-H), 2·93 (d, *J* 9·1 Hz, 6′-H), 3·10 (s, 8-H), 3·25 (d, *J* 9·1 Hz, 5′-H), 5·99 (s, two $OC\underline{H}_3$), 6·10 (s, two $OC\underline{H}_3$). 6·18 (s, one $OC\underline{H}_3$). MS: M 372 (100%), *m/e* (%): 357 (7), 341 (70), 329 (4), 325 (12), 311 (4), 299 (6), 192 (5), 191 (8), 181 (26), 171 (13), 157 (3), 149 (3).

(±)-2′,3′,4′,6,7-*Pentamethoxyisoflavanone*, was obtained by hydrogenation of Ic in EtOH over Pd/C at room temp., m.p. 145–147°. $\nu_{\max}^{\text{KBr}}$ (cm^{-1}): 1658, 1631, 1608, 1490, 1484, 1264, 1096, 1033, 884 793. $\lambda_{\max}^{\text{EtOH}}$ 234, 272, 334 nm (ϵ 22,500, 12,500, 7100). NMR ($CDCl_3$, τ): 2·61 (s, 5-H), 3·21 (d, *J* 8·0 Hz, 6′-H), 3·36 (d, *J* 8·0 Hz, 5′-H), 3·54 (s, 8-H), 5·5 (m, 2-H_2), 6·2 (m, 3-H), 6·08 (s, two $OC\underline{H}_3$), 6·12 (s, two $OC\underline{H}_3$), 6·14 (s, one $OC\underline{H}_3$).

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