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FLAVONOIDS FROM *DERRIS* SPECIES*

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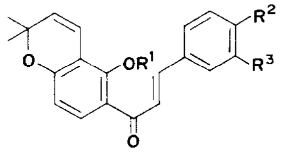
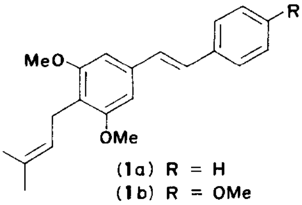
Key Word Index—*Derris floribunda*; *D. amazonica*; *D. urucu*; Leguminosae–Lotoideae; chalcone; stilbene; isoflavan; hydroxyrotenone.

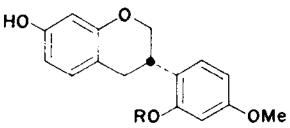
Plants. Derris floribunda (Benth.) Ducke, trivial name "timbó venenoso", *D. amazonica* Killip, trivial name "timbó-rana" and *D. urucu* (Killip et Smith) Macbr., trivial name "timbó urucú", "timbó verdadeiro" (="true timbó") [2], were collected in the vicinity of Manaus, Amazonas, and identified by the botanist W. Rodrigues, INPA, Manaus. *Constituents of* D. floribunda. Powdered root (1·3 kg) was extracted with petrol. The $CHCl_3$-soluble portion (22 g) of the extract (30 g) was chromatographed on silica (600 g) giving the following fractions with the indicated eluants: A_1 (petrol–C_6H_6 9:1), A_2, A_3 (C_6H_6), A_4-A_7 (C_6H_6–$CHCl_3$ 9:1). A_1 was crystallized from petrol giving 3,5-dimethoxy-4-prenylstilbene (**1**a, 40 mg), mp and mmp with an authentic sample from *D. rariflora* (Mart.) Macbr. [3] 84–86°. A_2 was crystallized from petrol giving lonchocarpin (**2**a, 40 mg), mp and mmp with an authentic sample from *D. sericea* (H.B.K.) Ducke [4] 108–109°. A_3 was crystallized from petrol giving 3,5,4′-trimethoxy-4-prenylstilbene (**1**b, 30 mg). A_4 was crystallized from petrol giving derricidin (25 mg), mp and mmp with an authentic sample from *D. sericea* [4] 115–116°. A_5 was crystallized from petrol–C_6H_6 giving isocordoin (40 mg), all data, incl. mp 162–163°, as reported for a sample from an undetermined *Lonchocarpus* sp. [5] A_6 was crystallized from C_6H_6 giving 5,7-dihydroxy-6-prenylflavanone (35 mg), mp and mmp with an authentic sample from *D. rariflora* [3] 212–214°. A_7 was crystallized from C_6H_6 giving 4-hydroxylonchocarpin (**2**b, 30 mg), 1st crop, and a mixture of **2**b and possibly **2**c, 2nd crop.



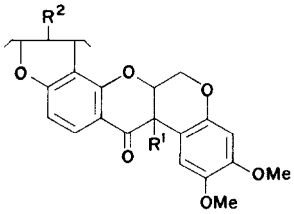
(**2**a) $R^1 = R^2 = R^3 = H$
(**2**b) $R^1 = R^3 = H$, $R^2 = OH$
(**2**c) $R^1 = H$, $R^2 = R^3 = OH$
(**2**d) $R^1 = Ac$, $R^2 = OAc$, $R^3 = H$



(**1**a) R = H
(**1**b) R = OMe



(**3**a) R = H
(**3**b) R = Me



(**4**a) $R^1 = H$, $R^2 = CH_2{=}CMeCH-CH_2$
(**4**b) $R^1 = OH$, $R^2 = CH_2{=}CMeCH-CH_2$
(**4**c) $R^1 = OH$, $R^2 = Me_2C-CH{=}CH$
(**4**d) $R^1 = OAc$, $R^2 = CH_2{=}CMeCH-CH_2$
(**4**e) $R^1 = OAc$, $R^2 = Me_2C-CH{=}CH$

3,5,4′-*Trimethoxy*-4-*prenylstilbene* (**1**b), crystals, mp 92–94° (Found: C, 78·20; H, 7·70. $C_{22}H_{26}O_3$ requires: C, 78·07; H, 7·74%). Comparison of the IR [ν_{max}^{KCl} (cm^{-1}): 1600, 1580, 1520, 970, 840] and PMR [τ(CCl_4): 2·75 (~*d*, *J* 8·5 Hz, H-2′, H-6′), 3·30 (~*d*, *J* 8·5 Hz, H-3′, H-5′), 3·20 (*s*, CH=CH), 3·52 (*s*, H-2, H-6), 4·95 (*t*, *J* 6·5 Hz, =CH), 6·20 (*s*, 2 OMe), 6·26 (*s*, OMe), 6·80 (*t*, *J* 6·5 Hz, CH_2), 8·30 (*s*, Me), 8·40 (*s*, Me)] spectra with the analogous spectra [3] of **1**a identified the compound with the symmetrically substituted methoxy-derivative **1**b. 4-*Hydroxylonchocarpin* (**2**b), crystals, mp 201–203° (Found: C, 74·35; H, 5·55. $C_{20}H_{18}O_4$ requires: C, 74·52; H, 5·63%). Comparison of the IR [ν_{max}^{KCl} (cm^{-1}):

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3180, 1630, 1610, 1580, 1510, 825, 800] and PMR [$\tau((CD_3)_2CO)$: −3·83 (*s*, CH–2′), 2·20 (*d*, *J* 9 Hz, H–6′), 2·25 (*d*, *J* 15 Hz, H–β), 2·41 (~*d*, *J* 8·5 Hz, H–2, H–6), 2·46 (*d*, *J* 15 Hz, H–α), 3·16 (~ *d*, *J* 8·5 Hz, H–3, H–5), 3·30 (*d*, *J* 9 *Hz*, *H*–4″), 3·75 (*d*, *J* 9 Hz, H–5′), 4·40 (*d*, *J* 9 Hz, H–5″), 8·50 (*s*, 2 Me–6″)] spectra with the analogous spectra [4] of **2**a identified the compound with the symmetrically substituted hydroxy-derivative **2**b. The PMR spectrum of the diacetate (**2**d) showed all the expected features [$\tau(CDCl_3)$: 2·47 (*d*, *J* 15 Hz, H–β), 2·46 (~ *d*, *J* 9 Hz, H–2, H–6, H–6′), 2·56 (*d*, *J* 15 Hz, H–α), 2·88 (~*d*, *J* 9·0 Hz, H–3, H–5), 3·30 (*d*, *J* 9·0 Hz, H–5′), 3·65 (*d*, *J* 10 Hz, H–4″), 4·30 (*d*, *J* 10 Hz, H–5″), 7·72 (*s*, 2 COMe), 8·57 (*s*, 2 Me–6″). This compound occurs also in an unidentified *Lonchocarpus* sp. [6].

Constituents of D. amazonica. Powdered aerial wood (0·8 kg) of the creeper was extracted with EtOH. The C_6H_6-soluble portion (3 g) of the extract (27 g) was chromatographed on silica (450 g). Elution with solvent of increasing polarity gave, in succession, sitosterol (20 mg), (3S)-2′-*O*-methylvestitol (**3**b) (15 mg), lupenone (20 mg), lupeol (10 mg) and (6aS,11aS)-demethylhomopterocarpin (20 mg), mp and mmp with an authentic sample from *Dalbergia decipularis* Rizz. et Matt. [7] 127–128°.

(3S)-7-*Hydroxy-2′,4′,dimethoxyisoflavan* (**3**b), crystals, mp 128–129° ($CHCl_3$–EtOH) (Found: C, 71·40; H, 6·39. $C_{17}H_{18}O_4$ requires: C, 71·31; H, 6·34%). Comparison of the IR [ν_{max}^{KCl} (cm^{-1}): 3360, 1600, 1585, 1495, 835], PMR [$\tau(CDCl_3)$: 3·05 (*d*, *J* 9 Hz, H–5 or H–6′), 3·16 (*d*, *J* 9 Hz, H–6′ or H–5), 3·45–3·80 (*m*, H–6, 8, 3′, 5′), 4·58 (*s*, OH), 5·75 (*dd*, *J* 9, 3·5 Hz, H_{eq}–2), 5·97 (*d*, *J* 9 Hz, H_{ax}–2), 6·24 (*s*, 2 OMe), 6·30–6·90 (*m*, H–3), 7·15 (*d*, *J* 7 Hz, $ArCH_2$)] and ORD [(c 2 mg/100 ml, EtOH, 300–274 nm) $[\phi]_{298}$ 0, $[\phi]^{tr}{}_{283}$ −7200, $[\phi]_{274}$ −4500] curves with the analogous curves of **3**a [8, 9] revealed the compound as a hydroxydimethoxyisoflavan of identical absolute configuration and oxygenation pattern. Base peak of the MS [(*m/e*): 286 (91%) M, 164 (100), 152 (36), 151 (91), 149 (59), 135 (9), 121 (54)] was compatible only with a dimethoxylated B-ring and identified the compound with the 2′-O-methyl derivative of (3S)-vestitol (**3**b).

Constituents of D. urucu. Powdered aerial wood (3·4 kg) of the creeper was extracted with EtOH. The extract was chromatographed on silica giving the following fractions with the indicated eluants: A_1 (light petrol.), A_2 ($CHCl_3$). A_1 was rechromatographed on silica giving, upon elution with solvent of increasing polarity, in succession, aliphatic acids (1·5 g, mp 70–72°), rotenone (**4**a, 6 g), mp and mmp with an authentic sample 162–164° [10], and 6a,12a-dehydrorotenone (0·6 g), mp and mmp with a sample prepared by treatment of rotenone with I_2–AcONa 228–230° [10]. A_2 was rechromatographed on silica giving, upon elution with solvent of increasing polarity, 3-methoxy-8,9-methylenedioxy-6a,11a-dehydropterocarpan (26 mg), all data, incl. mp 179–180°, as reported for a sample of flemichapparin-B [11], and a mixture of 12a-hydroxyrotenone and tephrosin, (**4**b + **4**c, 0·5 g).

12a-*Hydroxyrotenone* (**4**b) *and tephrosin* (**4**c), crystals, mp 80–84° (one TLC-spot upon devel. with several solvent systems). The nature of the mixture was indicated by MS [(*m/e*): 410 (52%) M, 209 (29), 208 (100), 207 (37), 203 (21), 193 (8), 187 (8), 181 (10), 165 (10). Acetate, (*m/e*): 452 (41%) M, 393 (12), 392 (29), 250 (94), 208 (100), 207 (29), 203 (9), 194 (9), 193 (11), 192 (29), 191 (9), 187 (18), 182 (24), 181 (12), 165 (12), 159 (53), 151 (17)]. The respective proportion, 65:35, of its components was determined by PMR [$\tau(CDCl_3)$, **4**b: 2·20 (*d*, *J* 8 Hz, H-11), 3·45 (*s*, H–1), 3·50 (*d*, *J* 8 Hz, H–10), 3·55 (*s*, H–4), 4·80 (*dd*, *J* 9, 8 Hz, OCH), 5·00 (*m*, =CH_2), 5·30–5·70 (*m*, H–6a, 2H–6, OH), 6·22 (*s*, OMe), 6·30 (*s*, OMe), 6·78 (*dd*, *J* 16, 9 Hz H–1′), 7·08 (*dd*, *J* 16, 8 Hz, $ArCH_2$), 8·22 (*s*, = CMe). **4**c: 2·30 (*d*, *J* 8 Hz, H–11), 3·45 (*s*, H–1), 3·45 (*d*, *J* 10 Hz, ArCH=), 3·55 (*s*, H–4), 3·60 (*d*, *J* 8 Hz, H–10), 4·45 (*d*, *J* 10 Hz, =CH), 5·30–5·70 (*m*, H–6a, 2H–6), 6·22 (*s*, OMe), 6·30 (*s*, OMe), 8·55 (*s*, OMe), 8·61 (*s*, OMe)]. Resolution of all PMR features was achieved in the spectrum of the mixture of the acetates (also one TLC-spot) [$\tau(CDCl_3)$, **4**d: 2·16 (*d*, *J* 8 Hz, H–11), 3·12 (*s*, H–1), 3·45 (*d*, *J* 8 Hz, H–10), 3·54 (*s*, H–4), 4·59 (*dd*, *J* 4, 2 Hz, H–6a), 4·80 (*dd*, *J* 9, 8 Hz, OCH), 5·00 (*m*, =CH_2), 5·42 (*dd*, *J* 13, 4 Hz, H–6), 5·72 (*dd*, *J* 13, 2 Hz, H–6), 6·20 (*s*, OMe), 6·23 (*s*, OMe), 6·73 (*dd*, *J* 16, 9 Hz, ArCH), 7·07 (*dd*, *J* 16, 8 Hz, ArCH), 7·80 (*s*, COMe), 8·21 (*s*,

=CMe). **4e**: 2·28 (*d*, *J* 8 Hz, H–11), 3·12 (*s*, H–1), 3·42 (*d*, *J* 10 Hz, ArCH=), 3·54 (*s*, H–4), 3·60 (*d*, *J* 8 Hz, H–10), 4·45 (*d*, *J* 10 Hz, =CH), 4·59 (*dd*, *J* 4, 2 Hz, H–6a), 5·42 (dd, *J* 13, 4 Hz, H–6), 5·72 (*dd*, *J* 13, 2 Hz, H–6), 6·20 (*s*, OMe), 6·23 (*s*, OMe), 7·80 (*s*, COMe), 8·54 (*s*, CMe), 8·60 (CMe)]. The PMR data show that the stereochemistry of both components is unexceptional [10]. Reflux of the mixture in 10% methanolic H_2SO_4 (40 min) gave a product from which only 6a,12a-dehydrorotenone was isolated by TLC.

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TRITERPENOIDS FROM *BYRSONIMA VERBASCIFOLIA*[*]

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Key Word Index—*Byrosonima verbascifolia*; Malpighiaceae; triterpenoids; glochidone.

Plant—*Byrosonima verbascifolia* (L.) Rich. (Malpighiaceae), trivial name "murici", was collected near Brasilia, D.F., and identified by the botanists A. P. Duarte and C. T. Rizzini. *Bark.* The C_6H_6 extract (134 g *ex* 11 kg) was recrystallized from MeOH giving β-amyrin (120 g). The mother-liquor was evaporated and the residue (14 g) was chromatographed on silica. Elution with solvent of gradually increasing polarity gave fractions which, after crystallization from the indicated solvents, gave sitosterol (MeOH–$CHCl_3$, 165 mg), friedelin (MeOH–$CHCl_3$, 67 mg), 3-*O*-acetyloleanolic acid (EtOAc, 51 mg), β-amyrin (500 mg), β-amyrenone (MeOH–$CHCl_3$, 16 mg), 3-*O*-acetyllupeol (MeOH–$CHCl_3$, 220 mg) and glochidone (MeOH–$CHCl_3$, 65 mg). β-Amyrenone was identified by direct comparison with a sample prepared by oxidation of β-amyrin with Jones reagent. Glochidone was identified by direct comparison with an authentic sample *ex Glochidium* sp. (Euphorbiaceae) [1] kindly supplied by Prof. T. R. Govindachari.

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