Identification of the constituents relied upon direct comparison (m.m.p., IR, PMR, co-TLC) of IIIb and of IV resp. with (6*S*)-dihydromethysticin[3] and anibine;[2] and upon comparison of m.p. and UV spectra of IIIa and of IIIc with lit. data resp. of dihydrokawain[6,7] and tetrahydroiangonin.[6,7]

Tetrahydro-11-methoxyiangonin (IIId). White plates, m.p. 121–123° (C_6H_6). ν_{max} (cm^{-1}): 1708, 1694, 1623, 1526, 1412, 1389, 1370, 1281, 1252, 1230, 1220, 1154, 1134, 1040, 1028, 1002, 988, 830, 817, 645. λ_{max}^{EtOH} (nm): 231, 277, 284sh (τ 17 800, 3400, 2800). PMR ($CDCl_3$, τ) of IIIa,b,c,d: 4·88 (*s*, H-3), 5·40–5·90 (*m*, H-6), 6·33 (*s*, OCH_3), 7·15–7·35 (*m*, $ArCH_2$), 7·55–7·75 (*m*, two H-5), 7·80–8·25 (*m*, $ArCH_2CH_2$). Additional features of the PMR spectra of IIIa: 2·87 (*s*, five ArH). IIIb: 3·37 (*s*, three ArH), 4·14 (*s*, O_2CH_2). IIIc: 2·90 and 3·20 (approx. doublets, *J* 8 Hz, *AA'BB'* system), 6·23 (*s*, OCH_3). IIId: 3·30 (*s*, three ArH), 6·21 (*s*, OCH_3), 6·25 (*s*, OCH_3). MS. IIIa: M 232 (60%), *m/e* 91 (100%). IIIb: M 276 (97%), *m/e* 135 (70%). IIIc: M 262 (37%), *m/e* 121 (100%). IIId: 292 (45%), *m/e* 151 (100%). ORD (EtOH, *c* 1·0, 400–210 nm). IIIa: $[\phi]_{317}$ O, $[\phi]_{257}$ +9280, $[\phi]_{248}$ O, $[\phi]_{235}$ −20 880. IIIb: $[\phi]_{298}$ O, $[\phi]_{260}$ +12 420, $[\phi]_{249}$ O, $[\phi]_{232}$ −26 220. IIIc: $[\phi]_{315}$ O, $[\phi]_{257}$ +13 100, $[\phi]_{248}$ O, $[\phi]_{235}$ −26 200. IIId: $[\phi]_{305}$ O, $[\phi]_{262}$ +14 600, $[\phi]_{249}$ O, $[\phi]_{233}$ −39 420.

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FLAVONOIDS FROM AMAZONIAN LEGUMINOSAE*

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Key Word Index—*Aldina heterophylla*; *Crudia amazonica*; *Eperua bijuga*; *Andira parviflora*; *Diplotropis purpurea*; Leguminosae; flavonoids.

Plant. Aldina heterophylla Bth., trivial name 'macucú', tree, subfamily Leguminosae–Caesalpinioideae.[2] *Source.* Manaus, Brasil.

Trunk wood. The C_6H_6 extract was chromatographed on silica giving sitosterol, aliphatic ketones and esters, and as major crystalline constituent (+)-maackiain [(6*aS*,11*aS*)-3-hydroxy-8,9-methylenedioxypterocarpan], m.p. and lit.[3] m.p. 180–181°, besides much smaller quantities of (±)-maackiain, m.p. and lit.[3] m.p. 195–196°, and (±)-demethylhomopterocarpin (3-hydroxy-9-methoxypterocarpan), m.p. and lit.[4] m.p. 194–195°. MS, NMR, UV and IR spectral measurements corroborated the identifications.

Plant. Crudia amazonica Spr. ex Bth., tree, subfamily Leguminosae–Caesalpinioideae.[2] *Source.* Manaus, Brasil.

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Trunk wood. The EtOH extract was chromatographed on silica. The principal crystalline fraction was purified by sublimation giving apigenin (5,7,4′-trihydroxyflavone), m.p. 310°, triacetate, m.p. 183–185°, trimethylether, m.p. 155–157° [lit.[5] m.ps resp. 348–350°, 185–187°, 156–157°]. MS, NMR, UV and IR spectral measurements corroborated the identifications.

Plant. Eperua bijuga Mart. ex Bth., trivial name 'muirapiranga', tree, sub-family Leguminosae–Caesalpinioideae.[2] *Source.* Manaus, Brasil.

Leaves. The EtOH extract was fractionated into C_6H_6 soluble and C_6H_6 insoluble portions. Chromatography on silica of the soluble portion gave an alkane fraction, m.p. 68–70°, and friedelan-3α-ol, m.p. 304–306°, acetate m.p. 304–306° [lit.[6,7] m.ps respectively 302–304°, 315–316°]. Direct comparison with an authentic sample, kindly provided by Prof. E. Wenkert, Indiana University, Bloomington, U.S.A., confirmed the identification. Chromatography on silica of the insoluble portion, and crystallization of the main fraction from $CHCl_3$ gave tricin (5,7,4′-trihydroxy-3′,5′-dimethoxyflavone), m.p. 287–288°, triacetate, m.p. 249–250°, trimethyl ether, m.p. 191–193° [lit.[5] m.ps respectively 288–290°, 249–251°, 192–193°]. MS, NMR, UV and IR spectral measurements corroborated the identification.

Plant. Andira parviflora Ducke, trivial name 'angelim', tree, subfamily Leguminosae–Lotoideae.[2] *Source.* Manaus, Brasil.

Trunk wood. The C_6H_6 extract was chromatographed on silica giving cycloartenone, m.p. and lit.[8] m.p. 105–106°, cycloartenol, m.p. and lit.[8] m.p. 114–115°, biochanin-*A* (5,7-dihydroxy-4′-methoxyisoflavone), m.p. and lit.[9] m.p. 211–213° and (±)-5,7-dihydroxy-4′-methoxyisoflavanone, m.p. 167–169°. MS, PMR, UV and IR spectral measurements corroborated the identification of the former three compounds. The constitutional proposal for the fourth compound was based on the following evidence.

(±)-5,7-*Dihydroxy-4′-methoxyisoflavanone.* Determination of the MW (MS) and functional analysis led to the formula $C_{15}H_9O_2(OH)_2OMe$, suggestive of a diarylpropanoid skeleton. The PMR spectrum [in $(CD_3)_2CO$] defined its isoflavanone type (τ 5·55, *d*, *J* 6·3 Hz, two H-2; τ 6·02, *d*, *J* 6·3 Hz, H-3)[10] and indicated the presence of a hydroxyl at C-5 (τ −1·21, *s*, O$\underline{H}$ . . . O=C). The additional hydroxyl and the methoxyl (τ 6·28, *s*, [3H]) must be situated at C-4′ and at C-7. Indeed, ring *B* is *para* substituted (*AA′BB′* signal, τ 2·70–2·92 and 3·07–3·29) and ring *A* sustains hydrogens at C-6 and C-8 (τ 4·08, *s*, [2H]). Only the signals due to these two aromatic protons suffer paramagnetic shifts upon acetylation of the compound (τ 3·53 and 3·58, doublets, *J* 2·0 Hz), a fact which establishes the presence of the hydroxyl at C-7 and leaves C-4′ for the methoxyl. The ORD curve (close to base line), IR (ν_{max}^{KBr} 3375, 1640, 1253, 1166 cm^{-1}), UV (λ_{max}^{EtOH} 222, 294, 330 nm, ϵ 24 000, 14 300, 3200; $\lambda_{max}^{EtOH+NaOH}$ 231, 250 inf., 331, ϵ 22 900, 12 850, 24 600) and MS were in agreement with the proposed constitution. The retro-Diels–Alder cleavage of the molecular ion ($M^{+\cdot}$ 286) led to major fragments at 152 ($C_7H_4O_4^{+\cdot}$), 134 ($CH_2{=}CH.C_6H_4OMe^{+\cdot}$) and 119 ($CH_2{=}CH.C_6H_4O^+$) a.m.u.

Comments. According to a recent paper,[10] the natural occurrence of nine isoflavanones has been reported previously. These include padmakastein, a constituent of *Prunus puddum*[11]

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which shows the same oxygenation pattern as the novel isoflavanone here described. Padmakastein is 2,3-dihydroprunetin, and, indeed, prunetin (5,4′-dihydroxy-7-methoxyisoflavone) is found in the same plant.[12] This situation is paralleled in the present case. 5,7-Dihydroxy-4′-methoxyisoflavanone is 2,3-dihydrobiochanin-*A*, and co-occurs with biochanin-*A* in *Andira parviflora.*

Plant. Diplotropis purpurea (Rich.) Amsh., trivial name 'sapupira', tree, subfamily Leguminosae–Lotoideae.[2] *Source.* Manaus, Brasil.

Trunk wood. The C_6H_6 extract was chromatographed on silica giving sitosterol, stigmasterol, lupeol, (−)-maackiain [(6*aR*,11*aR*)-3-hydroxy-8,9-methylenedioxypterocarpan], m.p. and lit.[3] m.p. 178–179°, (2*R*)-7-hydroxyflavanone, m.p. and lit.[1] m.p. 190–191°, formononetin, m.p. and lit.[13] m.p. 260–261°, isoliquiritigenin (4,2′,4′-trihydroxychalcone), m.p. and lit.[14] m.p. 202–203°, liquiritigenin [(±)-7,4′-dihydroxyflavanone], m.p. and lit.[15] m.p. 206–207°.

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PHYSCION AND PHYTOSTEROL FROM THE ROOTS OF *CASSIA OCCIDENTALIS*

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Key Word Index—*Cassia occidentalis*; Leguminosae; physcion; phytosterol.

Plant. Cassia occidentalis L. *Uses.* Medicinal.[1] *Previous work.* Seeds,[2–6] Roots.[7]

Present work. Air dried *Cassia occidentalis* roots were powdered and extracted with light petrol. (60–80°) and benzene. The light petrol. extract was saponified with 5% alcoholic KOH. Non saponifiable matter (chromatographed over neutral alumina) yielded a mixture[6] of equal portions of sitosterol and campesterol.

The benzene extract (chromatographed over silica gel) yielded golden yellow needles, m.p. 204–206°, acetate m.p. 185–186°, methyl derivative m.p. 226–227°, demethylation yielded emodin, these studies along with IR and UV spectra showed it to be physcion, identity confirmed by m.m.p. and co-chromatography with an authentic sample of physcion.

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