C_6H_6–$CHCl_3$ (1:1) with the aid of a few ml of EtOH. Addition of 100 g of silica gel followed by evaporation of solvent gave a free-flowing powder which was placed on a column of 500 g of silicic acid and rechromatographed in the usual manner, 1 l. fractions being collected. The only solid material was found in fractions 91–93 ($CHCl_3$–MeOH 99:1). Recrystallization afforded 0·25 g of 5,4′-dihydroxy-3,7-dimethoxyflavone, m.p. 246–248° (lit 253–254°,[3] 246–247° [4]), NMR signals (DMSO-d_6) at 7·91 *d* and 6·90 *d* (*J* 9, A_2B_2 system of H-2′, H-3′, H-5′ and H-6′), 6·62 *d* and 6·27 *d* (*J* 2, *AB* system of H-6 and H-8), 3·82 and 3·78 (two methoxyls), UV λ_{max} 352·5 and 267 nm, with added NaOAc 355 and 268 nm, with added $AlCl_3$ 352·5, 305 and 277 nm, with added NaOEt 395 and 270 nm, with added NaOAc–H_3BO_3 350 and 267 nm. Direct comparison with an authentic sample of 5,4′-dihydroxy-3,7-dimethoxyflavone supplied by Prof. P. R. Jefferies established identity. Extraction of Barr No. 65-191 gave similar results.

The present report corroborates the findings of Higo *et al.*[1] that *A. eriocentra* yields no easily crystallizable homogeneous sesquiterpene lactone components. 5,4′-Dihydroxy-3,7-dimethoxyflavone has previously been isolated from an unnamed new *Beyeria* species,[3] from *Alpinia Kumatake*,[4] *A. japonica*,[5] *Eucryphia lucida*,[6] *Cistus ladanifera*,[7] *Cheilanthes farinosa*[8] and *Larrea cuneifolia*,[9] but not, to the best of our knowledge, from a Composite.

Acknowledgement—We wish to thank Professor P. R. Jefferies for an authentic specimen of 5,4′-dihydroxy-3,7-dimethoxyflavone. This work was supported in part by a grant from the United States Public Health Service (CA-13121).

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Phytochemistry, 1973, Vol. 12, pp. 1182 to 1184. Pergamon Press. Printed in England.

6-PHENYLETHYL-5,6-DIHYDRO-2-PYRONES FROM *ANIBA GIGANTIFOLIA**

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(*Received* 12 *December* 1972. *Accepted* 28 *December* 1972)

Key Word Index—*Aniba gigantifolia*; Lauraceae; anibine, substituted (6*S*)-phenylethyl-5,6-dihydro-2-pyrones.

Several *Aniba* species contain 4-methoxy-6-styryl-2-pyrones (I).[2] Metabolites of this type are accompanied in two *Piper* species by dihydro (II) and tetrahydro (III) deriva-

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* Part XXV in the series "The Chemistry of Brazilian Lauraceae". For Part XXIV see Ref. 1. Sponsored by Instituto Nacional de Pesquisas da Amazônia, Conselho Nacional de Pesquisas, Manaus.

† Multinational Program in Chemistry, Organization of American States, graduate fellow, 1971–1972.

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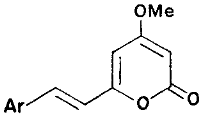
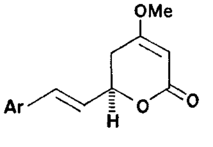
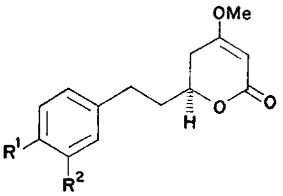
tives.[3,4] We wish to report on the occurrence, now also in an *Aniba* species, *A. gigantifolia* O. C. Schmidt*, of tetrahydroderivatives: the known dihydrokawain (IIIa), dihydromethysticin (IIIb)[3] and tetrahydroiangonin (IIIc)[4] and the new tetrahydro-11-methoxyiangonin (IIId). Additionally, anibine (IV), the pseudoalkaloid of *A. duckei* Kosterm., *A. rosaeodora* Ducke and *A. coto* (Rusby) Kosterm.[2] was also found to be present.



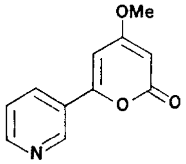
(I)



(II)



(IIIa) $R^1 = R^2 = H$
(IIIb) $R^1 = R^2 = OCH_2O$
(IIIc) $R^1 = OMe; R^2 = H$
(IIId) $R^1 = R^2 = OMe$



(IV)

The separation of type III compounds is notoriously difficult,[3,4] and only partial separation of the crude C_6H_6 or EtOH extracts into sitosterol, a mixture, IIId and IV, in order of increasing polarity, was achieved by silica column chromatography. The mixture was resolved by fractional crystallization from C_6H_6 which gave pure IIIb in the first crop. The residual material was fractionated by careful chromatography on an alumina column. Light petrol.–Et_2O eluted successively pure IIIa, pure IIIc and impure IIIb.

The structure of IIId was deduced from its PMR spectrum which was identical with the spectra of IIIa, IIIb and IIIc with the exception, of course, of the signals due to the protons and the substituents of the aromatic ring. The constitution of this ring was established through oxidation of IIId to veratric acid.

The absolute configuration of the *Piper* products IIIa and IIIb is known.[5] The ORD curve of a sample of IIIb ex *Piper methysticum* Forster, kindly supplied by Prof. R. Hänsel, Freie Universität Berlin, was superimposable on the analogous curves given by all type III constituents of *A. gigantifolia*. The same (6*S*)-configuration was consequently ascribed to all of them.

EXPERIMENTAL

Isolation of the constituents of Aniba gigantifolia. Powdered trunk wood (1·0 kg) was extracted successively with C_6H_6 and EtOH. The C_6H_6 extract (27·5 g), redissolved in a little C_6H_6, crystallized in the refrigerator. The crystals (IIIb, 4·5 g) were separated by filtration. The filtrate was evaporated and the residue was chromatographed on a column of Merck's Kieselgel 0·05–0·20 mm. C_6H_6 eluted sitosterol (100 mg), C_6H_6–AcOEt, 9:1 eluted a mixture (12 g), C_6H_6–AcOEt, 4:1 eluted IIId (6·5 g) and AcOEt–MeOH, 19:1 eluted IV (420 mg). The mixture was fractionally crystallized from C_6H_6 giving IIIb (9 g). The mother liquor was rechromatographed on a column of Merck's alumina G. Light petrol.–Et_2O 9:1 eluted IIIa (210 mg) and light petrol.–EtO_2, 4:1 eluted IIIc (150 mg). Other fractions contained mixtures of IIIa, IIIb and IIIc. The EtOH extract (21·8 g) was treated in the same way as the C_6H_6 extract. IIIb (680 mg) crystallized directly. Sitosterol (120 mg), IIIa + IIIc (380 mg), IIIb (730 mg), IIId (790 mg) and IV (1·5 g) were obtained by chromatographic techniques.

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* Herbarium specimen INPA (Manaus) 37397. The botanist W. Rodrigues, to whom we are indebted for the classification, reports that *A. gigantifolia* has previously only been located at the Tapajós river (Pará State, Brasil) and in Peru. Near Manaus, where our specimen was collected, occurs *A. hostmanniana* (Nees) Mez, which differs from *A. gigantifolia* only with respect to the pillosity of the ovary, a fact which makes distinction between the two species very difficult.

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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*, $OC\underline{H}_3$), 7·15–7·35 (*m*, $ArC\underline{H}_2$), 7·55–7·75 (*m*, two H-5), 7·80–8·25 (*m*, $ArCH_2C\underline{H}_2$). Additional features of the PMR spectra of IIIa: 2·87 (*s*, five $Ar\underline{H}$). IIIb: 3·37 (*s*, three $Ar\underline{H}$), 4·14 (*s*, $O_2C\underline{H}_2$). IIIc: 2·90 and 3·20 (approx. doublets, *J* 8 Hz, *AA'BB'* system), 6·23 (*s*, $OC\underline{H}_3$). IIId: 3·30 (*s*, three $Ar\underline{H}$), 6·21 (*s*, $OC\underline{H}_3$), 6·25 (*s*, $OC\underline{H}_3$). 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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Phytochemistry, 1973, Vol. 12, pp. 1184 to 1186. Pergamon Press. Printed in England.

FLAVONOIDS FROM AMAZONIAN LEGUMINOSAE*

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(*Received* 12 *December* 1972. *Accepted* 28 *December* 1972)

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.

* Part XXXIX in the series "The Chemistry of Brazilian Leguminosae". For part XXXVIII see Ref. 1.

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