$OC\underline{H}_3$). MS. M 312 (100%), *m/e* (%) 298 (33), 283 (5), 277 (10), 255 (3), 239 (4), 166 (19), 146 (19), 141 (7), 127 (10), 123 (6).

7-O-Glycosylcaviunin. White crystals, m.p. 190–192° (EtOH–H_2O, 4:1). λ_{max}^{EtOH} (nm): 267, 295 (ε 38 050, 23 050); no shift upon addition of NaOAc; $\lambda_{max}^{EtOH+AlCl_3}$ (nm): 278, 300, 390 (ε 38 050, 28 950, 6400). ν_{max}^{KBr} (cm^{-1}): 3452, 1660, 1627, 1591, 1526, 1492. MS. M 536 (2%), *m/e* (%) 374 (100), 359 (34), 356 (12), 345 (4), 344 (6), 343 (12), 341 (7), 330 (21), 192 (3), 191 (6), 183 (3), 149 (4), 145 (3), 144 (5). *Pentaacetate.* White crystals, m.p. 184–185° (purified by silica chromatography). ν_{max}^{KBr} (cm^{-1}): 1740, 1640, 1620, 1515. PMR ($CDCl_3$, τ): 2·18 (*s*, H-2), 2·93 (*s*, H-6′), 3·18 (*s*, H-8), 3·41 (*s*, H-3′), 4·30–4·50 (*m*, five H), 5·60–5·80 (*m*, two H), 6·06 (*s*, $OC\underline{H}_3$), 6·13 (*s*, $OC\underline{H}_3$), 6·16 (*s*, $OC\underline{H}_3$), 6·23 (*s*, $OC\underline{H}_3$), 7·55 (*s*, $OCOC\underline{H}_3$ at C-5), 7·84 (*s*, $OCOC\underline{H}_3$), 7·90 (*s*, three $OCOC\underline{H}_3$). *Hydrolysis.* 7-*O*-Glycosylcaviunin (25 mg), MeOH (2 ml) and 2 N HCl (15 ml) were heated under reflux (48 hr). The mixture was cooled and extracted with $CHCl_3$. The $CHCl_3$ was washed, dried and evaporated. The residue was recrystallized from MeOH, giving caviunin (5 mg).

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FLAVONOIDS FROM *POECILANTHE PARVIFLORA**

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Key Word Index—*Poecilanthe parviflora*; Leguminosae; flavanone; isoflavones; isoflavanone.

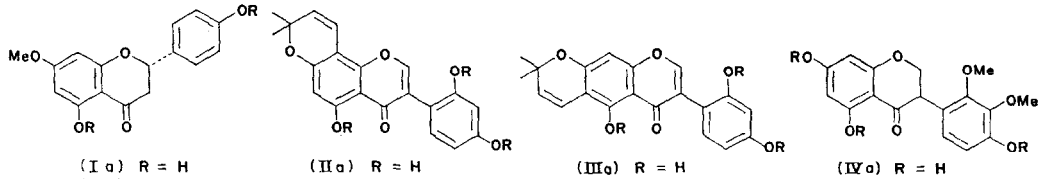
In central Brazil 'coração de negro' or 'pau-ferro' designate a number of species belonging to different families which, such as *Poecilanthe parviflora* Benth. (Leguminosae–Lotoideae), yield durable timber. In an attempt to isolate the antifungal principles, the trunk wood of *P. parviflora*, collected in the Linhares Reserve, near Vitória, Espirito Santo State, was examined and found to contain, besides nerolidol and (2*S*)-sakuranetin (Ia),[2] a colourless compound and a yelllw crystalline product which was apparently homogenous upon examination by TLC. Elementary, MS and functional analysis established the formula $C_{20}H_{13}O_3(OH)_3$ for this yellow compound. This and the UV spectrum were consistent with a feebly acidic (absence of 7-OH) 5-hydroxyisoflavone ($AlCl_3$-shift). While the PMR

* Part XLI in the series "The Chemistry of Brazilian Leguminosae". For Part XL see Ref. 1. Taken from part of the doctorate thesis presented by R. M. Viegas Assumpção to the Universidade de São Paulo.

[1] BRAZ FILHO, R., GOTTLIEB, O. R. and LEITE DE ALMEIDA, M. E. (1973) *Phytochemistry* **12**, 1187.

[2] VIEGAS ASSUMPÇÃO, R. M., KOPP SILVA, S. M. and GOTTLIEB, O. R. (1968) *An. Acad. Brasil. Ciênc.* **40**, 297.

spectrum clearly confirmed this assumption (τ 1·90, *s*, H-2)[3] and assigned the 5 additional carbons to a 6,6-dimethylpyrano group, it also proved that the product was a 1:1 mixture of two isomers. This was appreciated upon inspection of the signals due to three spin coupled protons at C-3′ (τ 3·54, *d*, *J* indet.), C-5′ (τ 3·60, *dd*, *J* 8·0 and 2·5 Hz) and C-6′, since not one but two *ortho* split doublets of close chemical shift (τ 2·90 and 2·92, *J* 8·0 Hz, rel. areas 1/2 H:1/2 H) represented H-6′. Alternative substitution patterns for ring B are excluded, due to the absence of *ortho* or *para* quinol systems. On the other hand, the two signals representing the lone aromatic protons of the *A*-rings had sufficiently differing chemical shifts, allowing to assign one to a proton at C-6 (τ 3·86, *s*, rel. area 1/2 H) for parvisoflavone-*A* (IIa) and at C-8 (τ 3·52, *s*, rel. area 1/2 H) for parvisoflavone-*B* (IIIa).



(I a) R = H
(I b) R = Ac

(II a) R = H
(II b) R = Ac
(II c) R = Me

(III a) R = H
(III b) R = Ac
(III c) R = Me

(IV a) R = H
(IV b) R = Me

All attempts to separate either the natural products (IIa + IIIa) or its acetylated derivatives (IIb + IIIb) into the separate constituents failed, but the fully methylated derivatives (IIc + IIIc) were easily resolved into IIc and IIIc. The analysis of the MS and PMR spectra of these trimethyl ethers fully confirmed the structural proposals. Indeed, the MS of both compounds are very similar. The molecular ions loose 31 m.u. (MeO·) as expected for 2′-methoxyisoflavones.[4] The loss of 15 m.u. (Me·) leads to the most abundant fragment ions which, in turn, generate ions of the correct mass due to cleavage of the heterocycle. Here, as in the case of the phenolic compounds, a distinction between the isomers was possible by PMR spectrometry, since the C-6 proton (τ 3·77, *s*) is considerably more shielded than the C-8 proton (τ 3·38, *s*), located at the *peri*-position with respect to the heterocycle.

Elementary, MS and functional analysis established the formula $C_{15}H_7O_2(OH)_3(OMe)_2$ for the colourless compound, parvisoflavone. Its PMR spectrum contained a multiplet (τ 5·3–5·9, 3 [H]) indicative of an isoflavone skeleton.[5] Indeed, dehydrogenation of parvisoflavone trimethyl ether by active MnO_2[6] led to an isoflavone, as ascertained by the presence of the typical H-2 singlet (τ 2·07),[3] in the PMR spectrum of the derivative.

The heterocycle of parvisoflavanone suffers a retro-Diels—Alder cleavage upon electron impact. The masses of the major fragments allocate two hydroxyls to ring *A* and one hydroxyl together with the two methoxyls to ring *B*. Clearly, ring *A* must possess the usual 5,7-dihydroxy substitution: one of its hydroxyls is relatively acidic (AcONa UV-shift), and the compound gives an $AlCl_3$ UV-shift; both its protons are *meta*-related to the carbonyl, giving rise to a PMR singlet at relatively high field [τ (d_6-acetone) 4·08]. That these protons are indeed also *meta*-related to each other was confirmed by the PMR spectrum in d_5-pyridine, where they are represented by two doublets (τ 3·68 and 3·75, *J* 2·2 Hz).

The comparison of the spectra in the two solvents showed, furthermore, that one of the

[3] JACKMAN, L. M. (1965) in *Progress in the Chemistry of Organic Natural Products* (ZECHMEISTER, L., ed.), Vol. XXIII, p. 315, Springer, Wien.
[4] CAMPBELL, R. V. M., HARPER, S. H. and KEMP, A. D. (1969) *J. Chem. Soc.* C, 1787.
[5] FARKAS, L., GOTTSEGEN, Á., NÓGRÁDI, M. and ANTUS, S. (1971) *J. Chem. Soc.* C, 1944.
[6] CROMBIE, L. and WHITTING, D. A. (1963) *J. Chem. Soc.* 1569.

two vicinal protons of ring *B* is *ortho*-related to the hydroxy. The original doublets of the PMR spectrum [τ (d_6-acetone) 3·21 and 3·44, J 8·6 Hz] collapsed to a singlet [τ (d_5-pyridine) 3·15], due to paramagnetic shifts of 0·29 ppm (typical of *ortho*-H) and 0·06 ppm (typical of *meta*-H).[7] These data are consistent only with 3′-hydroxy-2′,6′-dimethoxy, 6′-hydroxy-2′,3′-dimethoxy and 4′-hydroxy-2,3′-dimethoxy structures for ring *B*. The former two alternatives being improbable on biogenetic grounds, the constitution of 5,7,4′-trihydroxy-2′,3′-dimethoxyisoflavanone (IVa) is podoised for parvisoflavanone.

The mixture of parvisoflavones-*A* and -*B* was found to possess high fungistatic activity. At 260 ppm concentration and with reference to the control, growth of *Polyporus fumosus* Pers. ex Fries and of *Fomes connatus* (Weinm.) Gill. reached about 15%, and growth of *Lenzites trabea* Pers. ex Fries attained less than 5%. At the same concentration, the inhibitory activity of sakuranetin proved smaller. Growth of the same wood rotting fungi reached 70% of the control.

EXPERIMENTAL

Isolation of the constituents of Poecilanthe parviflora. (a) Ground trunk wood (5 kg) was extracted with benzene (Soxhlet). Partial concentration and cooling gave an oil (35 ml) which was submitted to vapour entrainment giving an essential oil (5 ml). This was analysed by GLC and found to contain 26% of *nerolidol*. The benzene solution was extracted with 5% aq. Na_2CO_3, washed (H_2O), dried and evaporated. The residue (9 g) was chromatographed on a silica column. Elution with $CHCl_3$ produced IIa + IIIa (200 mg). The Na_2CO_3-soln. was acidified and extracted with Et_2O. The residue (4 g) from the Et_2O was chromatographed on a silica column. Elution with C_6H_6–Me_2CO (4:1) gave IVa (60 mg). Elution with $CHCl_3$–acetone (1:1) gave an additional quantity of IIa + IIIa (100 mg). (b) Ground heart wood was extracted with EtOH. The solvent was evaporated. The residue was taken up in a small volume of EtOH filtered and evaporated. The residue was recrystallized repeatedly from EtOH giving Ia, m.p. 150–152° [lit.[8] m.p. 151–152°], $[\alpha]_D^{25°}$ −21° (c 1·85, EtOH) [(+)-sakuranetin: config. 2*R*],[9] UV spectrum as required.[9,10] *Diacetate* (Ib), m.p. 105–106° [lit.[8] m.p. 98–99°], IR spectrum as required.[11]

Parvisoflavones-A (IIa) + B (IIIa). Yellow crystals, m.p. 235–239° (Me_2CO–$CHCl_3$) (Found: C, 68·10; H, 4·55. $C_{20}H_{16}O_6$ requires: C, 68·18; H, 4·58%). ν_{max}^{KBr} (cm^{-1}): 3220, 1645, 1620, 1590, 1540, 1500. λ_{max}^{EtOH} (nm). 268, 306 (ϵ 46 950, 6300); no shift upon addition of NaOAc and of H_3BO_3 + NaOAc; $\lambda_{max}^{EtOH+NaOH}$ (nm). 275, 320; $\lambda_{max}^{EtOH+AlCl_3}$ (nm). 275, 285. PMR ($CDCl_3$, τ). 1·90 (*s*, H-2), 2·90 and 2·92 (two doublets, J 8·0 Hz; H-6′ of cmpds. *A* and *B*), 3·35 (*d*, J 10·2 Hz, H-4″), 3·54 (*d*, J indet., H-3′), 3·60 (*d*, J 8·0 and 2·5 Hz, H-5′), 3·52 (*s*, H-8 of cmpd. *B*), 3·86 (*s*, H-6 of cmpd. *A*), 4·34 (*d*, J 10·2 Hz, H-3″), 8·58 (*s*, two CH_3). MS. M 352 (10%), *m/e* (%) 351 (28), 340 (21), 337 (100), 319 (10), 276 (3), 261 (5), 204 (9), 203 (79), 169 (13), 135 (5). *Acetate* (IIb + IIIb), m.p. 178–185° (C_6H_6), ν_{max}^{KBr} (cm^{-1}). 1772, 1644, 1381, 1370, 1260, 1195, 1139, 1103, 1024, 909, 818, 800. *Methyl ether* (Me_2SO_4, K_2CO_3 in Me_2CO) was resolved by preparative TLC (SiO_2, C_6H_6–AcOEt, 1:1) into the slower moving IIc and the faster moving IIIc.

Tri-O-*methylparvisoflavone*-A (IIc). Colourless crystals, m.p. 166–168° (Found: C, 70·00; H, 5·59. $C_{23}H_{22}O_6$ requires: C, 70·04; H, 5·62%). ν_{max}^{KBr} (cm^{-1}). 1640, 1635, 1590, 1560, 1500. λ_{max}^{EtOH} (nm). 258, 263 (ϵ 35 900, 36 000). PMR ($CDCl_3$, τ). 2·25 (*s*, H-2), 2·75 (*d*, J 9·4 Hz, H-6′), 3·45 (*m*, H-3′, H-5′), 3·77 (*s*, H-6), 3·25 (*d*, J 10·6 Hz, H-4″), 4·40 (*d*, J 10·6 Hz, H-3″), 6·05 (*s*, $OC\underline{H}_3$), 6·12 (*s*, $OC\underline{H}_3$), 6·23 (*s*, $OC\underline{H}_3$), 8·50 (*s*, two $C\underline{H}_3$). MS. M 394 (67%), m/e (%) 379 (100), 363 (12), 217 (17).

Tri-O-*methylparvisoflavone*-B (IIIc). Colourless crystals, m.p. 149–151° (Found: C, 69·99; H, 5·59; $C_{23}H_{22}O_6$ requires: C, 70·04; H, 5·62%. ν_{max}^{KBr} (cm^{-1}). 1650, 1640, 1590, 1500. λ_{max}^{EtOH} (nm). 267 (ϵ 45 150). PMR ($CDCl_3$, τ). 2·26 (*s*, H-2), 2·73 (*d*, J 9·4 Hz, H-6′), 3·22 (*d*, J 10·6 Hz, H-4″), 3·38 (*s*, H-8), 3·43 (*m*, H-3′, H-5′), 4·28 (*d*, J 10·6 Hz, H-3″), 6·06 (*s*, $OC\underline{H}_3$), 6·10 (*s*, $OC\underline{H}_3$), 6·20 (*s*, $OC\underline{H}_3$), 8·48 (*s*, two $C\underline{H}_3$). MS. M 394 (80%), *m/e* (%) 379 (100), 363 (13), 217 (19).

[7] DEMARCO, P. V., FARKAS, E., DODDRELL, D., MYLARI, B. L. and WENKERT, E. (1968) *J. Am. Chem. Soc.* **90**, 5480.
[8] GOEL, R. N. and SESHADRI, T. R. (1959) *Tetrahedron* **5**, 91.
[9] ARAKAWA, H. and NAKAZAKI, M. (1960) *Ann. Chem.* **636**, 111.
[10] HOROWITZ, R. M. and JURD, L. (1961) *J. Org. Chem.* **26**, 2446.
[11] SADTLER STANDARD SPECTRA (1967) *Infared*, Vol. 20, No. 20844, Sadtler Res. Lab., Philadelphia.

Parvisoflavanone (IVa). Colourless prisms, m.p. 203–205° (MeOH) (Found: C, 61·39; H, 4·80. $C_{17}H_{16}O_7$ requires: C, 61·44; H, 4·85%). ν_{max}^{KBr} (cm^{-1}). 3335, 1641, 1589, 1506, 1472, 1451, 1311, 1292, 1252, 1165, 1024, 963, 955, 825, 812. λ_{max}^{MeOH} (nm). 287, 320 inf (ϵ 22 250, 3800), $\lambda_{max}^{MeOH+NaOH}$ (nm). 243, 322 ϵ 28 000, 46 000), $\lambda_{max}^{MeOH+NaOAc}$ (nm). 292, 323 (ϵ 22 200, 12 000), $\lambda_{max}^{MeOH+AlCl_3}$ (nm). 273 inf, 310 (ϵ 7500, 26 000). PMR [$(CD_3)_2CO$, τ]: 3·21 (*d*, *J* 8·6 Hz, H-6′), 3·44 (*d*, *J* 8·6 Hz, H-5′), 4·08 (*s*, H-6, H-8), 5·3–5·9 (*m*, CH_2CH), 6·20 (*s*, two OCH_3); (C_5D_5N, τ): 3·15 (*s*, H-5′, H-6′), 3·68 (*d*, *J* 2·2 Hz, H-6), 3·75 (*d*, *J* 2·2 Hz, H-8), 5·1–5·8 (*m*, CH_2CH), 6·00 (*s*, OCH_3), 6·08 (*s*, OCH_3). MS. M 332 (100%), *m/e* (%) 299 (4), 180 (40), 179 (9), 165 (44), 153 (61), 152 (25), 133 (58), 124 (11). ORD curve superimposable on base line.

Di-O-methylparvisoflavanone (IVb). IVa, methylated with Me_2SO_4, K_2CO_3 in acetone, gave colourless needles, m.p. 159–162° (MeOH). MPR ($CDCl_3$, τ). 3·22 (*d*, *J* 8·8 Hz, H-2′), 3·43 (*d*, *J* 8·8 Hz, H-3′), 3·95 (*s*, H-6, H-8), 5·3–5·9 (*m*, CH_2CH), ~ 6·2 (5 OCH_3). IVb (10 mg) and active MnO_2 (80 mg) were refluxed in acetone (3 ml, 3 hr). The mixture was filtered and the solvent evaporated. The residue was submitted to PMR spectrometry without purification [$(CD_3)_2CO$, τ]: 2·07 (*s*).

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ISOLEMENT DE DERIVES SECO-IRIDOIDES D'*ANTHOCLEISTA ZAMBESIACA*

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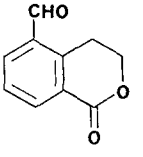
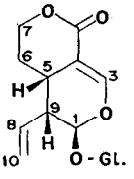
Key Word Index—*Anthocleista zambesiaca*; Loganiaceae; seco-iridoïde; erythrocentaurine; sweroside.

Plante. Anthocleista zambesiaca Baker, récoltée en 1971 au Rwanda (Forêt de Nyungwe). Herbier Bouxin No. 263 Bruxelles. *Usages.* Au Rwanda, pour combattre les accès fébriles et délirants; au Transvaal, comme antimalarique.[1] *Travaux précédents.* Isolement du swertiamaroside des feuilles d'*A. procera* Afzel.[2] L'érythrocentaurine[3] et le swéroside[4] ont été isolés de *Swertia japonica* Makino.

Les écorces séchées (1,5 kg) réduites en poudre sont épuisées au moyen de CH_3OH. Le résidu d'évaporation est repris par H_2O. La solution aqueuse est extraite par $CHCl_3$, puis par un mélange $CHCl_3$–isopropanol, 3:2. L'évaporation des solutions extractives fournit respectivement un résidu *A* (2,2 g) et un résidu *B* (2,8 g), qui par chromatographie préparative (épaisseur 1 mm) donnent I (300 mg) et II (1 g).



(I)



(II)

Erythrocentaurine (I). PF: 135–137°; λ_{max} nm (log ϵ): 223 (4,84) 290 (3,54); λ_{max} cm^{-1}

[1] WATT, J. M. et BREYER-BRANDWIJK, M. G. (1962) *Medicinal and Poisonous Plants of Southern and Eastern Africa*, 2nd Edn, p. 727, Livingstone, Edinburgh.
[2] KOCH, M. (1964–1965) Thèse, Série E—141, Fac. de Pharm. Univ. de Paris.
[3] KUBOTA, T. et TOMITA, Y. (1958) *Chem. Ind. (London)* 230.
[4] INOUYE, H., UEDA, S. et NAKAMURA, Y. (1966) *Tetrahedron Letters* 5229–5234.