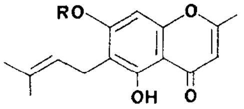
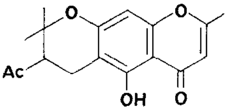
the MS of its mixture with osthol. The identity was proved by direct comparison with authentic material.



(1) R = H
(2) R = Me



(3)

Compound **3** is optically active $[\alpha]^{30}_{\lambda\,\mathrm{nm}}$ −34·1° (589), −31·6° (578), −34·1° (546), −49·4° (436) and −55·7° (405) (*c* 0·79) and has a molecular weight of 318 (from mass spectrum), $C_{17}H_{18}O_6$. Its UV-spectrum, especially the high intensity of the band at 258 nm characterizes it as a chromone derivative [5]. $\lambda^{\mathrm{MeOH}}_{(\mathrm{max})}$ 250 sh, 258, 268 sh, 294 nm, log ε 4·35, 4·33, 4·20, 3·95). In its IR spectrum two −C=O bands are present at 1750 and 1670 cm^{-1}. The latter is due to the conjugated chromone carbonyl group, the former can be attributed to an ester C=O group on the non-chromone part of the molecule. NMR ($CDCl_3$, TMS as internal reference δ ppm) 1·4 (6H, *s*, 2 Me at C-8), 2·1 (3H, *s*, MeCOO at C-7), 2·4 (3H, *s*, Me at C-2), 2·9 (2H, *m*, CH_2 at C-6), 5·2 (1H, *m*, CH at C-7), 6·05 (1H, *s*, CH= at C-3), 6·4 (1H, *s*, H at C-10) and 13·0 (1H, *s*, O–H . .O= at C-5). MS: M$^+$ (6%), 258 (22%), M-60), (100%, M-60-15). The parent alcohol hamaudol was isolated by Nitta [6] from roots of *Angelica japonica*. An ester described as hamaudol-7-*O*-acetate having a mp 127–128° was isolated from *Xanthogalum sachokianum* by Sokolova and Pimenov [7, 8] and its spectroscopic properties are comparable to those described above.

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ELLAGIC ACIDS FROM VOCHYSIACEAE*

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(*Received* 10 *September* 1974)

Key Word Index—*Erisma calcaratum*; *Salvertia convallariodora*; *Vochysia acuminata*; *V. tyrsoidea*; Vochysiaceae; ellagic acids.

The Vochysiaceae include only five south American genera, namely *Callisthene*, *Erisma*, *Qualea*, *Salvertia* and *Vochysia*. Ellagic acids were found in *E. calcaratum* (Link) Warm. (**1b**, **1c**), *S. convallariodora* St. Hil. (**1b**, **1d**, **1e**, **1f**), *V. acuminata* Bongard (**1a**, **1b**) and *V. tyrsoidea* Pohl (**1b**, **1d**). The last named species contains additionally physcion and 2,6-dimethoxy-1,4-benzoquinone. These and the ellagic acids of known natural occurrence **1a**, **1b**, **1d** were identified by comparison of their physical and spectral data with published data, preparation of derivatives and interconversions. 3,3′,4-Tri-*O*-methyl-4′-*O*-rutinosylellagic acid (**1c**) was hydrolyzed to rhamnose, glucose and **1b**. The PMR spectrum of its hexaacetate contained the characteristic signals of the hexa-*O*-acetylrutinosyl group [1]. A product, isolated in small amount, was shown by MS to be an *O*-methyl-*O*,*O*-methyli-

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* Part I in the proposed series "The Chemistry of Brazilian Vochysiaceae". Sponsored by Conselho Nacional de Pesquisas, Brasil.

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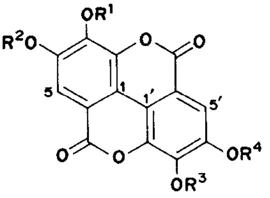
deneellagic acid, possibly **1e**, whose natural occurrence was reported previously without citation of data [2]. MS peaks of a less pure sample were consistent with the additional presence of di-*O*-methyl-*O*,*O*-methylidene- (**1f**), tri-*O*-methyl- (**1b**) and tetra-*O*-methylellagic acids (**1d**).



(**1a**) $R^1 = R^2 = R^3 = R^4 = H$
(**1b**) $R^1 = R^2 = R^3 = Me$, $R^4 = H$
(**1c**) $R^1 = R^2 = R^3 = Me$, $R^4 =$ rutinosyl
(**1d**) $R^1 = R^2 = R^3 = R^4 = Me$
(**1e**) $R^1 - R^2 = CH_2$, $R^3 = Me$, $R^4 = H$
(**1f**) $R^1 - R^2 = CH_2$, $R^3 = R^4 = Me$

EXPERIMENTAL

Isolation of the constituents of Erisma calcaratum. Collection site: Vicinity of Manaus, Amazonas. Identified by the botanist J. E. de Paula. A sample of ground trunk wood (1·3 kg) was extd. with C_6H_6. The extract (5 g) was chromatographed on a silica column, giving, by elution with the indicated solvent systems, the following products (after crystallization from the indicated solvents). C_6H_6: oil, C_6H_6–$CHCl_3$ 1:1: aliphatic alcohol (50 mg, EtOH), $CHCl_3$ and $CHCl_3$–MeOH 19:1: **1b** (350 mg, dioxane), $CHCl_3$–MeOH 1:1: **1c** (100 mg, dioxane).

Isolation of the constituents of Salvertia convallariodora. Collection site: Cipó Ridge, Minas Gerais. Identified by the botanist J. L. Pedersoli. A sample of trunk wood was separated into softwood and heartwood. Ground softwood (1·2 kg) was extd successively with C_6H_6 and EtOH. Silica column chromatography of the C_6H_6 extract (5 g) gave oil (500 mg), sitosterol (100 mg) and a triterpene (100 mg), and of the EtOH extract (11 g) gave aliphatic alcohol (200 mg). Ground heartwood (0·9 kg) was extd with C_6H_6. The extract (10 g) was chromatographed on silica giving upon elution with C_6H_6 aliphatic ester (2 g, EtOH), and with C_6H_6–$CHCl_3$ 1:1 **1e** (50 mg, dioxane). The dioxane soln contained **1e**, **1d**, **1b**, **1f**.

Isolation of the constituents of Vochysia acuminata. Collection site: Tijuca Forest, Guanabara. Identified by the botanist M. C. Vianna. A sample of ground branch wood (0·3 kg) was extd with C_6H_6. The extract (2 g) was chromatographed on a silica column giving upon elution with C_6H_6–$CHCl_3$ 3:2 oil, with C_6H_6–$CHCl_3$ 2:3 **1a** (10 mg, dioxane), and with $CHCl_3$ **1b** (100 mg, dioxane).

Isolation of the constituents of Vochysia tyrsoidea. Collection site: Serro region, Minas Gerais. Identified by the botanist A. Pereira Duarte. A sample of ground trunk wood (2·8 kg) was extd successively with C_6H_6 and EtOH. The C_6H_6 extract (25 g) was washed with light petrol. (b. 60–70°) at reflux temp. The light petrol. soluble (18 g) and insol (7 g) parts were separately chromatographed on silica columns giving, by elution with the indicated solvent systems, the following products (after crystallization from the indicated solvents). Sol part C_6H_6: oil (6 g), C_6H_6–$CHCl_3$ 1:1: physcion (7 mg, EtOH), C_6H_6–$CHCl_3$ 1:2: sitosterol (1·5 g, EtOH), $CHCl_3$: **1b** (10 mg, dioxane). Insol part C_6H_6–$CHCl_3$ 1:1: resin, C_6H_6–$CHCl_3$ 1:2: 2,6-dimethoxy-1,4-benzoquinone (5 mg, EtOH), **1d** (7 mg, subl). The EtOH extract (55 g) was resuspended in EtOH and filtered. The EtOH-soluble part (45 g) did not afford a pure cmpd. The EtOH-insoluble part (10 g) was chromatographed on a silica column giving with $CHCl_3$–MeOH 99:1 resin, with $CHCl_3$–MeOH 24:1 **1b** (24 mg, dioxane), with $CHCl_3$–MeOH 19:1 resin, with $CHCl_3$–MeOH 9:1 aliphatic alcohol (8 mg, EtOH).

2,6-*Dimethoxy*-1,4-*benzoquinone* was identified by direct comparison with an authentic sample [3]. 1,8-*Dihydroxy*-6-*methoxy*-3-*methylanthraquinone* (physcion) [4] was identified by direct comparison with an authentic sample obtained by partial demethylation of 1-hydroxy-6,8-dimethoxy-3-methylanthraquinone [5] with H_2SO_4 conc. *Ellagic acid* (**1a**) [6], 3,3′,4-*tri*-O-*methylellagic acid* (**1b**) [7] and 3,3′,4,4′-*tetra*-O-*methylellagic acid* (**1d**) [8] were identified by their mps. UV, IR, NMR and MS data which corresponded to the resp lit values. Methylation (Me_2SO_4, K_2CO_3, Me_2CO, reflux) of **1a** and **1b** gave **1d**. Demethylation (H_2SO_4 conc, 140°, 10 min) [7] of **1b** and **1d** gave **1a**. Acetylation of **1a** and **1b** gave the known corresp. acetates [7].

3,3′,4-*Tri*-O-*methyl*-4′-O-*rutinosylellagic acid* (**1c**), crystals, mp 260–263° (dioxane). (Found: C, 53·75; H, 5·10; $C_{29}H_{32}O_{17}$ requires: C, 53·38; H, 4·94%.) λ_{max}^{EtOH} (nm): 249, 287 inf., 350 inf., 368 (ϵ 54700, 14000, 14700, 16700); no NaOAc or $AlCl_3$ shift. ν_{max}^{KBr} (cm^{-1}): 3400, 1745, 1605, 1565, 1485, 1405, 1350, 1250, 1112, 1090,1070,980, 910, 758. MS: identical to MS of **1b**. *Hexaacetate* (**1c**, Ac_2O, C_6H_5N, room temp), colourless crystals, mp 137–139° (EtOH). ν_{max}^{KBr} (cm^{-1}): 1740, 1607, 1575, 1490, 1410, 1353, 1250, 1220, 1050, 990, 905, 750. PMR ($CDCl_3$, τ): 2·12 (*s*, ArH), 2·32 (*s*, ArH), 4·75 (*m*, glucose H-1,2,3,4; rhamnose H-2,3,4), 5·30 (*s*, rhamnose H-1), 5·82 (*s*, Me), 5·85 (*s*, Me), 5·99 (*s*, Me), 6·3 (*m*, glucose H-5 and CH_2, rhamnose H-5), 7·94 (*m*, 6 COMe), 8·85 (*d*, *J* 3·0 Hz, rhamnose Me). *Hydrolysis* [**1c** (40 mg), MeOH–aq conc HCl 9:1 (4 ml), reflux, 4h] gave **1b** (identified by direct comparison with natural **1b**), rhamnose and glucose (identified by PC and through their osazones).

3′-O-*Methyl*-3,4-O,O-*methylideneellagic acid* (**1e**), crystals, mp > 300° (dioxane), subl with dec (Found: M 328·0229. $C_{16}H_8O_8$ requires: M 328·0219). λ_{max}^{EtOH} (nm): 253, 372, 380 inf., 410 (ϵ 28800, 6200, 4900, 6900); $\lambda_{max}^{EtOH+NaOH}$ (nm): 290 inf., 310 (ϵ 9500, 6200); $\lambda_{max}^{EtOH+NaOAc}$ (nm): 256, 274, 315 inf., 410 (ϵ 24000, 19300, 6500, 7500). ν_{max}^{KBr} (cm^{-1}): 3450, 1755, 1613, 1585, 1528, 1493, 1478, 1350, 1275, 1213, 1158, 1100, 1013, 901, 760. MS (*m/e*): 329 (20%) M + 1, 328 (100%) M, 313 (40), 285 (20), 207 (19), 194 (45), 201 (15). Evap of the crystallization dioxane gave a solid, MS (*m/e*): 358 (20%) M (**1d**), 344 (11%) M (**1b**), 342 (15%) M (**1f**), 329 (20%) M + 1 (**1e**), 328 (100%) M (**1e**).

Acknowledgement—The MS were registered by Dr. A. Aragão Craveiro, by courtesy of Prof. E. Wenkert, Rice University, Houston, U.S.A.

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