Precipitate (11 g) was distributed on DCC using lower layer of $CHCl_3$–MeOH–H_2O (35:65:40) as a stationary phase and upper layer as a moving phase. Two new compounds were obtained as crystals. (2: 2.0 g, 3; 0.5 g). Sissotrin, irisolidone-7-*O*-glucoside and rutin were identified by the comparison of IR (KBr) and PMR spectrum with authentic samples. The gentiobioside was obtained as colourless prisms (MeOH–H_2O), mp 224–226°, $[\alpha]_D^{24}$ − 38.2° (C = 1.79 in MeOH–H_2O 4:1) Anal. Calcd. for $C_{28}H_{32}O_{15}$; C, 55.26; H, 5.26. Found: C, 55.15; H, 5.24 UV λ_{max}^{MeOH} nm (log ε); 262 (4.61), 324 (3.61), $\lambda_{max}^{MeOH+AlCl_3}$ nm 272, $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm 272, $\lambda_{max}^{MeOH+NaOAc}$ nm 262. PMR (d_5-Py); 3.70 (3H, *s*, —OMe), 4.20–4.00 (19H, *m*), 4.62 (1H, *d*, *J* = 10Hz), 4.84 (1H, *d*, *J* = 6), 6.66 (1H, *d*, *J* = 2, H-6), 6.94 (1H, *d*, *J* = 2, H-8), 6.98 (2H, *d*, *J* = 8, H-3′,5′), 7.56 (2H, *q*, *J* = 2,8,H-2′,6′), 8.06 (1H, *s*, H-2), 13.30 (1H, —OH). Permethyl ether was obtained as colourless needles, mp 78.5–80.5°. MS M^+ 720, *m/e* 423 (6.5%), 298 (13.9%), 219 (1.7%), 187 (100%). PMR (δ ppm in $CDCl_3$); 3.36, 3, 46, 3.48, 3.50 (2 × OMe), 3.68 (2 × OMe), 3.84, 3.96, 4.24 (1H, *d*, *J* = 8Hz), 4.96 (1H, *d*, *J* = 8), 6.44 (1H, *d*, *J* = 3), 6.73 (1H, *d*, *J* = 3), 6.92 (2H, *d*, *J* = 10), 7.47 (2H, *d*, *J* = 10), 7.76 (1H, *s*). The octa-acetate crystallized as needles, mp 253–255°, PMR (δ ppm in $CDCl_3$) 1.90, 1.96, 2.02 (2 × —OCOMe), 2.06 (3 × —OCOMe), 2.40 (Arom. —OCOMe), 3.82 (OMe), 4.28 (1H, *d*, *J* = 8Hz), 4.62 (1H, *d*, *J* = 8), 5.0–5.3 (12H, *m*), 6.66 (1H, *d*, *J* = 2) 6.92 (2H, *d*, *J* = 8), 7.08 (1H, *d*, *J* = 2), 7.44 (2H, *d*, *J* = 8), 7.98 (1H, *s*). The 7-xylosylglucoside was isolated as needles (MeOH–H_2O) mp 228–230°, $[\alpha]_D^{24}$ − 79.5° (*c* = 0.52 in MeOH–H_2O 4:1). Anal. Calcd. for $C_{27}H_{30}O_{14}\cdot H_2O$; C, 54.36 H, 5.41. Found; C, 54.15 H, 5.22 UV λ_{max}^{MeOH} nm (log ε) 263 (4.55), 324 (3.56) $\lambda_{max}^{MeOH+NaOAc}$ nm 263, $\lambda_{max}^{MeOH+AlCl_3}$ nm 272, $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm 273. PMR (δ ppm in d_5-pyridine) 3.72 (3H, *s*, —OMe), 4.40–4.10 (17H, *m*), 4.76 (1H, *d*, *J* = 7Hz), 4.90 (1H, *d*, *J* = 10), 6.79 (1H, *d*, *J* = 2, H-6), 7.02 (1H, *d*, *J* = 2, H-8), 7.04 (2H, *d*, *J* = 9, H-3′,5′), 7.60 (2H, *d*, *J* = 9, H-2′,6′), 8.10 (1H, *s*, H-2). Permethyl ether, needles mmp 154–156.5°. MS M^+ 676, *m/e* 379, 298, 175, 143. PMR (δ ppm in $CDCl_3$) 3.46, 3.48, 3.60 (2 × —OMe), 3.68 (2 × OMe), 3.84, 3.95, 4.22 (1H, *d*, *J* = 7), 4.87 (1H, *d*, *J* = 10), 4.94 (11H, *m*), 6.48 (1H, *d*, *J* = 2, H-6), 6.68 (1H, *d*, *J* = 2, H-8), 6.94 (2H, *d*, *J* = 8, H-3′5′), 7.50 (2H, *d*, *J* = 8, H-2′,6′), 7.80 (1H, *s*, H-2). Acetate was obtained as needles, mp 143–145°. PMR (δ ppm in $CDCl_3$) 1.92, 2.04 (3 × —OCOMe), 2.08 (2 × —OCOMe), 2.40 (Arom. —OCOMe), 3.84 (OMe), 4.56 (1H, *d*, *J* = 8Hz), 4.96 (1H. *d*, *J* = 7), 5.0–5.3 (11H, *m*), 6.64 (1H, *d*, *J* = 2), 6.94 (2H, *d*, *J* = 8), 7.00 (1H, *d*, *J* = 2), 7.44 (2H, *d*, *J* = 8), 7.94 (1H, *s*).

Acknowledgement—The authors thank Hôansha for grants.

REFERENCES

1. Szavo, V. (1958) *Chem. Abstr.* **52**, 16502.
2. Shibata, S. and Nishikawa, Y. (1963) *Chem. Pharm. Bull. (Tokyo)* **11**, 167.
3. Komatsu, M., Yokoe, I. and Shirataki, Y. (1976) *Yakugaku Zasshi* **96**, 254.
4. Banerji, A., Multi, V. V. S. and Seshadri, T. R. (1966) *Indian J. Chem.* **4**, 70.
5. Kubo, M. and Fujita, K. (1973) *Phytochemistry* **12**, 2547.
6. Stanev, St. (1962) *Chem. Abstr.* **56**, 6092.
7. Tanimura, T. Pisano, J. J., Ito, Y. and Bowman, R. L. (1970) *Science* **169**, 54.
8. Kawai, K., Akiyama, T., Ogihara, Y. and Shibata, S. (1974) *Phytochemistry* **13**, 2829.
9. Mabry, T. J. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*. Springer Verlag, New York.

Phytochemistry, 1977, Vol 16, pp 620–621 Pergamon Press Printed in England

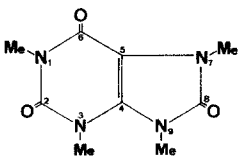
A NEW TETRAMETHYLURIC ACID FROM *COFFEA LIBERICA* AND *C. DEWEVREI*

JOSEF PETERMANN, THOMAS W. BAUMANN and HANS WANNER
Institut für Pflanzenbiologie der Universität, Zollikerstrasse 107, CH-8008 Zürich

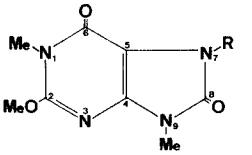
(*Received* 24 *September* 1976)

Key Word Index—*Coffea*; Rubiaceae; leaves, *O*(2),1,7,9-tetramethyluric acid.

In an earlier communication [1], we reported the presence of 1,3,7,9-tetramethyluric acid (**1**) and *O*(2),1,9-trimethyluric acid (**2**) in the genus *Coffea*. In a detailed study on the distribution of caffeine and these methylated uric acids during vegetative development of *C. liberica* [2], we noticed that, at a certain developmental stage of the plant, the leaves contain a third uric acid in concentrations mostly less than 0.1%. Based upon its transient occurrence which coincides with a decrease in concentration of (**1**) and an increase of (**2**), we supposed that it could be the metabolic intermediate and may have the structure of (**3**). The chromatographic comparison with an authentic sample of (**3**), which was synthesized earlier for proper identification of (**2**), confirmed our suggestion. We isolated the substance in pure form for identification from *C. liberica* Bull ex Hiern as well as from two varieties of *C.*



1



2 R = H **3** R = Me

dewevrei (*C. dewevrei* De Wild. et Durand var. *excelsa* Chev. and *C. dewevrei* De Wild. et Durand var. *aruwimiensis* (De Wild.) Chev.).

The dried and finely ground leaf material (portions of 1 g) was boiled in 125 ml 0.01 n H_2SO_4 (20 min), mixed with 13 g MgO, cooled and filtered through glass filter G4. The filtrate was extracted with $CHCl_3$ (100 ml × 3). Following evaporation of $CHCl_3$, the concentrate was chromatographed by preparative TLC on Si gel ($CHCl_3$–MeOH 9:1). The zone with R_f 0.52 was eluted with MeOH and rechromatographed. Crystallization from MeOH (and few drops of H_2O) yielded needles (mp 202°) with mass, UV and IR spectra [1] identicl to those of the authentic sample of 3 with mp 205° prepared by methylation of 7,9-dimethyluric acid [3,4]. Thermal rearrangement of both the natural and synthesized sample gave 1,3,7,9-tetramethyluric acid (1).

Acknowledgements—This work was supported by the Swiss National Science Foundation. We wish to thank Professor M. Hesse and Mr. A. Guggisberg for MS, mp determination and thermal rearrangement study.

REFERENCES

1. Wanner, H., Pešáková, M., Baumann, T. W., Charubala, R., Guggisberg, A., Hesse, M. and Schmid, H. (1975) *Phytochemistry* **14**, 747.
2. Baumann, T. W., Oechslin, M. and Wanner, H. (1976) *Biochem. Physiol. Pflanz.* **170**, 217.
3. Biltz, H. and Bülow, H (1921) *Ann. Chem.* **423**, 159.
4. Biltz, H. und Max, F. (1920) *Ber. Deut. Chem. Ges.* **53**, 2327.

Phytochemistry, 1977, Vol 16, pp. 621–622 Pergamon Press Printed in England.

CHONDROFOLINE FROM *UVARIA OVATA**

KRISANA PANICHPOL,† ROGER D. WAIGH‡ and PETER G. WATERMAN†

† Department of Pharmaceutical Chemistry, University of Strathclyde, Glasgow G1 1XW, Scotland
† Department of Pharmacy, University of Manchester, Manchester M13 9PL, England

(*Received* 30 *October* 1976)

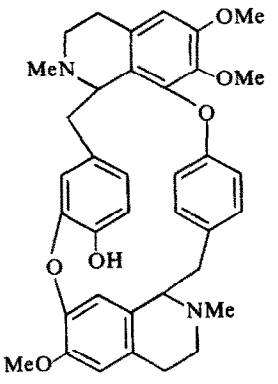
Key Word Index—*Uvaria ovata*; Annonaceae; chondrofoline; *bis*-1-benzyltetrahydroisoquinoline alkaloid.

Chondrofoline, a member of the rare group of 7,3‴–8′,4″-linked *bis*-benzylisoquinolines, has been found in *Uvaria ovata* (Annonaceae); it has previously been found only in *Chondrodendron platyphyllum* Miers (Menispermaceae) [1]. Alkaloids of this type have previously been isolated only from Menispermaceae and Lauraceae [2] and their discovery in another, closely allied, Ranalean family yet again illustrates the potential value of alkaloids in the systematics of the Ranales.

EXPERIMENTAL

Plant. Uvaria ovata A. DC; Voucher. Enti 1284, deposited at the herbarium of the Royal Botanic Garden, Edinburgh; Source. Achimota, Ghana.

Alkaloid isolation. Powdered leaf (650g) was extracted successively with petrol (40–60°), $CHCl_3$ and MeOH. Acid extraction of the $CHCl_3$ concn., basification of the acid extract with NH_3 and re-extraction into $CHCl_3$ gave a mixture of alkaloids. Col. chr. of the mixture over Al gave, on elution with $CHCl_3$–MeOH (99:1), a single alkaloid. Recrystallisation of the alkaloid from $CHCl_3$–Et_2O and finally Et_2O gave plates (97 mg) mp 136–140°. $[\alpha]_{546}^{20}$ − 257 (*c* 0.10 in 0.1 N HCl). Found, M^+ 608.2877; $C_{37}H_{40}N_2O_6$ requires 608.2886. UV λ_{max}^{EtOH} nm (log ε) 232 (4.57), 281 (3.97), undergoing a bathochromic shift on the addition of alkali. IR ν_{max} (KBr) cm^{-1} 3450 (OH). PMR ($CDCl_3$) δ 2.30 (3H, *s* N-Me), 2.58 (3H, *s* N-Me), 3.78 (3H, *s* OMe), 3.92 (6H, *s* 2 × OMe), 2.60–3.85 (14H, *m* CH_2 and CH), 6.00 (1H, *s* C-8′-H), 6.65–7.35 (9H, *m* Har). MS 608 (91), 607 (50), 487 (2), 312 (92), 311 (19), 299 (24), 298 (100), 266 (10), 204 (23), 192 (12), 190 (15), 176 (11.5), 174 (19), 161 (6.5), 159 (10), 146 (11), 145 (15). From UV, IR and PMR spectra and accurate mass measurement of the molecular ion, it appeared likely that the alkaloid was of the *bis*-1-benzyltetrahydroisoquinoline type, with one OH, 3 × OMe and 2 × NMe substituents. The significance of MS fragmentation patterns in the identification of *bis*-benzylisoquinoline alkaloids and the probable origin of the fragments observed have been thoroughly discussed [3]. The major ions, at *m/e* 312 ($C_{19}H_{22}NO_3$) and *m/e* 298 ($C_{18}H_{20}NO_3$), indicated that the two benzylisoquinoline moieties were linked head to tail. In addition, the relatively high abundance of an ion at *m/e* 204 ($C_{12}H_{14}NO_2$) suggested the presence of a 6,7-dimethoxyisoquinoline fragment, and the relatively low abundance of an ion corresponding to loss of Me from the other benzylisoquinoline subunit indicated MeO substitution in this isoquinoline unit rather than in the benzyl group attached to it. A detailed comparison of the complete MS with those of known head to tail linked *bis*-benzylisoquinolines [4] suggested that the alkaloid



1

* Part 3 in the series 'Chemical Studies on the Annonaceae'. For Part 2 see Panichpol, K., Waigh, R. D. and Waterman, P. G. (1976) *J. Pharm. Pharmacol.* **28**, 71p.