(380 mg) and 1,3,6,8-tetrahydroxyanthraquinone (32 mg). The intermediate fraction between versicolorin B and 1, 3, 6, 8-tetrahydroxyanthraquinone was subjected to TLC (0.25 mm Si gel; toluene–EtOAc, 4 : 1). The orange material at R_f 0.44 was eluted with CH_2Cl_2 and re-crystallized (Me_2CO) to give pure versicolorone (135 mg).

Versicolorone (**1**). Orange-red needles (Me_2CO), mp 210°. Found: C, 65.1; H, 4.2. $C_{20}H_{16}O_7$ requires: C, 65.2; H, 4.3%. UV λ_{max}^{EtOH} nm (log ϵ): 224 (4.38) 254 (4.07), 263 (4.14), 291 (4.39), 320 (3.92) and 454 (4.03); IR ν_{max}^{KBr} cm^{-1}: 3350, 2920, 1700, 1670, 1620, 1395, 1320, 1260, 1170 and 758; ^1H NMR (250 MHz, DMSO-d_6, TMS): δ 2.04 (2H, *m*, H-4′) 2.07 (3H, *s*, H-6′) 2.37 (2H, *m*, *H*-3′), 3.41 (2H, *m*, H-1′), 3.80 (1H, *m*, J = 7.3 Hz, H-2′), 6.65 (1H, *d*, J = 2.5 Hz, H-7), 7.17 (1H, *d*, J = 2.5 Hz, H-5), 7.88 (1H, *s*, H-4), 11.81 (1H, *s*(*br*), 6-OH), 12.33 (1H, *s*, 8-OH), 12.89 (1H, *s*, 1-OH); ^{13}C NMR (62.86 MHz, DMSO-d_6, TMS): δ 23.75 (*t*, ^1J = 126 Hz, C-3′), 30.37 (*q*, ^1J = 126 Hz, C-6′), 38.32 (*d*, ^1J = 125 Hz, C-2′), 42.06 (*t*, ^1J = 122 Hz, C-4′), 63.56 (*t*, ^1J = 140 Hz, C-1′), 108.70 (*dd*, ^1J = 161 Hz, ^3J = 4 Hz, C-7), 108.85 (*d*, ^3J = 4 Hz, C-13), 109.20 (*t*, ^3J = 5 Hz, C-12), 109.22 (*d*, ^1J = 166 Hz, C-4), 109.38 (*dd*, ^1J = 166 Hz, ^3J = 5 Hz, C-5), 122.50 (*s*(*br*), C-2), 132.88 (*d*, ^2J = 4 Hz, C-14), 135.27 (*d*, ^2J = 4 Hz, C-11), 162.90 (*t*, ^2J = 4.5 Hz, C-6), 164.81 (*d*, ^2J = 5.5 Hz, C-8), 165.55 (*s*, C-1), 181.73 (*t*, ^3J = 4.5 Hz, C-10), 189.35 (*s*, C-9), 210.18 (*s*, C-5′); MS (probe) 70 eV *m/z* (rel. int.): 368 $[M]^+$ (5), 325(2), 310(32), 297(6), 58(46) and 43(100); high resolution MS *m/z* 368.0900 ($C_{20}H_{16}O_7$ requires 368.0895), 325.0713 ($C_{18}H_{13}O_6$ requires 325.0710), 310.0478 ($C_{17}H_{10}O_6$ requires 310.0476), 297.0401 ($C_{16}H_9O_6$ requires 297.0398).

REFERENCES

1. Berger, Y. and Jadot, J. (1976) *Bull. Soc. Chim. Belg.* **85**, 271.
2. Berger, Y. and Jadot, J. (1975) *Bull. Soc. R. Sci. Liege* 157.
3. Berger Y., Jadot, J. and Ramaut, J. (11976) *Bull. Soc. Chim. Belg.* **85**, 161.
4. Berger, Y. (1980) *Phytochemistry* **19**, 2779.
5. Cox, R. H., Churchill, F., Cole, R. J. and Doner, J. W. (1977) *J. Am. Chem. Soc.* **99**, 3159.
6. Aucamp, P. S. and Holzapfel, C. W. (1970) *F. S. Afr. Chem. Inst.* **23**, 40.
7. Gorst-Allman, C. P., Pachler, K. G. R., Steyn, P. S. and Wessels, P. L. (1977) *J. Chem. Perkin Trans.* 1, 2181.
8. Steyn, P. S., Vleggaar, R., Wessel, P. L. and De Buys, S. (1979) *J. Chem. Soc. Perkin Trans.* 1, 460.

Phytochemistry, Vol. 21, No. 6, pp. 1451–1453, 1982.
Printed in Great Britain.

0031-9422/82/061451-03$03.00/0

ISOLATION AND CRYSTAL STRUCTURE OF 5-HYDROXY-2,8-DIMETHYL-6,7-DIMETHOXYBENZOPYRAN-4-ONE FROM *COUEPIA PARAENSIS*

RADHIKA SANDUJA*, KENNETH L. EULER*, MAKTOOB ALAM*, JAMES D. KORP† and IVAN BERNAL†

*Department of Medicinal Chemistry and Pharmacognosy; †Department of Chemistry, University of Houston, Houston, TX 77004, U.S.A.

(*Received* 2 *August* 1981)

Key Word Index—*Couepia paraensis*; Rosaceae; 5-hydroxy-2, 8-dimethyl-6, 7-dimethyloxychromone.

Abstract—A highly substituted chromone constituent of *Couepia paraensis* was isolated and identified as 5-hydroxy-2,8-dimethyl-6,7-dimethoxychromone by spectroscopic and X-ray crystallographic methods.

Couepia paraensis (M & Z) Benth. is a small tree belonging to the tribe Chrysobalanoideae of the Rosaceae. This plant has not previously been investigated for its chemical constituents. Members of the Chrysobalanoideae tribe have been reported to contain flavonoids and proanthocyanidins[1], and in this communication we wish to report the isolation and chemical characterization of a highly substituted chromone from *C. paraensis*.

The chloroform extract of *C. paraensis* upon column chromatography followed by prep. TLC gave a yellow crystalline compound (**1**), mp 125°, MW 250 (found: C, 62.36; H, 5.6; O, 31.98. $C_{13}H_{14}O_5$ requires: C, 62.5; H, 5.6; O, 31.9%). **1** gave a green color with $FeCl_3$, indicating the presence of one or more phenolic hydroxyl groups, which was also supported by the $AlCl_3$ induced bathochromic shifts in the UV spectra (λ_{max}^{MeOH} nm: 227, 264 and 330; $\lambda_{max}^{MeOH+AlCl_3}$ nm: 280 and 380). The IR spectrum (ν_{max}^{KBr} cm^{-1}: 3020, 2950, 1660 (>C=O), 1640 and 1575) indicated the presence of a γ-pyrone moiety in **1**[2]. The mass spectral fragmentation pattern of **1** [*m/z* (rel. int.) 250 $[M^+]$ (70), 235 $[M-CH_3]^+$ (94), 207 $[M-CH_3CO]^+$ (100), 192 $[M-C_3H_6O]^+$ (13); 164 $[M-C_4H_6O_2]^+$ (15), and 136 $[M-C_6H_{10}O_2]^+$ (44)] was characteristic of chromones and coumarins with methoxy groups at

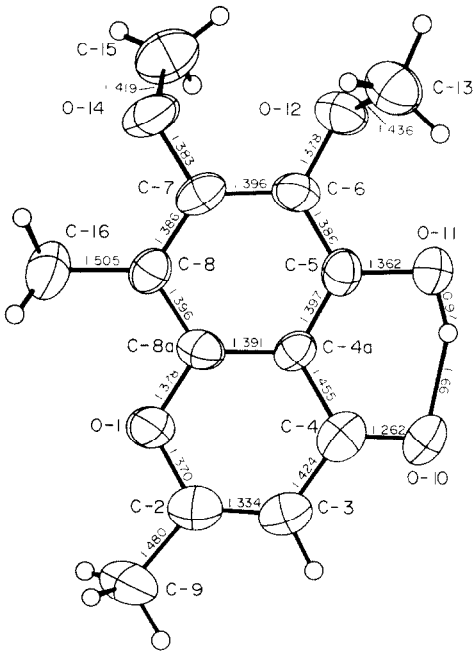

Fig. 1. Computer generated perspective drawing of 5-hydroxy-2, 8-dimethyl-6, 7-dimethoxybenzopyran-4-one.

C-6 and C-7 [3]. The spectral data alone did not allow unambiguous determination of the position of ring substituents, and so the X-ray structure was undertaken. **1** was then identified as 5-hydroxy-2,8-dimethyl-6,7-dimethoxybenzopyran-4-one. The ^{1}H-NMR spectrum of **1** [δ 2.20 (3H, *s*, H-16); 2.37 (3H, *s*, H-9), 3.90 (3H, *s*, H-15), 3.96 (3H, *s*, H-13), 6.1 (1H, *s*, H-3), and 12.65 (1H, *s*, H-11)] indicates the presence of one methyl group, two methoxy groups and a hydrogen-bonded hydroxy group (δ 12.65) on ring A of a chromone molecule. The remaining methyl group assigned to the C-2 position on the basis of biogenic considerations and the vinylic proton (δ 6.1). This structure was also supported by the ^{1}H-NMR spectrum of the hydrogenation product $[MSM]^+$ (252) of **1** [δ 1.55 (3H, *d*, J = 6.2 Hz, H-9), 2.13 (3H, *s*, H-16), 2.59 (2H, ABX, J = 6 Hz and 2.5 Hz, H-3)[4], 3.83 (3H, *s*, H-15), 3.9 (3H, *s*, H-13), 4.20 (1H, *m*, H-2) and 11.91 (1H, *s*, H-11)]. Figure 1 shows a computer-generated perspective drawing of **1**. The bond distances shown are all well within the ranges expected for the atoms and hybridization states involved [6].

There is an intramolecular hydrogen bond between the keto- and hydroxy-oxygens, and this explains why bond C-4–O-10 appears to be slightly elongated. The O · · · O separation is 2.56 Å, and the H-11 · · · O-10 distance is 1.66 Å, making this a reasonably strong bond. As would be expected, the benzopyranone moiety is quite flat, with only a 3° bend between the planes of the two six-membered rings. Atom O-1 shows the greatest deviation from the plane. The methoxy carbons, C-13 and C-15, are both bent out of the mean plane of the ring system, in opposite directions as necessitated by steric considerations. The torsion angles involved are C-7–C-6–O-12–C-13 (111°) and C-6–C-7–O-14–C-15 (58°), although it is unclear why they are so different in magnitude. Details of the molecular parameters are deposited at the Cambridge crystallographic centre.

EXPERIMENTAL

Mp was uncorr. The ^{1}H NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard. Chemical shifts are expressed in δ ppm. The EIMS (direct probe) was recorded on a HP 5930A GC–MS spectrometer equipped with a HP 5933 data system and operating at 70 eV.

For the X-ray analysis, a single crystal was mounted on an Enraf-Nonius CAD4 automatic diffractometer using Mo Kα-radiation, and 1985 unique reflections were collected out to 50° in 2θ. The space group is monoclinic, $C2/c$, with a = 11.091(8), b = 11.757(8), c = 19.358(9) Å, β = 104.22(5)° and Z = 8 molecules/cell. The structure was solved by MULTAN [5], which showed all of the non-hydrogen atoms in the initial E map. All hydrogens were found in subsequent difference Fourier syntheses and were allowed to vary independently. Full-matrix least squares refinement, with anisotropic thermal parameters for the non-hydrogens and isotropic for hydrogens, led to the final agreement factors of R = 0.038 and R_w = 0.033, where the weights used were $[\sigma(|F|)]^{-2}$. The atom labeling scheme is shown in Fig. 1.

Isolation and purification. The plant material used in this study was collected and dried in Brazil in 1971 by the Instituto Nacional de Pesquisas de Amazonia, Manaus, Brazil. Dried and coarsely powdered plant material (42 g) was exhaustively extracted with EtOH. The EtOH was removed under reduced pressure, and the residue (10.9 g) was extracted with hexanes to remove lipids. The hexane insoluble residue (10.5 g) was extracted with chloroform followed by EtOH. The residue (3.1 g) from the chloroform extract was chromatographed on a Si gel 60 (230–400 mesh, E. Merck) column (2.5 × 100 cm) which was eluted with a linear gradient of ethyl acetate (0–20%) in benzene. Fractions 27–31 (10 ml each) were combined and evaporated to dryness. The residue (950 mg) was applied to three Si gel prep. TLC plates (1 mm thick) which were developed in benzene–ethyl acetate (4:1). The bands were located by UV and the absorbent after scraping was eluted with benzene–ethyl acetate (1:1) to yield a yellow crystalline (**1**) (0.41 g).

Hydrogenation of 1. 5.2 mg of 1 was dissolved in 20 ml of ethyl acetate and 10 mg 10% Pd-charcoal was added. The hydrogenation was carried out at room temp. and 1 atm pressure for 8 hr. After hydrogenation the reaction mixture was processed by the standard method.

Acknowledgements—This research was supported by grants (E-594 to I.B. and E-745 to M.A.) from the Robert A. Welch Foundation, Houston, Texas. I.B. thanks the U.S. National Science Foundation for providing funds used in the purchase of the X-ray diffractometer. The authors wish to thank Dr. N. M. Ferguson and Dr. D. Batista (Director, Instituto Nacional de Pesquisas de Amazonia, Manaus, Brazil) for providing the plant material used in this study, and Mrs. Cathy Meier for her assistance in preparing this manuscript.

REFERENCES

1. Hegnauer, R. (1963) *Chemotaxonomie der Pflanzen*, Vol. VI, p. 92. Birkhäuser, Basel.
2. Nakanishi, K. and Solomon, P. H. (1977) *Infrared Absorption Spectroscopy*, p. 47. Holden-Day, San Francisco.

3. Budzikiewicz, H., Djerassi, C. and Williams, D. H. (1964). *Structure Elucidation of Natural Products by Mass Spectrometry* Vol. II, pp. 254–261. Holden-Day, San Francisco.
4. Abraham, R. J. and Loftus, P. (1979) *Proton and Carbon-13 NMR Spectroscopy*, p. 79. Heyden & Son, Philadelphia.
5. Germain, G., Main, P. and Woolfson, N. M. (1971) *Acta Cryst.* **A27**, 368.
6. Pauling, L. (1960) *The Nature of the Chemical Bond*, 3rd edn. Cornell University Press, Ithaca, N.Y.

Phytochemistry, Vol. 21, No. 6, pp. 1453–1454, 1982.
Printed in Great Britain.

0031-9422/82/061453-02$03.00/0

A PHLOROGLUCINOL DERIVATIVE OF *DRYOPTERIS ABBREVIATA*

MAKSUT COŞKUN,† AKIYO SAKUSHIMA, SANSEI NISHIBE, SUEO HISADA and NEVIN TANKER*

Faculty of Pharmaceutical Science, Higashi Nippon Gakuen University, Ishikari-Tobetsu, Hokkaido, 061-02, Japan; *Department of Pharmaceutical Botany, Faculty of Pharmacy, University of Ankara, Ankara, Turkey

(*Received* 29 *September* 1981)

Key Word Index—*Dryopteris abbreviata*; Aspidiaceae; fern; methylene-bis-methylphlorobutyrophenone; abbreviatin BB.

Abstract—A new phloroglucinol derivative, abbreviatin BB, has been isolated from *Dryopteris abbreviata*. Its structure was elucidated to be methylene-bis-methylphlorobutyrophenone on the basis of spectroscopic data.

Dryopteris abbreviata (DC.) Newman is a diploid species which grows locally in Europe and Turkey. It is a member of the *D. filix-mas* complex. These ferns contain variable amounts of filixic acid, large amounts of flavaspidic acid, and small amounts of *para*-aspidin[1, 2]. Widén *et al.*[3] examined the rhizomes of this species from Scotland and Italy and reported the occurrence of flavaspidic acid and filixic acid. In addition, Tanker and Coşkun[2] detected the presence of *para*-aspidin and some unknown compounds in the rhizomes of *D. abbreviata* collected from Turkey.

This paper deals with the isolation of a new phloroglucinol derivative lacking the filicinic acid ring, designated abbreviatin BB(**1**), from rhizomes of *D. abbreviata* of Turkish origin.

The HPLC chromatogram[4] of the crude filicin obtained by the magnesium oxide method[5] is shown in Fig. 1, indicating that this material also contains much flavaspidic acid and filixic acid, and a small quantity of **1**. After removal of flavaspidic acid AB, the Et_2O solution of crude filicin was subjected to CC on Si gel with a cyclohexane–tetrahydrofuran(THF) gradient to yield **1**. **1** was re-crystallized from chloroform to give pale-yellow needles, mp 200–202°. (Found: $[M]^+$ at m/z 432.1786; $C_{23}H_{28}O_8$ requires: 432.1783.)

The IR spectrum showed absorption bands at 3500 (OH), 2950 (CH), 1610 (C=O), 1570 (C=C), 1480, 1160

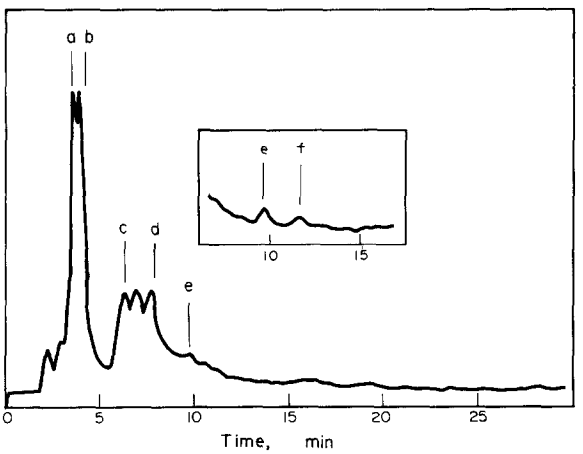

Fig. 1. HPLC chromatogram of the crude filicin. (a), Flavaspidic acid AB; (b), flavaspidic acid PB; (c), filixic acid ABA; (d), filixic acid ABB; (e), filixic acid BBB; (f), abbreviatin BB.

†Present address: Department of Pharmaceutical Botany, Faculty of Pharmacy, University of Ankara, Ankara, Turkey.