rinsed with Me_2CO to dissolve the exudate material and the soln evapd to dryness. Fronds of *N. dealbata* (12.5 g) yielded 0.596 g of crude extract (4% dry wt); fronds of *N. limitanea* (4.67 g) yielded 0.158 g of crude extract (3.4% dry wt). This material was crystallized ×3 from MeOH, then twice from C_6H_6. In both cases the major component of the farina was obtained as colourless fine needles, mp 148–149° (*N. dealbata*, *ca* 250 mg) and 149–150° (*N. limitanea*, *ca* 100 mg), respectively. The solvent used for TLC on polyamide DC-11 was toluene–petrol (100–140°)–MeCOEt–MeOH, 12:6:2:1 (corresponding to E.W.'s former standard solvent 60:26:7:7 [7]. C_6H_6 has been replaced by toluene, which in some solvent mixtures requires slight alterations in proportions). The plates were viewed in UV light before and after spraying with 'Naturstoff-reagenz A' (β-aminoethyl ester of diphenyl boric acid). MS were measured at 70 eV at the Institute of Organic Chemistry of the TH Darmstadt. ^1H NMR spectra were recorded in MeOH-d_4 at 100 MHz at the Université Cl. Bernard Lyon I.

Acknowledgements—E.W. is most greateful to Dr. David Seigler (Urbana, Ill.) for supplying the fern material. Thanks are due also to M. Fischer (Darmstadt) for MS and to M. Pétiaud (Lyon) for ^1H NMR.

REFERENCES

1. Tryon, R. (1956) *Contrib. Gray Herb. Harv. Univ.* **179**, 1.
2. Wollenweber, E. (1978) *Am. Fern. J.* **68**, 13.
3. Wollenweber, E. (1976) *Ber. Dtsch. Bot. Ges.* **89**, 243.
4. Letcher, R. M., Nhamo, L. R. M. and Gumiro, I. T. (1972) *J. Chem. Soc.* 206.
5. Devon, T. K. and Scott, A. I. (1975) *Handbook of Naturally Occurring Compounds*, Vol. I. Acacemic Press, New York.
6. Wollenweber, E., Favre-Bonvin, J. and Jay, M. (1978) *Z. Naturforsch. Teil C* **33**, 831.
7. Wollenweber, E. (1976) *Phytochemistry* **15**, 438.

NOTE ADDED IN PROOF

Three further bibenzyls had been described previously: 3-OMe-bibenzyl from *Radula complanata* (see Asakawa, Y., Kusube, E., Takemoto, T. and Suire, C. (1978) *Phytochemistry* **17**, 2115), 3,4,5,3′,4′,5′-hexaOMe-bibenzyl (brittonin A) from *Frullania brittoniae* subsp. *truncatifolia* (Asakawa, Y., Tanikawa, K. and Aratoni, T. (1976) *Phytochemistry* **15**, 1057) (both liverworts), and 3,3′-diOH-5-OMe-bibenzyl from yam bulbils, *Dioscorea batatas* (Hashimoto, T. and Hasegawa, H. (1974) *Phytochemistry* **13**, 2849).

Phytochemistry, 1979, Vol. 18, pp. 1244–1245. © Pergamon Press Ltd. Printed in England. 0031-9422/79/0701-1244 $02.00/0

8-HYDROXYCAPILLARIN—EIN NEUES ISOCUMARIN AUS *ARTEMISIA DRACUNCULUS*

HARALD GREGER und FERDINAND BOHLMANN*

Institut für Botanik der Universität Wien, A-1030 Wien, Rennweg 14, Austria und *Institut für Organische Chemie der Technischen Universität Berlin, D-1000 Berlin 12, Straße des 17. Juni 135, W. Germany

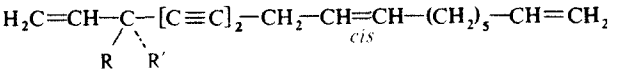
(*Eingegangen am* 7 *November* 1978)

Key Word Index—*Artemisia dracunculus*; Compositae; Anthemideae; root acetylenes; 8-hydroxycapillarin.

Im Rahmen vergleichender Untersuchungen über aromatische Polyine und Dehydrofalcarinon-Derivate in der *Artemisia dracunculus*-Gruppe wurden die Wurzel-Acetylene einer decaploiden Gartenherkunft von *Artemisia dracunculus* L. isoliert und aufgeklärt. Neben Dehydrofalcarinon (**1**) und Dehydrofalcarinol (**2**) wurde hier in Übereinstimmung mit früheren Befunden [1] Capillen (**3**) und in hoher Konzentration Capillarin (**4**) festgestellt. Außerdem wurde ein Derivat des Capillarins isoliert, das bisher noch nicht bekannt war.

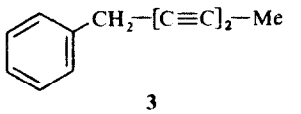
Die massenspektroskopisch ermittelte Summenformel $C_{13}H_{10}O_3$ deutet bereits an, daß die Verbindung eine zusätzliche OH-Gruppe besitzt. Entsprechend erkennt man im ^1H-NMR-Spektrum ein tiefliegendes Singulett bei 10.03 für eine wasserstoffbrückengebundene OH-Gruppe, die demnach nur an C-8 stehen kann. Die Aromatensignale zeigen, daß die Verbindung drei vicinale Wasserstoffe besitzt [*dd* 6.88 (J = 7.5, 1.0), *dd* 7.59 (J = 8, 7.5), *dd* 6.95 (J = 8, 0.7)]. Die gegenüber Capillarin unveränderten Signale der Seitenkette zeigen, daß nur die Konstitution (**5**) für den neuen Naturstoff in Betracht kommt.

Im Gegensatz zu einer kürzlich untersuchten, octoploiden *A. dracunculus* aus Taschkent [2] konnten hier keine Buten-(1)-yl-isocumarine nachgewiesen werden.

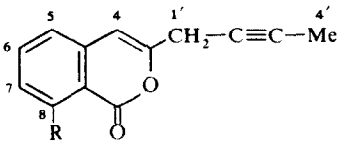


1 R, R′ = O

2 R = OH, R′ = H



3



4 R = H
5 R = OH

EXPERIMENTELLES

A. dracunculus (AR-913) wurde aus Achänen vom Botanischen Garten Krefeld (BRD) im Botanischen Garten der Universität Wien angezogen. Davon extrahierte man 150 g frische, zerkleinerte Wurzeln 2 Tage bei Zimmertemperatur mit Ether–Petrol (1:2). Der Extrakt wurde zunächst grob durch SC (Si gel, Akt. St. 2–3) und dann durch DC (Si gel, GF_{254}) getrennt. Als Laufmittel dienten Ether–Petrol (60–80°)-Gemische.

8-Hydroxycapillarin (**5**). Farblose Kristalle aus Ether, Schmp. 158°. IR ($CHCl_3$, Beckman IR 9) cm^{-1}: OH 3600–2700; C=O 1690; C=COR 1650; Aromat 1610, 1570. UV $\lambda_{max}^{Et_2O}$ nm: 338, 257, 235. MS (Varian MAT 711, 70 eV, Direkteinlaß): M^+ *m/e* 214.063 (100%) (ber. für $C_{13}H_{10}O_3$ 214.06); $-{}^{\cdot}Me$ 199 (5); $-CO$ 186 (11); $-{}^{\cdot}CHO$ 185 (7); $-{}^{\cdot}CH_2C{\equiv}CMe$ 161 (51); 161 $-CO$ 133 (11); 133 $-CO$ 105 (81). ^1H-NMR (Bruker WH 270, TMS als innerer Standard, $CDCl_3$): *t* 6.62 (4-H, *J* = 1); *dd* 6.95 (5-H, *J* = 8, 0.7); *dd* 7.59 (6-H, *J* = 8, 7.5); *dd* 6.88 (7-H, *J* = 7.5), 1.0); *dq* 3.45 (1′-H, *J* = 2.5, 1); *t* 1.91 (4′-H, *J* = 2.5); *s* 10.03 (OH).

Der Herbarbeleg wurde im Herbarium des Instituts für Botanik der Universität Wien (WU) hinterlegt.

Anerkennung—Wir danken Herrn P. Ambros vom Institut für Botanik der Universität Wien für die Ermittlung der Chromosomenzahlen.

LITERATUR

1. Bohlmann, F. und Kleine, K.-M. (1962) *Chem. Ber.* **95**, 39.
2. Greger, H., Bohlmann, F. und Zdero, C. (1977) *Phytochemistry* **16**, 795.

Phytochemistry, 1979, Vol. 18, p. 1245. © Pergamon Press Ltd. Printed in England. 0031-9422/79/0701-1245 $02.00/0

A NEW FLAVONE FROM *TERMINALIA ARJUNA* FRUITS

ASHISH NAGAR, V. K. GUJRAL and S. R. GUPTA
Department of Chemistry, University of Delhi, Delhi-110007, India

(*Revised received* 1 *February* 1979)

Key Word Index—*Terminalia arjuna*; Combretaceae; 5,7,2′,4′-tetramethoxy flavone.

Earlier work [1] on the fruits of *Terminalia arjuna* W & A led to the isolation of sitosterol, arjunic acid, mannitol and tannins. A re-investigation of the fruits of *T. arjuna* has now yielded a new flavone from the ether-soluble portion of the alcohol extract of *T. arjuna* fruits.

Its colour reactions and UV data indicated it to be a flavone lacking free hydroxyl groups. Its NMR spectrum in $CDCl_3$ showed the presence of four methoxyl groups, in addition to other expected signals. On degradation with alcoholic KOH, it gave 2,4-dimethoxybenzoic acid and 2,4-di-*O*-methylphloroacetophenone along with a small amount of the corresponding diketone, 2,4-dimethoxy-benzoyl-(2-hydroxy-4,6-dimethoxybenzoyl)-methane indicating the structure as 5,7,2′,4′-tetramethoxy flavone. This was confirmed by its synthesis using the Baker–Venkataraman method.

EXPERIMENTAL

Extraction and isolation. Air-dried *T. arjuna* fruits (5 kg) were successively extracted with hot petrol and EtOH. The EtOH extract was partitioned between Et_2O-soluble and Et_2O-insoluble portions. Et_2O-soluble portion on column chromatography and subsequent PLC yielded the new flavone.

5,7,2′,4′-Tetramethoxy flavone crystallized as needles from alcohol (20 mg), mp 179–80°. R_f: 0.29 (TEF, 5:4:1); 0.25 (C_6H_6–MeCOMe, 8:2). (Found: C, 66.8; H, 5.4. $C_{19}H_{18}O_6$ requires: C, 66.7; H, 5.3%). λ_{max}^{MeOH} nm log (ε): 245 (4.34), 340 (4.51); ν_{max}^{KBr} cm^{-1}: 1630, 1425, 1340, 1280. NMR ($CDCl_3$): δ 3.88 (3H, *s*,—OMe), 3.91 (3H, *s*,—OMe), 3.94 (3H, *s*,—OMe), 3.97 (3H, *s*,—OMe), 6.36 (1H, *d*, *J* = 2.5 Hz, C-6 proton), 6.5 (1H, *s*, C-8 proton), 6.6 (2H, *q*, C-3′, 5′ protons), 6.95 (1H, *s*, C-3 proton), 7.82 (1H, *d*, *J* = 9.5 Hz, C-6′ proton).

Synthesis. A mixture of 2,4-di-*O*-methylphloroacetophenone (2 g), 2,4-dimethoxybenzoyl chloride (2.5 g) and C_5H_5N (20 ml) was heated at 100° for 3 hr. The resulting ester was purified by column chromatography and crystallized from EtOH (1.5 g), mp 89–90°. (Found: C, 63.6; H, 6.0. $C_{19}H_{20}O_7$ requires: C, 63.3; H, 5.6%). ν_{max}^{KBr} cm^{-1}: 1730, 1630, 1600, 1450 and 1410. 2-(2,4-Dimethoxybenzoyloxy)-4,6-dimethoxy acetophenone (1 g) in dry C_5H_5N (10 ml) was treated with powdered KOH (1 g) and the mixture shaken vigorously for 2 hr with occasional warming. The resulting 2,4-dimethoxybenzoyl-(2-hydroxy-4,6-dimethoxybenzoyl)-methane [2] crystallized from EtOH (800 mg), mp 120°; ν_{max}^{KBr} cm^{-1}: 3246, 1600, 1425. The diketone (500 mg) was gently refluxed with HOAc (5 ml) and fused NaOAc (1 g) in an oil bath for 3 hr. The resulting flavone [2, 3] crystallized from EtOH (300 mg), mp 179–80°. It was identical with the natural sample (mmp, co-TLC, UV and IR).

REFERENCES

1. Erfan Ali, Nurhul Haq and Mojibur Rahman, A. K. M. (1966) *Sci. Res. (Dacca)* **3**, 157.
2. Doporto, M. L., Gallagher, K. M., Gowan, J. E., Hughes, A. C., Philbin, E. M., Swain, T. and Wheeler, T. S. (1955) *J. Chem. Soc.* 4249.
3. Dave, K. G., Telang, S. A. and Venkataraman, K. (1960) *J. Sci. Ind. Res. India* **19B**, 470.