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ISOPRENYLCOUMARINS FROM *BOENNINGHAUSENIA ALBIFLORA*

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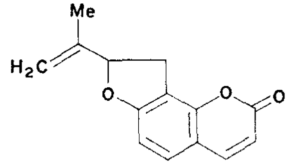
Key Word Index—*Boenninghausenia albiflora*; Rutaceae; angenomalin; micropubscin.

In an earlier communication[1] the isolation of 3-(1,1-dimethylallyl) xanthyletin was reported from the above plant. We now report the isolation and characterization of two more coumarins from the petrol. extract of the plant. Chromatography of the concentrated petrol. extract on alumina gave two more crystalline compounds which after recrystallization from acetone–petrol. melted at 107–108° and 118–119° respectively and gave single fluorescent spots on TLC (silica gel G).

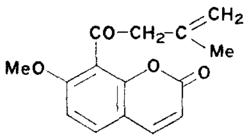
The compound m.p. 107–108° analysed for $C_{14}H_{12}O_3$ (M^+ 228). UV: EtOH: λ_{max} 253 (log ϵ 3·4) 262(3·52) 328 nm (4·15). IR: Nujol ν_{max} 1745 cm^{-1} (lactone C=O) 1615 cm^{-1} (C=C) 1260 cm^{-1} (=C–O–C) 900 and 3080 cm^{-1} (vinylidene group).

NMR* ($CDCl_3$): *AB* quartet centred at δ 6·15 (1H) and 7·6 (1H) (*J* 9·5 Hz) assigned to C-3 and C-4 hydrogens AB quartet at δ 7·24 (1H) and 6·72 (1H) (*J* 9·5 Hz) assigned to C-5 and C-6 hydrogens. The presence of C-5 and C-6 hydrogens and the absence of other aromatic protons indicated the angular fusion of the dihydrofuran ring. The C-2′ and C-3′ hydrogens appeared as an *ABX* system where the *AB* part of the spectrum showed itself as an octet centred at δ 3·31 and the *X* part of the spectrum as a triplet centred at δ 5·32. A singlet three proton signal at δ 1·8 is assigned to the methyl protons. The vinyl portons gave signals at δ 4·92 (1H) and 5·08 (1H).

The MS in addition to its molecular ion peak at *m/e* 228 showed prominent peaks at *m/e* 213, 200 and 185 characteristic of angularly fused dihydrofurano coumarins[2] was in full agreement with the structure assigned. On the basis of these the compound was identified as angenomalin (I) previously isolated by Hata *et al.*[3] from the roots of *Angelica anomala* Lall and *Angelica cartilaginomarginata* (Makino) Nakai (Umbelliferae).



(I)



(II)

Masquin, isolated from *Pimpinella rupicola* (Rutaceae) by Martinez *et al.*[4], and majurin, isolated from *Ammi majus* (Umbelliferae) by Mustafa *et al.*,[5] have identical structures to

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* 60 MHz spectra with TMS as internal reference.

[1] NAYAR, M. N. S., BHAN, M. K. and GEORGE, V. (1973) *Phytochemistry* **12**, 2073.

[2] SHIPCHANDLER, M. and SOINE, T. O. (1968) *J. Pharm. Sci.* **57**, 741–52.

[3] HATA, K., KOZAWA, M. and IKESHIRO, Y. (1967) *Yakugaku Zasshi* **87**, (a), 1118–1124.

[4] MARTINEZ, E. A., REYES, R. E., GONZALEZ, A. and LUIS, F. R. (1967) *An. Real Soc. Espan. Fis. Quim.* **63B** (2), 205–212; *Chem. Abst.* **67**, 47087 g.

[5] ABU MUSTAFA, E. A., EL-BAY, F. K. A. and FAYEZ, M. B. E. (1971) *Tetrahedron Letters* 1657.

angenomalin, but majurin is reported to be present in the plant as the glucoside in which the sugar residue is bound to the phenolic hydroxyl of the corresponding open coumarinic acid. Hence we suggest that the name majurin should be retained exclusively for the glucoside and not the coumarin.

The second compound m.p. 118–119°, analysed for $C_{15}H_{14}O_4$ (M^+ 258) had the following spectral characteristics. UV: EtOH: λ_{max} 257 (log ϵ 3·75) 323 nm (4·2). IR: Nujol ν_{max} 1730 cm^{-1} (lactone C=O) 1710 cm^{-1} (keto C=O) 1610 cm^{-1} (C=C) 1595 cm^{-1}, 1500 cm^{-1} (aromatic) 895 and 3075 cm^{-1} (*vinylidene* group).

NMR* ($CDCl_3$): *AB* quartets centred at δ 6·22 (1H) 7·65 (1H) (*J* 9·5 Hz) δ 7·42 (1H) and δ 6·85 (1H) (*J* 9·5 Hz) were assigned to C-3, C-4, C-5 and C-6 hydrogens. The vinylidene proton gave signals at δ 5·05 and 5·29 respectively. In the methoxy region there was a singlet signal of five protons due to the overlap of the protons of the aromatic methoxy and the keto methylene group protons. The vinylic methyl gave a singlet signal at δ 1·85 accounting for all the protons in the molecule.

On the basis of these data the compound was identified as micropubscin (II) isolated previously from *Micromelum pubescens* (Rutaceae) by Chatterjee *et al.*[6]

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[6] CHATTERJEE, A., DATTA, C. P. and BHATTACHARYYA, S. (1968) *Sci. Cult.* **34**, 366.

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COUMARINS OF *CITRUS MACROPTERA**

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From a chemical standpoint, the commercial *Citrus* species (Rutaceae) constitute one of the most intensely investigated plant groups.[1] On the other hand, relatively little is known

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* Part IX in the series "Chemotaxonomy of the Rutaceae". For Part VIII see DREYER, D. L. and LEE, A. (1972) *Phytochemistry* **11**, 763.

[1] KEFFORD, J. F. and CHANDLER, B. V. (1970) *The Chemical Constituents of Citrus Fruits, Advances in Food Research, Suppl.* 2, Academic Press, New York; GOODWIN, T. W. and GOAD, L. J., *The Biochemistry of Fruit and Their Products* (A. C. HULME, ed.), Vol. 1, Academic Press, London (1970).