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]

Acknowledgements—The authors wish to thank Dr. J. D. Connolly, Glasgow University for the spectral data and Mr. Y. K. Sarin of this Laboratory for the collection and identification of the plant material.

[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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(*Revised received* 9 *May* 1973. *Accepted* 23 *May* 1973)

Key Word Index—*Citrus macroptera*; Rutaceae; chemotaxonomy; furocoumarins.

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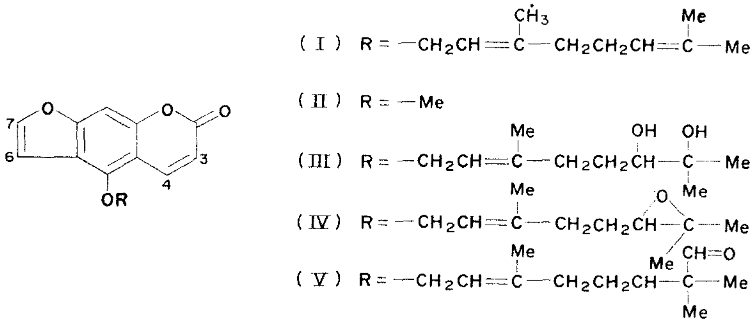
* Part IX in the series "Chemotaxonomy of the Rutaceae". For Part VIII see DREYER, D. L. and LEE, A. (1972) *Phytochemistry* **11**, 763.

[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).

about the chemical constituents of non-commercial *Citrus* species. This paper describes studies on the non-volatile constituents of the fruit of *Citrus macroptera* Montr., a species native to islands of the S. Pacific.[2] Previous studies on this species reported the presence of limonin and deacetylnomilin in the seeds[3] and a quinoline alkaloid in the bark.[4] The latter study is the only report of a quinoline (or biogenetically related furoquinoline) alkaloid in the genus *Citrus*. Furoquinoline alkaloids are otherwise frequent in plants of the Rutaceae.[5]



(I) R = $-CH_2CH{=}C(CH_3)-CH_2CH_2CH{=}C(Me)-Me$

(II) R = —Me

(III) R = $-CH_2CH{=}C(Me)-CH_2CH_2CH(OH)-C(OH)(Me)-Me$

(IV) R = $-CH_2CH{=}C(Me)-CH_2CH_2\overset{O}{CH-C}(Me)-Me$

(V) R = $-CH_2CH{=}C(Me)-CH_2CH_2CH-C(CH{=}O)(Me)-Me$

Extracts of the whole dried fruit, after chromatography on alumina yielded two coumarins. The less polar coumarin was identified as bergamottin(I). This coumarin has been found in many *Citrus* species.[6] The more polar coumarin, m.p. 104–106°, showed the same UV spectrum as bergamottin(I) or bergapten(II).[7] The IR spectrum showed, in addition to the hydroxy band, the usual bergapten bands in the 1730–1550 cm^{-1} region. The new coumarin was optically active. The NMR spectrum showed the expected aromatic resonances for a bergapten system.[8] In addition, resonances were present which corresponded to a geranyloxy side chain. Of the three *C*-methyl resonances in such a side chain, one was due to a vinyl *C*-methyl group while singlets at δ 1·18 and 1·16 indicated two *C*-methyls in a saturated environment. These data suggest the presence of a dihydroxy geranyloxy system(III).

Proof of the structure for 5-[(6′,7′-dihydroxy-3′,7′-dimethyl-2-octenyl)oxy-]-psoralen(III) was provided by relating bergamottin(I) to the new coumarin (III). Selective epoxidation of the terminal double bond of I with *m*-chloroperbenzoic acid gave the epoxide, IV. Acid catalyzed hydrolysis of IV with dilute perchloric acid[9] gave the diol(III), which proved to be identical with natural material by m.p., IR and TLC criteria.

The epoxide(IV) is a probable biogenetic intermediate in the formation of III. Comparison of the synthetic epoxide with the crude plant extracts by TLC showed the apparent absence

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[2] SWINGLE, W. T. znd REECE, P. C. (1967) *The Citrus Industry* (REUTHER, W., WEBBER, H. J. and BATCHELOR, L. D., eds.), Vol. 1, Rev. Edn, p. 395, University of California Press, California.

[3] DREYER, D. L. (1966) *Phytochemistry* **5**, 367.

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[5] PRICE, J. R. (1963) *Chemical Plant Taxonomy* (SWAIN, T. ed.), p. 429, Academic Press, London.

[6] STANLEY, W. L. and JURD, L. (1971) *Agric. Food Chem.* **19**, 1106.

[7] STANLEY, W. L. and VANNIER, S. H. (1967) *Phytochemistry* **6**, 585.

[8] DREYER, D. L. (1965) *J. Org. Chem.* **30**, 749.

[9] BOHLMANN, F., ZDERO, C. and KAPTEYN, H. (1968) *Ann.* **717**, 186; DREYER, D. L. (1970) *Tetrahedron* **26**, 5745; COATES, R. M. and MELVIN, JR., L. S. (1970) *ibid.* **26**, 5699.

of any fluorescent material which corresponded in R_f to the synthetic material. A pinacol like rearrangement of III (or IV) would account for the biosynthesis of the aldehyde (V), which has been found in extracts of *Citrus paradisi.*[10] III constitutes another member of the growing list of 6′,7′-disubstituted geranyloxy derivatives found in the Rutaceae, other members being marmin,[11,12] severine[13] and geiparvarin.[12]

EXPERIMENTAL

NMR data are given in δ. The areas of the peaks were consistent with their assignments. TLC in CHCl$_3$–EtOAc (1:1) with silicic acid was used as a monitoring system.

Isolation. Whole fruit of *Citrus macroptera*, collected at the Citrus Research Center, University of California, Riverside, California was cut up and dried. The dried and ground fruit was extracted with benzene. Solvent was removed from the extracts and the residue chromatographed on alumina. The fractions from the column were monitored by TLC and coumarins detected in UV light. Elution of the column with pentane gave mostly oils. Elution with 10–20% C$_6$H$_6$ in pentane gave fractions from which begamottin(I) was recovered, m.p. 56–58°, from EtOAc–hexane; λ_{max}^{EtOH} ~ 245, 251, 259, 268, 310 nm; NMR 7·86 (*d, J* 10 Hz) H-4, 7·32 (*d, J* 2 Hz) H-7, 6·9 (s) H-8, 6·70 (*d, J* 2 Hz) H-6, 6·05 (*d, J* 10 Hz) H-3, 5·34 (*t*, J 7 Hz) H-2′, 4·88 (unresolved) H-6′, 4·75 (*d, J* 7 Hz) H-1′, 2·02, 2·00 (s) H-4′ and H-5′, 1·62, 1·62, 1·54 C-methyls. Further elution of the column with Me$_2$CO-C$_6$H$_6$ (1:1) gave fractions from which III was recovered, m.p. 104–106°, $[\alpha]_D$ + 12·7° (CHCl$_3$); λ_{max}^{EtOH} 221, ~245, 251, 259, 268, 310 nm; NMR 7·85 (*d, J* 10 Hz) H-4, 7·30 (*d, J* 2 Hz) H-7, 6·88 (s) H-8, 6·68 (*d, J* 2 Hz) H-6, 6·02 (*d, J* 10 Hz) H-3, 5·38 (*t, J* 7 Hz) H-2′, 4·75 (*d, J* 7 Hz) H-1′, 3·18 (*q, J* 7, 3 Hz) H-6′, 2·28–1·98 (m) H-4′, 1·62 (s) vinyl methyl, 1·18, 1·16 C-methyls.

Epoxidation of bergamottin. 270 mg bergamottin and 148 mg *m*-chloroperbenzoic acid in CHCl$_3$ were left to stand overnight at room temp. The CHCl$_3$ was extracted with 5% Na$_2$CO$_3$ and the CHCl$_3$ phase dried. Solvent was removed and the residue crystallized from MeOH to give IV. It was recrystallized from EtOAc–pentane, m.p. 67–70°; λ_{max}^{EtOH} 221, ~245, 251, 259, 268, 310 nm; NMR 7·86 (*d, J* 10 Hz) H-4, 7·32 (*d, J* 2 Hz) H-7, 6·88 (s) H-8, 6·68 (*d, J* 2 Hz) H-6, 6·04 (*d, J* 10 Hz) H-3, 5·39 (*t, J* 7 Hz) H-2′, 4·76 (*d, J* 7 Hz) H-1′, 2·58 (*t, J* 6 Hz) H-6′, 2·10 (*q, J* 6 Hz) H-4′, 1·66 (s) vinyl methyl, 1·23, 1·23 *C*-methyls (Found: C, 71·4; H, 6·35. C$_{21}$H$_{22}$O$_5$ requires: C, 71·17; H, 6·26%).

Racemic 5-[(*6′,7′-dihydroxy-*3′,7′*-dimethyl-*2*-octenyl*)*oxy-*]*-psoralen*(III). To 132 mg IV in 18 ml of dioxane was added 9 ml 3% HClO$_4$ and the solution allowed to stand 1 hr at room temp. The solution was then diluted with H$_2$O and extracted with EtOAc. The extracts were washed, dried, solvent removed and the residue crystallized from EtOAc–hexane to give racemic III, m.p. 104–107° (Found: C, 67·70; H, 6·67. C$_{21}$H$_{24}$O$_6$ required: C, 67·73; H, 6·50%.

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[13] DREYER, D. L. (1967) *Tetrahedron* **23,** 4613.