Les résultats obtenus à partir du *B. verticillata* africain contredisent donc formellement ceux concernant l'espèce sud-américaine et rendent nécessaire une nouvelle étude de celle-ci. On doit noter l'intérêt présenté par la condensation d'une unité tryptaminique et d'une unité isoprénoïde pour former un alcaloïde indolique, qui est à rapprocher de celle d'une unité de phényléthylamine et d'une unité en C_5 dans la biosynthèse de certains alcaloïdes des cactus tels que la lophocerine[6] et la pilocerine.[7]

EXPÉRIMENTALE

Les spectres de masse ont été mesurés sur le spectromètre MS9 et les spectres de RMN sur Varian A-60A; les produits étant en solution dans $CDCl_3$, les déplacements chimiques sont exprimés en ppm, référence zéro, tétraméthylsilane.

Remerciements—Nouse remercions le Professeur M.-M. Janot pour l'intérêt qu'il porte à ces recherches.

[7] O'Donovan, D. G. et Horan, H. (1969) *J. Chem. Soc.* C, 1737.

Phytochemistry, 1973 Vol. 12, pp. 2310 to 2312. Pergamon Press. Printed in England.

COUMARINS AND OTHER COMPONENTS OF *AFRAEGLE PANICULATA*

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Key Word Index—*Afraegle paniculata*; Rutaceae; imperatorin, heraclenin; aurapten; marmesin; 6,7-dimethoxycoumarin; dictamine; sitosterol; hydroquinone.

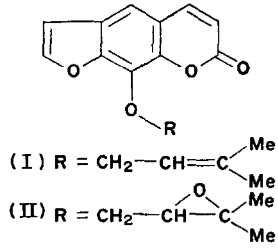
Afraegle paniculata Schum and Thonn (Rutaceae) is found in West Africa from Senegal to Nigeria. Earlier work[1,2] revealed that the chemical composition of the species varied considerably depending on the locality from which collection was made. Torto *et al.*[1] isolated three furocoumarins, imperatorin (I), heraclenin (II) and xanthotoxin (III), and two chromenocoumarins, xanthyletin (IV), xanthoxyletin (V) from a Ghanian plant while Abe[2] isolated imperatorin, sitosterol and the alkaloid dictamine (VI) from a specimen collected from Fiditi in Nigeria. We now report the isolation and characterization of the crystalline products from the stem. Two plant materials were collected from Fiditi and Akure in Nigeria, both towns are about 150 miles (225 km) apart. In each case the ground stem of *A. paniculata* was successively extracted with light petrol. (60–80°), and isopropyl ether. The residue from each extract was separated on a silica gel or deactivated alumina column. (The alumina was deactivated by shaking with 5% by volume of 10% HOAc.)

Fiditi sample. Light petrol. extract. Light petrol. extracted an oil and sitosterol, yield 30 mg/kg. Light petrol.: Et_2O (9:1) eluted white needle-like crystals, yield 2·3 mg/kg, m.p. 113–114°, $[\alpha]_D^{25}$ +24° ($CHCl_3$), M^+ 286, and which analysed for $C_{16}H_{14}O_5$. Detailed study of the NMR, IR, UV, MS showed the compound to be (+)-heraclenin. *isoProply*

[1] Adjangba, M. S. Torto, F. G., Asomaning, W. A. and Sefcovic, P. (1969) *J. West Afr. Sci. Ass.* **14**, 9.

[2] Abe, M. O. (1970) Ph.D. Thesis, Ibadan.

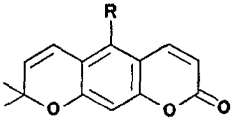
ether extract. Light petrol.–Et_2O (9:1) eluted more sitosterol while the mixed solvent (4:1) eluted a white crystalline solid, yield 16 mg/kg, m.p. 131–132°, M^+ 199, $C_{12}H_9O_2N$. There was a conspicuous absence of H-3 and H-4 of a coumarin while the aromatic methoxy resonance at δ 4·4 was more deshielded than normal. The compound was confirmed to be dictamine by comparison of physical and spectra data with those of an authentic specimen.*



(I) R = $CH_2-CH=C\begin{smallmatrix}Me\\Me\end{smallmatrix}$

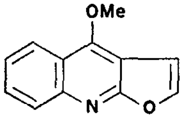
(II) R = $CH_2-\overset{O}{CH-C}\begin{smallmatrix}Me\\Me\end{smallmatrix}$

(III) R = Me

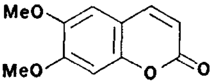


(IV) R = H

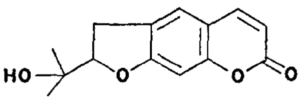
(V) R = OMe



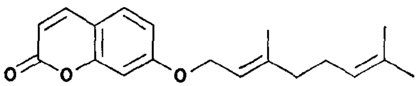
(VI)



(VII)



(VIII)



(IX)

Akure sample. Light petrol. extract. Crude solid separated from the extract. Recrystallization afforded a clean compound, yield 240 mg/kg, m.p. 144–146°, M^+ 206 which analysed for $C_{11}H_{20}O_4$. It had a very simple NMR; two methoxy resonances (δ 3·90 and δ 3·95); H-4 and H-3 of a coumarin (δ 6·25 and δ 7·60; $J_{3,4}$ 10 Hz); and two aromatic protons δ 6·80, *s* and δ 6·90, *s*. The singlet nature of the aromatic protons indicated para coupling: the compound was probably 6,7-dimethylcoumarin. To confirm that the substitution was at 6,7- and not 5,7- as in citropten, the compound was demethylated with H_2SO_4 to give a diol m.p. 270–274° which with $FeCl_3$ turned green, and remained green not turning red as observed for citropten.[3] All the facts unambiguously confirm the compound to be 6,7-dimethoxycoumarin (aesculin dimethyl ether) (VII). The filtrate from the extract was put on a column. Light petrol. extracted an oil, sitosterol (50 mg/kg), while light petrol.–Et_2O (1:1) eluted imperatorin (14 mg/kg) m.p. 100°. The structure was readily characterized from the NMR and confirmed by comparison of the analytical and spectra data with those of an authentic specimen.* Ether eluted marmesin (VIII), 9 mg/kg, m.p. 190–192°, M^+ 246. The tertiary hydroxy function, the splitting patterns and the chemical shifts of the various protons allowed a ready assignment of the structure which has been confirmed by m.m.p. IR, and UV of an authentic specimen.† *isoPropyl ether extract.* Et_2O eluted a white crystalline solid (0·001%), m.p. 66–67°, M^+ 298, $C_{19}H_{22}O_3$. The base peak *m/e* 162 indicated a ready loss of 136 m.u. Since the NMR showed the presence of three allylic Me (δ 1·60,

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* Spectra data were from records on Dr. Abe's work in this Department.

† We are grateful to Dr. S. K. Talapatra, University College of Science, Calcutta, India for authentic specimens of aurapten and marmesin.

[3] ANON (1965) *Dictionary of Organic Compounds* Vols. 1 and 2, 4th Edn., Eyre & Spottiswoode, London.

1·67, 1·75); two vinyl protons, and three allylic methylene protons, the loss of 136 was rationalized as being due to an allylic ether cleavage with H transfer from an allylic 3-Me to the ether oxygen in a 6-membered transition state of a geranyloxy or neryloxy side chain. Since the H-3 and H-4 of coumarin were readily discernible, the compound must be geranyloxycoumarin or neryloxycoumarin with the substituent at 5-, 6- or 7-position. Comparison of our specimen with authentic auraptenf allow the confirmation of our compound as 7-geranyloxycoumarin (aurapten (IX)). Et_2O–MeOH (1:1) eluted a white crystalline solid (0·01 %) m.p. 171–173°, M^+ 110°, soluble in H_2O, EtOH, alcohol, acetone, but only sparingly soluble in $CHCl_3$. Alcoholic solution gave a purple colour which slowly crystallized as dark purple needles with $FeCl_3$, m.m.p., and comparison of spectra data with those for an authentic sample showed the compound to be hydroquinone.

Hydroquinone has been found in the Ericaceae, Rosaceae, Proteaceae, compositae, and recently in the Labiatae[4] and Bignoniaceae.[5] To our knowledge this is the first record of the isolation of this phenol, the only C_6 phenol of systematic interest,[6] in the Rutaceae.

[4] SUBRAMANIAN, S. S., NAIR, A. G. R., RODRIGUEZ, E. and MABRY, T. J. (1972) *Current Sci.* **41,** 202.

[5] SUBRAMANIAN, S. S., NAGARAJAN, S. and SULOCHANA, N. (1973) *Phytochemistry* **12,** 220.

[6] HARBORNE, J. B. and SIMMONDS, N. W. (1964) *Biochemistry of Phenolic Compounds* (HARBORNE, J. B., ed.), p. 77, Academic Press, New York.

Phytochemistry, 1973, Vol. 12, pp. 2312 to 2314. Pergamon Press. Printed in England.

NODAKENETIN ACETATE: A NEW COUMARIN FROM *BOENNINGHAUSENIA ALBIFLORA*

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Key Word Index—*Boenninghausenia albiflora*; Rutaceae; xanthyletin; bergapten; sitosterol; isopimpinellin; nodakenetin acetate; daphnetin-8-methyl ether; xanthotoxin.

Boenninghausenia albiflora Reichb. (Rutaceae), a common plant growing all over temperate Himalaya (altitude 1500–2500 m), is a slender, erect branching, perennial rooted herb of 25–50 cm height with small leaves.[1] Earlier work on the leaves and stems resulted in the isolation of dictamnine,[2] bergapten[2] and matsukaze lactone[3] (a dimeric coumarin) from the MeOH extract and rutin[4] from the EtOH extract. We now report the isolation of six coumarins,[5] viz. xanthyletin (I), bergapten (II), isopimpinellin (III), nodakenetin

[1] BISWAS, K. P. (1966) *Plants of Darjeeling and Sikkim Hymalayas*, Vol. 1, p. 214, West Bengal Government Press, Alipore.

[2] OHTA, T. and MIYAZAKI, T. (1958), *Yakugaku Zasshi* **78,** 1067; (1959) *Chem. Abstr.* **53,** 1636.

[3] MIYAZAKI, T. and MIHASHI, S., (1964) *Chem. Pharm. Bull.* (*Tokyo*) **12** (10), 1232 (Eng.); (1965) *Chem. Abstr.* **62,** 2755g.

[4] MATSUNO, T. and AMANO, Y. (1962) *Kyoto Yakka Daigaku Gakuho* **10,** 17; (1964) *Chem. Abstr.* **60,** 3264b.

[5] For a review on coumarins, see SOINE, T. O. (1964) *J. Pharm. Sci.* **53** (3), 231.