Cyclization of atalaphyllinine. Atalaphyllinine (25 mg) was heated at 80–100° for 4 hr with HCO_2H (2 ml) and then left at room temp overnight. H_2O was added and the soln extracted with CH_2Cl_2. The extract was washed with $NaHCO_3$ aq. H_2O, dried (Na_2SO_4) and evaporated. The residue was chromatographed over Si gel (2 g) in C_6H_6–EtOAc (1:1) to yield a gummy mass, homogeneous by TLC in several solvent systems.

Hydrogenation of cyclized product of atalaphyllinine. A soln of above gummy mass in dry EtOH (5 ml) was shaken with H_2 (1 atom) in the presence of PtO_2 (30 mg) for 6 hr. The soln was filtered, evaporated and preparative TLC of the residue (solvent: C_6H_6–EtOAc MeOH, 40:10:1) furnished a product yield 40%) which was crystallised from CH_2Cl_2–hexane in yellow crystals, mp 250° (dec.) (M^+ 379). This product gave brown colour with $FeCl_3$.

Acknowledgements—Sincere thanks are due to Dr. R. D. Bennett, U.S.D.A., California (U.S.) for help with the NMR spectra; Dr. R. S. Kapil, CDRI, Lucknow for MS and Dr. N. Viswanathan, Ciba Research Centre, for a generous gift of an authentic sample of bicycloatalaphylline. Thanks are also due to Prof. P. K. Jena and Dr. S. N. Mahapatra of this Laboratory for their keen interest in this work.

REFERENCES

1. Kirtikar, K. R. and Basu, B. D. (1933) *Indian Med. Plants* **1**, 482.
2. Basu, D. and Basa, S. C. (1972) *J. Org. Chem.* **37**, 3035.
3. Thakar, M. R. and Sabata, B. K. (1969) *Ind. J. Chem.* **7**, 870.
4. Govindachari, T. R., Viswanathan, N., Pai, B. R., Ramachandran, V. N. and Subramanium, P. S. (1970) *Tetrahedron* **26**, 2905.
5. Talapatra, S. K., Bhattacharyya, S. and Talapatra, B. (1970) *J. Ind. Chem. Soc.* **47**, 600.
6. Sangster, A. W. and Stuart, K. L. (1965) *Chem. Rev.* **65**, 69; Reisch, J., Szendrei, K., Minker, E. and Novak, I. (1972) *Pharmazie* **27**, 208.

Phytochemistry, 1975, Vol. 14, pp. 836–837. Pergamon Press. Printed in England.

MINOR COUMARINS OF *BOENNINGHAUSENIA ALBIFLORA*

SUNIL K. TALAPATRA, SWAPAN K. MUKHOPADHYAY and BANI TALAPATRA

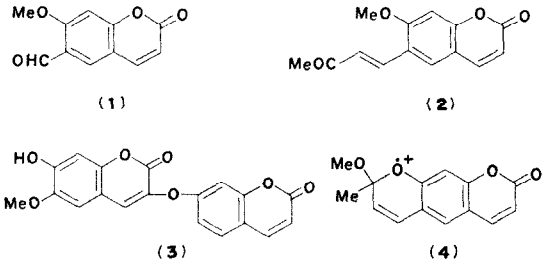
Department of Chemistry, University College of Science, Calcutta 700009, India

(*Received* 2 *October* 1974)

Key Word Index—*Boenninghausenia albiflora*; Rutaceae; angelical; 6-(*trans*-1-buten-3-onyl)-7-methoxycoumarin; daphnoretin; methyl *p*-coumarate.

Like many other Rutaceae, *Boenninghausenia albiflora* contains many coumarins [1–4] only three of which are novel: nodakenetin acetate [1], 3-(1,1-dimethyl allyl)-xanthyletin [2] and the dimeric coumarin, matsukaze lactone [4]. Investigation of the minor constituents of leaves and stems of *B. albiflora* led to the isolation of three further coumarins; angelical (**1**), 6-(*trans*-1-buten-3-onyl)-7-methoxycoumarin (**2**) and daphnoretin (**3**) along with methyl *p*-coumarate. All these compounds were characterised mainly on the basis of their spectral properties.

Coumarin (**2**), $C_{14}H_{12}O_4$ (M^+ 244), mp 225°, showed UV absorption at λ_{max}^{EtOH} 285 nm (log ϵ 4·4) and 225 (4·09); IR, ν_{max}^{KBr} 1718 cm^{-1} (coumarin lactone CO), 1664 (α,β-unsaturated CO) and 976 (*trans*-disubstituted alkene). The PMR spectrum (100 MHz, $CDCl_3$, δ) had signals for a ketomethyl group (2·38, *s*, 3H), two *trans*-disubstituted olefinic protons (6·74 *d* and 7·80 *d*, *J* 16 Hz), coumarin 3- and 4-protons (6·29 *d* and 7·64 *d*, AB system, *J* 10 Hz), two aromatic protons (6·83 *s* and 7·62 *s*, 1H each, H-8 and H-5) and a methoxy group (3·96, *s*, 3H). The MS showed the base peak at *m/e* 213, the genesis of which may be rationalised by the loss of OMe from the ion (**4**), the latter being formed by isomerisation of the side chain double bond of the



molecular ion (M^+ 244, 60·3%) from *trans* to *cis* followed by cyclization. The presence of the keto-methyl group was indicated by the appearance of an intense peak at *m/e* 43 (38%). All the above data showed the structure of (**2**) as 6-(*trans*-1-buten-3-onyl)-7-methoxycoumarin. Recently [5], a new coumarin, named suberenon, possessing the same structure as (**2**) has been reported from *Ruta graveolens* but no direct comparison could be made because of the nonavailability of a sample of the latter.

The two other rare coumarins angelical (**1**) [6] and daphnoretin (**3**) [7] and methyl *p*-coumarate were characterized by UV, IR, PMR and MS and daphnoretin, also by direct comparison. Angelical showed expected PMR signals [8]. MS of (**1**) (M^+ 204, 100%), not reported earlier, was consistent with its structure.

EXPERIMENTAL

Extraction. Dried, powdered leaves and stems (2 kg) were soxhletted with light petrol (60–80°) and $CHCl_3$ respectively. The basic components were separated in the usual way and the neutral fraction of both light petrol and $CHCl_3$ extracts were separately chromatographed over Si gel, elution being carried out with solvents of increasing polarity. *Angelical* (**1**). C_6H_6–$CHCl_3$ (1:1) eluate of light petrol extract furnished angelical crystallizing from $CHCl_3$ as colourless needles (yield 0·001%), mp 250° (lit. [6] 256°); IR: ν_{max}^{KBr} 1727 cm^{-1} (coumarin lactone CO), 1664 (aromatic aldehyde CO); PMR spectrum was similar to that reported earlier [8]. MS: (*m/e*, % base peak): 204 (100, M^+), 187 (32·5), 186 (22), 175 (29), 159 (26), 158 (26), 147 (19). 6-(*trans*-1-*Buten*-3-*onyl*)-7-*methoxycoumarin* (**2**). C_6H_6–$CHCl_3$ (1:1) eluted portion of $CHCl_3$ extract on rechromatography over Si gel furnished (**2**), crystallizing from light petrol–MeOH in pale, dirty yellow needles (0·0005%), mp 225°; MS: (*m/e*, % base peak) 244 (60·3, M^+), 229 (76·4, M^+-Me), 214 (29·4, 229-Me), 213 [100, M^+-OMe], 201 (7, 229-CO), 186 (18·6, 214-CO), 185 [6·3, ion (a)-CO], 158 (25·6, 186-CO), 157 (1·3, 185-CO). *Daphnoretin* (**3**). Fractions eluted by $CHCl_3$–MeOH (95:5) were combined together and concentrated to yield (**3**), purified through repeated chromatography and crystallized from light petrol–acetone mixture as pale yellow needles (0·003%), mp 244°; IR: ν_{max}^{KBr} 3344 cm^{-1} (OH), 1720 (coumarin lactone CO), 1282 (ether linkage); PMR (100 MHz, CD_3SOCD_3, δ): 6·39 *d* and 8·05 *d* (2H, AB system, *J* 9·5 Hz, H-3′ and H-4′), 7·73 *d* (1H, *J* 8·5, H-5′), 7·12 *dd* (1H, *J* 8·5 Hz and 2·0 Hz, H-6′), the lower field component of this *dd* merged with the doublet for H-8′ resulting into a broad singlet at 7·17 (1·5 H), 7·88 *s* (1H, H-4), 7·23 *s* (1H, H-5), 6·89 *s* (1H, H-8) and 3·82 *s* (3H, 6-OMe). MS: (*m/e*, % base peak): 352 (100, M^+), 337 (1·4), 324 (1·5), 309 (6·3), 295 (1), 240 (4), 191 (1·7), 179 (32·2), 176 (5), 164 (7), 145 (7), 89 (38), (**3**) formed acetate (Ac_2O, pyridine, 24 hr, room temp), mp 233°; IR superimposable on that of authentic daphnoretin, and (**3**) showed no mp depression on admixture with authentic daphnoretin.

Methyl p-*coumarate.* C_6H_6–$CHCl_3$ (1:1) eluted fraction of light petrol extract upon several rechromatography furnished methyl *p*-coumarate from light petrol–$CHCl_3$ as colourless needles (0·004%), mp 138°; the latter developed deep yellow colour with alcoholic KOH; UV: λ_{max}^{EtOH} (log ϵ) 228 nm (3·86) and 313 (4·18); IR: ν_{max}^{KBr} (cm^{-1}) 3509 (OH), 1695 (ester CO), 1639, 1605, 1587, 1515, 1433, 1325, 1279, 1190, 1176, 986, 833; PMR (100 MHz, $CDCl_3$, δ): 6·27 *d* and 7·63 *d* (2H, *J* 16 Hz, two *trans*-olefinic protons of the side chain), 6·86 *d* and 7·38 *d* (4H, A_2B_2 quartet, *J* 8·5, aromatic protons), 6·6 *s* (1H, phenolic proton) and 3·8 *s* (3H, OMe group); MS (*m/e*, % base peak): 178 (76, M^+), 147 (100, M^+-OMe), 119 (22·4, 147-CO), 91 (12, 119-CO); (**4**) formed acetate, mp 84°.

Acknowledgements—We are indebted to Drs. B. C. Das (CNRS, Gif-sur-Yvette), R. S. Kapil (CDRI, Lucknow) and A. Chakrabarty (IIT, Kanpur) for MS and IR spectral measurements, to Dr. P. L. Mazumdar (University College of Science, Calcutta, India) for the gift of authentic daphnoretin and to U.G.C., New Delhi, for the award of a Junior Fellowship (to S.M.).

REFERENCES

1. Talapatra, S. K., Mukhopadhyay, S. K. and Talapatra, B. (1973) *Phytochemistry* **12,** 2312.
2. Nayer, M. N. S., Bhan, M. K. and George, V. (1973) *Phytochemistry* **12,** 2073.
3. Ohta, T. and Miyazaki, T. (1958) *Yakugaku Zasshi* **78,** 1067; (1959) *Chem. Abstr.* **53,** 1636.
4. Miyazaki, T. and Mihashi, S. (1964) *Chem. Pharm. Bull. (Tokyo)* **12,** 1232; (1965) *Chem. Abstr.*, **62,** 2755g.
5. Reisch, J., Szendrei, K., Novak, I. and Minker, E. (1972); *Magy. Kem. Foly. (Hung.)* **78,** 6; (1972) *Chem. Abstr.*, **76,** 138149f.
6. Hata, K. and Tanaka, Y. (1957) *Yakugaku Zasshi* **77,** 937; (1958) *Chem. Abstr.* **52,** 3799h.
7. Tschesche, R., Schacht, U. and Hegler, G. (1963) *Ann.*, **662,** 113; (1963) *Chem. Abstr.* **59,** 548e.
8. Guise, G. B., Ritchie, E., Senior, R. G. and Taylor, W. C. (1967) *Aust. J. Chem.* **20,** 2429.