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SESQUITERPENE HYDROCARBONS OF *BAZZANIA TRILOBATA**

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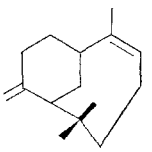
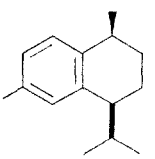
Key Word Index—*Bazzania trilobata*; Hepaticae; Riverwort; bazzanene, calamenene; barbatene.

Plant. Bazzania trilobata; (L.) Gray[1], *Source.* Thüringer Wald, June 1970; *Previous work*: On *Bazzania trilobata*,[2] *B. pompeana*,[3] and *B. tricenata*.[4]

Present work. 720 g of dried ground plant material yielded 25 g of green oil on hexane extraction. The hydrocarbon portion was obtained by hexane elution from a 300-g column of Al_2O_3 (Act. II, neutral): 13·7 g GC analysis[5] on Apiezon L (190°) revealed ten significant sesquiterpene components. The four major ones were identified: α-barbatene ($I_A^{190} = 1501$, 4%),[6] β-barbatene ($I_A^{190} = 1538$, 26%),[6] calamenene ($I_A^{190} = 1568$, 8%),[7] and bazzanene ($I_A^{190} = 1590{\cdot}5$, 48%).



(I)



(II)

Bazzanene (I: $[\alpha]_D$ +68°, lit.[3] +48°) was identified by the spectral data (MS, NMR, IR) which corresponded to the literature reports.[3] The barbatenes were identified from NMR and GC (3 stationary phases) comparison with the barbatenes isolated from *Barbilophozia barbata*.[6] In the case of β-barbatene $[\alpha]_D$ −21°, $[\alpha]_{300}$ −42°; reported[6] $[\alpha]_{300}$ −50°), the

* Part XIV in the series "Constituents of Mosses and Liverworts". For Part XIII see Ref. 6.

[1] Voucher specimens are to be found in the herbarium of S. Huneck, Halle.
[2] HUNECK, S. and KLEIN, E. (1967) *Phytochemistry* **6**, 383; HUNECK, S. (1967) *Z. Naturforsch.* **22b**, 462; HUNECK, S. and KLEIN, E. (1970) *Journ. Hattori Bot. Lab.* **33**, 1.
[3] HAYASHI, S. and MATSUO, A. (1969) *Experientia* **25**, 1139; (1970) *Ibid.* (1970) **26**, 347; MATSUO, A. (1971) *Tetrahedron* **27**, 2757.
[4] HUNECK, S., GROLLE, R. and VEVLE, O. (1973) *J. Hattori Bot. Lab.*, in press.
[5] ANDERSEN, N. H. and FALCONE, M. S. (1969) *J. Chromatog.* **44**, 52.
[6] ANDERSEN, N. H., COSTIN, C. R., KRAMER, C. M., OHTA, Y. and HUNECK, S. (1973) *Phytochemistry* **12**, in press.
[7] ANDERSEN, N. H. and SYRDAL, D. D. (1970) *Phytochemistry* **9**, 1325.

identity in absolute configuration was established by CD comparison—$\Delta\epsilon_{196}$ +7·2 from either source. The NMR spectrum of the isolated calamenene showed it to be the *cis*-isomer[8] essentially free of diastereomeric material. The negative ^1L_b band ($\Delta\epsilon_{278} = -0{\cdot}25$) suggests structure II.[8]

Acknowledgement—The work at U.W. was supported by NIH Grant GM-18143.

[8] ANDERSEN, N. H., SYRDAL, D. D. and GRAHAM, C. (1972) *Tetrahedron Letters* 905.

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FILICES, etc.

PHYTOSTEROLS IN PLANTS

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Key Word Index—*Cyathea spinulosa*; Filices; Fern; lupeol; *Antidesma diandra*; *Euphorbia jacquemontii*; *Gelonium bifarium*; Euphorbiaceae; Angiospermae taraxerone; sitosterol; epimultiflorenol; multiflorenol; bauerenol; *Soymida febrifuga*; Meliaceae; methyl angolensate; sitosterol.

Plant. Cyathea spinulosa Wall[1] (Syn. *Hemitelia decipines* J. Scott). Filices. *Occurrence.* Middle and upper hill forest, rarely found near Kalimpong and Darjeeling, India. *Previous work.* None.

Isolation and identification. The powdered whole plant was extracted with C_6H_6 and the neutral fraction gave *lupeol*,[2] m.p. 214–215°, $[\alpha]_D$ +26·4°, its acetate m.p. 216–217°, $[\alpha]_D$ +47·5° confirmed by m.m.p., IR and co-TLC with an authentic sample. The second solid has been identified as *sitosterol.*

Plant. Antidesma diandrum Roth.[3] Euphorbiaceae. *Occurrence.* Tropical Himalaya, from Garwhal eastwards and southwards to Travancore, India.

Isolation and identification. The powdered trunk was extracted with benzene and the neutral part afforded *sitosterol.*

Plant. Euphorbia jacquemontii Boiss; Euphorbiaceae.[4] *Occurrence.* Throughout the Western Himalayan region of India. *Previous work.* None.

Isolation and identification. The powdered trunk bark was extracted with C_6H_6 and the neutral part on chromatography first gave *taraxerone*, $C_{30}H_{50}O$,* m.p. 238–240°, $[\alpha]_D$ 10·8°[5] confirmed by IR, NMR and co-TLC with authentic specimen and by conversion to

* Satisfactory analysis, $[\alpha]_D$ in $CHCl_3$, 60 Mc NMR in $CDCl_3$ with TMS as internal standard.

[1] COWAN, A. M. and COWAN, J. M. (1929) *The Trees of Northern Bengal*, p. 143, Bengal Secretariat Book Depot, Calcutta.
[2] HALSALL, T. G., JONES, E. R. H. and MEAKINS, G. D. (1952) *J. Chem. Soc.* 2862.
[3] HOOKER, J. D. (1954) *Flora of British India*, Vol. 5, p. 361, Reeve, London.
[4] HOOKER, J. D. (1954) *Flora of British India*, p. 238, Reeve, London.
[5] POLLOCK, J. R. A. and STEVENS, R. (1965) *Dictionary of Organic Compounds*, 4*th* Ed., Vol. 5, p. 2943, Eyre & Spottiswoode, London and references cited therein.