

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<sup>8</sup> essentially free of diastereomeric material. The negative  $^1L_b$  band ( $\Delta\epsilon_{278} = -0.25$ ) suggests structure II.<sup>8</sup>

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

<sup>8</sup> ANDERSEN, N. H., SYRDAL, D. D. and GRAHAM, C. (1972) *Tetrahedron Letters* 905.

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## FILICES, etc.

### PHYTOSTEROLS IN PLANTS

D. R. MISRA, D. B. NASIKAR, T. K. RAY and H. N. KHASTGIR

Chemistry Department, North Bengal University, Darjeeling, India

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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; *Soyimida febrifuga*; Meliaceae; methyl angolensate; sitosterol.

*Plant.* *Cyathea spinulosa* Wall<sup>1</sup> (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,<sup>2</sup> m.p. 214–215°,  $[\alpha]_D +26.4^\circ$ , its acetate m.p. 216–217°,  $[\alpha]_D +47.5^\circ$  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.<sup>3</sup> 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.<sup>4</sup> *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.

<sup>1</sup> COWAN, A. M. and COWAN, J. M. (1929) *The Trees of Northern Bengal*, p. 143, Bengal Secretariat Book Depot, Calcutta.

<sup>2</sup> HALSALL, T. G., JONES, E. R. H. and MEAKINS, G. D. (1952) *J. Chem. Soc.* 2862.

<sup>3</sup> HOOKER, J. D. (1954) *Flora of British India*, Vol. 5, p. 361, Reeve, London.

<sup>4</sup> HOOKER, J. D. (1954) *Flora of British India*, p. 238, Reeve, London.

<sup>5</sup> POLLOCK, J. R. A. and STEVENS, R. (1965) *Dictionary of Organic Compounds*, 4th Ed., Vol. 5, p. 2943, Eyre & Spottiswoode, London and references cited therein.

taraxerol, m.p. 278–280°,  $[\alpha]_D + 3.7^\circ$ , acetate, m.p. 295–297°,  $[\alpha]_D + 9.16^\circ$ . The second solid was an alcohol,  $C_{23}H_{48}O$ , m.p. 87–88°,  $[\alpha]_D - 22.42^\circ$  (IR: 3275  $cm^{-1}$ ); acetate,  $C_{25}H_{50}O_2$ , m.p. 70–71° (IR: 1725 and 1245  $cm^{-1}$ ) but could not be identified for want of sufficient material. The last solid *sitosterol*,  $C_{29}H_{50}O$ , m.p. 137–138°,  $[\alpha]_D - 36^\circ$  confirmed by m.m.p., IR and co-TLC with authentic specimen. Acetate, m.p. 127°,  $[\alpha]_D - 4^\circ$ .

*Plant.* *Gelonium bifarium* Roxb;<sup>6</sup> Euphorbiaceae. *Occurrence.* Andaman islands, Malay islands. *Previous work.* Other sister species.<sup>7,8</sup>

*Isolation and identification.* The powdered trunk bark was extracted with  $C_6H_6$ . The neutral part gave a complex mixture of crystalline substances which on acetylation afforded a mixture of at least 3 acetates (TLC). On fractional crystallization it first afforded *bauerenol* acetate,  $C_{32}H_{52}O_2$ , m.p. 282–284°,  $[\alpha]_D 0^\circ$ , hydrolysis of which gave *bauerenol*,  $C_{30}H_{50}O$ , m.p. 208–209°,  $[\alpha]_D - 20^\circ$  confirmed by m.m.p., IR and co-TLC with authentic specimen. From the mother liquor two other solids were separated by fractional crystallization. The first solid multiflorenol acetate  $C_{32}H_{52}O_2$ , m.p. 220–222°,  $[\alpha]_D 0^\circ$  and its corresponding alcohol, *multiflorenol*,  $C_{30}H_{50}O$ , m.p. 188–190°,  $[\alpha]_D - 30^\circ$  confirmed by m.m.p. and IR comparison with authentic specimen. The third solid isolated from the mother liquor has been identified as epimultiflorenol acetate,  $C_{32}H_{52}O_2$ , m.p. 220–222°,  $[\alpha]_D 0^\circ$  and its corresponding alcohol *epimultiflorenol*, m.p. 206–208°,  $[\alpha]_D 0^\circ$  and its identity has been confirmed by preparing the alcohol from multiflorenone by the method of Paton *et al.*<sup>9</sup> The last solid m.p. 135–137° has been identified as *sitosterol*.

*Plant.* *Soyimida febrifuga* A. Juss.<sup>10</sup> Meliaceae. *Occurrence.* Dry forests of Western Peninsula, extending northwards to Marwara, the Mirzapur Hill and Chot Nagpur of India. *Medicinal use.* Bark, astringent, bitter tonic, febrifuge, used in general debility, intermittent fevers, diarrhoea and dysentery. *Previous work.* bitter substances from bark.<sup>11</sup>

*Isolation and identification.* The powdered trunk bark was extracted with  $C_6H_6$  and the chromatography of the neutral part over alumina first afforded *sitosterol*, m.p. 137–138°,  $[\alpha]_D - 36^\circ$  confirmed by m.m.p. and IR comparison with authentic specimen. The second solid, m.p. 202–204°,  $[\alpha]_D - 42^\circ$  coming out in  $C_6H_6$ –petrol. (4:1) showed in the NMR spectrum the presence of two  $\alpha$  ( $\delta$  7.37) and one  $\beta$ -furanic protons ( $\delta$  6.35), the H-17 proton ( $\delta$  5.62)  $\alpha$ -to the furan ring, two vinyl proton singlet  $\sim$   $\delta$  5.00, characteristic of the vinylidene group exocyclic to a cyclohexane ring, two doublets ( $J$  14 Hz) each one proton, assignable to the isolated geminal protons at C-15 and five three proton singlet assignable to one methyl ester and for quaternary methyls. All the above spectral data are in accord with *methyl angolensate*<sup>12</sup> and the compound has been found to be identical with the same confirmed by m.m.p. IR, co-TLC and NMR spectra with an authentic specimen.

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<sup>10</sup> CHOPRA, R. N., NAYAR, S. L. and CHOPRA, I. C. (1956) *Glossary of Indian Medicinal Plants*, CSTR, p. 232, Calcutta.

<sup>11</sup> ANON (1851) *Arch Pharm. (Berl.)* 271.

<sup>12</sup> BEVAN, C. W. L., POWELL, J. W., TAYLOR, D. A. H., TOFT, P., WELFORD, M., CHAN, W. R., MOOTOO, B. S. and HALSALL, T. G. (1964) *Chem. Ind. (London)* 1751.