Phytosterols. 10 kg of wood was extracted with Et_2O at room temp. for 10 days. The Et_2O extract was evaporated dryness. Chromatography on silica gel over *n*-hexane and EtOAc (5:1) gave a white crystalline substance (1·0 g, 0·01 %). TLC R_f 0·28, *n*-hexane–EtOAc (5:1). β-Sitosterol, stigmasterol and campesterol were detected by GLC comparison with authentic specimens (SE-30 5 % on Celite 545 at 280°). The ratio of β-sitosterol–stigmasterol–camphesterol (31:3:68).

Phytochemistry, 1971, Vol. 10, pp 1954 to 1955. Pergamon Press. Printed in England.

LEGUMINOSAE

CONSTITUENTS OF *SAMANEA SAMAN* BARK

S. K. NIGAM, G. MISRA and C. R. MITRA

Utilization Research Laboratory, National Botanic Gardens, Lucknow, India

(*Received* 29 *December* 1970, *in revised form* 5 *April* 1971)

Plant. Samanea saman[1] Merrill. syn. *Pithecellobium saman, Inga saman.*

Uses. Medicinal.[2,3]

Previous work. Seeds and leaves.[2,3] On sister species, *Pithecellobium dulce.*[4–8]

Bark. Extr. EtOH; *n*-hexane soluble neutral fraction, chromatography (Al_2O_3): *Hexacosanol*, $C_{26}H_{54}O$, m.p., mixed[7] m.p., IR, acetate, m.p. *Lupeol*, $C_{30}H_{50}O$, m.p., mixed[9] m.p., $[\alpha]_D$, IR, co-TLC, m.p. and $[\alpha]_D$ of acetate, $C_{32}H_{52}O_2$ and benzoate, $C_{37}H_{54}O_2$. *α-Spinasterol*, m.p., mixed[7] m.p., $[\alpha]_D$, IR co-TLC, m.p. and $[\alpha]_D$ of acetate, $C_{31}H_{50}O_2$ and benzoate, $C_{36}H_{52}O_2$.

n-Hexane soluble acidic fraction, chromatography (silica gel): *Octacosanoic acid*, $C_{28}H_{56}O_2$, m.p., mixed, m.p., IR, methyl ester, m.p. 66–67°, mol. wt. 424 (mass).

n-Hexane insoluble middle layer: *β-D-Glucoside of α-spinasterol*, $C_{35}H_{58}O_6$, m.p., mixed[8] m.p., $[\alpha]_D$, IR, co-TLC, tetra-acetate, $C_{43}H_{66}O_{10}$, m.p.; acid hydrolysis to α-spinasterol and glucose.

Ether soluble $FeCl_3$ and Mg–HCl positive fraction: *Flavonoid mixture* one, separated through preparative paper chromatography, had R_f 0·68 (BzOH–H_2O, 4:1) and 0·69 (*n*-BuOH–AcOH–H_2O, 4:1:3), $\lambda_{\max}^{\text{alc}}$ 250, 349 nm, with NaOAc → 275 nm, could not be identified due to its paucity.

[1] G. WATT, *The Economic Products of India*, Vol. VI, p. 283.
[2] K. WIESNER, D. M. MACDONALD, C. BANKIEWICZ and D. E. ORR, *Canad. J. Chem.* **46**, 1881 (1968).
[3] K. E. MAGNUS and C. E. SEAFORTH, *Tropical Science* **VII**, 6 (1965).
[4] S. K. NIGAM, C. R. MITRA and K. N. KAUL, *J. Pharm. Sci.*, U.S.A. **52**, 459 (1962).
[5] S. K. NIGAM and C. R. MITRA, *Chem. Proc. Engg., India* **1**, 156 (1967).
[6] S. K. NIGAM and C. R. MITRA, *Ind. J. Chem.* **5**, 395 (1967).
[7] S. K. NIGAM and C. R. MITRA, *Planta Medica* **16**, 335 (1968).
[8] S K. NIGAM and C. R. MITRA, *Planta Medica* **18**, 44 (1970).
[9] G. MISRA and C. R. MITRA, *Phytochem.* **7**, 501 (1968).

New compound. Another L–B positive and Tortelli–Jaffe negative compound from the hexane soluble neutral fraction (*vide supra*), m.p. 164–165° (Found: C, 84·97; H, 11·43. $C_{29}H_{46}O$ required: C, 84·88; H, 11·22%), mol. wt. 410 (mass), its IR spectrum showed absence of hydroxyl band and the lone oxygen function in the molecule was a >CO group having absorption at 1720 cm^{-1} (6 membered ketone[10]) besides the other important peaks[11] of a steroid.

The mass spectrum of the compound is in excellent agreement with the cracking pattern reported[12,13] for stigmastane skeleton. The molecular ion peak appearing at *m/e* 410(M^+) undergoes loss of 139 mass units to give the peak at *m/e* 271(M^+—C_{10} side chain). The other peaks are at *m/e* 298(M^+—ring A and CH_3), 229(M^+—side chain and 42 mass units for ring D fragment) and 367(M^+—isopropyl fragment, mass 43), a prominent peak characteristic of the Δ^7-sterols with Δ^{22}-side chain. The absence of the peak at *m/e* 253(M^+—C_{10} side chain and C-3 OH) confirmed that the C-3 constituted the carbonyl group which would not undergo fragmentation;[12] the peak at *m/e* 269 was, however, the base peak.

The NMR spectrum of the ketone showed a broad signal at δ 2·3 ppm(4H) which may be attributed to the proton alpha to the carbonyl group in ring A and the methyl signals between δ 0·6 and 1·1 ppm along with the olefinic protons(3H) as a multiplet centred at δ 5·2 ppm.

The ketone was finally identified as *α-spinasterone* (5α-stigmasta-7,22-dien-3 one) by mixed m.p. and superposable IR spectrum with the derived[14] α-spinasterone from α-spinasterol.

The L-B positive and TLC pure natural and the derived samples of α-spinasterone do not respond to Tortelli-Jaffe colour test which otherwise should have been positive as it is specific for α-spinasterol. Clark-Lewis *et al.*[13] observed that pure α-spinasterol is negative to this test; it is positive only when it is contaminated with stigmast-$\Delta^{8(14)}$-enol. This contention has since been substantiated by our observations too and the ketone further proved to be a single entity.

The mother liquor of α-spinasterone on co-TLC (silica gel G, benzene) showed the presence of *lupenone* besides other compounds (*vide supra*).

The presence of α-spinasterone, α-spinasterol and its glucoside in the same plant part is of biogenetic interest.

Acknowledgements—Authors' thanks are due to Mr. J. Saran for microanalyses, to Messrs R. K. Singh and B. P. P. Srivastava for recording the mass and the NMR spectra respectively and to the Director, National Botanic Gardens, Lucknow for his interest in the work.

[10] P. SENGUPTA and H. N. KHASTGIR, *Tetrahedron* **19,** 123 (1963).

[11] R. N. JONES and A. R. H. COLE, *J. Am. Chem. Soc.* **74,** 5648 (1952).

[12] S. S. FRIEDLAND, G. H. LANE, JR., R. T. LONGMAN, K. E. TRAIN and M. J. O'NEAL, JR., *Anal. Chem.* **31,** 169 (1959).

[13] J. W. CLARK-LEWIS and I. DAINIS, *Aust. J. Chem.* **20,** 1961 (1967).

[14] K. BOWDEN, I. M. HEILBRON, E. R. H. JONES and B. C. L. WEEDON, *J. Chem. Soc.* 39 (1946).

Phytochemistry, 1971, Vol. 10, pp. 1955 to 1956. Pergamon Press. Printed in England.

MELIACEAE

TETRANORTRITERPENOIDS FROM *CEDRELA FISSILIS*

R. ZELNIK and C. ROSITO

Serviço de Química Orgânica, Instituto Butantan, São Paulo, Brasil

(*Received* 10 *November* 1970)

Abstract—The co-occurrence of mexicanolide and 3-β-hydroxy-isomexicanolide in the seeds of *Cedrela fissilis* Velloso is recorded.