[Reprinted from the *Journal of Scientific & Industrial Research*, 1957, Vol. 16B, No. 2, pp. 72-74]

Chemical Investigation of *Asteracantha longifolia* & *Strobilanthes auriculatus*

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(*Manuscript received* 25 *June* 1956)

Lupeol has been isolated from the roots of *Asteracantha longifolia* and *Strobilanthes auriculatus*. Hentriacontane has been isolated from the leaves of the former.

ASTERACANTHA longifolia Ness. (syn. *Hygrophilla spinosa* T. Anders) belongs to the natural order *Acanthaceae* and occurs widely throughout India and Ceylon. The plant, especially the root, has found extensive application as diuretic in indigenous systems of medicine[1]. Earlier work by Ghatak and Dutt[2] claims to have isolated from the roots, a sterol, hygrosterol, $C_{28}H_{46}O$, m.p. 194°, characterized as the acetate, m.p. 208°, $[\alpha]_D$, +27·8° in chloroform; Lagawanker *et al.*[3], however, reported a 'sterol', $C_{18}H_{34}O_3$, m.p. 136°. Basu *et al.*[4,5] and Chopra and Ghosh[6] have recorded the presence of alkaloidal material in the plant. The results of our systematic investigation of this plant are recorded in this paper.

Extraction of the plant material with alcohol containing acetic acid gave only traces of basic material which could not be characterized. Extraction of the powdered, dry roots with light petroleum gave a white

solid practically free from resinous matter. Chromatography, followed by crystallization, gave colourless needles, m.p. 212°-13°, showing positive Liebermann's reaction and forming an acetate, a benzoate and a 3:5-dinitrobenzoate. The substance was identified as the triterpenoid alcohol, lupeol, by analytical and specific rotation data, and comparison with authentic specimens of lupeol and its derivatives[7]. The hygrosterol of Ghatak and Dutt (loc. cit.) is obviously impure lupeol. The purification of the crude lupeol was more easily effected on a larger scale by conversion to the benzoate and hydrolysis of the purified derivative.

Extraction of the stem and leaves of the plant with petroleum ether gave a sticky material, which was separated by chromatography into small quantities of lupeol and a wax. Repeated crystallization of the wax from acetone gave glistening plates, m.p. 68°-70°. The substance gave no colour with tetranitromethane, was unaffected under oxidative, hydrolytic or acylating conditions, and analysed for $C_{31}H_{64}$. Its formula and melting point correspond to those reported for hentriacontane[8], a hydrocarbon which occurs frequently in nature.

The roots of another plant of the Acanthaceae family, provisionally identified as *Strobilanthes auriculatus* Nees. and reported[9] to be of use in treating intermittent fever, have been found to contain lupeol. No chemical examination of this plant seems to have been reported so far.

Experimental procedure

Isolation of lupeol from Asteracantha longifolia — Dry, powdered roots (4500 g.) were percolated in the cold with petroleum ether (40°-60°; 20 litres) for a week. The yellow extract was drained off and distilled to remove the solvent. The extraction was repeated twice when a pale yellow solid (total 25 g.) was obtained. A solution of the material (10 g.) in benzene (75 ml.) was passed through a column of alumina (160 g.). The following 150 ml. fractions were collected:

Fraction	Nature of product	Yield g.	M.P. °C.
1	Wax	2	—
2	White crystals	5·5	208-10
3	do	0·5	206-8
4	do	0·5	158
5	do	0·5	175

Two recrystallizations of material from the second and third fractions, from acetone gave white, slender needles, m.p. 212°-13°, mixed m.p. with lupeol, 211°-12°, $[\alpha]_D^{28°}$, +28·0° (*c* 1·95 in chloroform). (Found: C, 84·3; H, 11·4. $C_{30}H_{50}O$ requires C, 84·5; H, 11·7 per cent.)

The acetate, obtained by heating the compound with acetic anhydride in pyridine at 100°, crystallized from dilute alcohol as needles, m.p. 214°-15°, mixed m.p. with lupeol acetate, 214°-15°, $[\alpha]_D^{28°}$, +38·0° (*c* 5·47 in chloroform). (Found: C, 82·4; H, 10·8. $C_{32}H_{52}O_2$ requires C, 82·1; H, 11·1 per cent.)

The benzoate, prepared by heating with benzoyl chloride and pyridine at 100°, crystallized from acetone in stout needles, m.p. and mixed m.p. with lupeol benzoate, 265°-67°, $[\alpha]_D^{28°}$, +61·0 (*c* 1·8 in chloroform). (Found: C, 83·9; H, 9·8. $C_{37}H_{54}O_2$ requires C, 83·8; H, 10·2 per cent.)

The 3:5-dinitrobenzoate, prepared by heating lupeol and 3:5-dinitrobenzoyl chloride in pyridine at 100°, crystallized from acetone as brownish yellow plates, m.p. 272°-73°. (Found: C, 71·9; H, 8·3. $C_{37}H_{52}O_6N_2$ requires C, 71·6; H, 8·4 per cent.)

Purification of lupeol from Asteracantha longifolia — Crude lupeol (14 g., m.p. 205°-10°), benzoyl chloride (20 ml.) and pyridine (20 ml.) were heated at 100° for 4 hr. The mixture was diluted with water and filtered. The solid was washed successively with acid, alkali, water and alcohol. The crude benzoate (14 g., m.p. 261°-63°) was crystallized from acetone (5 litres) to give pure lupeol benzoate (11·2 g.), m.p. 263°-65°. This was hydrolysed by refluxing with alcohol (800 ml.) containing potassium hydroxide (20 g.) for 3 hr. The solution was cooled, diluted with water and filtered. The precipitate was recrystallized from a mixture of acetone (800 ml.) and methanol (300 ml.) to give colourless needles of pure lupeol (6·5 g.), m.p. 212°-13°. Concentration of the mother liquor gave more of the crystals (1·5 g.), m.p. 211°-12°.

Isolation of hentriacontane — Powdered, dry stem and leaves of the plant (6000 g.) were repeatedly percolated in the cold with petroleum ether (40°-60°). The combined extracts left on evaporation a yellow syrup (32 g.), which was taken up in benzene and passed through an alumina column. The earlier eluates on evaporation gave a wax

(8 g.), which on two crystallizations from acetone gave shining plates, m.p. 68°-70°. (Found: C, 85·6; H, 14·4. $C_{31}H_{64}$ requires C, 85·3; H, 14·7 per cent.) The later eluates from chromatography gave small amounts of lupeol, m.p. 210°-12°.

Isolation of lupeol from Strobilanthes auriculatus — Dry, powdered roots (2500 g.) were repeatedly percolated with cold petroleum ether, the combined extracts evaporated and the residual wax (5 g.) was taken up in benzene and chromatographed over alumina. The earlier eluates gave a yellow wax, while the later ones gave a solid (2·5 g.), needles from acetone-alcohol mixture; m.p. 211°-12°, undepressed on admixture with lupeol. The benzoate, m.p. 263°-65°, showed no depression in melting point when mixed with lupeol benzoate.

Acknowledgement

Our thanks are due to the Council of Scientific & Industrial Research, India, for a research grant, and to Prof. F. S. Spring for gift of samples of lupeol and its derivatives.

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