

CHEMICAL EXAMINATION OF LORANTHUS GREWINKII BOISS AND BUNGE

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Loranthus grewinkii is a fruit tree parasite found in West Pakistan and in many parts of Iran, especially in the northern provinces of Gilan and Mazandran, on pear, apricot and almond trees. Morphologically it is similar to *Viscum album*, but differs from it in the colour of the fruits and the size of the leaves.¹

The plant is locally known as "Keshmesh kowli" "Mavize Kohi" and also "Mavizaj-e-kohi". The dried berries which carry only one seed, are dark brown in colour, have a shrivelled surface and contain a sticky material which can be drawn out in threads. It is highly valued in the Unani system of medicine as a general nerve tonic, and is also reputed for its properties as a resolvent and a laxative,² but no chemical investigation of its constituents appears to have been carried out. The present studies have been carried out with the locally available, stored material. On extraction with light petroleum (b.p. 60-80°C.) a sticky resinous material was obtained (yield about 35%), which on hydrolysis with alcoholic potash gave about half of its weight as unsaponifiable matter (15% on the weight of the berries). From the unsaponifiable matter two triterpenoids have been obtained through their benzoyl derivatives, one of which has been identified as lupeol (C₃₀H₅₀O) while the other, which analyses for the formula, C₃₀H₅₀O₂, (m.p. 224-26°(sub.) [α]_D²⁰ = + 4.5 (CHCl₃) appears to be new and has been provisionally named as "loranthol" (yield 5.9% on the weight of the unsaponifiable fraction).

Loranthol gives crystalline diacetyl and dibenzoyl derivatives and would thus correspond to a dihydroxy compound, belonging most probably to the same series of triterpenoids as lupeol. This view finds a measure of support from the infra-red studies, which confirm the presence of two hydroxyl groups in loranthol as against one in lupeol and also point to their structural similarity (Figs. 1 & 2).

The two products were separated from each other on the basis of the varying solubilities of their benzoyl derivatives in hot light petroleum (b.p. 60-80°C.). Loranthol dibenzoate is almost insoluble in this solvent, while lupeol benzoate readily goes into solution in hot petroleum ether. The presence of lupeol was established by physical and chemical means through comparison with an

authentic sample prepared from the unsaponifiable fraction of *Holarrhena antidysenterica*.³

Further work on the mother liquor of the two benzoates and other constituents of the berries is in progress.

Experimental

500 g. of the berries were first Soxhleted with petroleum ether (b.p. 60-80°C.) and the exhausted material was then crushed and extracted by Soxhleting with ethyl alcohol. The latter extractive was freed of the solvent and digested with petroleum ether, and the combined ethereal extracts were freed of the solvent, yielding 175 g. of a brownish sticky mass (35%). This product was saponified with 7% alcoholic potassium hydroxide and worked up in the usual manner, when it yielded 75 g. of unsaponifiable matter (yield 15% on the weight of the berries). The unsaponifiable matter which gave a strong sterolic colour reaction (Liebermann-Burchard) resisted crystallization through the usual solvents.

Benzoylation of Unsaponifiable Matter: Lupeol and Loranthol Benzoates.— 45 g. of the unsaponifiable material was refluxed in benzene solution (50 cc.) with benzoyl chloride (20 cc.) and pyridine (15 cc.) for 10 hours on a water bath. Water was then added to the reaction mixture and the whole was extracted out with 1:1 mixture of benzene and petroleum ether. The extract was repeatedly washed with water, dried over anhydrous sodium sulphate, concentrated to a small volume under reduced pressure, and kept in the cold when it yielded 9.4 g. of a colourless crystallisate, the mother liquors failing to yield any further crystalline matter.

The crystallisate was extracted out with hot petroleum ether. The petroleum ether soluble portion gave on repeated crystallisation from this medium a product which finally melted at 265°C. (yield 5.5 g.) and gave on hydrolysis a product melting at 210-12°C. which analysed for lupeol, C₃₀H₅₀O, and gave no depression in melting point on admixture with an authentic sample of lupeol.

Calculated for C₃₀H₅₀O : C, 84.5 ; H, 11.7 ; O, 3.8 ; m.w., 426. Found : C, 84.76 ; H, 11.74 ; O, 3.88 ; m.w., 441.

The benzoate which analysed for $C_{37}H_{54}O_2$ also showed no depression in mixed melting point with a sample of lupeol benzoate.

Calculated for $C_{37}H_{54}O_2$: C, 83.7 ; H, 10.1 ; O, 6.04 ; m.w. 530. Found : C, 83.1 ; H, 10.11 ; O, 6.4 ; m.w., 464.

The petroleum ether insoluble fraction of the initial crystallisate was repeatedly crystallised through a mixture of chloroform and acetone till a product finally melting at $340^\circ C$. (dec.) was obtained (stout rods, yield 8.7%). This product which is nearly insoluble in petroleum ether, ether and alcohol, sparingly soluble in ethyl acetate readily so in benzene and chloroform, analysed for $C_{44}H_{58}O_4$.

Calculated for $C_{44}H_{58}O_4$: C, 81.19 ; H, 8.98 ; O, 9.83 ; m.w. 650. Found : C, 80.7 ; H, 8.93 ; O, 9.62 ; m.w., 573.

Loranthol.—0.147 g. of the dibenzoate as obtained above was refluxed with 10 cc. of 10% alcoholic

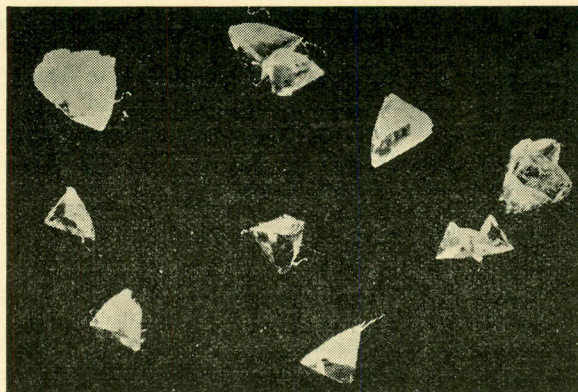


Fig. 3.—Tetrahedral loranthol crystals from acetone solution (x 5 nearly).

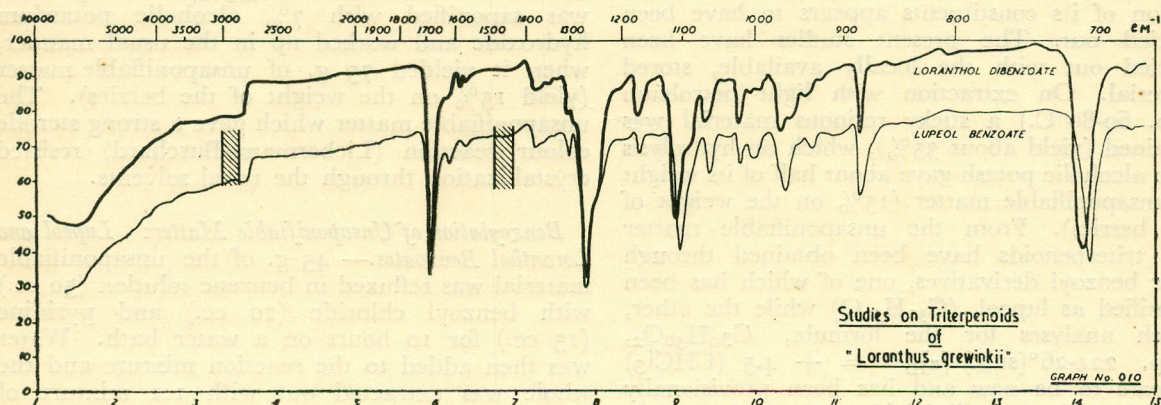


Fig. 1.—Infrared spectra of lupeol benzoate and loranthol dibenzoate (oil "mulls", concentration 2/3 mg./cm.²)

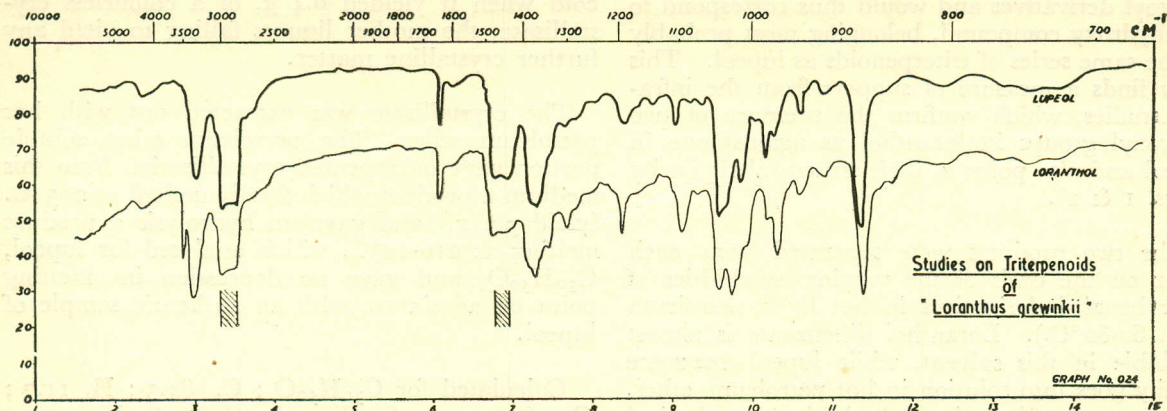


Fig. 2.—Infrared spectra of lupeol and loranthol (oil "mulls", concentration 2/3 mg./cm.²)

Potassium hydroxide till the solution became clear. The reaction mixture was nearly freed of the solvent *in vacuo* and after addition of water repeatedly extracted with benzene. The benzene extract was thoroughly washed with water, dried over anhydrous sodium sulphate, filtered and freed of the solvent *in vacuo*. On crystallisation of the oily residue from a mixture of ether and petroleum ether by slow evaporation at room temperature loranthol was obtained in nearly theoretical yield; m.p. 224-26°C. (with partial sublimation). On recrystallisation from acetone it gave tetrahedral type of crystals (Fig. 3). Loranthol is easily soluble in ether, ethyl acetate, alcohol, chloroform and benzene, sparingly soluble in hot petroleum ether and acetone. Loranthol analysed for $C_{30}H_{50}O_2$.

Calculated for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38; O, 7.23; m.w., 442. Found: C, 81.35; H, 11.49; O, 7.5; m.w., 418.

Loranthol Diacetate.—0.12 g. of loranthol was refluxed with 10 cc. of acetic anhydride for 6 hrs. with the addition of a drop of concentrated sulphuric acid. The reaction mixture was then poured over crushed ice and extracted with ethyl acetate. The ethyl acetate solution was repeatedly washed with sodium bicarbonate (10%) and then with water, dried over anhydrous sodium sulphate and freed of the solvent. On repeated crystallization of the glassy residue from methanol, loranthol diacetate was obtained as longish rectangular plates which melted at 220-21°C. and analysed for $C_{34}H_{54}O_2$.

Calculated for $C_{34}H_{54}O_2$: C, 77.52; H, 10.3; O, 12.15. Found: C, 77.70; H, 9.8; O, 12.25

Infra-red Studies.—The infra-red curves of lupeol benzoate and loranthol dibenzoate (Fig. 1) indicate a general similarity albeit with small but definite variations especially in the 900 cm^{-1} to 1200 cm^{-1} region. Further the graph for loranthol

(Fig. 2) shows two separate peaks in the hydroxyl region (3500 cm^{-1}), as against the single peak in case of lupeol. This difference is confirmed by definite differences in the 1000 cm^{-1} to 1100 cm^{-1} region, which is also sensitive to the hydroxyl groups.

The spectra were obtained on a Leitz double beam spectrometer equipped with a sodium chloride prism. All spectra were determined on oil suspensions or mulls of powdered substances, the concentration of the substance in the beam being nearly 2/3 mg./cm.²

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