

A NEW SESQUITERPENE ALCOHOL FROM *HIMANTANDRA BACCATA* BAIL.

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Summary

A new crystalline sesquiterpene alcohol has been isolated from the bark of *Himantandra baccata* Bail. (syn. *Galbulimima baccata*). It is a tricyclic saturated *tert.*-alcohol, $C_{15}H_{26}O$, which yields guaiazulene on dehydrogenation. The formulae I and II are suggested as possibilities.

I. INTRODUCTION

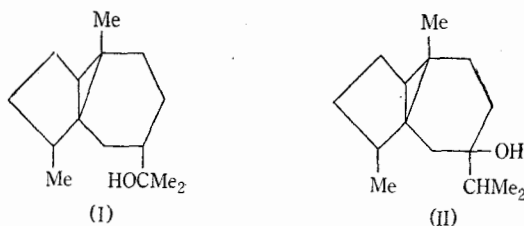
Solvent extraction of the milled bark of *Himantandra baccata* Bail. has yielded a number of compounds including an essential oil consisting largely of sesquiterpene derivatives (Hughes and Ritchie personal communication). Fractionation of the oil gave a considerable proportion of material, b.p. *c.* 100 °C/0.05 mm, which partly solidified. The purified material, himbaccol, $C_{15}H_{26}O$, has m.p. 76 °C, $[\alpha]_D -10^\circ$ (ethanol) and does not appear to be a known compound. It is saturated, gives no colour with tetranitromethane, cannot be hydrogenated at atmospheric pressure over palladium-charcoal, and resists the action of ozone, perbenzoic acid, and potassium permanganate in acetone. It must therefore be tricyclic. The infra-red spectrum, kindly examined by Dr. A. R. Cole, has a band at 2.95 μ indicative of the presence of an hydroxyl group. It was recovered unchanged after treatment with phthalic anhydride in boiling benzene, with 3,5-dinitrobenzoyl chloride in pyridine or with chromium trioxide in pyridine (Poos *et al.* 1953); heating with mineral acid under mild conditions resulted in dehydration. It must therefore be a *tert.*-alcohol.

Oxidation of himbaccol with chromic acid in acetic acid (Fieser 1948) gave rise to acetone and a ketone, $C_{12}H_{18}O$, isolated as their 2,4-dinitrophenylhydrazones. The tertiary hydroxyl group is therefore associated with the *isopropyl* group in the manner shown either in I or II.

Himbaccol readily produced guaiazulene (1,4-dimethyl-7-*isopropyl*azulene) on dehydrogenation with palladium-charcoal. It would therefore appear that one of the rings is very readily opened and is probably three-membered. The position of the ring is conjectural. Infra-red data show that a *cyclopropane* ring, if present, does not contain a methylene group (Cole personal communication). Furthermore, it probably does not terminate in a position adjacent to the *isopropyl* side-chain, since the 2,4-dinitrophenylhydrazone of the C_{12} -ketone

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is stable to acid under conditions where the derivative of thujone is readily converted to that of isothujone. Structures I or II are suggested as working hypotheses.



II. EXPERIMENTAL

(a) *Isolation*.—Crude himbaccol, kindly presented by Dr. G. K. Hughes and Dr. E. Ritchie, was drained on a porous tile. It was then chromatographed in light petroleum (b.p. 40–60 °C) on alumina (40 times its weight). Elution was with light petroleum with increasing admixture of ether up to equal volumes. Himbaccol appeared in the initial fractions, the later ones being contaminated by a liquid alcohol. Crystallization from aqueous methanol raised the m.p. to 76 °C. The action of potassium permanganate in cold acetone for 12 hr gave a more readily purified product (Found: C, 81.1; H, 11.8%. Calc. for $C_{15}H_{26}O$: C, 81.0; H, 11.8%).

(b) *Dehydrogenation*.—The alcohol (1.0 g) was heated at 225–235 °C for 2 hr with palladium-charcoal (10%) (cf. Linstead and Thomas 1940). The product was taken up in light petroleum (b.p. 40–70 °C) and chromatographed on alumina (35 g), the deep blue azulene band and the fraction immediately preceding it being collected separately. The latter fraction showed no signs of reaction with 2,4,6-trinitrobenzene (lack of cadalene) but the azulene readily gave an almost black complex. This was boiled several times with hexane and the undissolved residue recrystallized from methanol. It formed almost black needles, m.p. 149.5–150 °C, undepressed by an authentic specimen of the derivative of guaiazulene m.p. 150–151 °C.

(c) *Oxidation*.—To himbaccol (2 g) in pure acetic acid (15 c.c.) was added powdered chromium trioxide (1.1 g) in three portions over 1 hr with stirring, which was continued for a further 3 hr. Water (80 c.c.) was added and the mixture slowly distilled, the first 2 c.c. of distillate being added to 2,4-dinitrophenylhydrazine in 2N hydrochloric acid. The yellow derivative, m.p. 110–115 °C, was passed through alumina in benzene and crystallized from ethanol to give acetone 2,4-dinitrophenylhydrazone (145 mg), m.p. 123–124 °C undepressed by an authentic specimen m.p. 124 °C. The aqueous-acetic acid solution from the original oxidation was extracted with ether, the extract washed with aqueous sodium hydroxide, dried, and evaporated to give a sweet-smelling oil. This gave rise to a crystalline bisulphite compound, decomposed with dilute HCl. The oil so obtained (95 mg) gave a pale yellow 2,4-dinitrophenylhydrazone, crystallized from methanol, m.p. 94–95 °C (Found: C, 60.0; H, 6.3%. Calc. for $C_{18}H_{22}O_4N_4$: C, 60.3; 6.1%). Brief heating on the steam-bath with ethanolic sulphuric acid (10%) did not change this derivative.

III. REFERENCES

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