Chemical Structure of Hosenkol-A, the First Example of the Natural Baccharane Triterpenoid of the Missing Intermediate to Shionane and Lupane

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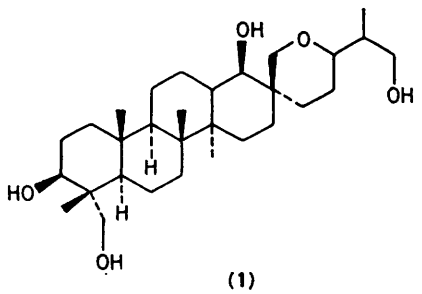
From the seeds of *Impatiens balsamina* L., hosenkol-A (**1**) was isolated and characterized as (3*S*,4*R*,17*R*,20*S*,-24*S*,25*S*)-3,17,26,28-tetrahydroxy-21,24-epoxybaccharane, which is the first baccharane triterpenoid from natural sources, on the basis of *X*-ray analysis.

The triterpenoids form the largest group among the terpenoid classes and all the triterpenoids originate biogenetically from squalene. Scheme 1 shows some biogenetic routes involving dammarane.[1] Among them baccharane† has so far only been postulated as an intermediate, although some baccharanes have been chemically derived.[2–6] The present communication deals with the chemical structure of hosenkol-A, the first naturally occurring baccharane triterpenoid, isolated from the seeds of *Impatiens balsamina* L. (Balsaminaceae).

Impatiens balsamina L., an annual native of India, is now widely cultivated as an ornamental plant. The seeds have been used to treat difficult labour, to suppress puerperal pain, and to act as an emmenagogue, expectorant, and as an antidote

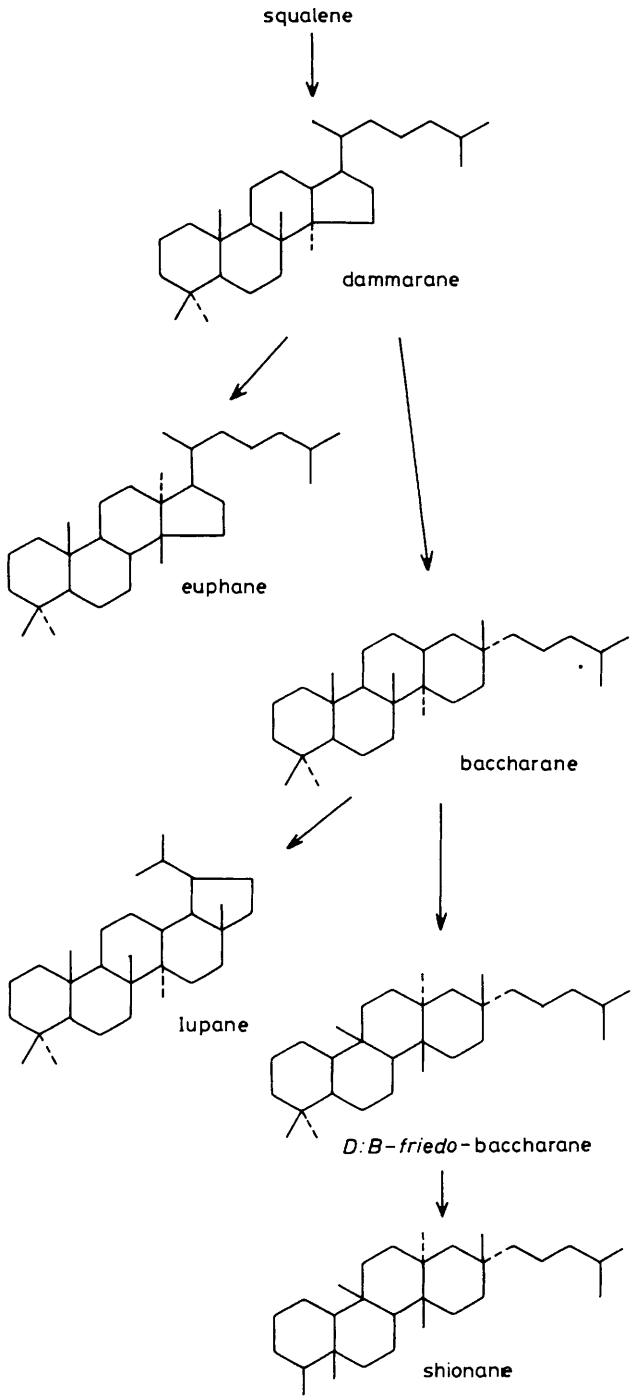
† The name baccharane is derived from baccharis oxide, which was isolated from *Baccharis halimifolia* L. (Compositae), but baccharis oxide has a *D*:*B-friedo*-baccharane skeleton, not a baccharane one.



(1)

for poisoning from fish in some Oriental countries.[7] Extraction of the seeds with methanol–water afforded a considerable quantity of saponins. One of the major saponins, hosenkoside-A, $C_{48}H_{82}O_{20}$, m.p. 233—236 °C, gave hosenkol-A (1) on acid or enzymic hydrolysis. Compound (1) crystallized from methanol as colourless plates, m.p. 225—227 °C, $[\alpha]_D$ +78.9° (*c* 1.51, pyridine). The empirical formula was established as $C_{30}H_{52}O_5$ by elemental analysis‡ and high-resolution mass spectrometry (calc. for $C_{30}H_{52}O_5$ 492.3814, found 492.3796). The i.r. spectrum showed hydroxy (ν 3400 cm^{-1}), but no carbonyl absorptions. The u.v. spectrum showed only end absorption. In the 360 MHz ^1H n.m.r. spectrum four tertiary methyl singlets (δ 0.85, 0.95, 0.97, 1.06) and a secondary methyl doublet (δ 1.10, *J* 6.5 Hz) were observed. The 25 MHz ^{13}C n.m.r. spectrum (shifts in p.p.m.) showed five methyl quartets (δ 12.8, 13.5, 15.0, 16.0, 17.1), three triplets (δ 64.6, 68.5, 72.8) due to a methylene carbon bearing an oxygen atom, three doublets (δ 73.8, 80.0, 80.0) ascribable to a methine carbon with an oxygen atom adjacent to it, and five quaternary carbon singlets (δ 36.1, 37.5, 39.3, 42.4, 43.0), but did not show any signals in the carbon–carbon double bond region. Acetylation of the baccharane (1) with acetic anhydride and pyridine gave a tetra-acetate (^1H n.m.r. four acetyl singlets, δ 1.82, 1.85, 1.86, 1.90). The i.r. spectrum of the tetra-acetate lacked hydroxy absorptions, suggesting that (1) has four hydroxy groups and an ethereal oxygen function. Since compound (1), with the structural features described above failed to be interpreted in terms of the known triterpenoid skeletons, the complete structure and relative stereochemistry were finally elucidated by *X*-ray crystallography.

X-Ray analysis was carried out§ on crystals of (1) obtained from ethanol–ethyl acetate. The thin, plate-shaped crystals belong to the orthorhombic space group $P2_12_12_1$, with a = 11.067(2), b = 35.785(5), c = 7.486(1) Å, U = 2964.7(9) Å^3. Intensity data were measured on a Rigaku RASA AFC-6B four-circle diffractometer using Mo-K_α radiation monochromated by a graphite plate and employing the $2\theta/\omega$ scan technique. The data were corrected for Lorentz, polarization, and background factors. Out of a total of 3042, 1954 reflections were observed [$I > 6\sigma(I)$]. The structure was determined by direct methods (MULTAN) and refined block-diagonal least-squares with anisotropic temperature factors for non-hydrogen atoms. The hydrogen atoms were located from a difference electron density map. The final R and R_w factors were 0.0606 and 0.0669 (w = 1.0), respectively.



Scheme 1. Some biogenetic routes involving dammarane.

Thus, compound (1) is shown to be either (3*S*,4*R*,17*R*,20*S*,-24*S*,25*S*)-3,17,26,28-tetrahydroxy-21,24-epoxybaccharane or its enantiomer. Of these alternatives, however, the former is chosen from a consideration of the biogenetic route of baccharane from dammarane. The isolation of hosenkol-A,

‡ Satisfactory elemental analysis was obtained for hosenkol-A.

§ The *X*-ray data were recorded at the Institute of Pharmacy, Tokushima-Bunri University, Tokushima 770, Japan. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

which has a unique spiro ring, strongly corroborates the postulated biosynthesis of lupane and shionane *via* baccharane.

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