109. *A New Triterpene from the Hong Kong Ericaceae: an Epoxyglutinane from* Rhododendron westlandii.

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A new triterpene, $C_{30}H_{50}O$, has been isolated from the leaves of *Rhododendron westlandii*. This compound, which has been related to glutinane, has been shown not to contain hydroxyl or carbonyl groups. Evidence for a cyclic oxide group has been obtained and structures (III and IV) are considered possibilities.

It has been shown [1] that ursolic acid, cerin, friedelin, epifriedelanol,* and a new triterpene * (from *Rhododendron westlandii*) occur in Hong Kong species of the Ericaceae. The new compound, $C_{30}H_{50}O$ (one atom of oxygen was shown to be present by difference and by a direct oxygen determination), which was twice chromatographed and then recrystallised before use, did not form acyl or carbonyl derivatives under mild or forcing conditions, and absence of hydroxyl and carbonyl groups was confirmed by comparison of its infrared spectrum with those for glutin-5(10)-en-3β-ol (I) and glutin-5(10)-en-3-one (Ia). It is thus presumably an epoxide, and in agreement with this it was eluted from the chromatographic column before the alcoholic and ketonic triterpenoids which the extract also contained.

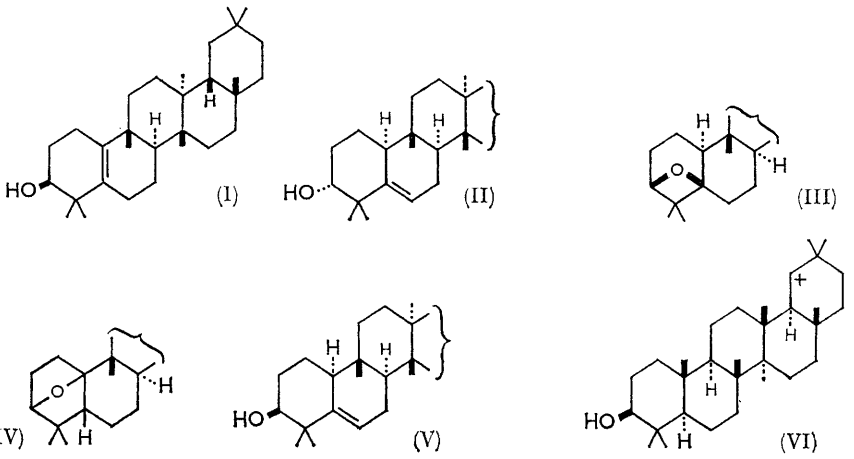
The new compound, which is stable to boiling alkali, is isomerised almost quantitatively under mild acid conditions to glutin-5(10)-en-3β-ol (I). Attempted oxidation with chromic and sulphuric acid gave a mixture of ketones.[2] These ketones could not be separated but were identified as glutin-5(10)-en-3-one and glutin-5-en-3-one since the mixture was reduced to the corresponding mixed alcohols, (I) and glutin-5-en-3α-ol (II), whose acetates were separated by recrystallisation. The ketones were presumably obtained by oxidation

* By error the sign of rotation was reversed for these compounds in a previous paper.[1b]

[1] (*a*) Arthur and Hui, *J.*, 1954, 2782, 4683; (*b*) Arthur, Lee, and Ma, *J.*, 1956, 1461.
[2] Beaton, Spring, Stevenson, and Stewart, *Tetrahedron*, 1958, **2**, 246.

of the alcohols (I) and (II) derived from the oxide by acid-isomerisation. In a separate experiment aqueous acid was found to isomerise the oxide to the alcohol mixture.

The oxide, unlike the alcohols (I) and (II) into which it can be isomerised, did not absorb at low wavelengths in the ultraviolet region (absence of tri- and tetra-substituted double bonds). Its light absorption throughout the entire ultraviolet region, in fact, was



negligible; it gave no colour with tetranitromethane whereas both alcohols gave strong colours; it did not undergo catalytic reduction or react with osmium tetroxide. These facts, considered together with the absence of hydroxyl and carbonyl groups and the ready isomerisation to the alcohol (I), suggest that the compound is a 3,*x*-epoxyglutinane, and structure (III) or (IV) seems probable.*

The oxide was recovered unchanged after treatment with lithium aluminium hydride in various solvents, so the possibility that it is a 1,2-epoxide seems to be excluded. Reaction with boron trifluoride in ether was unsuccessful in that the mixture of alcohols (I) and (V), but no ketone, was obtained. The oxide shows absorption in the region 980—970 cm.$^{-1}$ which might possibly represent that of a cyclic oxide group.[3] In a modification of the test [4] for cyclic oxides, using periodic acid, the oxide appeared to give a positive reaction, but we considered that the test was unreliable for triterpenoid compounds.

Glutin-5-en-3-one (glutinone, alnusenone) was first reported from *Alnus glutinosa* by Chapon and David.[5] Corey and Ursprung [6] converted friedelin into glutinone and the path which they used was re-investigated by Beaton *et al.*[2] who obtained mixed ketones as products [glutin-5-en-3-one and glutin-5(10)-en-3-one]; and the close relation between glutinone and friedelin has been noted.[2]

It is considered [7] that the biogenesis of the pentacyclic triterpenoids takes place from a squalenoid precursor *via* a common ion (VI or equivalent), and Beaton *et al.*[2] consider that degeneration of this ion may give rise to β-amyrin, taraxerol (taraxerone), glutin-5-en-3β-ol (glutinone), friedelin, and other compounds. In view of this, it is worth noting that, among other products, taraxerol and taraxerone occur in Canadian peat moss,[8] as do these two compounds [9] with glutinone [5] in *A. glutinosa*. 5β-Friedelan-3β-ol, with other triterpenoid

* We acknowledge gratefully suggestions from a Referee about the structure of the oxide.

[3] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1956.
[4] Fuchs, Waters, and Vanderwerf, *Analyt. Chem.*, 1952, **24**, 1514.
[5] Chapon and David, *Bull. Soc. chim. France*, 1953, 333.
[6] Corey and Ursprung, *J. Amer. Chem. Soc.*, 1955, **77**, 3667.
[7] Eschenmoser, Ruzicka, Jeger, and Arigoni, *Helv. Chim. Acta*, 1955, **38**, 1890.
[8] Ives and O'Neill, *Canad. J. Chem.*, 1958, **36**, 927.
[9] Koller, Hiestand, Dietrich, and Jeger, *Helv. Chim. Acta*, 1950, **33**, 1050.

compounds, occurs in humidified peat,[10] and this compound with friedelin, β-amyrin,[11] and the new epoxyglutinane occurs in *R. westlandii*.

Experimental

Analyses were by Dr. Zimmermann, Melbourne. M. p.s were taken on a Kofler block. Alumina used was of B.D.H. analysis grade; light petroleum had b. p. 60—80°. Rotations are for $CHCl_3$ solutions. Infrared spectra were taken for Nujol mulls on a Model 137 Infracord spectrophotometer. The spectrum of the oxide was also checked on a large instrument. Ultraviolet spectra were taken for EtOH solutions on a S.P. 500 Unicam instrument.

Isolation and Properties of the New Oxide.—Dried leaves (6·0 kg.) of *Rhododendron westlandii* were extracted with light petroleum, and the total extract, after removal of epifriedelanol as described in a previous paper,[1b] was chromatographed on alumina (2 kg.). Elution with light petroleum gave a wax from the first 500 ml. of eluate, and from the next 1500 ml. an *oxide*, which after two recrystallisations from light petroleum separated as stout needles (5·0 g.), m. p. 201—202°, $[\alpha]_D$ +74·8° (*c* 1·08) (Found: C, 84·4; H, 11·5; O, 4·0. $C_{30}H_{50}O$ requires C, 84·4; H, 11·8; O, 3·8%). Repeated chromatography and recrystallisation did not alter these properties. The oxide is soluble in chloroform, benzene, and light petroleum but very sparingly soluble in ethanol. It gave no colour with tetranitromethane but a deep red colour in the Liebermann–Burchardt test. It was identical with a triterpenoid substance reported previously [1b] from this plant. The oxide was recovered unchanged almost quantitatively after attempted benzoylation and acetylation under mild and forcing conditions, and after being heated with semicarbazide hydrochloride in aqueous pyridine for 12 hr. It did not react with potassium hydroxide in aqueous dioxan or with lithium aluminium hydride in boiling diethyl ether, tetrahydrofuran, or dibutyl ether, and it was recovered unchanged after being treated with osmium tetroxide in chloroform–pyridine for 15 days. It did not react with potassium cyanide in boiling ethylene glycol or with methylmagnesium iodide in boiling ether for 14 hr.

Isomerisation of the Oxide.—(a) *With hydrogen chloride.* Hydrogen chloride was passed into a solution of the oxide (0·5 g.) in dry chloroform (75 ml.). The solvent was removed in a vacuum and the residue crystallised from acetone, as plates of glutin-5(10)-en-3β-ol (0·45 g.), m. p. 243—244·5°, $[\alpha]_D$ −35·7° (*c* 1·01), λ 2070 Å (ε 5880) (Found: C, 84·9; H, 12·0. Calc. for $C_{30}H_{50}O$: C, 84·4; H, 11·8%). This product was also obtained, quantitatively, on treatment of the oxide with concentrated hydrobromic acid in acetic acid. It gave an acetate (acetic anhydride and pyridine) that separated from benzene as plates, m. p. 300—302°, $[\alpha]_D$ −18·0° (*c* 1·05) (Found: C, 81·7; H, 10·8. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%); glutin-5(10)-en-3-one, prepared by oxidation [12] with chromium trioxide of the alcohol (0·18 g.) in stabilised acetone, separated from acetone as prisms (0·14 g.), m. p. 255—257°, $[\alpha]_D$ −92·5° (*c* 0·80), $\lambda_{max.}$ 2900 (ε 87), 2070 Å (ε 5680) (Found: C, 84·8; H, 11·4. Calc. for $C_{30}H_{48}O$: C, 84·8; H, 11·4%). The alcohol, its acetate, and the ketone had infrared spectra identical with those of authentic specimens.

(b) *Attempted oxidation under aqueous acid conditions.* The oxide (1·0 g.) in stabilised acetone (1 l.) was oxidised as above.[12] Concentration of the solution yielded prisms (0·8 g.) of a mixture, m. p. 247—248·5° (Found: C, 85·1; H, 11·7. Calc. for $C_{30}H_{48}O$: C, 84·8; H, 11·4%) [Beaton *et al.*[2] give m. p. 247—249° for the mixed crystal of glutinone and glutin-5(10)-en-3-one], which was almost quantitatively converted into an oxime, m. p. 280—285° (Found: C, 81·5; H, 11·1; N, 3·4. Calc. for $C_{30}H_{49}NO$: C, 81·9; H, 11·2; N, 3·2%). The ketone mixture (0·47 g.) in dioxan (70 ml.) was boiled under reflux with sodium borohydride for 3 hr. The product (0·46 g.), which could not be purified by recrystallisation or chromatography,[2] was treated with acetic anhydride and pyridine at room temperature for 4 days. The product (0·41 g.) afforded (i) glutin-5(10)-en-3β-yl acetate which separated slowly as plates (0·26 g.) and after two recrystallisations from benzene had m. p. and mixed m. p. 299—301°, $[\alpha]_D$ −20·7° (*c* 1·55), and (ii) fine needles (0·15 g.) of glutin-5-en-3α-yl acetate,[13] m. p. 226—229°, $[\alpha]_D$ +42·9° (*c* 0·23), λ 2070 Å (ε 4460) (Found: C, 81·7; H, 10·9. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%),

[10] McLean, Rettie, Spring, *Chem. and Ind.*, 1958, 1515.
[11] Unpublished work in this laboratory.
[12] Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2555.
[13] Beaton, Spring, and Stevenson, *J.*, 1955, 2616.

which was obtained from the acetic anhydride–pyridine filtrate by addition of water followed by crystallisation from benzene–methanol. The acetates had infrared spectra identical with those of authentic samples.

(c) *With boron trifluoride in ether.* A solution of the oxide (0·9 g.) in ether (160 ml.) and 47% boron trifluoride–ether complex (4 ml.) was left at room temperature. Crystals quickly appeared. After 3 hr. water was added to decompose the complex. The washed ethereal phase was dried (Na_2SO_4) and distilled. The residual mixture (0·9 g.) could not be purified by recrystallisation or by chromatography. On treatment with acetic anhydride and pyridine for 2 days at room temperature, crystals which were deposited were collected and recrystallised from benzene. Glutin-5(10)-en-3β-yl acetate (0·76 g.), m. p. 298—299° (identified by mixed m. p. and infrared spectrum), separated. To the pyridine–acetic anhydride filtrate, water was added and the precipitate was collected and recrystallised from benzene–methanol. Flattened needles (0·14 g.) of glutin-5-en-3β-yl acetate, m. p. 191—193°, $[\alpha]_D$ +70·7° (*c* 1·85), separated {Paton *et al.*[14] give m. p. 192—194°, $[\alpha]_D$ +79°} (Found: C, 81·9; H, 11·4. Calc. for $C_{32}H_{52}O_2$: C, 82·0; H, 11·2%). A similar alcohol mixture, obtained after attempted hydrogenation in chloroform with Adams catalyst and also separated by acetylation, was shown to contain glutin-5(10)-en-3β-ol and probably glutin-5-en-3β-ol.

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[14] Paton, Spring, and Stevenson, *J.*, 1958, 2640.