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THE STRUCTURE OF SIMIARENOL FROM THE HONG KONG SPECIES OF RHODODENDRON SIMIARUM

H. R. Arthur, and W. H. Hui

Department of Chemistry, University of Hong Kong

R. T. Aplin, *

Department of Chemistry, Stanford University, Stanford, California.

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The structure of the triterpene alcohol, simiarenol, $C_{30}H_{50}O$, called **simiarol** when first reported (1) by Arthur, Tam, and Angsusingh has now been elucidated.

Simiarenol, (I, R = H) m.p. 209 - 210° , $[\alpha]_D$ + 50.8° was converted into simiarenone (II) m.p. 207 - 208 $[\alpha]_D$ + 24.0° which on Wolff-Kishner reduction gave a product, m.p. 189.5 - 191.5° $[\alpha]_D$ + 76.8° that was shown to be identical (m. s., i. r., and mixed m. p.) with adianene (III) obtained (2) by Ageta, et al. from a japanese fern, Adiantum monochlamys Eaton (Adiantaceae).

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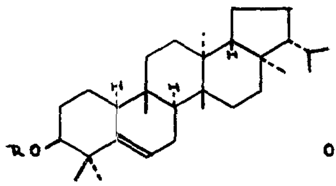
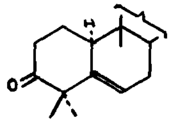
[*] Research Associate, Department of Chemistry, Stanford University present adress: Dyson Perrins Laboratory, Oxford University, England

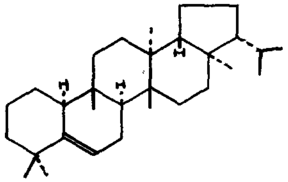


I, R = H

IV, R = CH$_3$CO



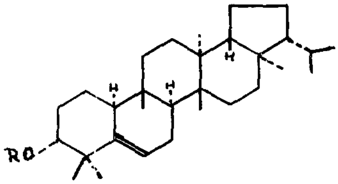
II



III

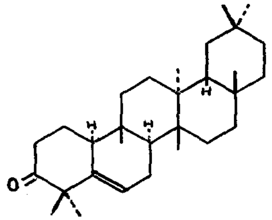
Simiarenyl acetate (IV, R = CH$_3$CO, 3β-axial acetate) shows a lowfield triplet (5.28τ) for a proton on carbon bearing an acetate. The coupling pattern is indicative of an equatorial C$_3$ proton having eq/ax and eq/eq coupling.

Furthermore reduction of simiarenone (II) by lithium aluminium hydride yields episimiarenol (V, R = H) whose acetyl derivative (VI, R = CH$_3$CO, 3α-equatorial acetate) shows a lowfield quartet (5.5τ) for a proton on carbon carrying an acetate. The coupling pattern (J ax/ax *ca.*10 cps; J ax/eq *ca.* 5 cps) being indicative of an axial C$_3$ proton.



V, R = H

VI, R = CH$_3$CO



VII

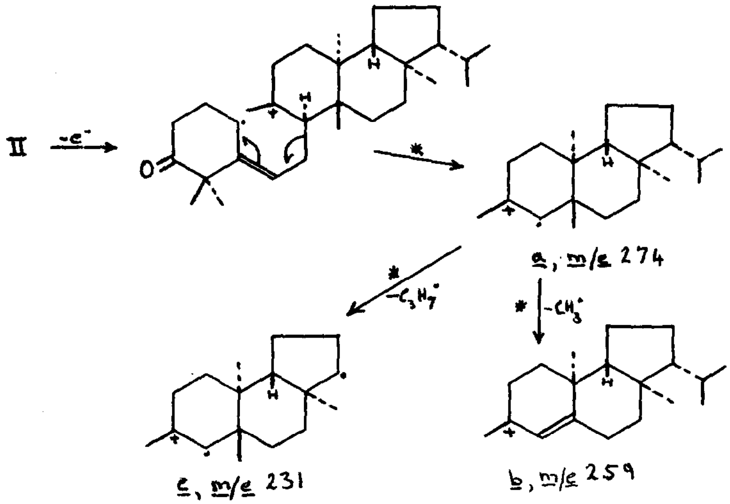
This situation is paralleled by the similar sequence of reactions of glutinol (3) and epifriedelanol (4). The near identity of the O.R.D. curves (Fig. I) of simiarenone (II) and glutinone (VII) confirms that the oxygen in simiarenol (I) is located at C_3. Further support for this conclusion comes from a comparison of the molecular rotation $[\phi]_D$ values and the changes observed in molecular rotation $[\Delta\phi]_D$ on acetylation and oxidation (Table I) with those for the glutane series. Thus simiarenol has structure I (R = H).

TABLE I

Comparison of $[\phi]_D$ and $[\Delta\phi]_D$ values

	$[\phi]_D$		$[\phi]_D$
simiarenol	+213	glutinol	+265
simiarenolacetate	+346	glutinolacetate	+375
simiarenone	+101	glutinone	+123
	$[\Delta\phi]_D$		$[\Delta\phi]_D$
Acetylation	+133	Acetylation	+110
Oxidation	-122	Oxidation	-142

The presence of a Δ^5 double bond and an isopropyl group in simiarenone is reflected in its mass spectrum Fig. 2, which is almost identical to that of glutinone Fig. 3. The base peak (a), m/e 274, of both spectra corresponds formally to a retro-Diels-Alder cleavage of ring B (5). The loss of the allylic C_{26} methyl group gives rise to the other major peak (b), m/e 259. A weak M-43 peak and a strong m/e 231 peak (c), in Fig. 2, which are absent in the spectrum of glutinone (Fig. 3), due to the loss of $C_3H_7^{\bullet}$ from the molecular ion and the ion (a) m/e 274, reflect the presence of an isopropyl group in simiarenone. The formation of the ions a, b, and c, in these spectra can be rationalised as is indicated for simiarenone.



*metastable peak observed.

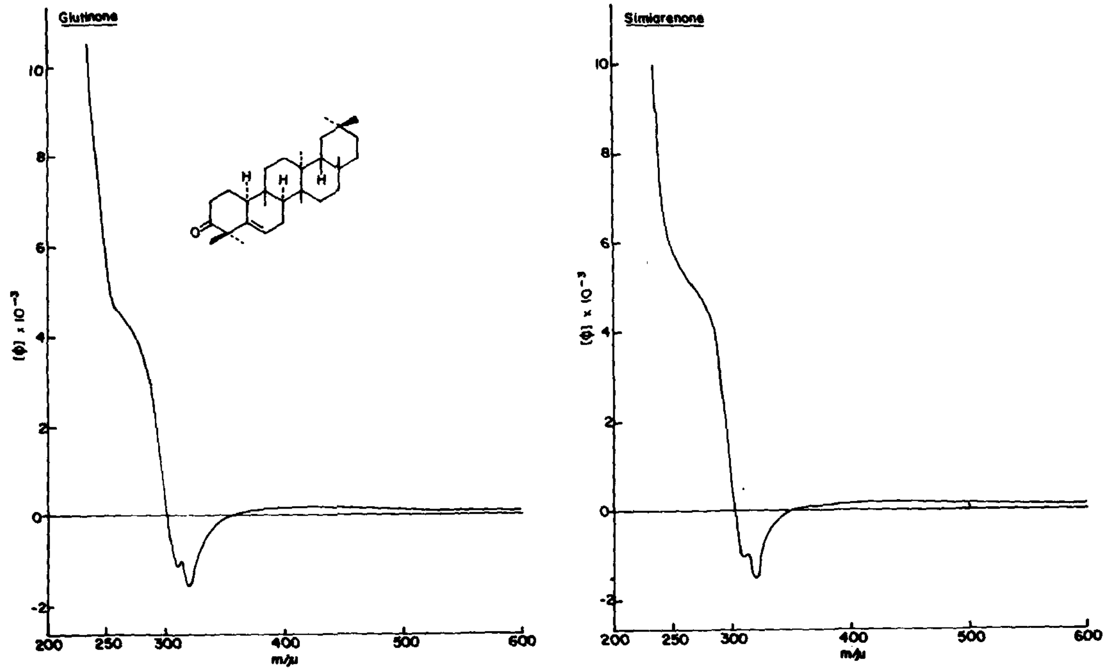


Fig.I Optical Rotatory Dispersion Curves

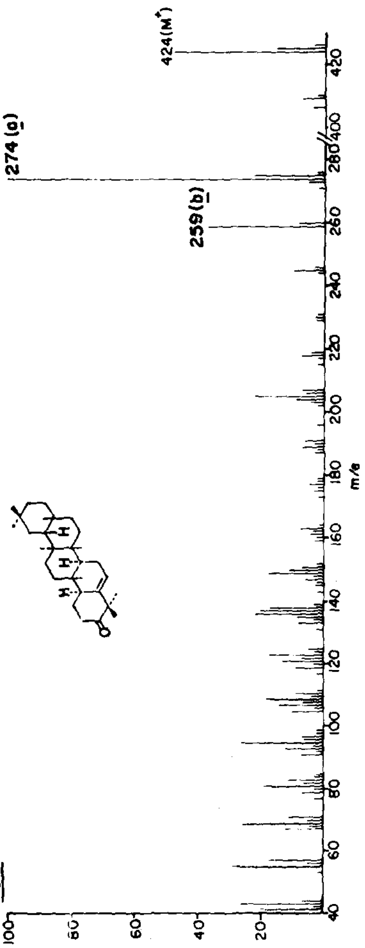


Fig.2 Glutinone

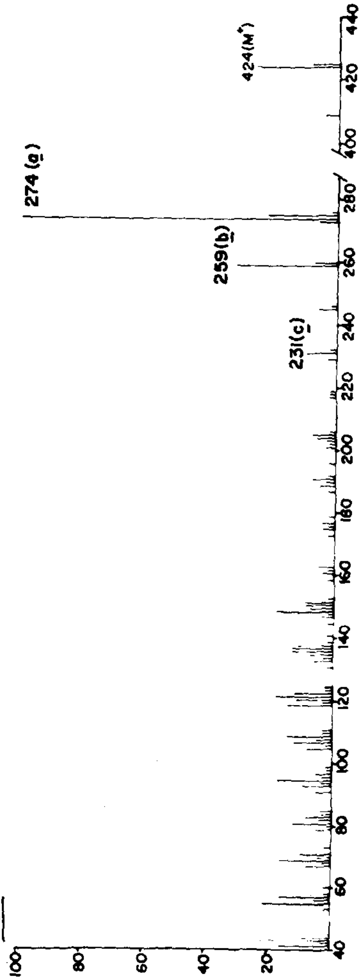


Fig.3 Simiarenone

Relative Abundance

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