

Synthesis and Structures of Edulan I and II

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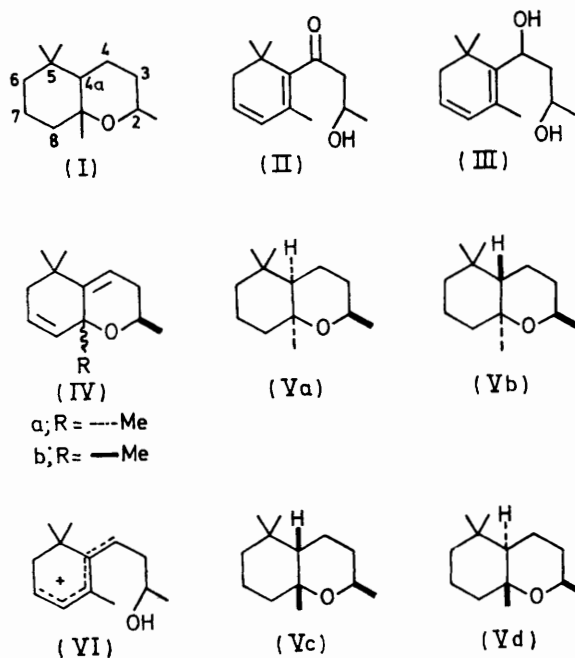
Summary Edulan I and edulan II have been shown by synthesis to be the stereoisomeric 2,3,5,6-tetrahydro-2,5,5,8a-tetramethyl-(8aH)-1-benzopyrans (IVa) and (IVb), the configurations of which are established by the results of microhydrogenation.

EDULAN I and EDULAN II, important trace components in the flavour of the purple passion fruit (*Passiflora edulis* Sims),¹ were recently shown to be isomeric tetramethyl-tetrahydrobenzopyrans with the skeleton (I) but the positions of the double bonds could not be assigned with

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certainty.³ Synthesis from an intermediate (II) in the preparation of β -damascenone³ now completes the elucidation of the structure of the edulans.



Reaction of the ketol (II) with sodium borohydride gave in approximately equal amounts two diastereoisomeric diols (III) which on treatment with 0.5M boron trifluoride in ether at 0° for 30 min gave a mixture,† with major components compounds X and Y (in order of their g.l.c. retention times on both Silicone SF 96 and Carbowax 20M) in a ratio of *ca.* 7:2. Longer reaction time or more vigorous conditions increased the proportion of Y. Treatment of the diol (III) with ion exchange resin IR 120 (H form) in ether at 20° for 3 h led to an equilibrium mixture of X and Y in a ratio of *ca.* 1:10, also formed from X or Y under the same conditions. Yields of the mixture of isomers from the ketol (II) averaged 85%.

† Minor components appear to be derived from the small quantities of double bond isomers³ present in the ketol (II).

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§ The absolute configuration has not been determined. Synthetic compounds are, of course, racemic.

¹ K. E. Murray, J. Shipton, and F. B. Whitfield, *Austral. J. Chem.*, 1972, 25, 1921.

² F. B. Whitfield, G. Stanley, and K. E. Murray, *Tetrahedron Letters*, 1973, 95.

³ K. S. Ayyar, R. C. Cookson, and D. A. Kagi, *J.C.S. Chem. Comm.*, 1973, 161.

Comparison of mass and i.r. spectra and g.l.c. retention times, together with the results of microhydrogenation by reaction gas chromatography, indicated² that compounds X and Y had the same structures as edulan II and I respectively. Subsequently the n.m.r. spectra of the natural edulans were found to be identical with those of the synthetic compounds. Despite this identification the synthetic and natural edulans have different aromas, no doubt because of the occurrence of both optical isomers in the synthetic compounds.

The 100 MHz n.m.r. spectra, including double irradiation and INDOR experiments, showed the presence of the groups C-CH₂-CH=CH-C and C=CH-CH₂-CHMe-O in both isomers. The disubstituted double bonds were shown to be Δ^7 ,⁸ in both edulans by observation of the chemical shifts produced by the addition of Eu(fod)₃ and Yb(fod)₃ reagents to solutions of the synthetic compounds.‡ Thus the edulans may be formulated as the stereoisomeric 2,3,5,6-tetrahydro-2,5,5,8a-tetramethyl-(8aH)-1-benzopyrans (IV).

Microhydrogenation of synthetic or natural edulan I using either the reaction gas chromatographic technique² or in acetic acid over PtO₂ gave the known octahydrobenzopyrans (Va, Vb) in a ratio of *ca.* 10:1. Under the same conditions edulan II gave the isomers (Vc, Vd) in a ratio of *ca.* 3:1 [Satisfactory mass spectral and g.l.c. data have been obtained to allow the positive identification of the isomeric octahydrobenzopyrans (Va-d)²]. The edulans therefore differ only in relative stereochemistry and hence edulan I and edulan II are assigned the relative configurations (IVa) and (IVb) respectively.§

While the mechanisms of the reactions have not been investigated, it seems likely that the acid-catalysed cyclisation of the diol (III) and the equilibration of the edulans (IV) take place through the common pentadienyl-carbonium ion (VI). Edulan I (IVa) with the 2-methyl group equatorial in a distorted chair conformation of the dihydropyran ring is more stable than edulan II (IVb) with the 2-methyl group equatorial in a distorted boat (or axial in a distorted chair).

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