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CONCERNING THE STRUCTURES OF EDULAN I AND II

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Two novel compounds with intense "rose-like" aromas have been reported in the juice of the purple passionfruit (Passiflora edulis, Sims)[1]. Previously referred to as the "rose compounds", the major one (1 p.p.m.) has been named edulan I and the other (0.1 p.p.m.) edulan II.

For the present study they were isolated by GC using successively high resolution polar and nonpolar columns[1]. This limited the amount of pure material available so that evidence of their structures is based on GC and mass spectral data, but is largely dependent on microhydrogenation studies using a recently developed technique[2]. New evidence has shown that the previously assigned structures[1] are in part incorrect and one or other of these structures is now suggested for edulan II (Scheme 2).

Edulan I and II have identical low resolution mass spectra[1]: m/e 192 (13)[b], 177 (100), 159 (13), 148 (21), 133 (80), 119 (17), 107 (14), 91 (27), 77 (16), 43 (23), which, except for the intense fragment m/e 133, closely resemble that of β-ionone. Their molecular formula was established as $C_{13}H_{20}O$ by high resolution mass spectrometry using a newly developed microsample introduction technique[3]. Edulan I gave an IR spectrum $\nu_{max}^{CCl_4}$ 3030, 2970, 2890, (methyl, methylene and methine) 1447, 1375 (gem dimethyl) 1240-1150 (ether C-O-C) 1098, 987, 955, 837 cm^{-1} and a UV spectrum, transparent in hexane above 210 nm, but insufficient material precluded us from obtaining IR data for edulan II.

Microhydrogenation of either edulan I or II over 10% Pt/C at 300°C (Scheme 2) gave a mixture of cis and trans tetrahydroionones. Consideration of this result together with the GC and MS data of edulan I and II and α- and β-ionone indicated that the edulans were bicyclic and structurally related to the ionones. Since the otherwise uninformative IR spectrum suggested

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[b] Percent relative intensity.

that edulan I was a cyclic ether, the photo-isomer of β-ionone (1) was prepared[4] and gave an MS resembling, in many respects, that of the edulans.

GC Retention Times expressed as Linear Retention Indexes

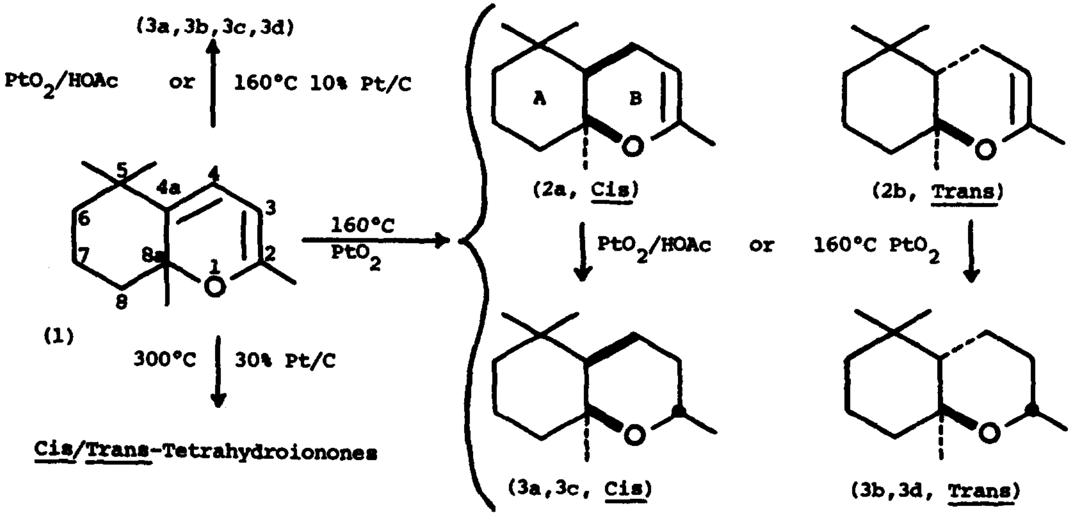
Compound	Silicone SF 96[a]	Carbowax 20M[a]
Edulan I	1309	1602
Edulan II	1258	1498
Photo-isomer of β-ionone (1)	1341	1664
α-Ionone	1420	1815
β-Ionone	1475	1900
Cis-hexahydrobenzopyran (2a)	1271	1461
Trans-hexahydrobenzopyran (2b)	1339	1586
Octahydrobenzopyran (3a)	1313	1502
Octahydrobenzopyran (3b)	1331	1549
Octahydrobenzopyran (3c)	1335	1549
Octahydrobenzopyran (3d)	1349	1580

[a] Glass GC columns (6m long, 2mm bore) 3% phase on Chromosorb G at 150°C.

Microhydrogenation of the photo-isomer (1) (Scheme 1) at 300°C over 10% Pt/C gave *cis* and *trans* tetrahydroiononés, while at 160°C over PtO_2, (1) gave the *cis* and *trans* hexahydrobenzopyrans (2a) and (2b) identical in mass spectra and GC data with specimens prepared by the method of Smit *et al*[5]. Also obtained were the four stereoisomers of the octahydrobenzopyrans (3a, 3b, 3c, 3d) named in order of their retention indexes (see Table) and identical in MS and retention times with specimens prepared according to the method of Büchi and Yang[4].

Microhydrogenation (Scheme 2) of edulan I at 160°C over PtO_2 gave one octahydrobenzopyran (3a) and dihydroedulan I[6] while under the same conditions edulan II gave two octahydrobenzopyrans (3c) and (3d) and dihydroedulan II[6]. The edulans thus have the carbon skeleton (3) and to satisfy the molecular formula $C_{13}H_{20}O$ edulan I and II each contain two double bonds. Structure (1) is eliminated by GC data, mass spectra and hydrogenation results (Schemes 1 and 2), hence rings A and B of edulan I and II each contain one double bond.

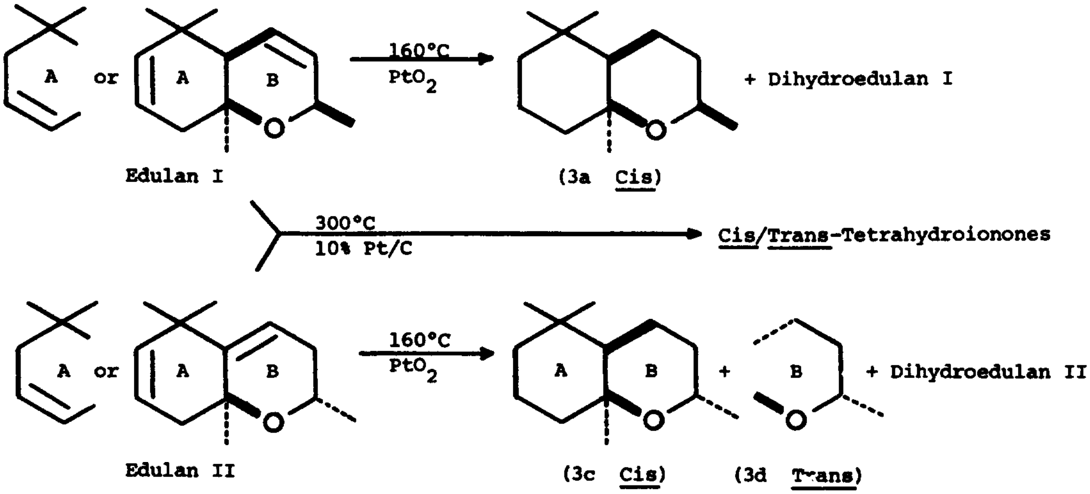
Hydrogenation of cis-hexahydrobenzopyran (2a) either in acetic acid or at 160°C over PtO_2 gave the octahydrobenzopyrans (3a, 3c) while under similar conditions trans-hexahydrobenzopyran (2b) gave the octahydrobenzopyrans (3b, 3d). Therefore rings A and B of the octahydrobenzopyrans (3a, 3c) have a cis fusion and the isomers (3b, 3d) a trans ring fusion.



SCHEME 1

From the NMR spectra[7] of the octahydrobenzopyrans (3a, 3b, 3c, 3d) it was possible to determine the relative stereochemistry at the asymmetric centres C_2, C_{4a}, C_{8a} and to show that the isomeric pairs (3a, 3b) and (3c, 3d) had different configurations at C_2. However, the absolute stereochemistry at C_2, C_{4a}, C_{8a} is unknown and hence an arbitrary geometry has been shown for these centres in Schemes 1 and 2.

As edulan I yields the cis-octahydrobenzopyran (3a) only (Scheme 2), the double bond in ring B is required in the 3,4 position and rings A and B have cis fusion. Edulan II on the other hand yields the cis and trans-octahydrobenzopyrans (3c, 3d) and hence the double bond is in the 4,4a position. From the hydrogenation results (Scheme 2) edulan I and II have different configurations at C_2. Since the double bond in ring A of both edulans is located in either the 6,7 or the 7,8 position, edulan I and II have one or other of the structures shown in Scheme 2. With the amounts of edulan I and II at present available it is not possible to assign the exact location of the double bond in ring A. Because of the importance of edulan I in passionfruit flavour[1] and of the possible value of the edulans to the flavouring industry larger amounts of these compounds are being prepared for further study.



SCHEME 2

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4. G. Büchi and N.C. Yang, J. Amer. Chem. Soc. **79**, 2318 (1957).
5. V.A. Smit, A.V. Semenovskii and V.F. Kucherov, Izv. Akad. Nauk. SSSR, Ser. Khim. 1601 (1963).
6. The MS of dihydroedulan I and dihydroedulan II together with their hydrogenation products indicate that these compounds are tetramethylhexahydrobenzopyrans.
7. The NMR, MS and IR spectra of the octahydrobenzopyrans (3a, 3b, 3c, 3d) will be discussed elsewhere.