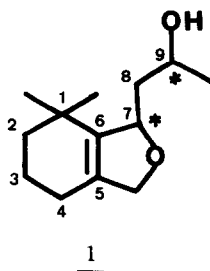


STRUCTURE AND SYNTHESIS OF TWO NOVEL IONONES IDENTIFIED IN THE PURPLE
PASSIONFRUIT (PASSIFLORA EDULIS SIMS)

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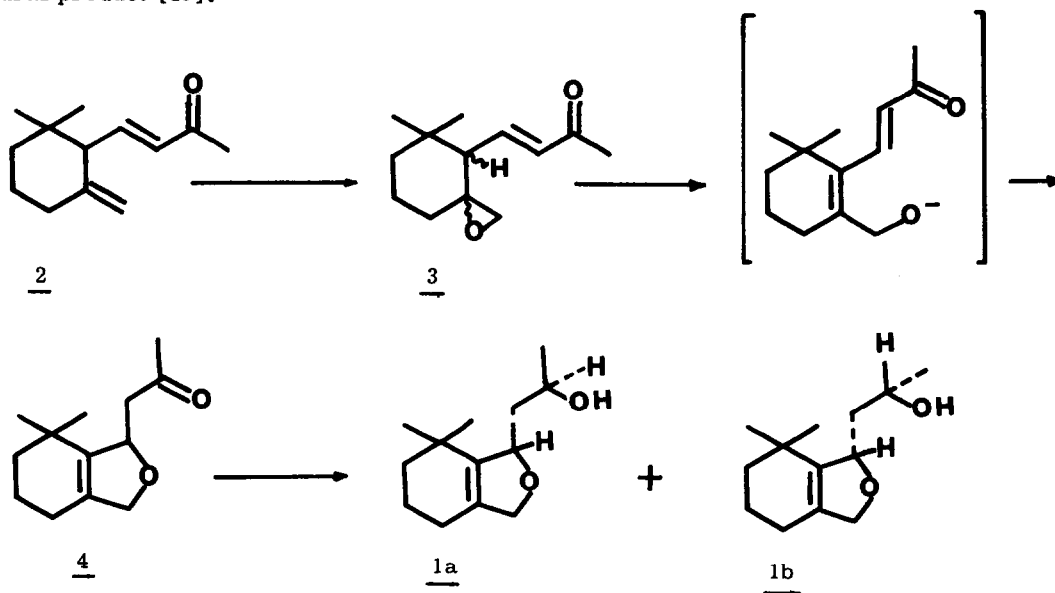
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Analysis of the volatiles of the purple-skinned passionfruit (Passiflora edulis Sims) [1] yielded about 500 μ g of a new compound from a neutral subfraction. On a Ucon HB 5100 column, the new compound was much more polar than β -ionone but slightly less polar than the lactone of 2-hydroxy-2,6,6-trimethylcyclohexylideneacetic acid (dihydroactinidiolide) [2], both identified [3] in the same fruit. The mass spectrum (MS) showed M.W. 210, the base peak being at m/e 151 (M - 59), with typical peaks at m/e 192 (M - 18) and 81 ($C_5H_5O^+$). $C_{13}H_{22}O_2$ is in good agreement with both the MS fragmentation pattern and the NMR integration curve. Presence of $CH_3-\overset{OH}{\underset{|}{CH}}-CH_2-$ was indicated by NMR signals at δ 1.17 (3H, d, J = 6 Hz, \underline{CH}_3-CH-O), 4.07 (1H, m, $\underline{H}-C-O$), and 4.23 (1H, s, OH, disappears on addition of D_2O) ppm, and decoupling experiments (irrad. at δ 1.17 and 4.07 ppm). Formation of a very stable fragment at m/e 151 (base peak) is by loss of the whole ($CH_3-\overset{OH}{\underset{|}{CH}}-CH_2$)^{*} group (M - 59), and the stability of this $C_{10}H_{15}O^+$ ion might suggest the presence of a six- or five-membered heterocycle. A gem-dimethyl group (NMR, δ 1.00 and 1.03 ppm) was present, and signals at δ 4.47 (2H, m) and 4.95 (1H, m) ppm were compatible with allylic hydrogens in a 2,5-dihydrofuran ring (see e.g. [4]). On these grounds and for biogenetic reasons we postulated structure 1 (for numbering see [5]) as a hypothesis.



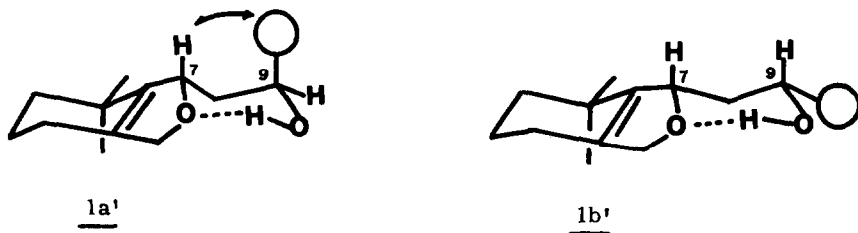
Structure 1 possesses two chiral carbon atoms, so there are four stereoisomers. In order to corroborate the structure and to assign the relative configuration of the natural product, the two racemic diastereoisomers, 1a and 1b, were synthesized by the following route.

γ -Ionone (2) and *m*-chloroperbenzoic acid gave a mixture of the two diastereoisomeric epoxides 3a [6] and 3b [6] ($\sim 2:1$ mixture, by NMR) in 87% yield. When this mixture was stirred with one equivalent of sodium methylate in dimethylformamide for 1 h at room temperature the ketone 4 [7] was isolated in 70% yield. Lithium aluminum hydride reduction of the ketone 4 furnished a mixture (94% yield) of the two diastereoisomers, 1a [8] and 1b [9] (4:1 ratio, by GC), which were separated by column chromatography on silica gel in ether-hexane (1 : 9 to 1 : 7). The more abundant isomer, 1a, proved identical in all respects with the natural product [10].



The configurational assignment of the two diastereoisomers 1a and 1b is based on two independent NMR arguments. (1) NMR dilution experiments demonstrated a strong intramolecular hydrogen bond between the hydroxyl group and the ether oxygen, yielding the two stable conformations 1a' and 1b'. The axial hydrogen at C(7) in 1a' (at δ 4.95 ppm) is, as expected, strongly shielded by the 1,3-diaxial methyl group at C(9) compared with the C(7) hydrogen (at δ 5.13 ppm) in 1b'. (2) Assuming a close similarity between the diamagnetic anisotropy of dioxanes [11] and the rings formed by intramolecular hydrogen bonding in formulae 1a' and 1b', the axial hydrogen or methyl group at C(9) should resonate at higher field than the equatorial isomer. This agrees with our assignments, and with the chromatographic behaviour, the isomer 1a (axial methyl) being less adsorbed ('less polar') than the epimer 1b.

The ketone 4 was subsequently identified in the purple [1] and in the yellow [12] passion-fruit, synthetic and natural compounds having identical mass spectra and retention times on a Ucon capillary column.



To the best of our knowledge 1a and 4 are the first examples of a new class of naturally occurring ionone derivatives bearing an ether bridge from the C(5) methyl group to the carbon C(7) [5].

Acknowledgment

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References and Notes

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- [2] a) T. Sakan, S. Iseo and S.B. Hyeon, *Tetrahedron Letters* 1967, 1623.
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- [3] K.E. Murray, J. Shipton and F.B. Whitfield, *Aust. J. Chem.* 25, 1921 (1972).
- [4] a) L.M. Jackman and S. Sternhell, *Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*, 2nd Edition, Pergamon Press, 1969, page 188.
 b) G. Ohloff, V. Rautenstrauch and K.-H. Schulte-Elte, *Helv. Chim. Acta* 56, 1503 (1973).
- [5] O. Isler, Editor, *Carotenoids*, Birkhäuser Verlag, Basel, 1971.
- [6] NMR, IR and mass spectrum are in agreement with this structure.

- [7] 90 MHz ^1H -NMR (CDCl_3): δ 1.05 (6H, 2s), 2.24 (3H, s), 2.64 (1H, d, $J = 5$ Hz), 2.66 (1H, d, $J = 9$ Hz), 4.46 (2H, m), 5.25 (1H, m) ppm. Irrad. at 5.25 \longrightarrow 2.64 + 2.66 \longrightarrow 2.65 (1H, 's') ppm.
 MS: $m/e = 150$ (100), 135 (98), 43 (70), 151 (51), 81 (43), 193 (25), 107 (23), 95 (20), M^+ = 208 (5).
 IR (neat): 1710, 1675, 1070, 1040, 1020 cm^{-1} .
- [8] 90 MHz ^1H -NMR (CDCl_3): δ 1.00 (3H, s), 1.03 (3H, s), 1.17 (3H, d, $J = 6$ Hz), 4.07 (1H, m), 4.23 (1H, s), 4.47 (2H, m), 4.95 (1H, m) ppm. Irrad. at 1.17 \longrightarrow 4.07 (1H, d of d, $J_1 = 6$ Hz, $J_2 = 2$ Hz), irrad. at 1.75 \longrightarrow 4.07 (1H, 'q'-like), irrad. at 4.07 \longrightarrow 1.17 (3H, s) + 1.75 (simplified multiplicity) ppm.
 MS: $m/e = 151$ (100), 81 (45), 43 (29), 95 (24), 177 (16), 133 (16), 192 (15), 109 (14), 107 (14), M^+ = 210 (8).
 IR (neat): 3480, 1678, 1133, 1070, 1054, 1040, 1020 cm^{-1} .
- [9] 90 MHz ^1H -NMR (CDCl_3): δ 1.04 (6H, s), 1.21 (1H, d, $J = 7$ Hz) 3.41 (1H, d, $J = 3$ Hz), 4.04 (1H, m), 4.5 (2H, m), 5.13 (1H, m) ppm. Irrad. at 1.21 \longrightarrow 4.04 (1H, d of d, $J_1 = 7$ Hz, $J_2 = 3$ Hz), irrad. at 1.8 \longrightarrow 4.04 (1H, simplified m), irrad. at 4.04 \longrightarrow 1.21 (3H, s) + 1.8 (simplified multiplicity) ppm.
 MS: $m/e = 151$ (100), 81 (48), 43 (30), 95 (25), 177 (22), 133 (17), 192 (17), 109 (16), 107 (16), M^+ = 210 (9).
 IR (neat): 3415, 1678, 1130, 1095, 1065, 1040, 1020 cm^{-1} .
- [10] Insufficient natural material precluded measurement of its optical rotation.
- [11] See e.g. reference [4a], page 240.
- [12] M. Winter et al., full paper in preparation.