

Mass Spectra of φ -Pelletierine, 9-Methyl-3-oxagranatan-7-one, and 9-Methyl-3-oxagranatan-7 α -ol

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The mass spectra of φ -pelletierine, 9-methyl-3-oxagranatan-7-one, and 9-methyl-3-oxagranatan-7 α -ol are discussed in relation to recent work by Djerassi and his co-workers on the tropane alkaloids.

IN connection with a structural problem in compounds believed to be related to 9-methyl-3-oxagranatan-7-one (I), it became necessary to examine the mass spectrum of this compound and of its parent hydrocarbon, ψ -pelletierine (II). In view of the recently published

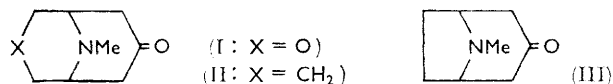
¹ E. C. Blosssey, H. Budzikiewicz, M. Ohashi, G. Fodor, and C. Djerassi, *Tetrahedron*, 1964, **20**, 585.

work ¹ on the mass spectra of tropane alkaloids, it was thought of interest to publish these results separately.

The reported methods for the synthesis of 9-methyl-3-oxagranatan-7-one are Dieckmann cyclisation from the appropriate *N*-methyilmorpholine derivative ² and use of oxybisacetaldehyde in the Robinson-Schöpf

² D. Jerchel and H. Weidmann, *Annalen*, 1957, **607**, 126.

synthesis.³ We have varied the latter method by a simpler procedure for preparation of the dialdehyde component, namely, the oxidation of 1,4-anhydroerythritol with aqueous sodium periodate.



The mass spectra of (I) and (II) would be expected to follow closely the pattern already described for tropinone (III) and its derivatives.¹ Spectra of both (I) and (II) clearly showed the molecular ion.

ψ -Pelletierine (II) (Figure 1).—It would be expected* that fragments retaining ring A would be m/e 14 greater than those from tropinone (III), whilst those in which

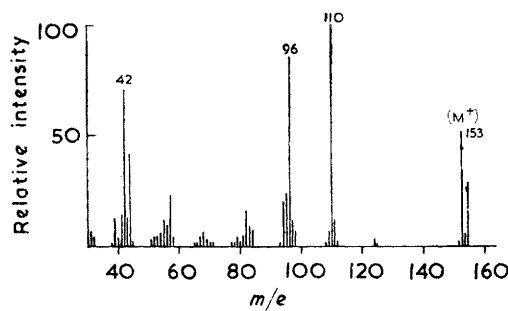
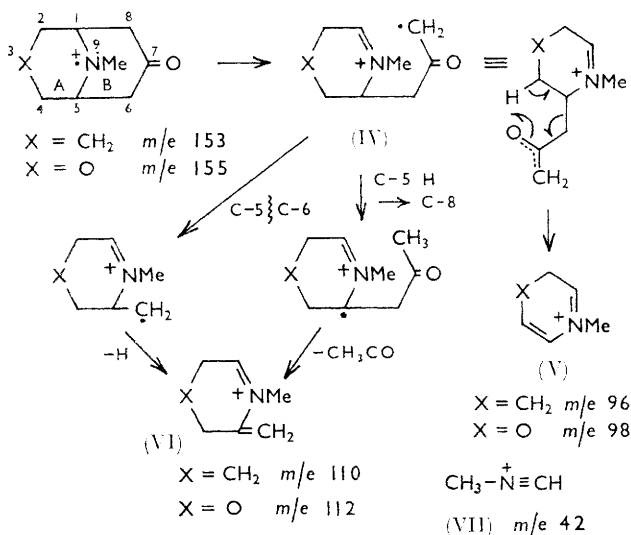


FIGURE 1 Mass spectrum of ψ -pelletierine

ring A is lost would be identical with those from (III). Two of the major peaks in tropinone are at m/e 82 and 96, and are derived from fragmentation of ring B. As

Route (a)



expected, therefore, in the spectrum of (I) the peaks at m/e 96 and 110 are prominent [route (a)]. The latter

³ C. L. Zirkle, F. R. Gerns, A. M. Pavloff, and A. Burger, *J. Org. Chem.*, 1961, **26**, 395.

* For the detailed reasoning behind the proposed fragmentation pattern see ref. 1.

peak is the more intense, since both species (VI) and (IX) ($\text{X} = \text{CH}_2$) contribute to it. Another intense peak is at m/e 42 (VII), characteristic¹ of tropane alkaloids. The loss of carbon monoxide from fragment (X) is supported by a metastable peak at m/e 62.5 (calc. 62.1). As expected, route (a) is preferred over route (b), since the intermediate (IV) is more stable than (VIII).

9-Methyl-3-oxagranatan-7-one (I) (Figure 2).—Here, fragments in which the heteroatom ring A is retained should be m/e 16 greater than in tropinone, and m/e 2

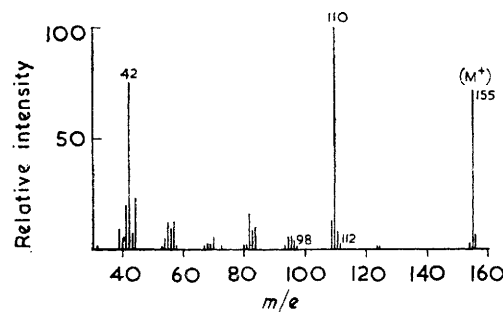
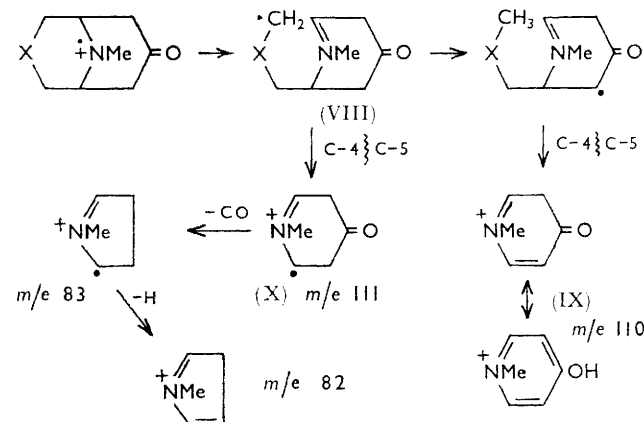


FIGURE 2 Mass spectrum of 9-methyl-3-oxagranatan-7-one

greater than in ψ -pelletierine (II). Introduction of the oxygen atom into ring A would be expected to favour greatly fragmentation of this ring compared with the

Route (b)



case of compound (II), because of the increased stability of intermediate (VIII; $\text{X} = \text{O}$) compared with (VIII; $\text{X} = \text{CH}_2$). The mass spectrum shows that this is so. The base peak at m/e 110 can now only arise from fragment (IX), formed by route (b), an obviously favoured process. Very little fragmentation occurs by route (a), as shown by the peaks at m/e 98 and 112 (V and VI; $\text{X} = \text{O}$). Again there is an intense peak at m/e 42 (VII).

9-Methyl-3-oxagranatan-7 α -ol (Figure 3).—The mass spectrum of this compound follows the expected¹ fragmentation pattern, with dominant rupture of ring A as for compound (I), above.

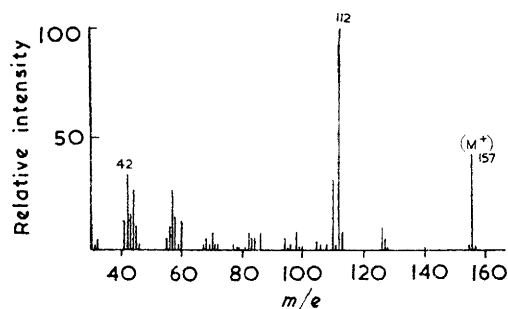


FIGURE 3 Mass spectrum of 9-methyl-3-oxagranatan-7 α -ol

EXPERIMENTAL

ψ -Pelletierine.—This compound, prepared by the literature method,⁴ but using a commercial 20% aqueous solution of glutaraldehyde, had m. p. 47–48° (lit.,⁴ 47–48.5°); it was characterised as the dibenzylidene derivative, m. p. 198–199° (from ethanol) (lit.,⁵ 197–199°).

9-Methyl-3-oxagranatan-7-one.—A solution of 1,4-anhydroerythritol⁶ (3.41 g., 0.033 mole) and sodium metaperiodate (7.06 g., 0.033 mole) in water (300 ml.) was allowed to stand in the dark for 24 hr. Dilute aqueous sodium hydrogen carbonate was carefully added to increase the pH from 3.5 to 6.0, followed by barium chloride dihydrate (4.02 g., 0.0165 mole). The resulting white suspension was poured into ethanol (900 ml.), and, after removal of the inorganic solids, the solution was evaporated below 35° to about 100 ml. Methylamine hydrochloride (4.45 g., 0.066 mole), sodium acetate trihydrate (13.5 g.,

0.099 mole), and acetonedicarboxylic acid (9.63 g., 0.066 mole) were added, and the resulting solution allowed to stand for 7 days at room temperature. During this time the solution became yellow, carbon dioxide was evolved, and the pH rose from 3.6 to 5.8. The solution was heated on a water-bath for 5 min., adjusted to pH 10 with sodium carbonate, and extracted continuously with chloroform for 5 days. Evaporation of the extract gave a dark brown syrup (5.07 g.) which was chromatographed on alumina (Spence, type H) and eluted with benzene-chloroform (1:1), to give an oil (3.89 g.). Crystallisation from cyclohexane gave the product (1.79 g., 35%), m. p. 76–77° (lit.,³ 79–80°) (Found: C, 62.0; H, 8.5; N, 8.9. Calc. for C₈H₁₃NO₂: C, 61.9; H, 8.5; N, 9.0%). The same yield was obtained if the chromatography was replaced by several recrystallisations.

The product was characterised as its *methiodide* (83%) (from water), m. p. 289–290° (decomp., subl.) (Found: C, 36.5; H, 5.5. C₁₉H₁₆INO₂ requires C, 36.4; H, 5.4%), and as its *dibenzylidene derivative* (83%), m. p. 183–184° (from propan-2-ol) (Found: C, 79.7; H, 6.3. C₂₂H₂₁NO₂ requires C, 79.7; H, 6.4%).

9-Methyl-3-oxagranatan-7 α -ol.—This was prepared by the literature method,³ m. p. 142.5–144° (from light petroleum) (lit.,³ 144–145°).

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BRIGHTON. [6/168 Received, February 8th, 1966]

⁵ B. J. Calvert and J. D. Hobson, *J. Chem. Soc.*, 1965, 2723.

⁶ J. S. Brimacombe, A. B. Foster, M. Stacey, and D. H. Whiffen, *Tetrahedron*, 1958, 4, 351.

⁴ A. C. Cope, H. L. Dryden, jun., and C. F. Howell, *Org. Synth.*, 1957, 37, 73.