A Mass Spectral Fragmentation Reaction Characteristic of 11-Oxo-α-amyrin and 11-Oxo-β-amyrin Derivatives

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In connection with an investigation of nonvolatile constituents from *Carphephorus odoratissimus* [1] the mass spectral fragmentation of 11-oxo-α-amyrin and 11-oxo-β-amyrin derivatives became of importance for structural elucidation purposes. In addition to the characteristic and well documented peaks due to retro-Diels-Alder and McLafferty fragmentation,[2] the mass spectra of these compounds also display a prominent *m/e* 135 peak, which apparently is of equal diagnostic significance.

The possible genesis of the *m/e* 135 ion had, to our knowledge, previously only been discussed in a study of mass spectra of dehydration and solvolysis products from β-amyrin and methyl glycyrrhetate [3] and in the structural elucidation of liquoric acid.[4] In these investigations the ion was formulated as a hydrocarbon fragment mainly comprising ring A and formed by rupture of the 6,7 and 9,10 bonds. However, as this formulation was not consistent with our results obtained for the acetates of 11-oxo-α-amyrin and 11-oxo-β-amyrin (*6* and *1*), we found it desirable to examine the reaction in further detail. While this work was in progress, a study of ring A transformed products derived from methyl glycyrrhetate was published by Askam and Bradley [5] in which the *m/e* 135 ion is suggested to comprise ring C and to be derived from the McLafferty fragment. Our results, discussed below, confirm their proposal and allow the formulation of a mechanism for the formation of the $C_9H_{11}O$ ion, now shown to be the dominating *m/e* 135 species, as a highly stabilised fragment.

In the spectra of all 11-oxo-α-amyrin and 11-oxo-β-amyrin derivatives available to us (*1* – *6*), the *m/e* 135 peak is prominent (30 – 90 %), but of considerably reduced intensity in the spectra of the 11-non-oxo derivatives *7* – *10* implying that the formation of the corresponding ion is triggered by the 11-oxo group.

Neither variation of the substituents in ring E (*cf.* *1* – *6*) nor alteration of ring A [5] (*cf.* *11* – *14*) cause a shift of the *m/e* 135 peak demonstrating that the formation of the species involves elimination of both terminal parts of the molecule.

High-resolution measurements revealed that the peak is mainly (85 %) due to an oxygen containing ion, $C_9H_{11}O$ (found 135.0813, calc. 135.0810), and only to a minor extent (15 %) to a $C_{10}H_{15}$ fragment. (Found 135.1175, calc. 135.1174.) It is evident therefore that the 11-oxo group is incorporated in the abundant $C_9H_{11}O$ ion.

Diffuse peaks (*m/e* 60.6), observed in the spectra of glabrolide (*4*) and isoglabrolide (*5*), indicate that the *m/e* 135 ion is derived from the McLafferty fragment.

A mechanism for this fragmentation reaction meeting the requirements detailed above and leading to a highly stabilised ion is given in Scheme 1. Thus, migration of the methyl group at C(14) to C(13) in the McLafferty fragment (a) – a reaction previously demonstrated to occur in similar systems [6,7] followed by cleavage of the now allylic 13,18 bond – provides an intermediate (b) in which ring C has become aromatic. Subsequent rupture of the allylic 15,16 bond in this intermediate with charge retention on the aromatic part gives the $C_9H_{11}O$ species of *m/e* 135.

Experimental. Low-resolution mass spectra were recorded on an LKB 9000 instrument using an electron energy of 70 eV and an ion source temperature of 290°. The high-resolution measurements were performed on an MS 902 instrument with an electron energy of 70 eV and at a temperature of 155°.

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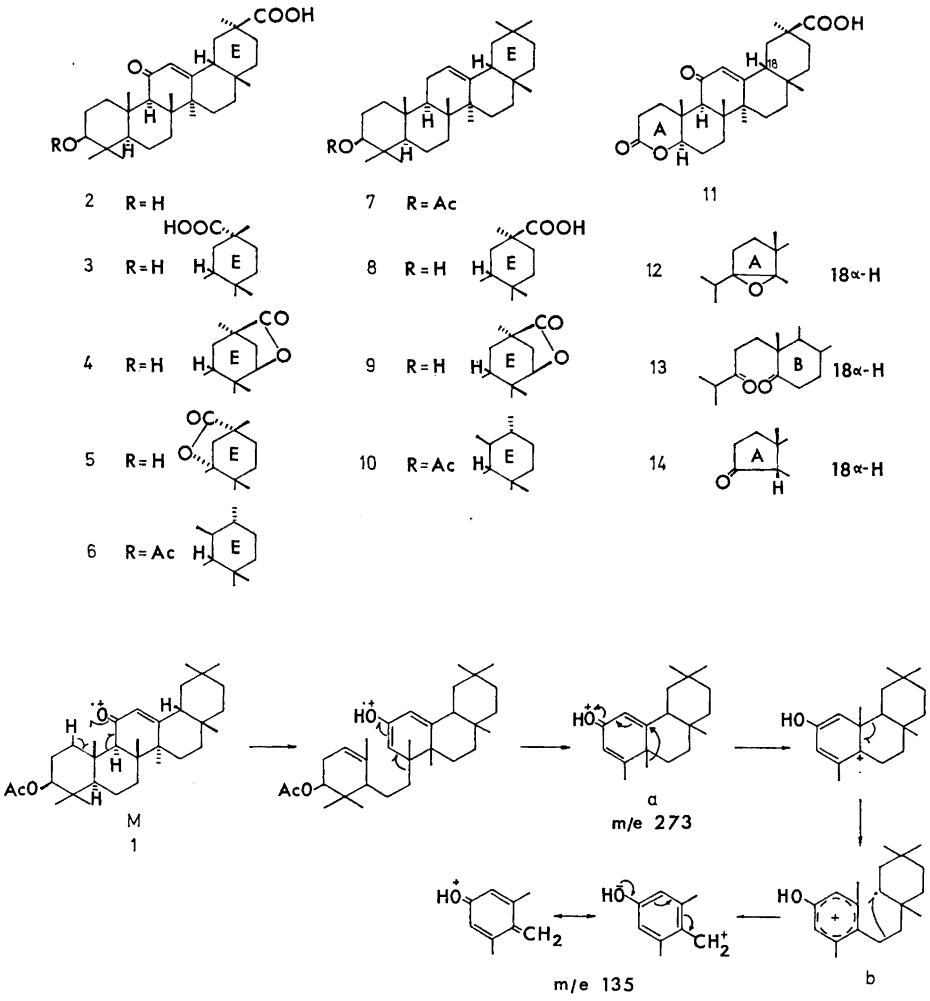

Scheme 1.

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