PHYTOECDYSONES OF Serratula

III. MASS SPECTROMETRIC STUDY OF THE ACETATES AND ACETONIDES OF ECDYSTERONE AND VITICOSTERONE E

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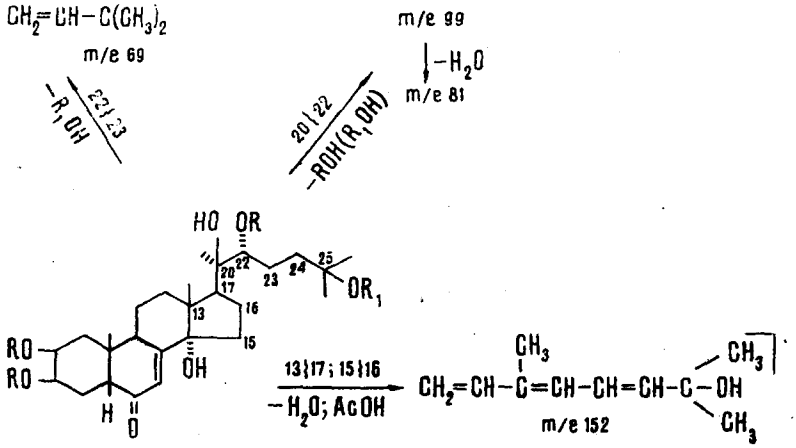
We have studied the mass spectra of some acetates and acetonides of ecdysterone and viticosterone E and have also compared them with the spectra of analogous derivatives of ecdysones not containing a hydroxy group at C_{25} [1]. In view of the identical nature of the fragmentation of the steroid nucleus, the main difference of analytical value in the mass-spectrometric behavior of these two series of compounds is connected with the nature of the decomposition of the side chain.

For ecdysterone (I) the predominating process is the cleavage of the $C_{20}-C_{22}$ bond, leading in the final account to the appearance of two strong peaks with m/e 99 and 81 [2] (Scheme 1 and Table 1). The fragment with m/e 81 is also characteristic for a whole series of acetates. The other types of cleavages of the side chain of ecdysterone are expressed considerably more feebly. However, in the mass spectrum of (I) there is an appreciable peak with m/e 69. This ion could obviously be formed as a result of the splitting out of a molecule of water at the expense of the hydroxyl at C_{25} followed by cleavage of the $C_{22}-C_{23}$ bond.

The intensity of this peak rises considerably in the spectra of viticosterone E (the 25-monoacetate of ecdysterone (II)) and of the 2,3,22-triacetate (III), while in the mass spectrum of the 2,3,22,25-tetraacetate (IV) the ion with m/e is the maximum ion (see Table 1). Decomposition of this type is not characteristic of the acetyl derivative of ponasterone A, of makisterones B and D, or of ajugasterones B and C, which have no oxygen-containing substituent at C_{25}. No intensive cleavage of the $C_{22}-C_{23}$ bond is found, either, for the acetates of makisterones A and C, which contain an alkyl substituent at C_{24} [1].



I R = R1 = H
II R = H; R1 = Ac
III R = Ac; R1 = H
IV R = R1 = Ac

Scheme 1

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 155-158, March-April, 1975. Original article submitted October 30, 1973.

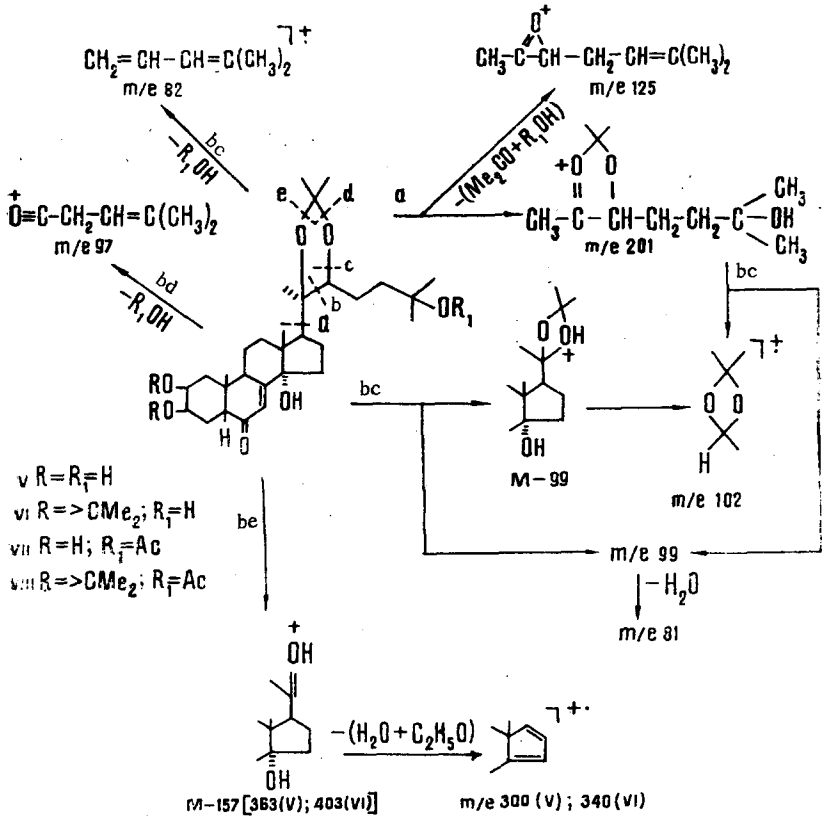
TABLE 1. Mass Numbers and Relative Intensities (%) of the Main Ions Characterizing the Fragmentation of the Side Chain of the Acetates of Ecdysterone and of Vitcosterone E

Compound	m/e			
	69	81	99	152
I	19	30	100	1
II	73	89	100	1
III	70	36	23	100
IV	100	50	2	14

In the mass spectrum of the triacetate (III), the maximum peak is that with m/e 152, obviously formed after the ejection of molecules of water and acetic acid from the side chain followed by the cleavage of the $C_{13}-C_{17}$ and $C_{15}-C_{16}$ bonds (see Scheme 1).

The mass spectra of the acetonides (V-VIII) (Scheme 2) in some acts of decomposition retain an analogy with the acetonides of ponasterone A [1] (the fragments of the steroid nucleus, the ejection of molecules of acetone, ketene, etc.) but differ by the decomposition of the side chain, which is also due to the oxygen-containing substituent at C_{25}.

In the mass spectrometry of the mono- and diacetonides of ecdysterone (V, VI), cleavage of type *a* (see Scheme 2) gives an ion with m/e 201, the structure of which is confirmed by the presence in the spectrum of the deuterated diacetonide of ecdysterone of a peak displaced by six units – with m/e 207.



Scheme 2

It is possible that the presence of a hydroxy function at C_{25} stimulates the decomposition of the fragment with m/e 201, and the strong peaks with m/e 99 and 102 are formed (see Scheme 2 and Table 2). The latter has an analog (m/e 108) in the spectrum of the deuterated diacetonide of ecdysterone. The ion with m/e 99, containing no isotopic label (no corresponding shift is observed in the spectrum of the deuterated diacetonide of ecdysterone), after the ejection of a molecule of water, gives a fragment with m/e 81. Like other acetonides [3], and also the diacetonide of ponasterone A [1], the ion with m/e 201, losing molecules of acetone and water successively, forms fragments with m/e 143 and 125.

Ions with m/e 99 and 102 can also arise by another competing direction. Under the action of electron impact, the acetonides (V) and (VI), undergoing cleavage of the bc type with the transfer of a hydrogen atom to the oxygen atom, fragment to ions with m/e 99 and M − 99. In the diacetonide of ecdysterone (VI), the ion with m/e M − 99 (461) corresponds to a deuterated analog with m/e 473. The fragment with m/e M − 99 decomposes with the cleavage of the $C_{17}-C_{20}$ bond, forming an ion with m/e 102.

In the mass spectrum of the diacetonide (VI), the maximum peak is that of the ion with m/e 403 (M − 157) arising by be cleavage. In the spectrum of the monoacetonide (V), the 100% peak of the ion with m/e

TABLE 2. Mass Numbers and Relative Intensities (%) of the Main Ions Characterizing the Fragmentation of the Side Chain of the Acetonides of Ecdysterone and Viticosterone E

Compound	m/e							
	81	82	97	99	102	125	201	M−157
V	11	2	4	52	31	8	11	22
VI	15	6	9	56	66	16	12	100
VII	18	100	33	8	0,5	35	1	1
VIII	17	100	38	14	1	47	5	1

300, which is a derivative of a fragment with m/e 363 (M − 157) also represents a fragment of the steroid nucleus [2].

Under the action of electron impact, the acetonides of viticosterone E (VII and VIII) decompose differently. The main initial process in this case is obviously the splitting off a molecule of acetic acid and the formation of an ion M − 60. The M − 60 fragment, undergoing bc cleavage with the transfer of the hydrogen atom from C_{23} to C_{22} gives the maximum ion, with m/e 82, in the spectra of compounds (VII) and (VIII). In addition, the M − 60 ion, on the decomposition of the dioxolane ring in the bd manner with the transfer of a hydrogen atom to the steroid fragment, forms a fairly strong peak of an ion with m/e 97 (see Scheme 2 and Table 2).

One of the strongest ions with m/e 125 may arise in the cleavage of bonds in M − 60 (VII, VIII) by type *a* with the subsequent ejection of a molecule of acetone. The ions with m/e 102 and 99 that are characteristic for compounds (V) and (VI) have a low intensity in the mass spectra of (VII) and (VIII).

EXPERIMENTAL METHOD

The mass spectra were taken on an MKh-1303 instrument (direct introduction of the sample) at 200-210°C for compounds (I-IV) and 130-140°C for (V-VIII) at an ionizing voltage of 40 V. The ecdysterone and viticosterone E used were isolated from Serratula sogdiana [4]. The preparation of the acetates (III, IV) and the acetonides (V-VIII) is described in the same paper.

SUMMARY

Features of the fragmentation of the side chain of the acetates and acetonides of ecdysterone and of viticosterone E have been studied. It has been shown that the presence of an oxygen-containing function at C_{25} in these compounds imparts to the spectra certain distinguishing features which have analytical value.

LITERATURE CITED

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