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# MASS SPECTROMETRY OF TETRACYCLIC TRITERPENES

## Part I - THE CUCURBITACIN GROUP

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During the past few years notable advances have been made in the mass spectrometric investigation of different groups of pentacyclic triterpenes and their fragmentation pattern has been elaborately discussed (1). However, there has been no record of a similar study in the field of tetracyclic triterpenes. It was therefore thought desirable to study the mass spectra of this class of natural products and in this communication we wish to report the preliminary results of our investigation on the mass spectral fragmentation of the cucurbitacin family (2) of tetracyclic triterpenes.

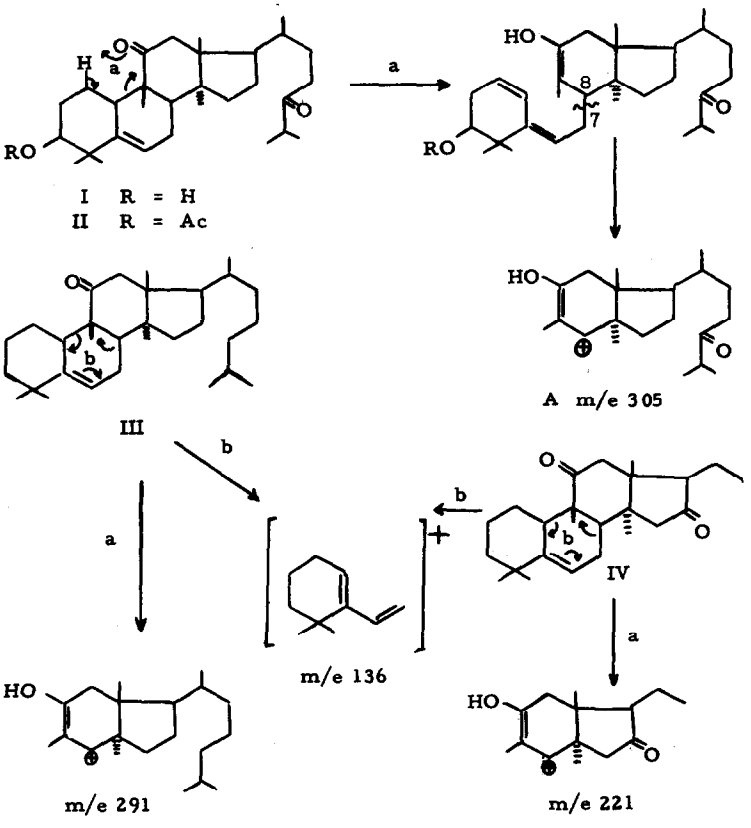
We have so far examined the mass spectra (3) of bryogenin (I), cucurbitacins A (V), B (VI), C (VII), D (VIII), E (IX), I (X) and two other compounds represented by structures (III) and (IV).

The mass spectrum of bryogenin (I) (m.w. 456), the simplest member of the cucurbitacin series, exhibited an intense peak at m/e 305. This peak corresponds to the ion A and it arises probably from the cleavage of the C-7 – C-8 bond preceded by a McLafferty (4) type of rearrangement (a) involving the participation of the 11-keto group and a hydrogen at C-1 as shown in Chart I. The same peak at m/e 305 is observed for bryogenin 3-acetate (II) but it is appropriately

shifted to m/e 291 and 221, respectively, in the mass spectra of compounds (III) and (IV).

On the other hand, a peak corresponding to a retro-Diels-Alder fragmentation (b) of ring B is not observed in the mass spectrum of bryogenin, while a small peak resulting from such a fragmentation is found at m/e 136 in the mass spectra of (III) and (IV) (see chart I)

Chart I



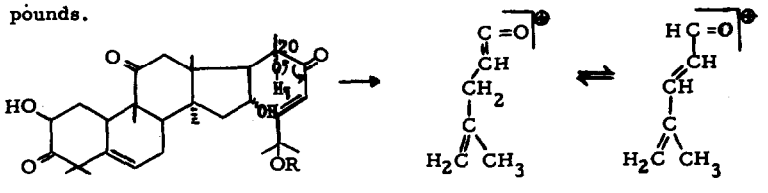
Mass spectra of cucurbitacins

Cucurbitacins A (V ), B (VI) and C (VII) did not show the molecular ion peak, but instead the M-60 peak appeared in the high mass region after loss of the elements of acetic acid from the molecule. The mass spectra of cucurbitacins D (VIII), E (IX) and I (X) exhibited small molecular ion peaks at m/e 516, 556 and 514, respectively.

In the case of cucurbitacins A (V), B (VI), C (VII), D (VIII), E (IX) and I (X) the relatively complex character of the side-chain seems to dominate the fragmentation. In fact, the peak corresponding to the McLafferty cleavage mentioned above (fragmentation a) is not visible in their mass spectra. Also, there is no sign of a retro-Diels-Alder fragmentation (b) of ring B except in the case of cucurbitacins E and I.

Side-chain of cucurbitacins A, B, C, D, E and I

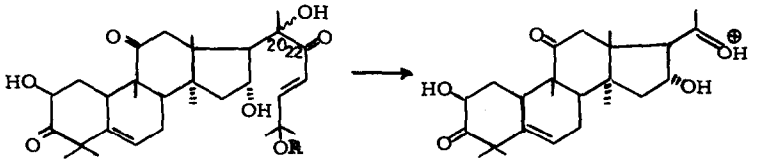
The nature of the side-chain in cucurbitacins A, B, C, D, E and I plays a significant role in their mass spectral fragmentation. The spectra of all these cucurbitacins [structures (V) - (X)], having the same side-chain, showed the most abundant ion peak at m/e 96, corresponding to the composition $C_6H_8O$ as was confirmed by high resolution mass measurement. The formation of this ion is most probably caused by a rupture of the side-chain with simultaneous migration of the hydrogen from the hydroxyl at C-20, according to the following mechanism. The appearance of this peak in the mass spectrum is useful in detecting this side-chain in this series of compounds.




VI R = Ac
VIII R = H

m/e 96 ($C_6H_8O$)

A simple cleavage of the C-20–C-22 bond of the cucurbitacins without a hydrogen transfer and with the retention of the positive charge on C-20 leads to an ion fragment which also merits discussion. This is exemplified by the mass spectra of cucurbitacins B (VI) and D (VIII) which exhibit a peak at m/e 403 due to this cleavage, as indicated below. This m/e 403 ion can then lose a molecule of water thus giving a peak at m/e 385 which is also observed in the mass spectra of these two compounds.



VI R = Ac

VIII R = H

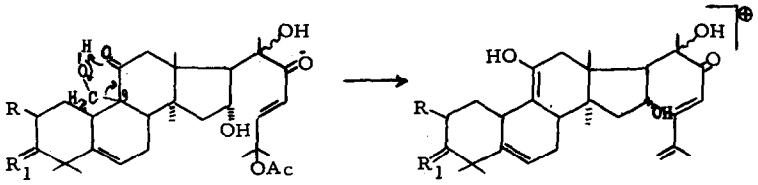
m/e 403

$-H_2O$

m/e 385

Presence of $-CH_2OH$ at C-9

The presence of a $-CH_2OH$ group at C-9 in cucurbitacins A (V) and C (VII) leads to a characteristic ion fragment M-60-30. This loss of 30 mass units is due to the expulsion of $CH_2O$ from the primary alcohol function by the transfer of the hydroxyl hydrogen on the carbonyl oxygen at C-11 in the following manner :



V R = OH (β) ; $R_1$ = O

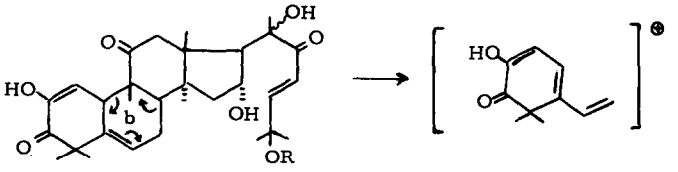
VII R = H ; $R_1$ = H / OH (α)

R = OH (β); $R_1$ = O m/e 484

R = H ; $R_1$ = H / OH (α) m/e 470

Presence of a double bond between C-1 and C-2

When a double bond is present in ring A between C-1 and C-2 (e.g. cucurbitacins E and I), cleavage of the McLafferty type involving the 11-keto group is, however, not possible. In this case a retro-Diels-Alder rupture (b) of ring B is indeed remarkable and affords an especially conjugated ion fragment which appears as an intense peak at m/e 164 (see below) in the mass spectra of cucurbitacins E (IX) and I (X). The composition ($C_{10}H_{12}O_2$) of this ion has been confirmed by accurate mass measurements.




IX R = Ac

X R = H

m/e 164 ($C_{10}H_{12}O_2$)

It is hoped that the findings available from the mass spectral fragmentation of the cucurbitacins will prove useful in the structure elucidation of similar substances. A detailed study of the mass spectra of these compounds and other groups of tetracyclic terpenes is now in progress in this laboratory.

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## References

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2. G. Ourisson, P. Crabbé and O. Rodig, Tetracyclic Triterpenes in the series chemistry of Natural Products, Edited by E. Lederer Hermann, Paris / Hoden-Day, Inc. San Francisco (1964).

3. All mass spectra were determined with an A. E. I. MS-9 mass spectrometer operating at 70 e. v.

4. F. W. McLafferty, Analyt. Chem., 31, 82 (1959).