Tetrahedron Letters No.36, pp. 4341-4347, 1966. Pergamon Press Ltd.
Printed in Great Britain.

MASS SPECTROMETRY OF TETRACYCLIC TRITERPENES
Part II. THE LANOSTANE GROUP : INFLUENCE OF THE 9:19-CYCLOPROPANE RING.

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(Received 30 June 1966)

Recently we reported (1) the preliminary results of the mass spectral fragmentation of the cucurbitacin series of tetracyclic triterpenes. We have now extended this investigation to several tetracyclic triterpenes of the lanostane group (2), particularly the compounds containing a 9:19-cyclopropane ring as in cycloartenol (I). The mass spectra of a large number of derivatives (I - XVII) belonging to this class of triterpenes, some of which were labelled with deuterium at C-2 and C-3, have been determined (3). Among several cleavage processes occurring upon electron impact in the mass spectrometer, the influence of the cyclopropane ring on the fragmentation pattern of this series of compounds is described in the present communication.

The mass spectra of these compounds demonstrated two distinct types of fragmentation : (i) formation of ion fragments induced by the presence of the cyclopropane ring; and (ii) fragments produced by the cleavage of the side-chain.

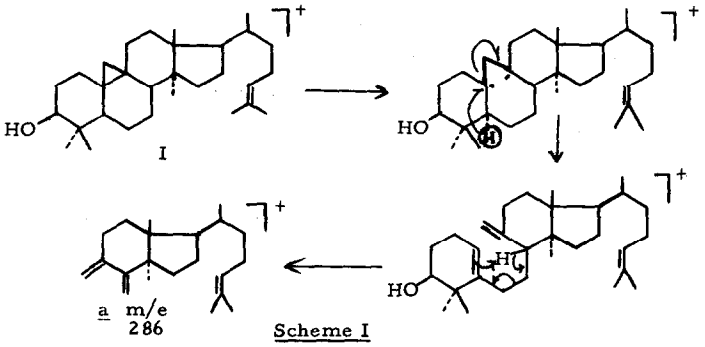
Presence of 9:19-cyclopropane ring

The influence of a cyclopropane ring on the fragmentation pattern is manifested in the mass spectra by the appearance of a charac-

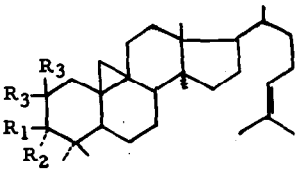
teristic peak a having an even number. The position of this peak is independent of the substitution at C-4 as well as of the oxygen function at C-3, but it is shifted in accordance with the substituents present in the side-chain (see Table I).

In the mass spectra of cycloartenol (I), its 3-acetate (II), 2:2-d_2 cycloartenol (IV), 2:2:3-d_3 cycloartenol (III), cycloartenone (V) and 2:2-d_2 cycloartenone (VI), this peak a is observed at m/e 286. It is shifted to m/e 288 in the mass spectrum of cycloartanol (VIII) indicating that the side-chain is retained in this ion fragment. Pollinastanol acetate (VII), having no methyl group at C-4 but possessing the same side-chain as in cycloartanol (VIII), also gave this ion peak at m/e 288. A similar peak, appropriately shifted is observed at m/e 300 in the case of cycloeucalenol 3-acetate (XV), 24-methylene cycloartanol 3-acetate (XVI) and cyclolaudenol (XII). It is therefore evident that the ring A in these triterpenes is lost in the course of the fragmentation leading to the ion a.

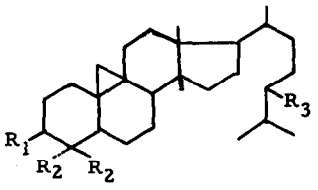
This characteristic ion fragment a originates probably by a rupture of the cyclopropane ring and its formation requires the loss of ring A along with C-6 or C-19. In the absence of a proper labelling experiment it cannot be definitely stated which of these two carbons is lost. A possible mode of formation of this ion a from cycloartenol is however shown in Scheme I.



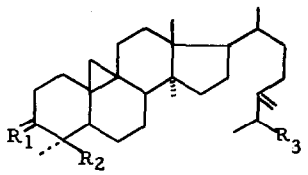
Scheme I

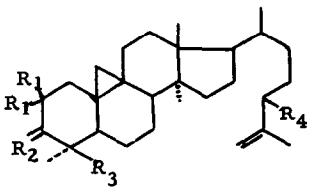


I R_1 = OH ; R_2 = R_3 = H
II R_1 = OAc ; R_2 = R_3 = H
III R_1 = OH ; R_2 = R_3 = D
IV R_1 = OH ; R_2 = H ; R_3 = D
V R_1 R_2 = O ; R_3 = H
VI R_1 R_2 = O ; R_3 = D



VII R_1 = OAc ; R_2 = R_3 = H
VIII R_1 = OH ; R_2 = Me ; R_3 = H
IX R_1 = OH ; R_2 = R_3 = Me





X R_1 = H ; R_2 = O ; R_3 = R_4 = Me
XI R_1 = H ; R_2 = $\overset{OAc}{H}$; R_3 = H ; R_4 = Me
XII R_1 = H ; R_2 = $\overset{OH}{H}$; R_3 = R_4 = Me
XIII R_1 = D ; R_2 = O ; R_3 = R_4 = Me
XIV R_1 = H ; R_2 = $\overset{OH}{H}$; R_3 = Me ; R_4 = OH

XV R_1 = $\overset{OAc}{H}$; R_2 = H ; R_3 = Me
XVI R_1 = $\overset{OAc}{H}$; R_2 = R_3 = Me
XVII R_1 = $\overset{OH}{H}$; R_2 = Me ; R_3 = COOMe

The mass spectrum of cycloartenol (I) also exhibited a peak b appearing at m/e 339 [(M-18) - 69] (M-60 - 69 in the case of cycloartenol acetate). A metastable peak found at m/e 282 (calculated for $339^2/408 = 281.67$) confirmed that this originated from the ion fragment m/e 408 (M-18). This peak at m/e 339 is not shifted in the mass spectra of 2,2,3-d_3 cycloartenol (III) or cycloartenol 3-acetate (II). A similar peak corresponding to ion b is exhibited by cyclolaudenol (XII) at m/e [(M-18) - 69]. Cycloeucalenol 3-acetate (XV) possessing only one methyl group at C-4 and pollinastanol 3-acetate (VII) having no substitution at C-4 showed this peak at [(M-60) - 55] and [(M-60) - 41], respectively. These results clearly indicate that carbons 2,3 and 4 are lost in the formation of the ion b from these compounds.

Another ion fragment c, which deserves mention, is observed at (M-18) - 43 in the mass spectra of some of the free 3-hydroxy compounds of this series possessing different C-terminal side-chains. Cycloeucalenol 3-acetate (XV) having one methyl substitution at C-4 also showed this peak at (M-60) - 43. It is therefore believed that neither the side-chain nor C-4 is involved in this particular fragmentation process. The origin of this peak could not be traced as yet but deuterium labelling at C-2 and C-3 (III, IV) suggests that these two carbon atoms are retained in this ion fragment.

Fragmentation of the side-chain

A peak d (Table I) corresponding to the rupture of the side-chain along the bond between C-17 and C-20 is observed in the mass spectra of all the compounds of this series studied by us. This may further lead to a peak appearing at d - 18 or d - 60 depending on the presence of a hydroxyl or an acetoxy group at C-3.

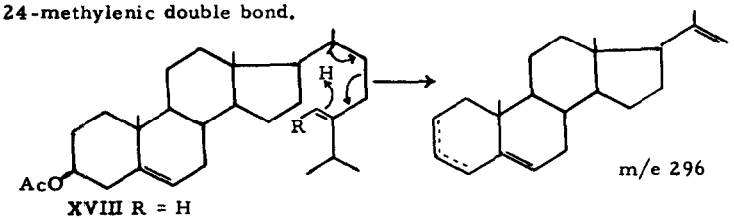
Table I

Compounds	M^+	ion a m/e	ion b m/e	ion c m/e	ion d m/e
I	426	286	339	365	315 → 297
II	468	286	339	365	357 → 297
III	429	286	339	368	318 → 300*
IV	428	286	339	367	317 → 299*
V	424	286	-	-	313
VI	426	286	-	-	315
VII	442	288	341	-	329 → 269
VIII	428	288	341	367	315 → 297
IX	442	302	355	381	315 → 297
X	438	300	-	-	313
XI	468	300	353	365	343 → 283
XII	440	300	353	379	315 → 297
XIII	440	300	-	-	315
XIV	442	302	355	381	315 → 297
XV	468	300	353	365	343 → 283
XVI	482	300	353	379	357 → 297
XVII	484	344	397	423	315 → 297

* Loss of 18 mass units (corresponding to elimination of H_2O) from these compounds deuterated at C-2 indicates that the hydrogens at this position are not involved in this particular dehydration process occurring in the mass spectrometer.

The side-chain bearing a double bond may sometimes be eliminated together with two hydrogens from the ring system although the peak arising out of such a cleavage process appears to be much less pronounced for these tetracyclic triterpenes than in the case of steroids (5).

The mass spectra of 24-methylene cholesterol 3-acetate (XVIII) and fucosterol 3-acetate (XIX) showed an intense peak at m/e 296 which probably originates by the mechanism shown in Scheme 2. A similar fragmentation is also found to occur in the case of citrostadienol (2) and it is believed to be typical for steroids containing a 24-methylenic double bond.



XVIII R = H
XIX R = CH_3

Scheme 2

Such a fragmentation does not, however, seem to operate for 9:19-cyclopropano tetracyclic triterpenes having a C-24 methylene group (XV, XVI, XVII).

The mass spectral fragmentation pattern discussed above has been found useful in the structure elucidation of compounds XI (6), XVII (7) and pollinastanol (4).

Acknowledgement. - We are grateful to Professors S. Corsano, C. Djerassi, G. Ourisson and to Drs. P. Benveniste and R. Goutarel for providing us with some of the samples utilized in this work.

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