A MASS SPECTROMETRIC STUDY OF SOME TRITERPENES OF THE DAMMARANE SERIES

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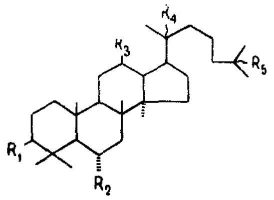
The results of a mass spectrometric study of tetracyclic triterpenes of the cucurbitacin [1] and lanostane [2] groups and also of a series of compounds of the dammarane series [3] have been published previously. The present paper gives the results of a wider investigation of these substances. We devoted particular attention to a study of the oxo derivatives, which are more convenient for mass spectrometric investigations [4]. The mass spectra of a considerable number of compounds of the dammarane series, including compounds labeled with deuterium, were obtained by introduction into the ion source. Among the various types of fragmentation, the most common for them are: the appearance of fragments from the decomposition of the side chain and the decomposition of ring C with the formation of ions of the "left-hand" and "right-hand" parts of the molecule.

Alcohols with the OH Group in the Ring System. The mass spectra of the triterpene alcohols (I, II, V-VII) (Figs. 1-5) are fairly complex because of the contribution of the products of fragmentation of partially dehydrated M^+ ions, for example a_1 and a_2 (Scheme 1). However, a reduction in the ionizing potential weakens the secondary processes and facilitates the determination of the main routes of decomposition of M^+, the peak of which is found with a very low intensity in the spectrum of compound (V) (see Fig. 3). Following on this, the decomposition of ring C of the primary ions leads to the fragments b_1, b_2, c_1, c_2, and c_3 [4]. The peaks of ions of type c, i.e., the right-hand part of the molecule, enable the size of the chain and the nature of the substituent at C-12 to be evaluated. Thus, the peaks of the ions c_2 and c_3 are shifted in the direction of higher mass numbers by 2 mu in the



I. $R_1 = R_3 = OH$ $R_2 = H$ $R_4 = R_5 = OH$
II. $R_1 = R_3 = OH$ $R_2 = H$ $R_4 = OH$ $R_5 = OMe$
III. $R_1 = R_3 = OAc$ $R_2 = H$ $R_4 = OH$ $R_5 = OMe$
IV. $R_1 = R_3 = OAc\text{-}d_3$ $R_2 = H$ $R_4 = OH$ $R_5 = OMe$
V. $R_1 = R_3 = OH$ $R_2 = R_3 = H$ $R_4 = OH$
VI. $R_1 = R_2 = R_3 = R_4 = OH$ $R_5 = H$
VII. $R_1 = R_2 = R_3 = OH$ $R_4 = OMe$ $R_5 = H$

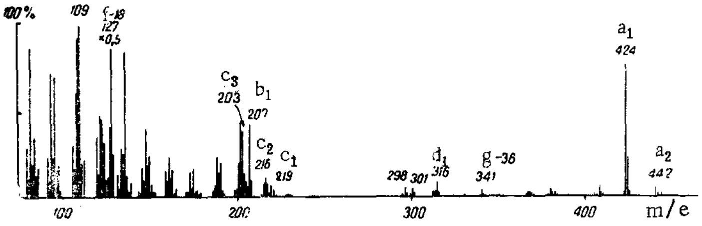


Fig. 1

Institute of Biologically Active Substances of the Far-Eastern Scientific Center of the Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 286-294, May-June, 1971. Original article submitted September 5, 1970.

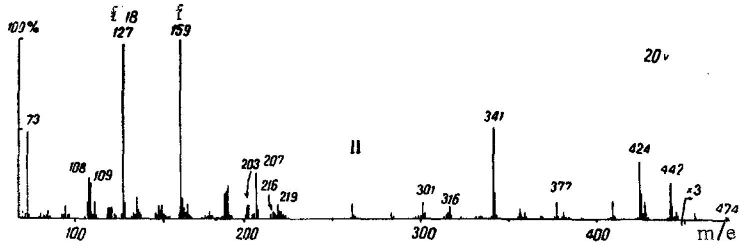
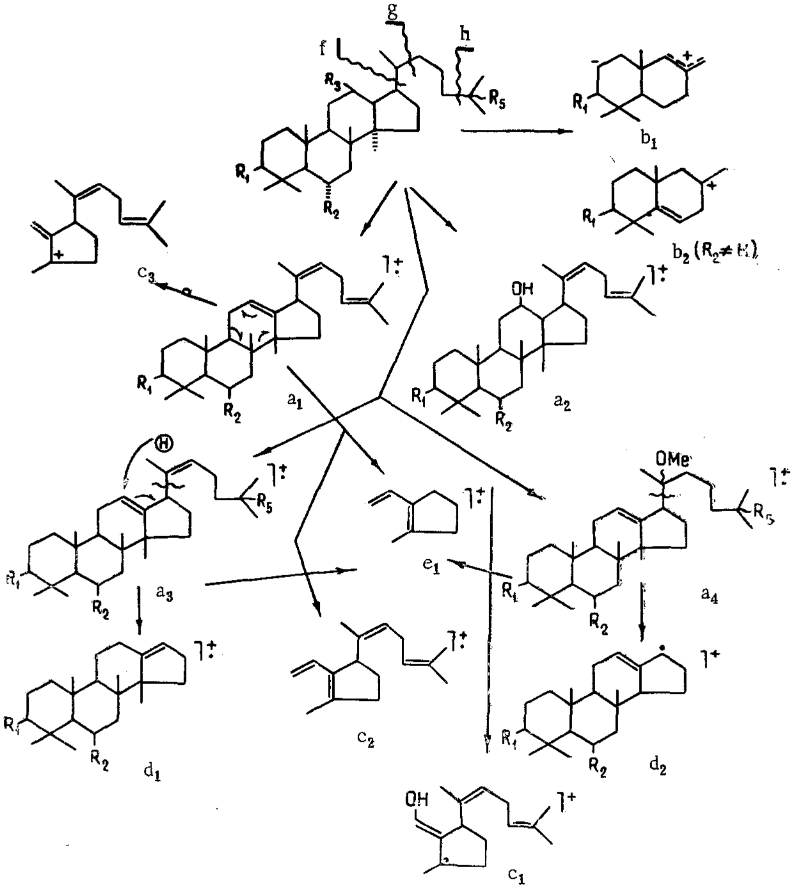


Fig. 2

the OAc group is less stable than the OH group, in the spectrum of the 3,12-diacetate (III) the peak of the c_1 ion is absent. Regardless of the presence of a C-6 OH group, the ions b_1 and b_2 of the AB rings give peaks of medium intensity at 207 mu in the spectra of C-20,25-substituted compounds. The most intense peaks in the spectra of these compounds are due to the ions f, g, and h. The intensity of the peaks of the ions f and g rises if there is a OMe group at C-20. The second type of fragmentation depends on whether there is a substituent at C-20 or not. Thus, in the spectra of compounds (V) and (VI) the main peak corresponds to the ion e_1 with m/e 108 formed by a retrodiene decomposition of ring C and the loss of the side chain in the ions a_1, a_3, and a_4. In addition to this, the rearrangement accompanied by the formation of the ions of the AB rings is weakened, in consequence of which considerable peaks of the ions with m/e 208 and 206 appear in the spectra of compounds (V) and (VI), respectively, and the intensity of the peak of the ion with m/e 316 of ring system d_1 rises.



Scheme 1

Ketones with the CO Group in the Ring System. The results of a comparison of the spectra of the oxo compounds (VIII) and (X-XIV) show that the compounds mentioned can be identified by means of a series of characteristic peaks.

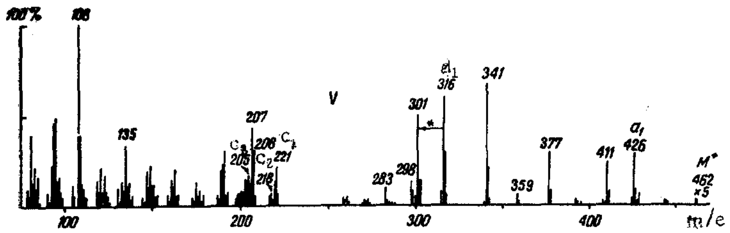


Fig. 3

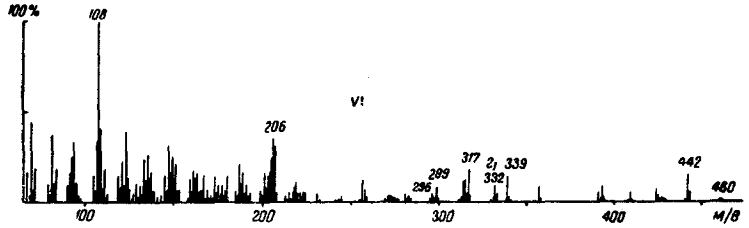
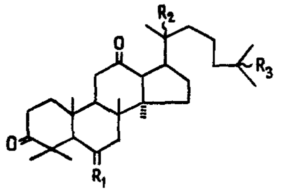
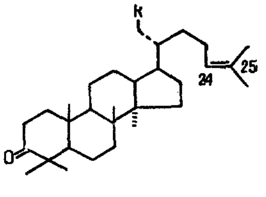


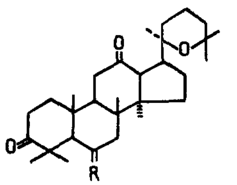
Fig. 4



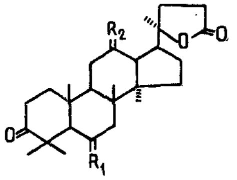
VIII $R_1 = H_2$ $R_2 = OH$ $R_3 = H$
IX 21, 21, 21, 22-d_4-VIII
X $R_1 = H_2$ $R_2 = R_3 = OH$
XI $R_1 = O$ $R_2 = OMe$ $R_3 = H$



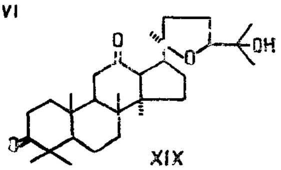
XII R=H
XIII R=OH
XIV R=H (H_2 at C-24,25)



XV $R = H_2$
XVI R=O
XVII 2,2-d_2-XV
XVIII 21, 21, 21, 22, 22 (C-24, C-26, C-27)-d_8-XVI



XX $R_1 = H$ $R_2 = O$
XXI $R_1 = R_2 = O$
XXII $R_1 = R_2 = H_2$



XIX

In the spectra of the diketones (VIII) and (X) (Figs. 6 and 7), the main peak corresponds to the ion e_2, with m/e 124, which is formed by the retrodiene decomposition of the enolic form of ring C with the loss of the side chain (Scheme 2). In actual fact, in the spectrum of the C-12 deoxo analog (XIV), this peak is absent, but the type of fragmentation is retained, and the peaks with appreciable intensity are probably due to the ions with m/e 82, 95, 108, and 109 containing ring D. The same statement is valid for the spectra of compounds (XII) and (XIII). The second strong peak of an ion with m/e 373 in the mass spectra of (VIII) and (X) arises by the detachment of the lateral alkyl radical from C-20. In the spectrum of the triketone (XI), the corresponding peak with 401 mu becomes the main peak. The considerable peaks in the central

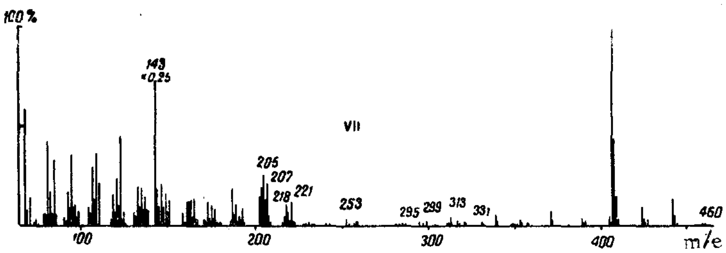


Fig. 5

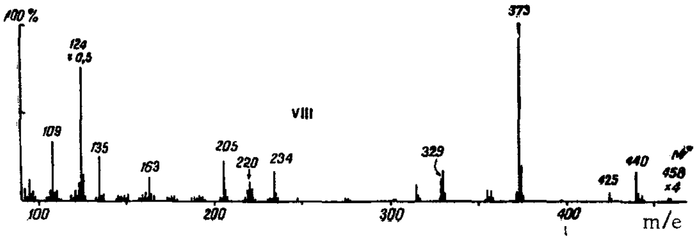


Fig. 6

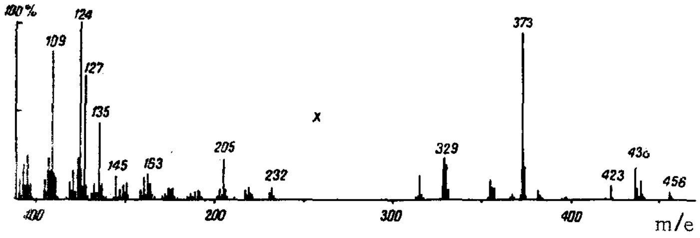


Fig. 7

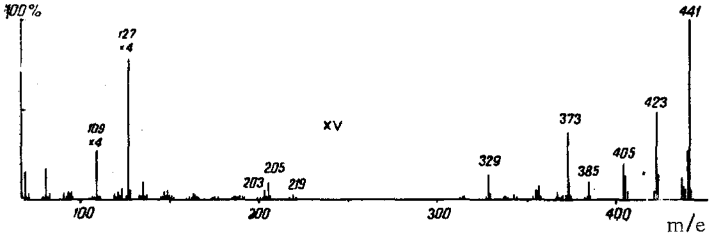


Fig. 8

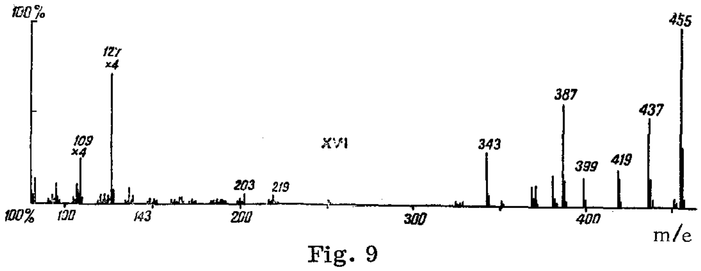


Fig. 9

Fig. 10

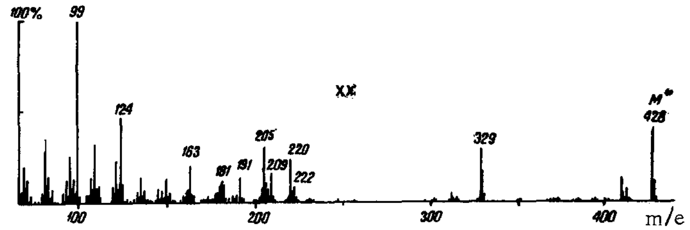
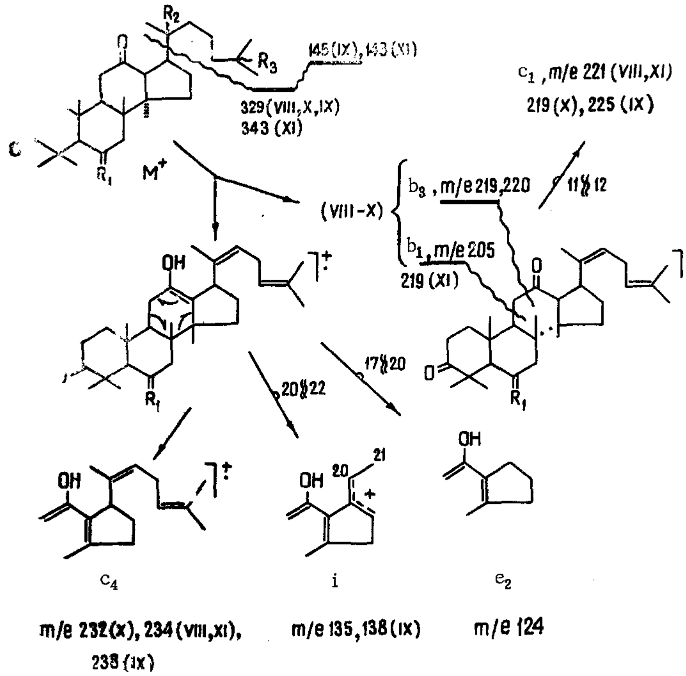


Fig. 11

part of the spectrum of the diketone (VIII) at 135, 205, 220, and 234 mu correspond to the ions c_1, b_1, b_3, and c_4, the formation of which is connected with the decomposition of ring C (see scheme 2).



Scheme 2

The mass spectra of (XV-XIX) with a closed side chain differ substantially from the spectra of the related compounds (VIII)-(XIV). Peaks with considerable intensity appear in the region of high mass numbers in the spectra of (XV), (XIV), and (XIX) (Figs. 8-10). These peaks correspond to the fragments formed in the decomposition of the side chain of M^+ (Scheme 3). For example, in the diketone (XV) these ions amount to 24.6% of the total intensity, and the ions arising in the decomposition of ring C to 6.3%. In the calculation, the peaks at 109 and 127 mu were excluded, since their high intensity is partially due to the thermal decomposition of the side chain, as was confirmed by reducing the ionizing voltage and the temperature of the evaporator. The intensity of the peak of the ion k with m/e 413 in the spectrum of the

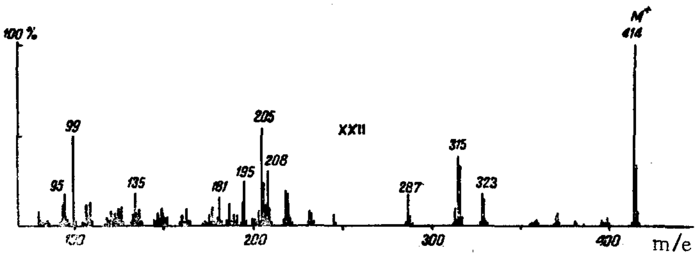
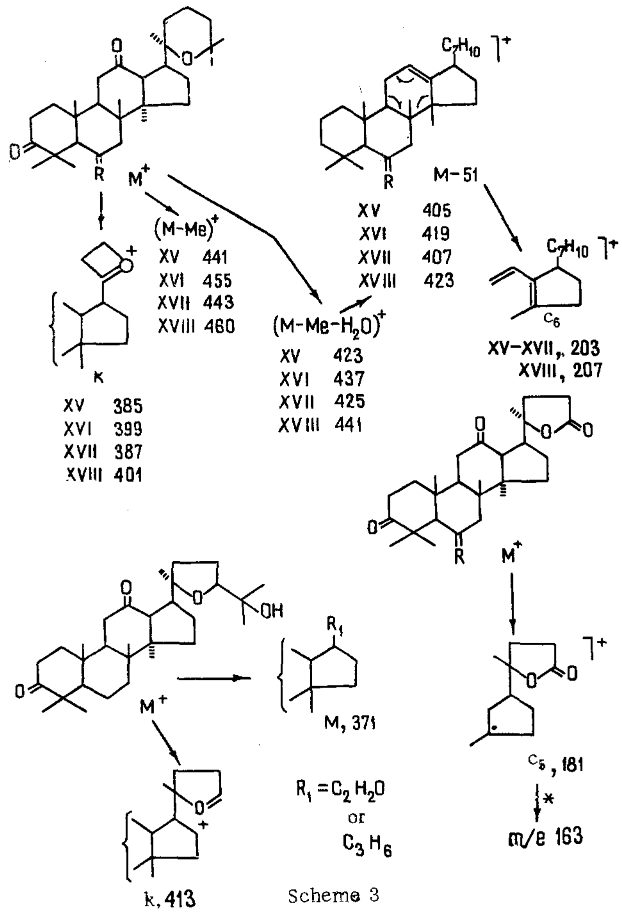


Fig. 12

diketone (XIX) does not change in the spectrum of its OD analog (XIX). The second intense peak at 371 mu belongs to the ion l.



Scheme 3

The ketones (XX) and (XXI), with smaller side chains, in contrast to the cases discussed above, give spectra containing M^+ peaks of considerable intensity. In this case, the second type of fragmentation is dominating. Thus, the most considerable peaks in the central part of the spectrum of compound (XX) (Fig. 11) are due to the ions b_1, b_3, c_1, c_4, and c_5 (see schemes 2 and 3). These ions amount to 15% of the total intensity, and all the peaks above 330 mu, if they are regarded as due to ions formed by the decomposition of the side chain, to 9.7%. Furthermore, the spectra of (XX) and (XXI) have the peak of the ion e_2 with m/e 124 which is not present in the spectrum of the corresponding monoketone (XXII) (Fig. 12). A characteristic feature of the spectrum of the latter is the appearance in it of peaks of the ions M−127 and M−86 at 287 and 328 mu, respectively. These ions probably have the same nature as the corresponding ions arising in the decomposition of steroids and terpenoids containing a 4,4-gem-dimethyl-3-one grouping [5].

EXPERIMENTAL

The mass spectra were obtained on an MKh-1303 instrument at an ionizing voltage of 50 V; the spectra of the alcohols were taken at a temperature of the evaporator of 140-150°C, and those of the ketones at 100-110°C. The rate of recording the spectrum was 5 mu/sec.

Samples (VII), (XI), (XVI), (XVII), (XVIII), and (XXI) were given to us by L. I. Strigina, (I)-(VI) and (VIII)-(XI) by É. V. Levina, (XIV) by Prof. J. Biellmann (France), (XX) and (XIX) by Prof. O. Tanaka (Japan), and (XII) and (XIII) by Dr. H. T. Cheung (Hong Kong).

SUMMARY

1. The mass spectra of tetracyclic triterpenes of the dammarane series with substituents at C-3, 6, and 12 and with side chains of various structures have been studied.

2. The main direction of fragmentation is the formation of ions as the result of the decomposition of the side chain and of ring C, the second type of fragmentation being controlled by the structure of the side chain.

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