FRAGMENTATION OF SESQUITERPENE LACTONES RELATED TO LEUCOMISIN

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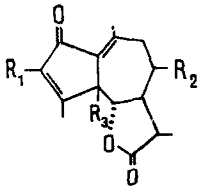
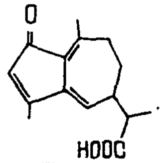
The mass spectra of seven sesquiterpene lactones — leucomisin, austricin, parishin B, parishin C, matricarin, artelin, and artelin diacetate — have been studied. It has been shown that the presence of the conjugated bonds C(1)=C(10), C(2)=O, and C(3)=C(4), and also C(5)=C(6), stabilizes M^+, and the main fragmentation process is that of the splitting out of the lactone ring. The presence of hydroxy substituents at C(3) and C(8) of the guaiane system does not change the stability of M^+ under electron impact. The directions of fragmentation have been confirmed by an analysis of spectra obtained by the metastable defocussing of daughter ions and by measuring the accurate masses of the main peaks of the fragmentary ions.

An analysis of literature information on the laws of fragmentation of sesquiterpene lactones of the guaiane series shows that their breakdown under electron impact depends totally on the nature of the substituents and on the presence of double bonds. Thus, in the case of 1,2-epoxyguaianolides [1], intensive processes of the breakdown of M^+ with the elimination of the substituents and the cleavage of rings A and B are observed. The mass spectra of 2,4-dihydroxyguaianolides [2] show the relatively high stability of M^+. The fragmentation of these compounds also takes place mainly with the elimination of the substituents and the elements of ring A.

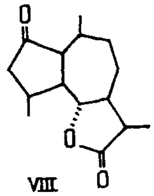
The mass spectrum of the lactone artelin recently isolated from *Artemisia leucodes* [3] showed an unusually high intensity of M^+ and a relatively low intensity of the fragmentary ions (Fig. 1). This impelled us to make a more detailed investigation of the mass spectra of a number of lactones of similar type — leucomisin (II), austricin (III) [4], matricarin (IV) [5], artelin (I) and its diacetate (V) [3], parishin C (VI) [6], and parishin B (VII) [7]. For comparison, we also studied the mass spectrum of tetrahydroleucomisin (VIII) [4].



	R₁	R₂	R₃
I	OH	OH	H
II	H	H	H
III	H	OH	H
IV	H	OAc	H
V	OAc	OAc	H
VI	H	H	OH



VII



VIII

In the spectra of compounds (I) and (III-VI), the processes in which the substituents R_1-R_3, and also methyl radicals, are split out are very weakly expressed, with the exception of the acetyl derivatives (Fig. 1). Only in the spectra of leucomisin (II) and of parishin C (VI) do the peaks of the ions due to the elimination of CH_3 and H_2O, respectively, amount

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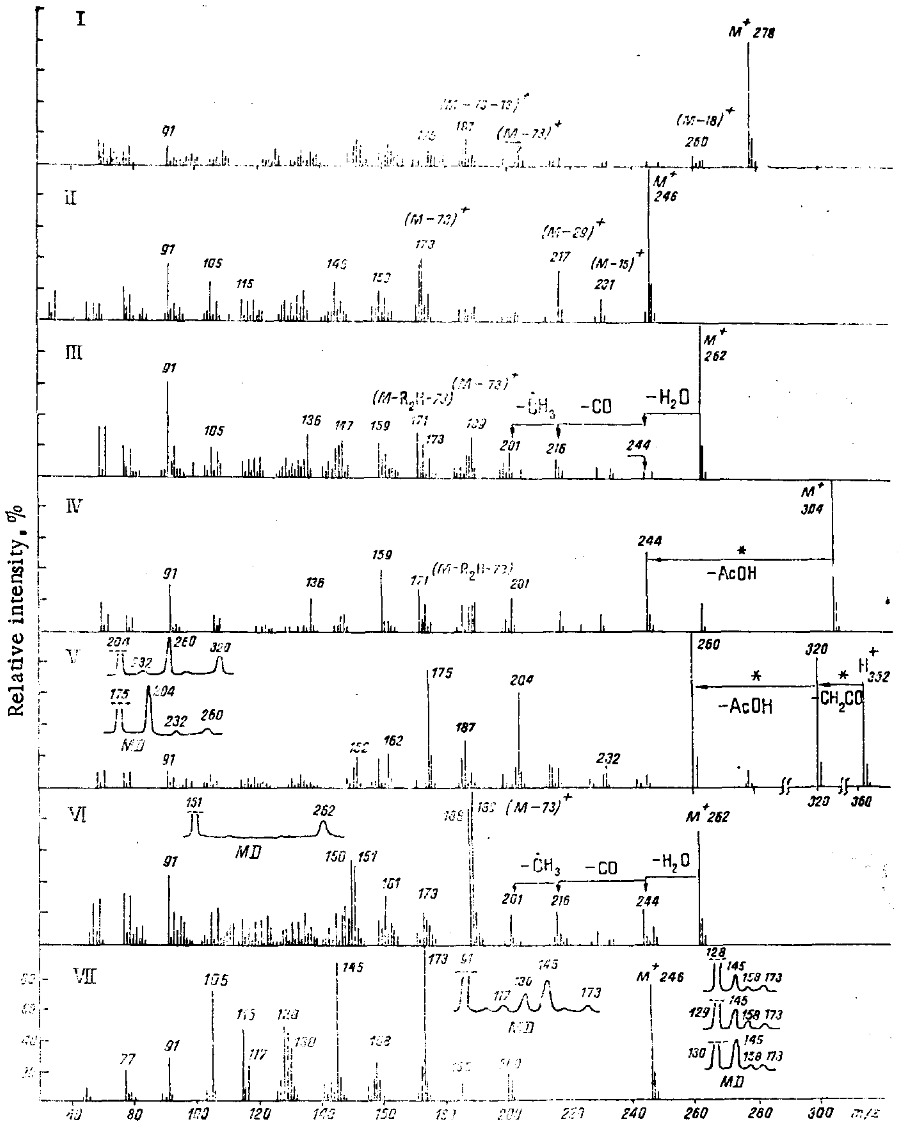
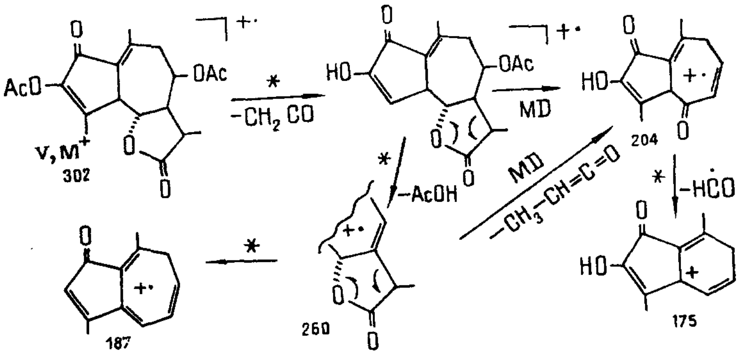


Fig. 1. Mass spectra of artelin (I), leucomisin (II), austricin (III), matricarin (IV), artelin diacetate (V), parishin C (VI), and parishin B (VII).

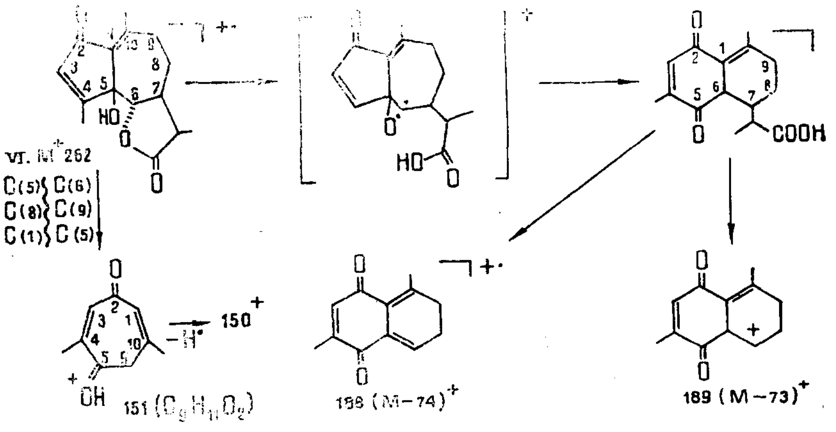
to 15-20% of the maximum peak. According to an accurate mass measurement, the $(M - 29)^+$ ion observed in the spectrum of (II) is due to the ejection of HCO.

The appearance of a hydroxy function at C(8) and also at both C(3) and C(8) in compounds (III) and (I) does not lower the stability of M^+ (Fig. 1). The presence of an OH group at C(3) stabilized by the neighboring carbonyl group in a position excluding isomerization means that the elimination of OH or H_2O from this position is energetically unfavorable. These conclusions are well confirmed by the mass spectra of the acetates (IV) and (V) (Fig. 1). In the spectrum of matricarin (IV), the main act of breakdown is the elimination of acetic acid, and the ejection of ketene is less characteristic. In the spectrum of the diacetate (V) an intense ejection of ketene at the expense of R_1 is observed, but even here, again, R_2 is eliminated in the form of AcOH (scheme 1, top, following page).

The appearance of an acetyl group at C(8) leads to another interesting act of fragmentation of compound (V). The peak of an ion with m/z 204 and the composition $C_{12}H_{12}O_3$ in the metastable defocussing (MD) spectrum showed as the parental ions those with m/z 232, 260, and 320 (Fig. 1). Making use of this fact and also of the elementary compositions of the ions (Table 1) and metastable transitions in the second field-free region, we assume the mechanism of the breakdown of M^+ of compound (V) given in scheme 1.



Scheme 1



Scheme 2

It is interesting to note that a hydroxy group at C(3) is retained in all the acts of the fragmentation of M^{+} for (V), which indicates a high stability of this structural element in the face of electron impact. According to its MD spectrum, the ion with m/z 175 (Fig. 1) can also be formed directly from the ion with m/z 260 through the cleavage of the C(5)—C(6), C(6)—C(7), and C(7)—C(11) bonds.

The presence of a tertiary OH group at C(5) in parishin C (VI) is responsible for the fact that in its spectrum the process of eliminating the lactone ring suffers strong competition from processes involving the successive ejection of water, carbon monoxide, and CH_3 (Fig. 1). The ease of formation of the corresponding fragmentary ions $(M - 73)^{+}$ and $(M - 74)^{+}$ is, in our opinion, due to the possibility of the occurrence of an intramolecular skeletal rearrangement (scheme 2).

The next in intensity in this spectrum are the peaks of ions with m/z 150 ($C_9H_{10}O_2$) and 151 ($C_9H_{11}O_2$). The MD spectrum of the ion with m/z 151 showed M^{+} of (VI) as the parental ion (Fig. 1). In this way it was possible to establish the occurrence of cleavage of the C(5)—C(6), C(8)—C(9), and C(1)—C(5) bonds of the guaiane system induced by a tertiary OH group (scheme 2).

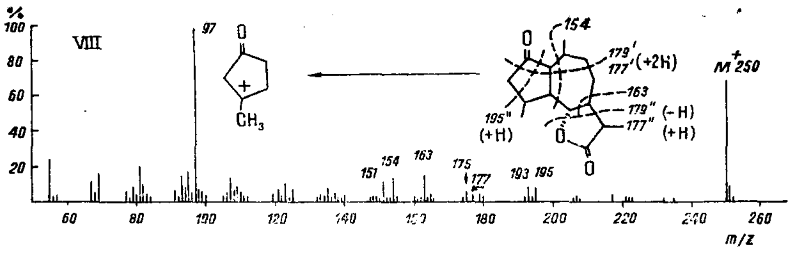


Fig. 2. Mass spectrum of tetrahydroleucomisin (VIII).

TABLE 1. Elementary Compositions of the Ions in the Mass Spectra of Compounds (II, V VI, VII, and VIII)

Accurate mass	Composition		
	C	H	O
II, M^+246,1255	15	18	3
217,1229	14	17	2
(1)* 175,1147	12	15	1
(1) 175,0774	11	11	2
173,0956	12	13	1
(2) 161,0973	11	13	1
(1) 161,0626	10	9	2
159,0821	11	11	1
145,0663	10	9	1
V, M^+362,1364	19	22	7
217,0854	12	12	3
(3) 187,0761	12	11	2
(2) 187,1136	13	15	1
(5) 175,0744	11	11	2
(1) 175,1134	12	15	1
159,0815	11	11	1
152,0846	9	12	2
VI, M^+262,1249	15	18	4
216,1143	14	16	2
189,0905	12	13	2
188,0817	12	12	2
(1) 173,0618	11	9	2
(1) 173,0972	12	13	1
(1) 161,0954	11	13	1
(1) 161,0604	10	9	2
159,0825	11	11	1
151,0757	9	11	2
150,0689	9	10	2
VII, M^+246,1254	15	18	3
185,0966	13	13	1
158,0743	11	10	2
145,1015	11	13	
130,0783	10	10	
129,0700	10	9	
128,0631	10	8	
117,0706	9	9	
115,0555	9	7	
105,0698	8	9	
91,0551	7	7	
VIII, M^+250,1569	15	22	3
(1) 195,1377	12	19	2
(1) 195,1011	11	15	3
(2) 193,1220	12	17	2
(1) 193,0861	11	13	3
(1) 179,1436	12	19	1
(1) 179,1059	11	15	2
(3) 177,1286	12	17	1
(1) 177,0924	11	13	2
174,1040	12	14	1
163,1145	11	15	1
154,0993	9	14	2
97,0666	6	9	1

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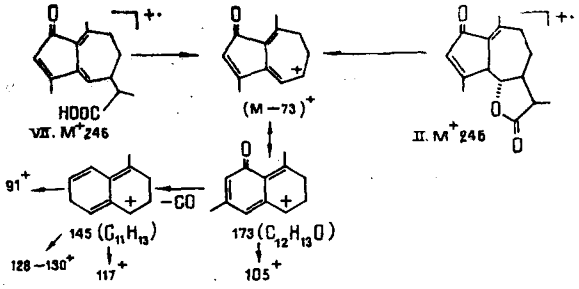
*Relative amount of this composition in the measured peak.

Processes involving the splitting out of ring C were also observed in the other spectra in the form of the peaks of the $(M - 73)^+$ and $(M - 74)^+$ or $(M - R_2H - 73)^+$ and $(M - R_2H - 74)^+$) ions of medium intensity (Fig. 1). As was shown by measurements of elementary composition (Table 1) and a study of the MD spectra (Fig 1), the subsequent breakdown of the $(M - 73)^+$ fragments was accompanied by the formation of tropylium cations with m/z 91 and of naphthalene ions with m/z 128. Using as an example parishin B (VII), the spectrum of which showed the strongest peaks of ions of these types (Fig. 1), this can be illustrated by scheme 3.



Scheme 3

The ions with m/z 128 ($C_{10}H_8$), 129 ($C_{10}H_9$), and 130 ($C_{10}H_{10}$) were, according to their MD spectra (Fig 1), formed predominantly from an ion with m/z 145 ($C_{11}H_{13}$) and, to a smaller extent, from ions with m/z 158 and 173 (Fig. 1).

To estimate the influence of a system of conjugate π-bonds on the distribution of the intensities of the main fragments, we studied the spectrum of tetrahydroleucomisin (VIII) (Fig. 2). The stability of M^+ from this lactone was considerably less than for leucomisin, and the peak of an ion with m/z 97 (C_6H_9O) formed by the cleavage of the C(1)—C(10) and C(5)—

C(6) bonds was the 100% peak (Fig. 2). The other directions of the breakdown of M$^+$ for (VIII) shown in Fig. 2 were confirmed by measurements of elementary compositions (Table 2) and by the MD spectra of the corresponding fragmentary ions.

EXPERIMENTAL

The total mass spectra, the accurate masses of the ions, and the MD spectra were obtained on a MKh-1310 instrument under the following conditions: SVP-5 system for the introduction of the sample; ionization voltage 50 V; temperature of the evaporator bulb 120-150°C; temperature of the ionization chamber 150°C; amplifier voltage 5 kV; resolving capacity of the instrument 1500 (total spectra) and 10,000 (accurate ion mass measurement); MD: E, H = const, U = 2.5 kV; scanning of U from 2.5 to 4.5 kV.

SUMMARY

The spectra of eight guaianolides have been studied. The presence of a system of C(1)=C(10), C(2)=O, and C(3)=C(4) conjugated bonds, and also of C(5)=C(6), stabilizes M$^+$, and the main fragmentation process is the elimination of the lactone ring. The presence of hydroxy substituents at C(3) and C(8) of the guaiane system does not change the stability of the M$^+$ ions in the face of electron impact.

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STRUCTURE OF SHONACHALIN D — A NEW ELEMANOLIDE

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The structure of a new elemanolide — shonachalin D from *Artemisia fragrans* — has been established on the basis of IR and NMR spectra.

Three new sesquiterpene lactones — shonachalins A, B, and C from *Artemisia fragrans* Willd. collected in the village of Shona-Chala, Lerik region, Azerbaidzhan SSR — have been reported previously [1-3]. A fourth lactone isolated from this plant material has the composition $C_{15}H_{22}O_3$, mp 110-112°C (from aqueous ethanol).

A comparison of the physicochemical properties and spectroscopic characteristics of the lactone under investigation with those of the known sesquiterpene lactones showed that the substance was new, not having been described in the literature, and for it we propose the name shonachalin D.

In the region of characteristic frequencies in the IR spectrum of shonachalin D were found maxima at (cm^{-1}) 3480 (OH group), 1750 (CO of a γ-lactone ring), and 1670 (double bonds). In the "fingerprint" region of the spectrum there were bands at 890, 930, and 958 cm^{-1}, which are characteristic for methylene groups [4]. Acetylation formed a monoacetate with the compo-

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