eter were regarded as having germinated. The experiments were performed in duplicate, and 200 spores were recorded in each Petri dish.

SUMMARY

From the stems of the cotton plant infected with the fungus Verticillium dahliae Kleb. has been isolated a quinone derivative of hemigossypol – hemigossypolone – for which the structure 8-formyl-6,7-dihydroxy-5-isopropyl-3-methyl-1,4-naphthoquinone is proposed, and its fungitoxicity has been determined.

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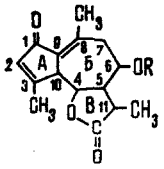
MASS-SPECTROMETRIC STUDY OF THE SESQUITERPENE LACTONE GROSSMISIN AND ITS DERIVATIVES

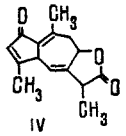
P. I. Zakharov, P. B. Terent'ev, O. A. Konovalova, and K. S. Rybalko

UDC 543.51+547.985

The structure of grossmisin isolated from the epigeal part of Artemisia caucasica Willd. (A. grossheimii Krasch. ex Poljak) (Caucasian wormwood) has been established previously [1]. We have studied the fragmentation under electron impact of grossmisin (I), its deuterium analog (II), and its derivatives acetylgrosssmisin (III) and anhydrogrossmisin (IV) in order to establish the main laws of the dissociative ionization of these compounds due to the presence of the structural elements characteristic for them.



I. R=–H
II. R=–D
III. R=–COCH$_3$

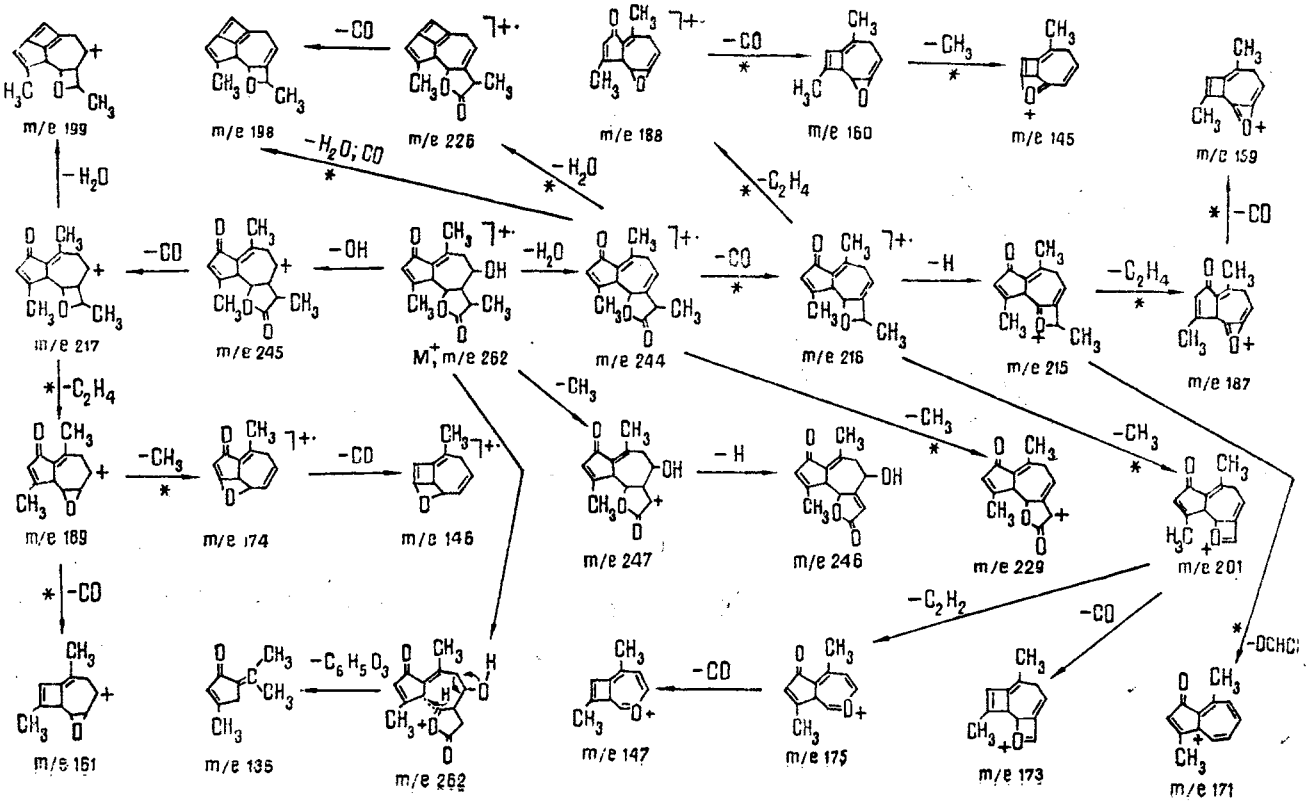


IV

The mass spectra of compounds (I-IV) areshown in Fig. 1. The appearance of ions in the mass spectrum of grossmisin (I) in the region of high masses and of the main ions in the region of moderate masses is shown in the scheme, and their accurate masses and elementary compositions are given in Table 1. The main direction of fragmentation of (I) is the elimination by the ion M^+ of an H_2O molecule (m/e 244) followed by the ejection of a CO group (m/e 216) or a CH_3 radical (m/e 229). A side direction of the decomposition of (I) is associated with the loss by the molecular ion of (I) of CH_3 and OH radicals (m/e 247 and 245, respectively).

M. V. Lomonosov Moscow State University. Patrice Lumumba International Friendship University, Moscow. All-Union Scientific-Research Institute of Medicinal Plants, Moscow. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 344-349, May-June, 1977. Original article submitted October 20, 1976.

The fact that the ion $(M - CH_3)^+$ is shifted by one mass unit in the direction of higher masses in the mass spectrum of [O–D]grossmisin (II) and the absence of the shift for the ions $(M - H_2O)^+$, $(M - OH)^+$, $(M - H_2O - CO)^+$, and $(M - H_2O - CH_3)^+$ confirms the route of their formation shown in the scheme. The appearance of a low-intensity ion with m/e 226 shows the loss of a second molecule of H_2O by the M^+ ion, which is due to the peri position of the exocyclic oxygen atom of the α,β-cyclopentanone ring and the CH_3 group in position 8 of the seven-membered ring (B). The presence of the metastable peak m* = 178, corresponding to the transition m/e 262 → m/e 216, shows that the formation of the fragment $(M - H_2O - CO)^+$ in the mass spectrum of (I) takes place not only through the elimination of a CO group by the $(M - H_2O)^+$ ion (m* = 199) but also as the result of the simultaneous elimination from the ion M^+ of the neutral particles CO and H_2O. A similar loss of these particles is undergone by the $(M - H_2O)^+$ fragment, as is shown by a metastable ion with m* = 161 corresponding to the transition m/e 244 → m/e 198.



The appearance of ions with m/e 246, 229, 215, and 201 in the mass spectrum of grossmisin (I) is due to the loss of a hydrogen atom or a CH_3 group, respectively from mother ions with m/e 247, 244, and 216, which leads to their partial aromatization. This process is one of the main causes for the detachment of H and CH_3 radicals in the subsequent (after the first) stage of the decomposition of the molecular ion (I) and explains the absence of the loss of a CH_3 radical by the ion with m/e 217 $(M - OH - CO)^+$.

The appearance of the main fragments in the region of medium masses in the decomposition of (I) is connected with the elimination by the ions $(M - H_2O - CO)^+$ and $(M - OH - CO)^+$ of a CO group and a CH_3 radical. An exception is the formation of fragments with m/e 175 and 136, which probably takes place through rearrangement processes. The routes of origin of these fragments are confirmed by their empirical formulas $C_{11}H_{11}O_2$ and $C_9H_{12}O$ obtained from the high-resolution mass spectrum of (I) (175.0762 and 136.0877 amu, respectively), and also by the dissociative ionization of [O–D]grossmisin (II), in the mass spectrum of which the fragment with m/e 175 does not undergo a shift and the ion with m/e 136 is shifted partially by one unit in the direction of higher masses. The intense fragment with m/e 91 in the mass spectrum of (I) has the empirical formula C_7H_7 (91.0567 amu) and evidently represents an ion with a tropylium structure [2].

Because of the absence of the OH group from the molecule of anhydrogrossmisin (IV), its the mass spectrum does not show the presence of ions with m/e 217, 189, and 161, which confirms the route of their origin from the ion with m/e 245 in the mass spectrum of (I), as shown in the scheme. The mass numbers of the other fragments, beginning with the ion having m/e 244 in the mass spectra of grossmisin (I) and anhydrogrossmisin (IV) coincide, which is due to the loss of the same neutral particles by this ion in the decomposition

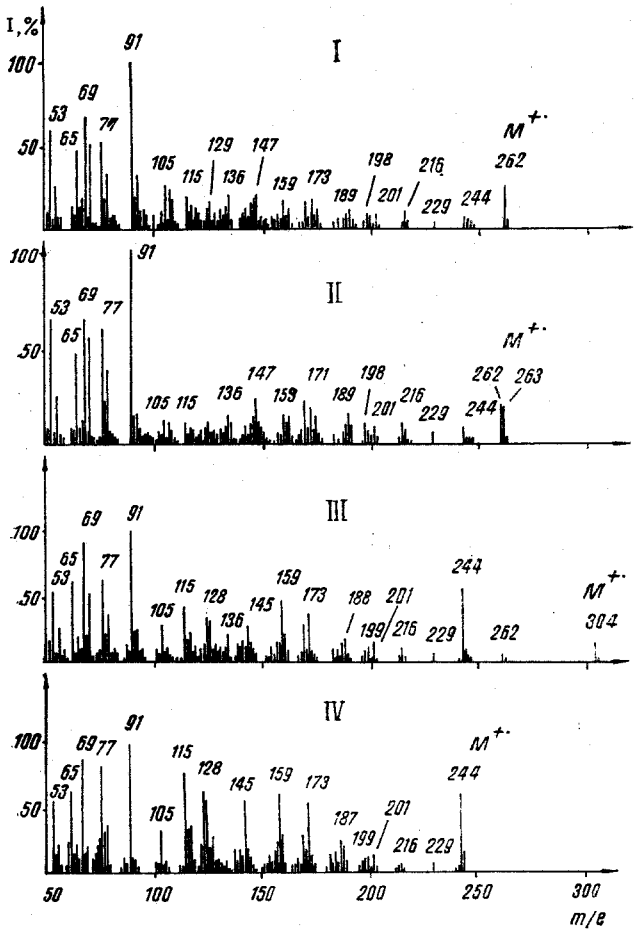


Fig. 1. Mass spectra of grossmisin (I), [D]grossmisin (II), acetylgrossmisin (III), and anhydrogrossmisin (IV).

TABLE 1. High-Resolution Mass Spectrum of Grossmisin (I) in the Region of High and Moderate Masses*

Mass		Error of measurement	Composition of the ion
measured	calc.		
262,1191	262,1204	−1,3	$C_{15}H_{18}O_4$
247,0974	247,0969	+0,5	$C_{14}H_{15}O_4$
246,0889	246,0891	−2,2	$C_{14}H_{14}O_4$
244,1113	244,1098	+1,5	$C_{15}O_{17}O_3$
226,0815	229,0863	−4,8	$C_{14}H_{13}O_3$
217,1135	217,1128	+0,7	$C_{14}O_{17}O_2$
216,1123	216,1149	−2,6	$C_{14}H_{16}O_2$
215,1069	215,1071	−0,2	$C_{14}H_{15}O_2$
201,0910	201,0914	−0,4	$C_{13}H_{13}O_2$
199,1109	199,1122	−1,3	$C_{14}H_{15}O$
198,1050	198,1044	+0,6	$C_{14}O_{14}O$
189,0891	189,0915	−2,4	$C_{12}H_{13}O_2$
188,0847	188,0837	+1,0	$C_{12}O_{12}O_2$
187,0755	187,0759	−0,4	$C_{12}H_{11}O_2$
175,0762	175,0759	+0,3	$C_{11}H_{11}O_2$
174,0676	174,0680	−0,4	$C_{11}H_{10}O_2$
173,0961	173,0966	−0,5	$C_{12}H_{13}O$
171,0802	171,0809	−0,7	$C_{12}O_{11}O$
161,0916	161,0966	−5,0	$C_{11}H_{13}O$
160,0880	160,0888	−0,8	$C_{11}H_{12}O$
159,0824	159,0809	+1,5	$C_{11}H_{11}O$
147,0803	147,0809	−0,6	$C_{10}H_{11}O$
146,0733	146,0731	+0,2	$C_{10}H_{10}O$
145,0657	145,0653	+0,4	$C_{10}H_9O$
136,0877	136,0888	−1,1	$C_9H_{12}O$

*The table gives ions of the greatest intensity, the formation of which is shown in the scheme.

of compounds (I) and (IV). However, the relative intensities of some of the ions in the mass spectra of (I) and (IV) (for example, the ions with m/e 244, 229, 198, 187, 173, 171, 147, and 145) differ appreciably, which can be explained by the different positions of the lactone ring (C) in compounds (I) and (IV). Conversely, the dissociative ionization of anhydrogrossmisin (IV) and of acetylgrossmisin (III), beginning with the fragment having m/e 244, leads to ions not only of the same mass but also of practically the same intensity. This fact can be explained by the assumption that on the elimination of a molecule of acetic acid by the M^+ ion of compound (III) the rearrangement of the lactone ring (C) from the C_4 to C_6 carbon atom of the seven-membered ring B takes place. As a result, the ion $(M - CH_3COOH)^+$, to which a metastable peak with m* = 196 corresponds, in the mass spectrum of (III) has the same structure as the molecular ion of compound (IV). This explains the identity of their subsequent decompositions. In the decomposition process, the molecular ion of acetylgrossmisin (III) also eliminates a ketene molecule, giving a fragment $(M - CH_2CO)^+$ with m/e 262 (m* = 226), i.e., it shows the fragmentation typical for acyl derivatives of other classes of compounds [3, 4]. We must also mention the multiline nature of the mass spectra of grossmisin (I) and its derivatives (II-IV), which is a distinguishing feature of the decomposition of other sesquiterpene lactones [5].

Thus, the mass spectra of grossmisin (I) and its derivatives do not contradict the structures adopted for these compounds. The main ions arising in the process of their fragmentation are due to the presence in the molecules of an alcoholic hydroxy group and carbonyls of lactone and of α,β-unsaturated cyclopentanone rings, and also of methyl groups present in the α and peri positions to the carbonyl groups of these rings.

EXPERIMENTAL

The mass spectra of the compounds were obtained on a standard MKh-1303 instrument fitted with a system for the direct introduction of the sample into the ion source at an ionizing voltage U = 70 V and recording temperatures of 90°C (I, II), 25°C (III), and 50°C (IV). The high-resolution mass spectrum of (I) was taken on a IMS-01 1G-2 instrument. The deuterium analog of grossmisin (II) was obtained by the method of Shipchandler and Joine [6]. The deuteration of (I) took place to the extent of 50% (from the mass spectrum).

SUMMARY

The dissociative ionization of grossmisin [O−D]grossmisin, and two of its derivatives have been studied. The appearance of the main fragments in the mass spectrum of grossmisin is due to the elimination by the M^+ ion of H_2O and CO molecules and CH_3 and OH radicals in various sequences. The hypothesis has been put forward that in the splitting off of a CH_3COOH molecule by the $M^{+\cdot}$ ion of acetylgrossmisin a rearrangement of the lactone ring takes place with its reclosure at the C_6 carbon atom of the seven-membered ring.

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