

FRAGMENTATION OF SOME 1,2-EROXYGUAIANOLIDES

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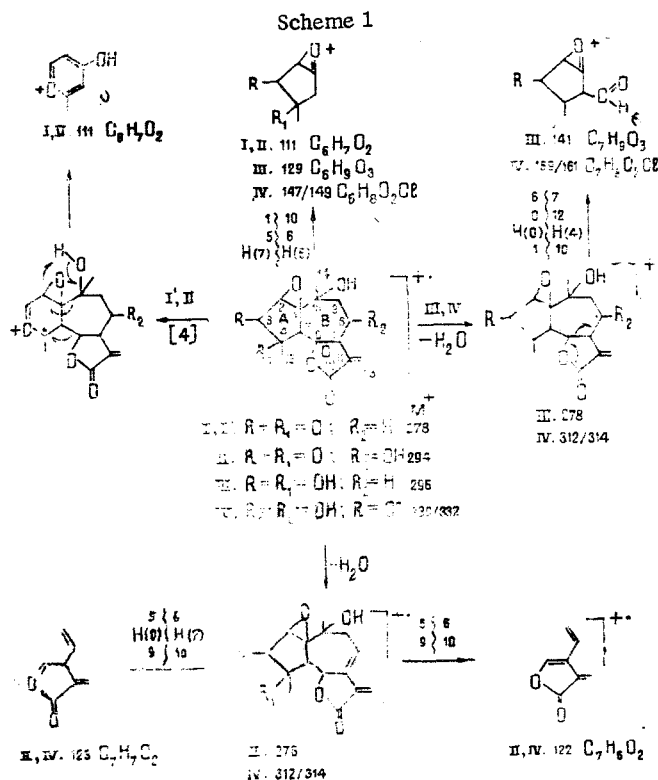
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The mass spectra of four guaianolides with epoxy groups of C_1 - C_2 have been studied. A mechanism is proposed for the formation of the main ions. The origin of the secondary fragments has been confirmed by measurements of elementary compositions.

In spite of the existence of a considerable number of sesquiterpene lactones of the guaiane type, there is extremely little information on the mass spectra of these compounds [1-4]. Continuing a study of the pathways of the fragmentation of lactones of sesquiterpene lactones, in this paper we consider the mass spectra of four lactones with a guaiane skeleton representing the 1,2-epoxyguaianolides - chrysartemin B (I) [5], rupin A (II) [4], ajafinin (III) [6], and biebsanin (IV) [7].

The intensities of the peaks of the molecular ions of (I-IV) are very low in comparison with the main peak of the spectra (Fig. 1), which is obviously due to the relative instability of the guaiane skeleton, aggravated by the presence of the epoxy groups. In the case of rupin A and biebsanin, the peaks of the ions of the protonated forms $(M+1)^+$ with m/e 295 ($C_{15}H_{19}O_6$) and 331 ($C_{15}H_{20}O_6Cl$), respectively, have a higher intensity. A similar phenomenon has been observed in the spectra of lactones, when the vapor pressure of the substances rises in the ion source of the mass spectrometer [8].

In contrast to the germacranolides [9], the presence of several OH groups does not lead to an appreciable increase in the role of the splitting out of substituents. At the same time, in the spectra of chrysartemin B (I) and rupin A (II) there are ions with m/e 111, the



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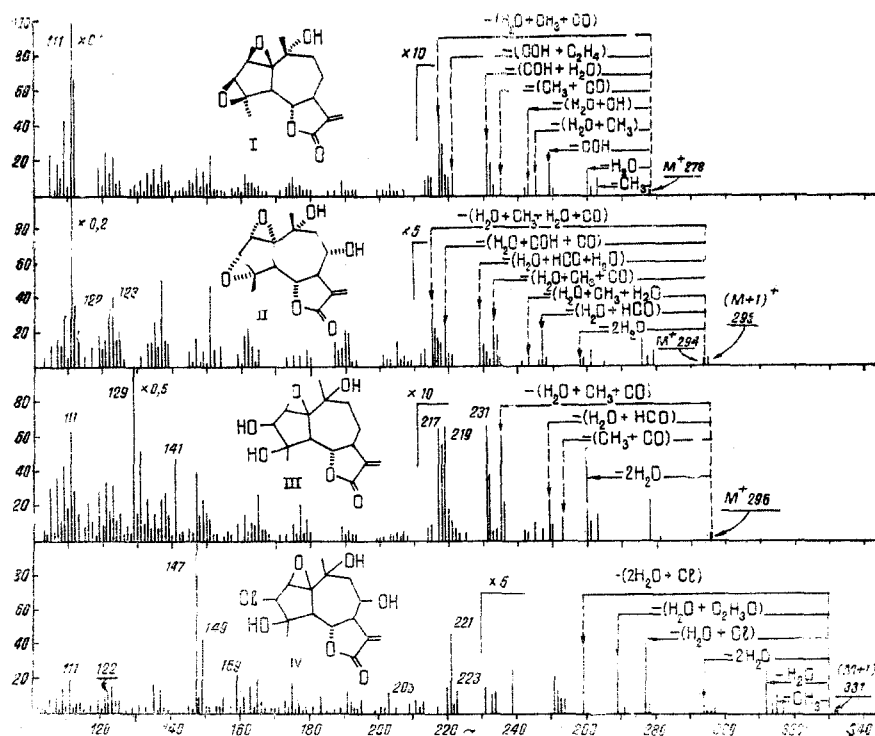


Fig. 1

intensity of the peaks of which far exceeds all the others. Irwin and Geissmann [4], comparing the spectra of rupin A and another 1,2,2,4-diepoxyguaianolide — anin (I') — suggested that this ion is formed as the result of the localization of the charge on the oxygen of the 3,4-epoxy group with the subsequent splitting out of rings B and C (Scheme 1).

A comparison of the spectra of the diepoxyguaianolides (I) and (II) in the spectra of compounds (III) and (IV), in the molecules of which the 3,4-epoxy groups are hydrated and hydrochlorinated, respectively, forced us to reconsider the mechanism of the appearance of the ion with m/e 111 suggested by Irwin and Geissman [4]. The spectra of (III) and (IV) each contain intense peaks of fragments with m/e 129 ($111 + H_2O$) and 147/149 ($111 + HCl$) (see Fig. 1). As an analysis of metastable transitions by the method of ion beam defocusing shows, the ions with m/e 111 in the spectra arise from the ions mentioned above by the elimination of a molecule of water (III) or of hydrogen chloride (IV).

It is natural to assume that the initial act of the fragmentation of the molecular ions of compounds (I-IV) by the direction considered is the cleavage of the C_1-C_{10} bond with the localization of the charge on the oxygen of the 1,2-epoxy group (see Scheme 1). The process is activated by the presence of an OH group at C_{10} .

The analogy in the positions of the OH groups in rupin A and biebsanin, and also in aja-finin and biebsanin, permits us to observe other, less characteristic, processes of the cleavages of the bonds in the skeletons in the spectra of these pairs of compounds. Thus, as the result of the 1,2-elimination of a molecule of water at the expense of the 8-OH-7-H atoms, activated by the formation of a conjugated chain, the cleavage of the C_5-C_6 and C_9-C_{10} bonds may take place, leading to the formation of ions of medium intensity with m/e 122 and 123 (see Scheme 1). The splitting out of water with the participation of the hydroxyl at C_4 in aja-finin and biebsanin initiates the fragmentation of rings B and C and the formation of ions with m/e 141 (III) and 159/161 (IV), as shown in the scheme.

Other, second-degree, methods of fragmentation of the guaiane skeleton of compounds (I-IV), as a rule accompanying the splitting out of substituents, are characterized briefly in Table 1. All the directions of fragmentation discussed have been confirmed by measurements of the elementary compositions of the ions. The processes of splitting out of the substituents are reflected directly in Fig. 1.

We have also analyzed the compositions of the ions $(M - 35)^+$ and $(M - 36)^+$ in the biebsanin spectrum and have established that the loss of Cl and HCl is responsible for 50% and 5%,

TABLE 1. Compositions of the Charged and Neutral Fragments in the Mass Spectra of the Guaianolides (I-IV)

m/e	Elementary composition	Particles eliminated from M ⁺	Position of cleavage of the bonds of the skeleton
Chrysartemin B (I)			
278M ⁺	C ₁₅ H ₁₈ O ₅		
215	C ₁₃ H ₁₁ O ₃	H ₂ O + CH ₃ + HC≡CH	
207	C ₁₁ H ₁₁ O ₄	C ₆ H ₉ O	1-10, 7-8
205	C ₁₁ H ₉ O ₄	C ₆ H ₉ O	1-10, 7-8
203	C ₁₃ H ₁₅ O ₂ 0.35*	HCO + H ₂ O + CO	
203	C ₁₂ H ₁₁ O ₃ 0.65	H ₂ O + C ₃ H ₅ O	2-3, 4-5
199	C ₁₃ H ₁₁ O ₂	CH ₃ + H ₂ O + CO + H ₂ O	
189	C ₁₂ H ₁₃ O ₂ 0.65	H ₂ O + C ₃ H ₅ O ₂	7-11, 12-0
189	C ₁₁ H ₉ O ₃ 0.35	CH ₃ + H ₂ O + CO + C ₂ H ₄	7-8, 9-10
177	C ₁₁ H ₁₃ O ₂ 0.25	C ₆ H ₇ + C ₂ H ₄ + CO ₂	
177	C ₁₀ H ₉ O ₃ 0.75	C ₆ H ₉ O + CO	
175	C ₁₁ H ₁₁ O ₂	H ₂ O + C ₃ H ₅ O + CO	
165	C ₁₀ H ₁₃ O ₂ 0.5	OH + C ₅ H ₅ O ₂	5-6, 7-8
165	C ₉ H ₉ O ₃ 0.5	CH ₃ + C ₅ H ₅ O ₂	5-6, 7-8
161	C ₁₁ H ₁₃ O 0.35	OH + CO + C ₅ H ₄ O ₂	6-0, 7-11
161	C ₁₀ H ₉ O ₂ 0.65	CH ₃ + H ₂ O + CO + C ₃ H ₄ O	2-3, 4-5
151	C ₉ H ₁₁ O ₂	H ₂ O + C ₅ H ₅ O ₂	1-10; 5-6 or 9-8; 5-6
Rupin A (II)			
295(M+1) ⁺	C ₁₅ H ₁₉ O ₆		
205	C ₁₂ H ₁₃ O ₃ 0.75	H ₂ O + C ₃ H ₃ O ₂	6-0, 7-11
205	C ₁₁ H ₉ O ₄ 0.25	C ₆ H ₃ O ₂	1-10, 7-8
191	C ₁₁ H ₁₁ O ₃	H ₂ O + CH ₃ + C ₃ H ₂ O ₂	6-0, 7-11
165	C ₉ H ₉ O ₃	H ₂ O + CH ₃ + C ₅ H ₄ O ₂	5-6, 7-8
162	C ₁₀ H ₁₀ O ₂	2H ₂ O + C ₅ H ₄ O ₂	5-6, 7-8
151	C ₉ H ₁₁ O ₂	2H ₂ O + C ₅ H ₃ O ₂	5-6, 8-9
Ajafinin (III)			
296M ⁺	C ₁₅ H ₂₀ O ₆		
231	C ₁₄ H ₁₅ O ₃	2H ₂ O + COH	
219	C ₁₃ H ₁₅ O ₃	H ₂ O + CH ₃ + CO ₂	
217	C ₁₃ H ₁₃ O ₃	2H ₂ O + CH ₃ + CO	
189	C ₁₂ H ₁₃ O ₂	H ₂ O + C ₃ H ₃ O ₂ + H ₂ O	6-0, 7-11
179	C ₁₁ H ₁₅ O ₂ 0.75	H ₂ O + C ₃ H ₃ O ₂ + CO	6-0, 7-11
179	C ₁₀ H ₁₁ O ₃ 0.25	H ₂ O + C ₄ H ₇ O - CO	1-10, 7-8
177	C ₁₁ H ₁₃ O ₂	H ₂ O + CO + C ₃ H ₅ O ₂	2-3, 4-5
175	C ₁₁ H ₁₁ O ₂	H ₂ O + CO + C ₃ H ₇ O ₂	2-3, 4-5
165	C ₁₀ H ₁₃ O ₂	2H ₂ O + C ₅ H ₃ O ₂	5-6, 7-8
161	C ₁₁ H ₁₃ O 0.45	2H ₂ O + CO + C ₃ H ₃ O ₂	6-0, 7-11
161	C ₁₀ H ₉ O ₂ 0.55	2H ₂ O + CO + CH ₃ + C ₃ H ₄ O	2-3, 4-5
159	C ₁₁ H ₁₁ O	H ₂ O + C ₃ H ₅ O ₂ + H ₂ O + C	2-3, 4-5
Biebsamin (IV)			
330M ⁺	C ₁₅ H ₁₉ O ₆ ³⁵ Cl		
252	C ₁₃ H ₁₃ O ₃ ³⁵ Cl	H ₂ O + C ₅ H ₅ O + OH	7-8, 9-10
251	C ₁₃ H ₁₅ O ₅	HCl + C ₂ H ₅ O	7-8, 9-10
251	C ₁₃ H ₁₂ O ₅ ³⁵ Cl 0.5	H ₂ O + C ₂ H ₃ O + H ₂ O	7-8, 9-10
239	C ₁₂ H ₁₅ O ₅	C ₃ H ₇ OCl	2-3, 4-5
223	C ₁₂ H ₁₅ O ₄ 0.5	HCl + C ₃ H ₃ O ₂	6-0, 7-11
223	C ₁₁ H ₁₁ O ₅ 0.5	CH ₃ + C ₅ H ₅ OCl	2-3, 4-5
221	C ₁₂ H ₁₃ O ₄	C ₃ H ₇ OCl + H ₂ O	2-3, 4-5
220	C ₁₂ H ₁₂ O ₄	H ₂ O + C ₃ H ₅ OCl	2-3, 4-5
191	C ₁₁ H ₁₁ O ₃	H ₂ O + Cl + C ₄ H ₅ O ₂	7-8, 1-10
165	C ₉ H ₉ O ₃	H ₂ O + C ₃ H ₅ OCl + C ₃ H ₃ O ₂	6-0, 7-11
163	C ₁₀ H ₁₁ O ₂	H ₂ O + Cl + C ₄ H ₅ O ₂ + CO	

*Relative proportion of the ion of the given composition in the peak measured.

respectively, of their intensities, the remainder of the ions of the given masses corresponding to the loss of H₂O + OH and 2H₂O. The ratio between the intensities of the peaks of the ions with m/e 221 and 223 in the spectrum of (IV) is approximately the same as that between the peaks of ions containing the isotopes ³⁵Cl and ³⁷Cl (3:1), but analysis of their composition showed the absence of a chlorine atom and, moreover, the ion with m/e 223 is a doublet. The origins of these ions are shown in Table 1. The ions with m/e 221 and 220, the methods of formation of which are similar, by losing a molecule of water each, are converted into ions with m/e 203 and 202, respectively (the peak m* = 186.5 amu.).

EXPERIMENTAL

The low-resolution mass spectra were obtained on an MKh-1303 instrument using a system for the direct introduction of the sample, at a temperature of 110-130°C with an ionizing voltage of 40 V.

The accurate masses of the ions were measured on an MKh-1310 mass spectrometer, the experimental conditions having been given previously [9].

SUMMARY

The mass spectra of four guaianolides with epoxy groups at C₁-C₂ have been studied. A mechanism is suggested for the formation of the fragmentary ions. The origin of the second-degree fragments has been confirmed by measurements of elementary compositions.

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COUMARINS OF THREE SPECIES OF THE GENUS *Haplophyllum*

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The results are given of an investigation of three species of the genus *Haplophyllum*: *H. villosum*, *H. kowalenskyi*, and *H. tenue*, from which five substances of coumarin nature have been isolated. Of them, two substances (I and II) have been identified as scopoletin and lomatin isovalerate, respectively, while suitable structures have been established for the new compounds tenuidin, villosin, and tenudiol. It has been shown that the coumarin composition of the plants changes with the growth site.

We have studied the coumarin composition of the epigeal part of three species of plants of the genus *Haplophyllum* (family Rutaceae): *H. villosum*, *H. kowalenskyi*, and *H. tenue*, collected in the Nakhichevan ASSR from various growth sites in the full-flowering stage (see Table 1). Five substances have been isolated (I, C₁₀H₈O₄, mp 204-205°C; II, C₁₉H₂₂O₅; III, C₁₄H₁₄O₃, mp 74-75.5°C; IV, C₂₀H₂₄O₅; V, C₂₀H₂₆O₆) all possessing the properties characteristic for compounds of the coumarin series.

In their physicochemical constants and IR and PMR spectra, substances (I) and (II) corresponded to the known coumarins scopoletin [1] and lomatin isovalerate [2]. Substances (III-V) proved to be new, not previously described in the literature. We have called them tenuidin, villosin, and tenudiol.

The IR spectra of tenuidin (III) showed absorption bands at (cm⁻¹) 1725 (C=O of an α -pyrone), 1700 (keto group), and 1655, 1610, and 1515 (-CH=CH bond in an aromatic ring).

In the PMR spectrum of (III), in addition to the signals of the protons of a 6,7-disubstituted coumarin ring (one-proton doublets at 6.26 and 7.66 ppm, J = 10 Hz, H-3 and H-4, and singlets at 6.80 and 6.91 ppm, H-8 and H-5), the signals of the protons of a methoxy group are observed at 3.95 ppm (singlet, 3 H) and those of a normal butyryl radical (triplet at 1.28 ppm, 3 H, and multiplet with its center at 2.88 ppm, 4 H). On the basis of these results, two structures are possible for compounds (III) - α and β . From biogenetic considerations, (IIIa) is the more probable:

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