SUMMARY

The stereochemistries of three oxides of the bicyclohomofarnesane series have been established by spectral and chemical methods.

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MASS SPECTROMETRY OF NEGATIVE IONS AND THE STEREOCHEMISTRY OF ORGANIC COMPOUNDS.

IV. ACETATES OF EPIMERIC DITERPENE GLYCOLS

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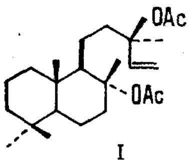
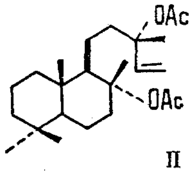
UDC 539.19.08+541.57

In an investigation of the mass spectra of the negative ions (NIs) from the dissociative capture of electrons (DCE) of a series of carbohydrate derivatives, the high stereospecificity of the fragmentation of the molecular NIs of the O-acetates and O-methyl derivatives of the monosaccharides on interaction with low-energy electrons has been established [1-4].

Continuing these investigations with the aim of showing the possibility of using the method of the mass spectrometry of NIs for investigating the stereochemistry of other classes of natural compounds, we have studied the DCE mass spectra of two acetyl derivatives of diterpenoids of the labdane group — the diacetates of sclareol (I) and of 13-episclareol (II) — which are given in Table 1.



I



II

It is known that the stereochemical differences of the sclareol and 13-episclareol molecules are connected with the different configurations of the asymmetric atom at C_{13}. Sclareol has the 13-R configuration and episclareol the 13-S configuration [5-10]. Consequently, the question of the influence of such fine differences in the molecules of the diacetates under consideration on the nature of the DCE mass spectra is a matter of interest.

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TABLE 1. Mass Number and Relative Intensities of the Negative Ions in the Mass Spectra of the Diacetates of Sclareol (I) and of 13-Episclareol (II)

m/e	I	II
391	[illegible] 0 (2,5)	77,0 (2,5)
349	[illegible],0 (2,3)	57,0 (2,3)
349	4.2 (7,5)	6,6 (7,5)
333	18.0 (6,6)	37,2 (6,6)
331	3,0 (2.7)	1,4 (2.7)
331	10,0 (7,0)	11,5 (7,0)
323	18,5 (6,8)	13,0 (6.8)
307	88,0 (2.5)	77,2 (2.5)
307	100 (7,0)	100 (7,0)
291	3,4 (8,0)	3,4 (8,0)
289	10,0 (2,3)	7.0 (2,3)
289	3,5 (7.5)	2,0 (7,5)
279	14,0 (6,8)	10,0 (6,8)
277	4,3 (1,0)	34,3 (1.0)
262	17,0 (0,8)	34,3 (0,8)
258	3.2 (7,0)	1,4 (7,0)
248	38,0 (0,7)	54,3 (1,0)
73	—	1140 (1,0)
59	116000 (0,9)	62500 (0,9)
43	24,3 (6,5)	11,5 (6,5)
41	250 (8,0)	100 (8.0)

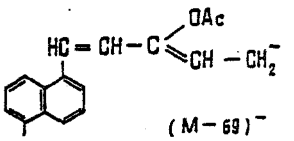
<u>Note.</u> The energy of the electrons of the maximum yield of ions is given in parentheses (eV±0.1 eV).

The dissociative capture of electrons by the molecules of the diacetates (I) and (II) is observed in three regions of electron energy (~1, ~ 2.5, and 7-8 eV).

In the mass spectra of compounds (I) and (II) given in Table 1, the intensities of the lines of the ions $(M - 85)^-$ (m/e 307) in the region of electron energies of ~7 eV are taken as 100%, and not the lines of the maximum peak, since the very high intensity of the lines of the ions with m/e 59 (OAc^-) in the spectra of the acetates (I) and (II) leads to the situation that the relative intensities of the other peaks are expressed in the form of fractions of a percentage part, which complicates the interpretation of the spectra. Furthermore, the intensities of the lines of the ions in NI mass spectrometry may depend on the width of the curve of the distribution of electrons with respect to energies [11], and therefore as the base line in the determination of the relative intensities of the peaks it is customary to take the line of the ions formed at an electron energy greater than 1 eV.

In the region of electron energies of ~2.5 eV, the fragmentation of the molecular negative ions is similar to the fragmentation of ions of pentose peracetates [1, 3]: the peaks of the ions $(M - Ac)^-$, $(M - Ac, AcOH)^-$, and $(M - Ac, C_2H_2O)^-$ are observed. The difference consists in the higher intensity of the peaks of the $(M - H)^-$ ions which apparently then lose a molecule of AcOH, forming the peak of the $(M - 61)^-$ ions (m/e 331).

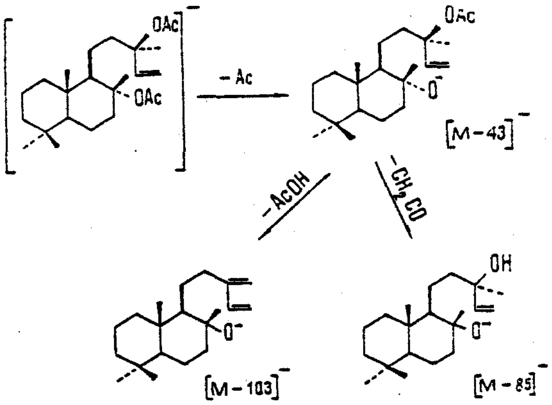
The mass spectra of the NIs formed at ~7-8 eV reflect the same fragmentation pathways as at 2.5 eV and, furthermore, lines also appear of $(M - OAc)^-$ ions (m/e 333), lines with m/e 323, 291, 279, and 136, and also the peaks of Ac^- (m/e 43) and OC_2H^- (m/e 41) ions. The appearance of ions with m/e 291 $(M - 101)^-$ is apparently connected with the splitting out from the $(M - OAc)^-$ ions of a molecule of ketene or of CH_3 and C_2H_5 groups. The ions with m/e 323 and 279 possibly have the structure:



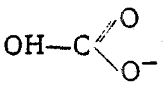
$(M - 69)^-$

(the replacement of one OAc group by a methyl group gives the ions with m/e 279), i.e., apparently, aromatization of the system takes place with the delocalization of the negative charge over the m system of electrons in a similar manner to the processes of forming ions in cyclic unsaturated system [1-4].

In the regions of electron energies considered, the mass spectra of the NIs of isomers (I) and (II) differ only slightly — a higher relative yield of the $(M - H)^-$ and $(M - Ac)^-$ ions is observed in the diacetate of 13-episclareol, but an increased relative yield of ions with m/e 41 ($^-OC{\equiv}CH$) in sclareol diacetate. One of the fragmentation pathways of the molecular ion of the diacetate (I) via the intermediate $(M - 43)^-$ ion may be the following possible scheme:



The greatest difference in the mass spectra of the negative ions of the isomers under consideration is observed in the region of electron energies of ~1 eV.

In episclareol diacetate (II) the relative intensity of the ions with m/e 277, 262, and 248 is considerably higher, and the very strong lines of the ions with m/e 73 $(OAcCH_2)^-$ or  $OH{-}C(=O)O^-$ are absent from the mass spectrum of (I).

Apparently, the origin of the ions with m/e 73 is connected with the close interaction of the OAc groups with one another in the molecular ion and in sclareol diacetate (I) such interaction is sterically hindered.

EXPERIMENTAL

The mass spectra of the NIs were recorded on an MKh-1303 mass spectrometer equipped for the recording of negative ions [12].

SUMMARY

1. It has been established that the fragmentation of the molecular negative ions of the diacetates of sclareol and of 13-episclareol takes place with the splitting out of the fragments Ac, OAc, CH_2CO, AcOH, CH_3, and $CH{=}CH_2$ without skeletal rearrangements.

2. The relative yields of the negative ions formed depend on the stereochemistry of the molecules of the compounds investigated.

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PHYTOECDYSONES OF *Rhaponticum integrifolium*

III. INTEGRISTERONE B

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Continuing a study of the phytoecdysones of the flower heads of *Rhaponticum integrifoliu* C. Winkl., in addition to the ecdysterone (I) and integristerone A (II) isolated previously [1, 2], we have isolated a new ecdysone — integristerone B (III), with the composition $C_{27}H_{44}O$ This compound has a lower chromatographic mobility than the other phytoecdysones obtained fro from this plant source.

In the mass spectrum of the ecdysone under investigation, the peak of the molecular ion is absent. The fragment with the highest mass number, m/e 476, and the ions with m/e 458, 440, and 422 are obviously formed by the loss from the molecular ion of integristerone B (M^+ 512) of from two to five molecules of water.

The fragmentation of the side chain of the new phytoecdysone is described by ions with m/e 143, 125, 99, 81, and 69. These ions, which are characteristic of ecdysones with the side chain of ecdysterone (I) [3,4], including integristerone A (II) [2], suggest the identity of the structure of the C-20—C-27 chains in ecdysones (I), (II), and (III).

The latter assumption is confirmed by the practical coincidence of the values of the chemical shifts of the C-21, C-26, and C-27 methyl groups and of the C-22 proton in the PMR spectra of compounds (II) and (III) (Table 1).

Experiments on the deuterium exchange of (I)-(III) showed that the fragments of the side chain with m/e 143 and 99 formed as the result of C-17—C-20 and C-20—C-22 cleavages, respectively, have a cyclic form (Scheme 1).

The steroid part of the molecule after analogous cleavages must lead to the ions $(M - 180)^+$, by C-17—C-20 cleavage, and $(M - 117)^+$, by C-20—C-22 cleavage [2, 3, 5]. The spectrum of integristerone B does actually have the weak peak of the ion $(M - 180)^+$ with m/e 332, a fragment with m/e 395 $(M - 117)^+$, and also the products of its successive dehydration — ions with m/e 377, 359, 341, and 323 (not shown in Scheme 1). The mass numbers of the ions of this series are displaced by 16 m.u. in the direction of high masses as compared with those of integristerone A [2], which shows the presence of five hydroxy groups in the steroid nucleus of phytoecdysone (III).

In addition to this, the mass spectrum of integristerone B showed strong peaks of fragments with m/e 390, 273, 272, 255, 229, and 228 (see Scheme 1) which are not characteristic of the spectra of ecdysterone and of integristerone A [1-3]. This can be explained by the characteristic decomposition of the hydroxy groups in the steroid part of the molecule of the phytoecdysone (III). We directed our attention to the fact that in the IR spectrum of integristerone B the maximum absorption of the 6-keto group appears at 1680 cm^{-1} and is displaced in comparison with the corresponding maximum of integristerone A (1665 cm^{-1}) by 15 cm^{-1} in the direction of high wave numbers. Such a displacement, which is possible if the C=O and the neighboring hydroxy group are coplanar, shows the presence of a 5β-hydroxy function in the molecule of phytoecdysone (III) [5-8].

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