MASS-SPECTROMETRIC STUDY OF THE COUMARINS MOGOLTIN, MOGOLTAVIN, AND MOGOLTAVININ

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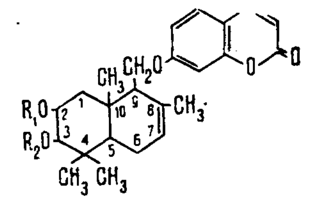
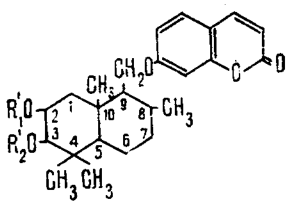
The structures of mogoltin (I), mogoltavin (IV), and mogoltavinin (VI), isolated from the roots of the plant Peucedanum mogoltavicum Korov. and belonging to the class of terpenoid coumarins have been established previously [1-3]. The present paper gives the results of a study of the mass spectra of these compounds and a number of their derivatives: mogoltin-d_2 (II), dihydromogoltin (III), mogoltavin-d (V), mogoltavinin-d (VII), mogoltavin acetate (VIII), mogoltavinin acetate (IX), and dihydromogoltin-d_2 (X):



I. $R_1 = -H$, $R_2 = -H$
II. $R_1' = -D$, $R_2' = -D$
III. $R_1' = -H$, $R_2' = -H$
IV. $R_1 = -H$, $R_2 = -COCH_3$
V. $R_1 = -D$, $R_2 = -COCH_3$
VI. $R_1 = -H$, $R_2 = -COC(CH_3){=}CHCH_3$
VII. $R_1 = -D$, $R_2 = -COC(CH_3){=}CHCH_3$
VIII. $R_1 = -COCH_3$, $R_2 = -COCH_3$
IX. $R_1' = -COCH_3$, $R_2 = -COC(CH_3){=}CHCH_3$
X. $R_1' = -D$, $R_2' = -D$



The figures in Table 1, which give the partial mass spectra of compounds (I-X), show that compounds (I-VII) and (X) are fairly stable to electron impact and give molecular ions of high and medium intensity. Compound (VIII) has a feeble molecular peak, and in the mass spectrum of substance (IX) the peak of the molecular ion is not observed at all. This shows the destabilization of the ions M^+ in the series of substances studied with an increase in the number and magnitude of the acyl groups in their molecules, which is characteristic for other classes of coumarins containing two acyloxy groups on vicinal carbon atoms [8].

The main direction of decomposition of compounds (I-X) on electron impact is the "β cleavage" of the ether bond with respect to the benzene ring of the coumarin nucleus which is typical for ethers of umbelliferone with a long side chain [4, 5]. It takes place with and without the transfer of one or two hydrogen atoms from the terpene to the coumarin moiety of the molecule and for compounds (IV and VI-X) is confirmed by metastable transitions. As illustrated by mogoltavin (IV) this process can be represented by Scheme 1.

In the mass spectra of mogoltin-d_2 (II) and dihydromogoltin-d_2 (X), obtained by deuterium-exchange reactions of substances (I) and (III) with vapors of methanol-d directly in the ionization chamber and containing 14 and 20% of the d_2-substituted compound, respectively, the ion corresponding to the terpene moiety

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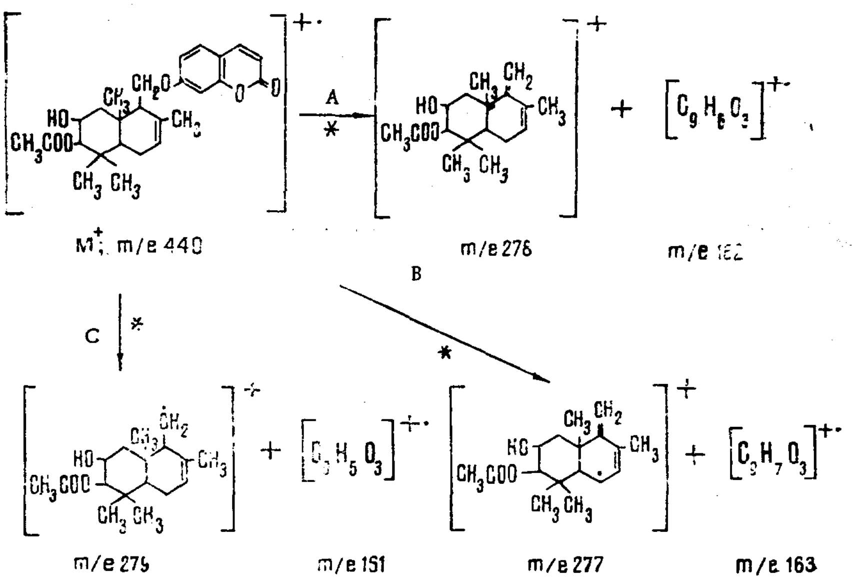
TABLE 1. Mass Numbers and Relative Intensities of the Peaks in the Mass Spectra of Compounds (I-X) in the Region of High and Medium Masses

Compound	Mass numbers (relative intensities, %)																		
I	398 (100) 177 (4,2)	397 (8,3) 176 (5,8)	396 (4,1) 175 (7,3)	383 (4,1) 174 (4,2)	382 (3.3) 163 (42)	381 (3,7) 162 (21)	380 (4,1) 161 (8,3)	365 (3,7) 159 (13)	364 (5,4) 145 (25)	363 (2,9)	237 (25)	236 (42)	219 (26)	218 (13)	203 (5,8)	201 (14)	192 (2,0)	191 (10)	198 (4,2)
II	400 (9,1) 221 (6.4) 162 (49)	399 (23) 220 (25) 161 (29)	398 (28) 219 (61) 159 (35)	397 (1,8) 218 (76) 145 (63)	396 (1,0) 205 (5,5)	385 (1,8) 204 (6,4)	384 (1,9) 203 (25)	383 (2 7) 202 (14)	382 (4,4) 201 (30)	381 (8,2) 199 (6,4)	380 (45) 198 (4,5)	366 (1,8) 192 (7,3)	365 (3.6) 191 (25)	364 (0,9) 189 (13)	363 (0,9) 177 (10)	239 (18) 176 (9,0)	238 (38) 175 (21)	237 (87) 174 (7,3)	236 (100) 163 (100)
III	400 (100) 206 (6,7)	382 (6,7) 205 (2,0)	381 (5,0) 203 (11)	367 (1,8) 191 (3,7)	366 (3,7) 190 (3,3)	338 (4,7) 189 (3,2)	257 (3.3) 179 (5,0)	256 (9,2) 178 (3,3)	239 (7,2) 177 (6,7)	238 (15) 176 (2,3)	224 (8,0) 175 (6,7)	223 (26) 165 (8,3)	222 (8,0) 164 (6,7)	221 (23) 163 (32)	220 (12) 162 (31)	212 (6,[illegible]) 161 (5,2)	209 (6,7) 147 (8,3)	208 (6,8)	207 (13)
IV	440 (97) 320 (2,8) 237 (8,3) 188 (5,6) 161 (30)	399 (1,4) 319 (1,8) 236 (1,6) 187 (19) 160 (9,7)	398 (2,7) 309 (1,8) 235 (1,4) 186 (5,5) 159 (30)	397 (1,4) 308 (1,8) 234 (0,7) 185 (14) 145 (31)	396 (1,4) 307 (3,2) 219 (100) 179 (3,3)	384 (1,4) 306 (2,8) 218 (22) 178 (3,6)	383 (2,8) 302 (0,8) 217 (6,2) 177 (17)	382 (1,2) 301 (0,8) 205 (8,3) 176 (15)	381 (1,4) 300 (1,6) 204 (6,0) 175 (33)	380 (2,8) 279 (21) 203 (25) 174 (9,6)	379 (1,4) 278 (86) 202 (19) 173 (9,7)	367 (1,4) 261 (2,8) 201 (86) 172 (5,6)	366 (2,8) 260 (3,8) 200 (9,7) 171 (7,0)	365 (5,0) 249 (1,4) 199 (6,0) 170 (2,8)	347 (1,4) 248 (2,8) 193 (3,6) 169 (5,6)	338 (1,4) 247 (14) 192 (3,3) 165 (5,6)	337 (0,7) 241 (8,3) 191 (15) 164 (15)	336 (0,7) 239 (0.9) 190 (5,6) 163 (83)	321 (0,7) 238 (1,4) 189 (11) 162 (44)
V	441 (54) 202 (13) 145 (31)	399 (5,0) 201 (97)	398 (2,5) 191 (11)	384 (3,8) 190 (3,9)	365 (3,8) 189 (21)	348 (3,7) 188 (3,9)	338 (3,7) 187 (12)	280 (9,7) 186 (3,9)	279 (31) 185 (12)	278 (5,8) 177 (12)	261 (7,7) 176 (15)	260 (3,8) 175 (39)	238 (3,9) 174 (11)	237 (8,8) 173 (10)	236 (7,7) 163 (100)	220 (24) 162 (48)	219 (34) 161 (44)	218 (7,8) 160 (7,8)	203 (12) 159 (57)
VI	480 (52) 363 (2,5) 229 (2,4) 178 (2,4)	466 (1,1) 337 (1,2) 219 (8,5) 177 (7,[illegible])	465 (1,2) 319 (2[illegible]) 218 (24) 176 (7,3)	464 (3,6) 318 (57) 217 (4,8) 175 (24)	428 (3,2) 304 (1,2) 216 (1,2) 174 (4,8)	427 (2,5) 303 (2,6) 205 (4,8) 173 (7,0)	426 (1,6) 302 (7,3) 204 (7,1) 172 (1,2)	425 (2,5) 301 (2,5) 203 (3[illegible]) 171 (2,4)	424 (4,1) 300 (2,5) 202 (16) 165 (3,7)	400 (2.5) 285 (2,5) 201 (68) 164 (9,7)	399 (3,2) 263 (1,6) 200 (7,3) 163 (50)	398 (3.8) 262 (2,3) 199 (3,7) 162 (29)	382 (24) 257 (1,6) 191 (9,7) 161 (27)	381 (100) 243 (2,0) 190 (4,8) 160 (2,4)	380 (9,8) 242 (1,7) 189 (9,7) 159 (4,8)	367 (1,6) 241 (2,0) 188 (2,9) 145 (22)	366 (2.5) 237 (2,4) 187 (9,7)	365 (4,9) 236 (3,7) 186 (2,9)	364 (1,6) 235 (7,1) 185 (9,7)
VII	481 (14) 203 (49) 164 (7,4)	466 (3,0) 202 (24) 163 (66)	465 (2,5) 201 (100) 162 (41)	399 (2,4) 199 (13) 161 (33)	398 (1,2) 198 (5,7) 160 (7,4)	382 (59) 191 (13) 159 (33)	366 (0,6) 190 (5,6) 145 (33)	365 (0,8) 189 (19)	364 (3,0) 188 (8,0)	320 (9,8) 187 (8,0)	319 (25) 186 (3,3)	303 (5 7) 185 (6,6)	302 (26) 178 (3,3)	301 (3,9) 177 (9,8)	237 (16) 176 (9,0)	236 (21) 175 (33)	235 (3,3) 174 (6,0)	220 (41) 173 (5,0)	219 (45) 165 (7,4)
VIII	482 (10) 218 (5,0) 175 (7,1)	320 (20) 217 (2,7) 174 (2,0)	279 (1.0) 205 (4,0) 173 (4,2)	278 (0.5) 204 (4,2) 172 (2,0)	277 (1,0) 203 (8.2) 171 (3,3)	276 (1,0) 202 (23) 165 (2,0)	262 (1,2) 201 (100) 164 (4,9)	261 (2,5) 200 (14) 163 (22)	260 (2,9) 199 (6,5) 162 (19)	245 (1,2) 191 (2,1) 161 (7,9)	244 (0,6) 190 (1,0) 160 (4,9)	243 (1,0) 189 (2,5) 159 (20)	242 (2,5) 188 (2,1) 145 (14)	237 (4,0) 187 (6,0)	236 (8,2) 186 (6,5)	235 (9,2) 185 (10)	234 (5,4) 184 (1,0)	233 (2,0) 177 (2,0)	219 (10) 176 (4,2)
IX	381 (0,8) 234 (2,5) 174 (0.8)	360 (13) 219 (7,0) 173 (3,3)	303 (0,3) 218 (3.5) 172 (0,8)	302 (0.5) 217 (2,5) 171 (2,7)	301 (1,0) 203 (8,3) 163 (36)	300 (1,7) 202 (17) 162 (21)	28[illegible] (0,5) 201 (100) 161 (11)	278 (0,5) 200 (12) 160 (3.3)	277 (1,0) 199 (2,1) 159 (31)	276 (0,5) 191 (0,8) 145 (28)	261 (0,5) 190 (0,4)	260 (1,0) 189 (1,2)	259 (0,5) 188 (1,2)	243 (0,5) 187 (7,5)	242 (0,6) 186 (2,1)	241 (0,6) 185 (10)	240 (0,6) 177 (1,0)	236 (1,7) 176 (2,7)	235 (4,2) 175 (7,5)
X	402 (19) 237 (5,6) 188 (2,5)	401 (38) 236 (1,4) 187 (6,2)	400 (32) 225 (6,8) 186 (1,2)	399 (2,5) 224 (14) 179 (4,3)	398 (1,2) 223 (18) 178 (8,0)	387 (0,3) 222 (6,2) 177 (17)	386 (0,4) 221 (24) 176 (4,3)	385 (0,4) 220 (9,[illegible]) 175 (7,4)	384 (0,2) 219 (2,5) 174 (1,9)	383 (0,2) 206 (5 6) 173 (1,9)	382 (0,7) 205 (18) 165 (19)	369 (0.1) 204 (10) 164 (25)	368 (0,7) 203 (38) 163 (100)	367 (0,7) 202 (4,3) 162 (93)	366 (0,2) 201 (3,7) 161 (11)	241 (0,7) 192 (2,8) 160 (1,9)	240 (1,9) 191 (5,1) 159 (5,6)	239 (5,6) 190 (1,1) 147 (20)	238 (7,4) 189 (3,7)

SCHEME 1

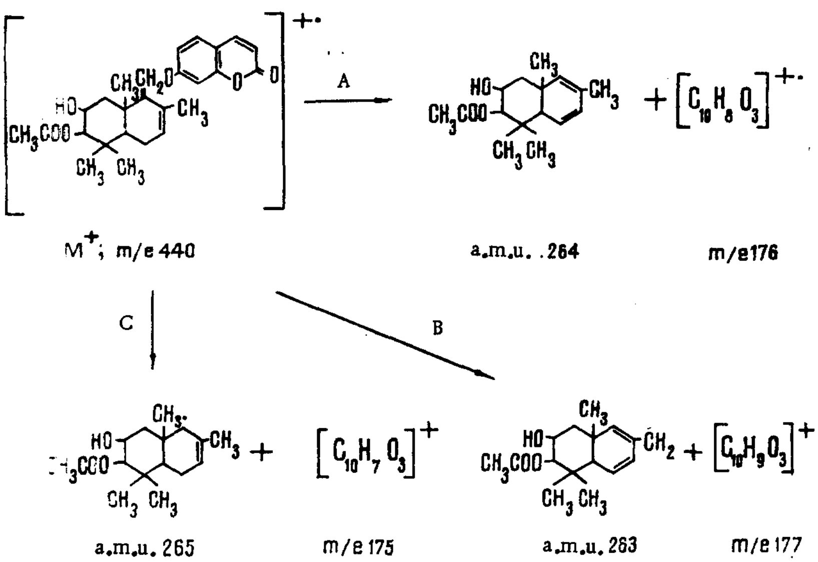


(route A) is shifted by two mass units, like the corresponding ion in mass spectrum of dihydromogoltin (III) (m/e 238). In the mass spectra of mogoltavin-d (V) and mogoltavinin-d (VII), these fragments undergo a total shift of one mass unit (m/e 219 and 279, respectively), which shows that these fragments belong to the terpene moiety of the molecules of these compounds, and they are formed by proposed Scheme 1. At the same time, in the mass spectra of (II, V, VII, and X) the ions with m/e 162 and 163 arising by routes A and B do not undergo a shift. Consequently, the migration of the hydrogen atoms accompanying these processes does not take place from the hydroxy groups of the terpene part of the molecules as might have been expected. The results of an analysis of Stuart–Briegleb and Dreiding spatial models, taking into account the trans linkage of the cyclohexane rings of the terpene moiety of compounds (I-X) belonging with respect to the structure of the carbon skeleton to bicyclic terpenoids of the labdane type [6], shows that the migration of hydrogen atoms accompanying processes A and B (see Scheme 1) is possible from positions 6 and 9. From the energy point of view, the process of eliminating these hydrogen atoms is also preferable for substances (I, II, and IV-IX) since these hydrogen atoms, located in the allyl position with respect to the double bond, have increased mobility and their splitting off leads to the formation of more stable ions. In dihydromogoltin (III), where there is no double bond in the terpene ring, the migration of hydrogen atoms evidently takes place with greater probability from positions 9 and 8, which again leads to the appearance of stable ions.

In the mass spectra of the diacyl derivatives of mogoltin (VIII and IX) the absence of free hydroxy groups does not prevent the fragmentation of their molecular ions by directions A and B, which again does not contradict the mechanism that we have proposed.

The second direction of decomposition of the ions M^+ in the mass spectra of compounds (I-X), which has a considerably lower intensity than the first, is "β cleavage" with respect to the oxygen of the ester bond. This process takes place with and without the transfer of one or two hydrogen atoms to the coumarin part of the molecule in which the positive charge of the fragmented ion M^+ is wholly localized, and this is responsible for the absence in the mass spectra of compounds (I-X) of fragments corresponding to their terpene moiety. In the case of substance (IV), as an example, this decomposition pathway can be represented by Scheme 2. In the mass spectra of the deuterium-substituted substances (II, V, VII, and X) no shift of the ions with m/e 176 and 177 into the region of heavy masses is observed, and it may therefore be assumed that their formation likewise takes place through the migration of hydrogen atoms from the positions shown above and not from the hydroxy groups.

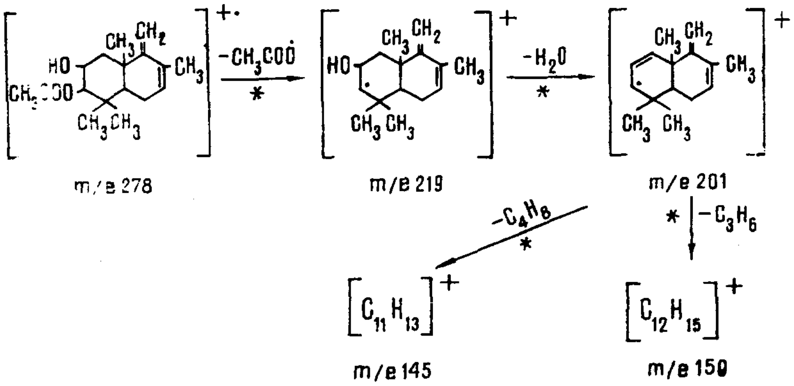
In addition to the directions considered, the decomposition of the molecular ions of compounds (I-X) takes place through the elimination of the substituents and their elements from the terpene moiety of the molecules. In the mass spectrum of mogoltin (I) the ejection by the ion M^+ of a CH_3 group and of a molecule of water, and also the successive elimination of these particles is observed, which leads to the appearance of the ions M^+-CH_3, M^+-H_2O, and $M^+-CH_3-H_2O$, respectively. The first of them loses one or two hydrogen atoms giving the ions M^+-CH_3-H and M^+-CH_3-2H which, as a result of the splitting out of a molecule of water, SCHEME 2



form the fragments $M^+-CH_3-H-H_2O$ and $M^+-CH_3-H-H_2O$ and $M^+-CH_3-2H-H_2O$. It is possible that the latter two ions also arise from the fragment $M^+-CH_3-H_2O$. These routes of decomposition have low rates, so that the ions formed are of feeble intensity. In the mass spectrum of mogoltin-d_2 (II), the fragments M^+-CH_3, $M^+-CH_3-H_3$ and M^+-CH_3-2H are shifted by two units and the remainder of the ions mentioned by one unit. These results confirm the method of formation proposed for these ions.

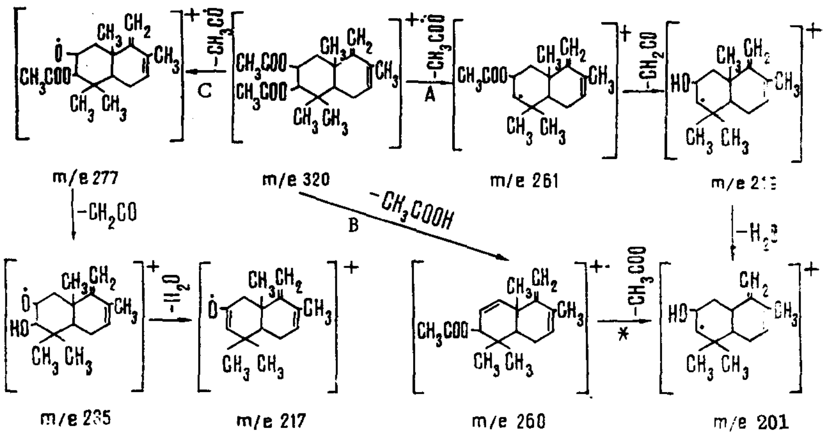
In the mass spectrum of dihydromogoltin (III), the fragments M^+-CH_3, M^+-CH_3-H, M^+-CH_3-2H, $M^+-CH_3-H_2O-H$, $M^+-CH^3-H_2O-2H$.are absent. It may therefore be assumed that the appearance of these ions in the mass spectrum of (I) and (II) is due to the presence of a double bond in the terpene moiety of the mogoltin molecule. In the monoacyl derivatives of mogoltin, the formation of such ions evidently depends on the rate of decomposition of the molecular ion by the other competing directions. Thus, in the mass spectrum of mogoltavin (IV) they are formed after the ejection by the M^+ ion of a molecule of ketene ($CH_2=C=O$), while in the mass spectrum of mogoltavinin (VI) the rate of appearance of these ions and the rate of splitting off of a molecule of ketene are apparently comparable, and these ions are present in the mass spectrum of (VI). These ions were not detected in the diacyl derivatives of mogoltin (VIII) and (IX). In the mass spectrum of mogoltavinin (VI) the molecular ion loses the fragment corresponding to the acid residue of angelic acid, forming the intense ion $M^+-CH_3CH=C(CH_3)COO$ (m/e 381). In compounds (VI) and (IX) there is the acyl residue of this acid which is characterized, as in the acyl derivatives of other classes of coumarins [7-9] by intensive fragments $[CH_3CH=C(CH_3)CO]^+$ (m/e 83) and $[CH_3CH=C(CH_3)]^+$ (m/e 55).

SCHEME 3



In the region of moderate mass numbers, the mass spectra of substances (I-X) contain strong peaks due to the decomposition of ions of terpene structure arising by directions A and B of Scheme 1. A typical example of such decomposition is the fragmentation of the terpene ion in the mass spectrum of mogoltavin (IV), which is illustrated in Scheme 3. This decomposition is confirmed by the shift of the ions with m/e 278 and 219 in the mass spectrum of mogoltavin-d (V) by one mass unit, and also by the presence of metastable peaks corresponding to the transitions 278 → 219, 219 → 201, 201 → 159, 201 → 145.

SCHEME 4



In the mass spectra of the diacyl derivatives of mogoltin (VIII) and (IX), the terpene ion formed by route A in Scheme 1 undergoes competing decomposition in three directions which, in the case of compounds (VIII), can be represented by Scheme 4. The last of them (route C, Scheme 4) is also characteristic for diacyl derivatives of other classes of coumarins [8, 9].

Thus, the laws of the decomposition of substances (I-X) under the action of electron impact that have been investigated well reflect their structural features and can be used for structural-analytical purposes among this class of compounds.

EXPERIMENTAL

The mass spectra of compounds (I-X) were taken on a modified MKh-1303 instrument with the direct introduction of the sample into the ion source at an ionizing voltage U = 40 V and the following temperatures of the samples: 165°C (I, II), 130°C (III), 140°C (IV), 160°C (V), 150°C (VI), 180°C (VII–X).

CONCLUSIONS

The mass spectra of six compounds belonging to the class of terpenoid coumarins and of four of their deuterium analogs have been studied. Decomposition pathways for these substances under the action of electron impact have been suggested. It has been shown that from the mass spectra of compounds of this series it is possible to determine their molecular weights and, in atomic mass units, the weights of their terpene moieties, and also to establish the presence of hydroxy and acyloxy groups in the bicyclic terpene moiety.

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