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Studies of Isosteviol Diterpenoid Derivatives by Mass Spectrometry: II.[1] Fragmentation of Isosteviol Esters under the Electronic Impact

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Abstract—Main rules of fragmentation of molecular ions of the esters of isosteviol diterpenoid (*ent*-16-oxobeieran-19-carboxylic acid) are established. It is shown that under the conditions of electron impact in the isosteviol esters the ester C–O and C^4–C^{19} bonds are ruptured. During the fragmentation of hydroxy derivatives of isosteviol at the C^{16} atom the elimination of H_2O molecules is observed.

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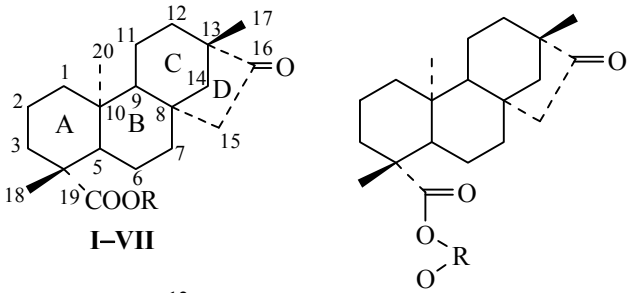
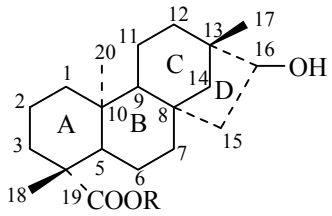
Nowadays mass spectrometry is one of the reliable methods for establishing the structure of organic compounds. Establishing and revealing main rules of the fragmentation of molecular ions of compounds permits to predict mass spectra of definite series of organic compounds.

Continuing the research on a detailed mass spectrometric investigation of the derivatives of isosteviol diterpenoid we have studied the pathways of fragmentation of isosteviol esters under the action of electron impact. Synthesis and spatial arrangement of these substances were described previously [2].

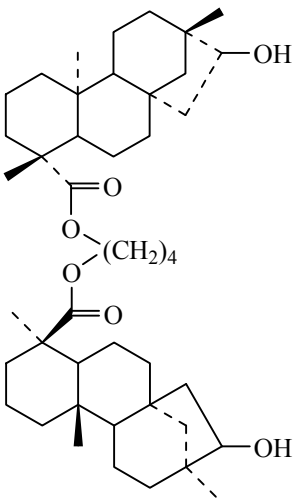


I–VII



VIII–IX

X–XIII

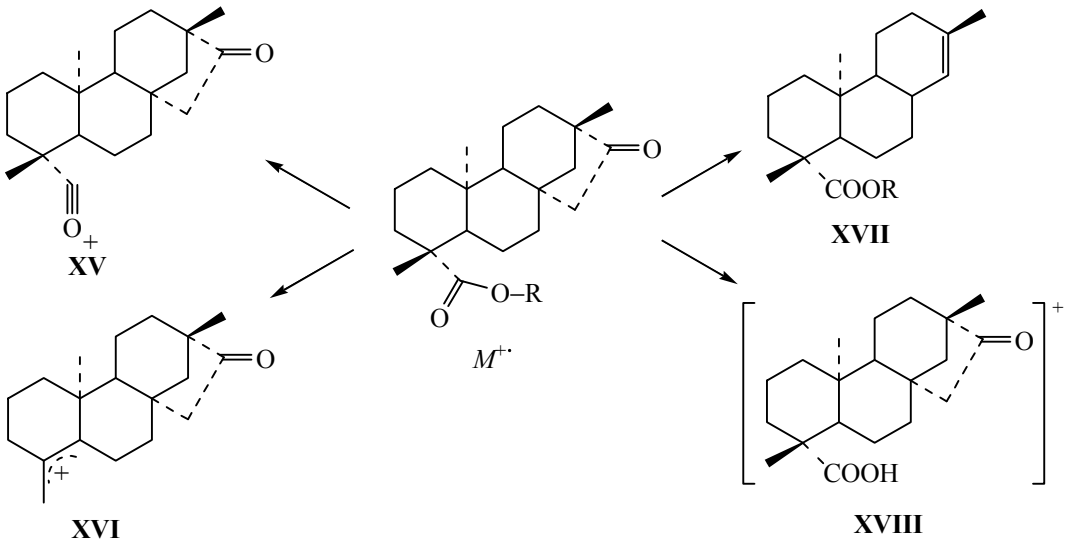


XIV

R = H (**I, VIII**), Me (**II, IX**), Et (**III**); *n*-Hex (**IV**), *n*-Dec (**V**), $CH_2CH{=}CH_2$ (**VI**), $(CH_2)_4OH$ (**VII**), C_3H_6 (**X**), C_4H_8 (**XI**), *n*-C_6H_4 (**XII**), $(CH_2)_2O(CH_2)_2$ (**XIII**).

[1] For communication I, see [1].

Scheme 1.



Experimental data concerning main characteristic ions formed under the action of electron impact of compounds **I–XIV** are presented in the table. Mass spectra of compounds under investigation contain the peaks of molecular ions $M^{+\cdot}$ having different intensity.

For the derivatives of isosteviol at the carboxy group **I–VII** the following pathways of fragmentation are characteristic. The formation of ions **XV** is connected with the cleavage of the ester C–O bond accompanied by the migration of hydrogen atom to the neutral fragment (Scheme 1). In the case of compounds **VIII, IX** having hydroxy group on C^{16} atom the fragmentation according to this pathway leads to the ions with *m/z* 302 that is shifted by two units as compared to the ions formed by fragmentation of compounds **I** and **II** which confirms this pathway of decomposition.

Relative intensities of peaks in mass spectra of compounds under study

Comp. no.	*m/z* Ratio and the intensities (*I*, %) of ions				
	M^+	**XV**	**XVI**	**XVII**	**XIX**
I	318 (27)	300 (53)	273 (28)	275 (38)	–
II	332 (28)	300 (53)	273 (100)	303 (1)	–
III	346 (21)	300 (32)	273 (56)	303 (6)	–
IV	402 (9)	300 (16)	273 (34)	359 (2)	–
V	458 (5)	300 (16)	273 (34)	415 (1)	–
VI	358 (32)	300 (37)	273 (58)	317 (8)	–
VII	390 (10)	300 (66)	273 (100)	347 (4)	–
VIII	320 (6)	302 (98)[a]	275 (70)[a]	275[a]	–
IX	334 (0.5)	302 (7)	275 (54)	289 (9)	–
X	676 (14)	300 (8)	273 (44)	–	359 (30)
XI	690 (2)	300 (22)	273 (63)	–	373 (8)
XII	710 (0.5)	–	273 (100)	–	–

[a] *m/z* Ratio corresponds to several fragments.

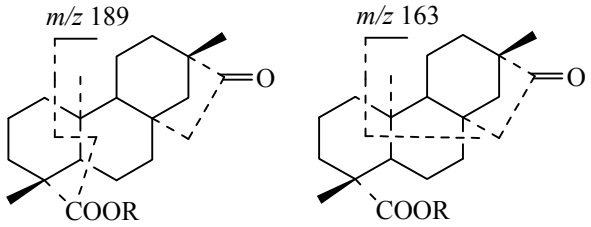
The ion **XVI** is formed probably by the rupture of C^4–C^{19} bonds. Analogous ion is formed also during the fragmentation of isosteviol derivatives having the fragment of Schiff base at the C^4 atom [1]. Similar to that in the spectra of compounds **I–VII** the peaks are observed corresponding to decomposition of ion **XVI** according to the previously suggested pathway [1]. For compounds **VIII** and **IX** the peak of ion with *m/z* 275 is observed.

Characteristic ions for compounds **I–VII** are $[M - 43]^{+\cdot}$ and $[M - 45]^{+\cdot}$. For compounds **VIII, IX** they correspond probably to structure **XVII**. Analogous fragmentation connected with the rupture of ions in the ring D was also observed previously [1, 3]. The formation of ion **XVIII**, the molecular ion of isosteviol, is caused by the pathway of decomposition including the abstraction of the substituent R from the ester group and the migration of hydrogen atom to the charged fragment.

In the range of medium mass values of the spectra of compounds **I–VII** the following characteristic peaks

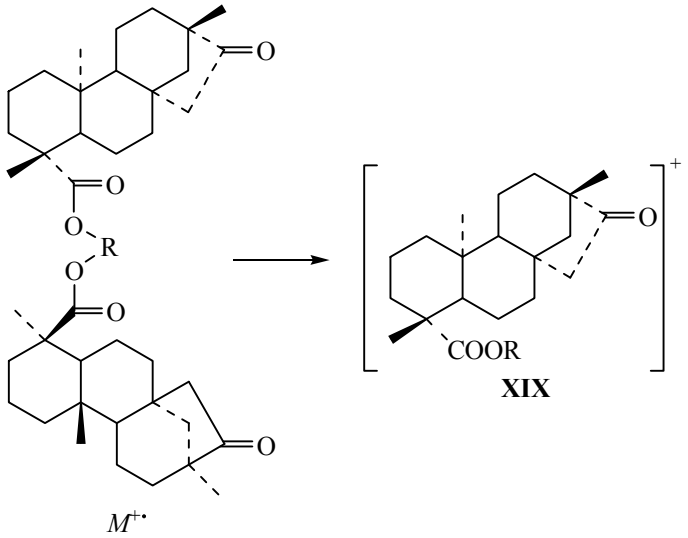
are observed[2]: *m/z* 203 $[C_{14}H_{19}O]^+$, *m/z* 229 $[C_{17}H_{25}]^+$, *m/z* 203 $[C_{14}H_{19}O]^+$, *m/z* 189 $[C_{13}H_{17}O]^+$, *m/z* 163 $[C_{11}H_{15}O]^+$, *m/z* 122 $[C_8H_{14}]^+$, *m/z* 109 $\{C_8H_{13}]^{+\cdot}$ For example, the formation of ions with *m/z* 189 and *m/z* 163 is possible only by the cleavage of bonds shown in the Scheme 2 in agreement with the reported data [4].

Scheme 2.



We shall discuss further the mass spectra of compounds **X**–**XIII**. In the range of high mass values the only characteristic peak is that of the ion $[M - 56]^+$ having low intensity. In the case of compounds **X**, **XI,** and **XII** the rupture of one of the O–R bonds of the ester fragment leads to ions **XIX** (Scheme 3). When the composition of spacer connecting two isosteviol molecules includes an aromatic fragment (compound **XII**) the decomposition according to this pathway does not take place. But for the compound **XII** the presence of ion **XV** with *m/z* 300 is characteristic.

Scheme 3.



$M^{+\cdot}$

X, XI, XIII

XIX

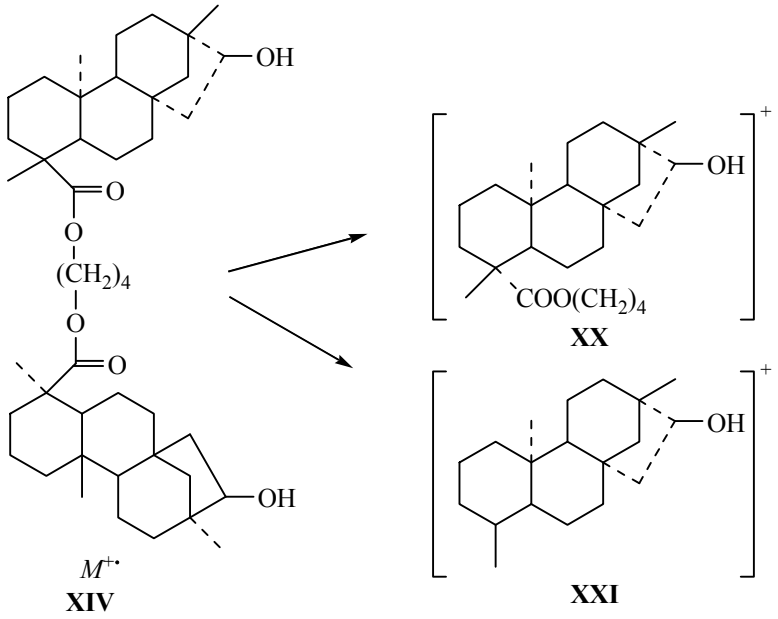
For the isosteviol derivatives **I**–**VII** and **X**–**XIII** as well as for those containing nitrogen at C^4 atom the ion with *m/z* 273 and the fragment ions formed by decomposition of the above-mentioned ion are characteristic. Note that the peak with *m/z* 273 in all the spectra has high intensity. Specific feature of compound **XIII** is the presence of ions formed due to the rupture of C–O bond of the spacer with *m/z* 345 and the intensity 15% with respect to the most intense peak.

In the spectrum of diester **XIV** having a secondary hydroxy groups at the C^{16} and $C^{16'}$ atoms the peak M^+ is absent which is characteristic of the secondary and tertiary alcohols [5]. The lability of the molecular ion of this compound is caused by the fragmentation initiated by the ionized hydroxy group. In the mass spectra of diester **XIV** the ions $[M - H_2O]^+$ and $[M - H_2O - H_2O]^+$ having low intensity and ions **XX** and **XXI** having medium intensity are observed. The latter are formed by the cleavage of O–R and C^4–C^{19} bonds respectively. The presence of ions **XX** and **XXI** once more confirms the pathways of decomposition of isosteviol esters suggested above.

Hence, main characteristic pathways of fragmentation of the ester derivatives of isosteviol diterpenoid **I**-

[2] Presented elemental compositions of fragment ions of isosteviol and its methyl ester are taken from the NIST mass spectral library, Version 2.0.

Scheme 4.



XIV observed in the course of electron impact include the cleavage of ester C–O and C^4–C^{19} bond. For the esters containing two isosteviol frames the elimination of two CO molecules from the molecular ion is observed. During the fragmentation of isosteviol esters containing secondary hydroxy group on the C^{16} atom the elimination of H_2O molecules takes place.

EXPERIMENTAL

Compounds **I–XIV** were prepared according to the procedures [2]. Their constants agree with the reported data.

Electron impact mass spectra were obtained on the TRACE MS Finnigan MAT instrument at the energy of ionizing electrons 70 eV and the ion source temperature 200°C. Heating of the evaporator ampule of the direct injection system was carried out in the programmed regime from 35°C to 250°C with the step 35°C/min. Processing of mass spectral data was carried out with the help of the XCalibur program. Mass spectra presented below include *m/z* values and relative intensities of the ion current (I_{rel}, %) with respect to the most intense peak. Intensities of peaks with the I_{rel} values no less than 10% are presented.

***Ent*-16-oxobeyeran-19-carboxylic acid (isosteviol) (I)**. 318(27) $[M]^+$, 300 (33), 275 (38), 273 (28), 259 (37), 257 (25), 229 (30), 203 (47), 189 (27), 175 (29), 165 (62), 163 (46), 152 (84), 147 (34), 133 (39), 123 (43), 121 (100), 109 (84), 107 (77), 93 (83), 81 (95), 79 (78), 67 (63), 55 (85).

Methyl *ent*-16-oxobeyeran-19-oate (II). 332 (28) $[M]^+$, 300 (53), 289 (18), 273 (100), 272 (45), 259 (22), 257 (19), 229 (20), 203 (22), 189 (18), 175 (18), 163 (21), 152 (16), 147 (18), 133 (18), 123 (28), 121 (64), 109 (43), 107 (42), 93 (32), 81 (34), 67 (20), 55 (42).

Ethyl *ent*-16-oxobeyeran-19-oate (III). 346 (21) $[M]^+$, 300 (32), 273(56), 272 (30), 259 (15), 257 (12), 229 (13), 203 (14), 189 (16), 175 (14), 167 (26), 163 (24), 152 (16), 149 (65), 133 (22), 123 (42), 121 (47), 109 (60), 107 (37), 97 (72), 93 (34), 81 (63), 71 (83), 57 (96), 55 (100).

Hexyl *ent*-16-oxobeyeran-19-oate (IV). 402 (9) $[M]^+$, 300 (16), 273 (34), 272 (33), 259 (13), 257 (9), 229 (8), 215 (7), 203 (8), 189 (12), 175 (10), 163 (21), 149 (13), 147 (15), 123 (23), 121 (41), 109 (39), 107 (43), 97 (17), 93 (40), 81 (52), 79 (35), 67 (32), 55 (56), 43 (100).

Decyl *ent*-16-oxobeyeran-19-oate (V). 458 (5) $[M]^+$, 300 (16), 273 (34), 272 (35), 259 (13), 257 (7), 229 (9), 215 (9), 203 (10), 189 (11), 175 (10), 163 (24), 149 (14), 147 (17), 133 (16), 123 (26), 121 (47), 109 (42), 107 (44), 93 (39), 81 (54), 79 (33), 67 (28), 57 (40), 55 (73), 43 (100).

2-Propenyl *ent*-16-oxobeyeran-19-oate (VI). 358 (32) $[M]^+$, 300 (37), 273 (58), 272 (78), 259 (28), 257

(26), 229 (28), 215 (15), 203 (19), 189 (26), 175 (16), 163 (13), 149 (11), 147 (17), 123 (28), 121 (60), 109 (57), 107 (60), 93 (62), 91 (68), 84 (98), 81 (69), 79 (67), 67 (68), 55 (100).

4-Hydroxybutyl *ent*-16-oxobeieran-19-oate (VII). 390 (10) $[M]^+$, 300 (66), 273 (100), 272 (93), 257 (38), 229 (26), 215 (16), 203 (17), 189 (17), 163 (24), 149 (16), 147 (17), 123 (33), 121 (47), 109 (46), 107 (45), 95 (34), 93 (34), 91 (24), 81 (40), 79 (24), 71 (81), 69 (26), 55 (46).

16-Hydroxy-*ent*-beieran-16-carboxylic acid (VIII). 320 (6) $[M]^+$, 302 (98), 287 (10), 275 (70), 274 (30), 257 (19), 229 (10), 205 (9), 201 (18), 187 (100), 177 (24), 161 (27), 159 (50), 147 (48), 137(46), 135 (47), 123 (88), 121 (90), 109 (91), 107 (67), 95 (64), 93 (66), 91 (55), 81 (85), 79 (57), 77 (25), 71 (26), 69 (44), 67 (63), 57 (45), 55 (93), 43 (82), 41 (80).

Methyl *ent*-16-hydroxybeieran-19-oate (IX). 334 $[M]^+$, 316 (44), 275 (50), 274 (19), 257 (20), 242 (22), 205 (9), 201 (14), 187 (47), 161 (24), 159 (29), 149 (23), 147 (21), 137 (19), 135 (21), 123 (74), 121 (67), 109 (74), 107 (54), 95(39), 93 (40), 91 (34), 81 (48), 79 (42), 67 (32), 55 (52), 45 (100), 43 (57), 41 (37).

Propan-1,3-diyl bis(*ent*-16-oxobeieran-19-oate) (X). 676 (14) $[M]^+$, 620 (8), 359 (28), 273 (44), 272 (15), 257 (10), 229 (13), 189 (14), 177 (16), 165 (13), 163 (11), 148 (40), 147 (26), 123 (43), 121 (42), 109 (72), 107 (43), 97 (100), 95 (72), 93 (31), 91 (44), 81 (62), 71 (62), 69 (61), 57 (62), 55 (43).

Butan-1,4-diyl bis(*ent*-16-oxobeieran-19-oate (XI). 690 (2) $[M]^+$, 373 (7), 300 (22), 273 (63), 272 (31), 257 (16), 229 (18), 203 (17), 189 (19), 177 (27), 163 (39), 147 (30), 123 (70), 121 (100), 109 (98), 107 (90), 97 (58), 95 (83), 93 (76), 91 (66), 81 (89), 71 (66), 69 (59), 57 (25), 55 (66).

1,4-Phenylenebis(*ent*-16-oxobeieran-19-oate) (XII). 710 $[M]^+$, 318 (11), 301 (15), 273 (100), 255 (30), 229 (29), 203 (15), 191 (50), 177 (78), 163 (22), 147 (26), 123 (50), 121 (30), 109 (54), 107 (38), 105 (25), 97 (73), 95 (44), 93 (25), 81 (70), 79 (27), 71 (30), 69 (28), 57 (25), 55 (70).

2,2'-Oxydiethylene-bis(*ent*-oxobeieran-19-oate) (XIII). 706 (12) $[M]^+$, 650 (5), 452 (4), 406 (6), 345 (15), 300 (30), 273 (82), 255 (18), 229 (24), 203 (27), 177 (25), 163 (27), 149 (28), 147 (32), 123 (56), 121 (83), 109 (90), 107 (77), 105 (50), 97 (54), 95 (72), 93 (45), 81 (83), 79 (47), 71 (45), 69 (39), 57 (25), 55 (70).

Butan-1,4-diyl bis(*ent*-16-hydroxybeieran-19-oate) (XIV). 694 $[M]^+$, 676 (8), 658 (4), 375 (14), 275 (44), 257 (51), 229 (20), 201 (12), 187 (22), 177 (13), 161 (35), 149 (37), 147 (49), 145 (34), 137 (37), 135 (43), 133 (47), 131 (32), 123 (59), 121 (65), 109 (60), 107 (61), 105 (70), 97 (55), 95 (60), 93 (65), 91 (63), 81 (100), 79 (68), 71 (55), 69 (66), 57 (45), 55 (86).

REFERENCES

1. Musin, R.Z., Babaev, V.M., Strobykin, I.Yu., Kataev, V.E., Gavrilov, V.I., and Musin, R.R., *Zh. Obshch. Khim*., 2009, vol. 79, no. 11, p. 1855.
2. Al'fonsov, V.A., Andreeva, O.V., Bakaleinik, G.I., Beskrovnyi, D.V., Gubaidullin, A.T., Kataev, V.E., Kovylyaeva, G.I., Konovalov, A.I., Korochkina, M.G., Latypov, Sh.K., Litvinov, I.A., Musin, R.Z., and Strobykin, I,Yu., *Zh. Obshch. Khim*., 2003, vol. 73, no. 7, p. 1186.
3. Compadre, C.M., Hussain, R.A., Nanayakkara, N.P.D., Pezzato, J.M., Kinghorn, A.D., *Biomedical and Environmental Mass Spectrometry*, 1988, vol. 15, p. 211.
4. Brooks, C.J.W., *Phil. Trans. R. Soc. Lond., A*, 1979, vol. 293, p. 53.
5. Lebedev, A.T., *Mass-spektrometriya v organicheskoi khimii* (Mass Spectrometry in Organic Chemistry), Moscow: BINOM, Laboratoriya Znaniiya, 2003.