Chemistry of Natural Compounds, Vol. 29, No. 4, 1993

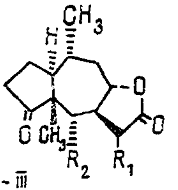
MASS SPECTRA OF PSEUDOGUAIANOLIDES RELATED TO CARPESIOLIN

V. N. Plugar', Ya. V. Rashkes, A. Ovezdurdyev, and I. D. Sham'yanov

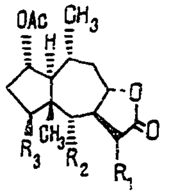
UDC 543.51+547.314

The main directions of fragmentation and the EI of six pseudoguaianolides related to carpesiolin have been studied. It has been established that acylation of the OH group at C-6 suppresses the selective breakdown of the guaiane skeleton, while the simultaneous presence of AcO groups at C-2 and C-4 favors the formation of a number of characteristic ions. The hydrogenation of the exomethylene group has no appreciable influence on direction of fragmentation.

The diversity of the structures and the nonstandard nature of the fragamentation pathways of sesquiterpenoids under EI limits the applicability of mass-spectrometric methods for investigating this class of compounds. At the same time, in the analysis of a group of related substances and the products of their transformation it is possible to make successful use of a correlation between structure and directions of fragmentation [1, 2]. We shall illustrate this with the use, as an example, of a group of pseudoguaianolides: ergolide (II), britanin (IV), and erigerolide (VI) isolated earlier from the plants *Erigeron khorasanicus* Bois. and *Inula aspera* Poir. [3, 4], and also some of their derivatives: carpesiolin (I), dihydroergolide (III), and dihydrobritanin (V). The formulas of the compounds studied are given below:



I-III



IV-VI

I. $R_1 = {=}CH_2$; $R_2 = -OH$
II. $R_1 = {=}CH_2$; $R_2 = -OAc$
III. $R_1 = -CH_3(\alpha)$; $R_2 = -OAc$

IV. $R_1 = {=}CH_2$; $R_2 = -OAc$; $R_3 = -OH$
V. $R_1 = -CH_3(\alpha)$; $R_2 = -OAc$; $R_3 = -OH$
VI. $R_1 = {=}CH_2$; $R_2 = -OH$; $R_3 = -OAc$

The behavior of similar substances under EI has been considered in a number of publications [5, 7]. Tsal et al. [7] have analyzed the direction of fragmentation of the seven-membered rings of 11 pseudoguaianolides of the helenamene series and have established the nature of the main fragments with m/z 95, 96, 122, 123, and 124. The presence of a voluminous substituent at C-6 of the arnifolin molecule [5] leads to the situation that the main fragments in the spectrum are due to the cleavage of bonds in the tiglic acid residue. In analyzing the spectra of compounds (I)-(VI), we set ourselves the task of following how the directions of fragmentation change with a variation in the nature of the substituents at C-4 and C-6, with the appearance of an acyl group at C-2, and with the hydrogenation of the exomethylene π-bond of the lactone ring and also with the characteristic features of the spectra of position isomers — britanin and erigerolide.

It follows from the general EI spectra (Table 1) that only carpesiolin (I) possesses a high selectivity of fragmentation, giving as the 100% peak an ion with m/z 97, consisting to the extent of 4/5 of particles with the composition C_6H_9O formed with the cleavage of the C-1–C-10 and C-4–C-6 bonds. The origin of a minor component, having the composition C_7H_{13}, is uncertain.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 530-535, July-August, 1993. Original article submitted December 15, 1992.

0009-3130/93/2904-0462$12.50

TABLE 1. Relative Intensities of the Ions (%) in the Mass Spectra of (I)-(VI)

m/z	I	II	III	IV	V	VI	m/z	I	II	III	IV	V	VI
369					0,2(MH)$^+$		178			25		26	
367				0,3(MH)$^+$		2	176				13	60	
308			18(MH)$^+$		5		175		15	30	12		
306		1(M$^+$)		3		7	174		5		15		
292					3		173		30		12		
264	3(M$^+$)	12	25		20		167			25			
262				12			165				10		13
248			100		100		161		25	18		11	
246	10	100		100		100	159				12	8	
233			23		8		147		13	37	15	23	
228		20		28		6	145	1	6	5	12	6	
222					28		133		10	15	16	26	35
220			50	10	25		132				10	6	30
218		15				17	121			12	25	37	40
217						12	119		18	24	20		12
205			26				109	3	6		15	15	37
204		13			50		108	4	10	13	65	40	80
203		14			6		107	2	8	28	75	65	75
202				25	6		106	1	4	4	18	13	63
194					18		105		15	12	12	12	25
193			4	12	12		97	100	65	75	15	13	27
192			28	5	13		95		8	20	18	28	25
191		10			20		93		10	12	13	15	30
189		11		23			91		12	18	17	15	37

TABLE 2. Mass Numbers of the Precursor Ions in the MD Spectra of (II)-(VI)

Compound	Daughter ions	Parental ions, m/z
II	105	120, 133, 147, 165
	119	134, 146, 161, 179
	133	148, 161, 175, 191
	145	160, 173, 189, 218
	147	165, 175, 189
	161	179, 189, 203, 218, 221, 246, 264
	173	191, 202, 218, 228, 246
III	107	122, 135, 149, 167, 178, 192, 205, 220, 264
	147	165, 175, 189, 201, 205, 218, 230
	167	210, 224, 237, 248, 266, 281
	175	192, 205, 220, 237, 248, 266, 308
	178	193, 206, 220, 237, 248, 266
	192	210, 220, 237, 248, 266
IV	189	204, 217, 231, 246
	220	262
	246	264, 306
	262	304, 322
V	107	135, 149, 194
	121	149, 165, 194
	133	148, 161, 176
	148	166, 204, 222
	161	176, 191, 204
	176	194, 204, 222, 230, 236
	178	206, 220
	204	248, 264
VI	121	246
	165	246
	216	246
	214	246
	246	264, 306

TABLE 3. Elementary Compositions of the Ions in the Spectra of (I)-(VI)

Compound	m/z	Elementary composition			Relative content, %
		C	H	O	
I	97	6	9	1	80
	97	7	13		20
II	97	7	13		100
	105	8	9		100
	119	9	11		100
	133	9	9	1	25
	133	10	13		75
	145	11	13		85
	145	10	9	1	15
	147	10	11	1	65
	147	11	15		35
	161	11	13	1	100
	173	12	13	1	100
	189	12	13	2	100
	191	12	15	2	100
	203	13	15	2	100
	204	13	16	2	65
	204	12	12	3	35
III	107	8	11		100
	119	9	11		100
	121	8	9	1	15
	121	9	13		85
	147	10	11	1	15
	147	11	15		85
	161	11	13	1	50
	161	12	17		50
	167	13	11		25
	167	10	15	2	75
	175	12	15	1	100
III	178	11	14	2	65
	178	12	18	1	35
	192	12	16	2	90
	192	13	20	1	10
	193	12	17	2	100
	220	14	20	2	100
IV	107	7	7	1	10
	107	8	11		90
	189	14	21		50
	189	12	13	2	50
	220	13	16	3	100
	262	15	18	4	100
V	95	7	11		60
	95	6	7	1	40
	107	7	7	1	100
	133	10	13		85
	133	9	9	1	15
	176	12	16	1	100
	178	11	14	2	80
	178	12	18	1	20
	204	13	16	2	75
	204	14	20	1	25
VI	107	8	11		100
	108	8	12		100
	121	8	9	1	10
	121	9	13		90
	165	9	9	3	100
	217	14	17	2	100
	264	15	20	4	100

Acylation of the OH group at C-6 strongly suppresses the selectivity of fragmentation (spectra of (II)-(VI)). Hydrogenation of the exomethylene groups ((III) and (V)) and the replacement of C=O at C-4 by CH−OH (IV) and (V)) give no additional effect. At the same time, the introduction of a second acyl substituent at C-2 (IV)-(VI)) sharply decreases the stability of the molecular ions. The peaks of MH^+ ion are observed in the molecular region of the spectra. The fragmentation of all the acetylated compounds proceeds via the stage of the stable cations $(M - AcOH)^+$ (II, III) or $(M - 2AcOH)^+$ (IV-VI). In their turn, as the metastable defocussing (MD) spectra (Table 2) show, these ions are the parental ions of all the main fragments of medium mass numbers.

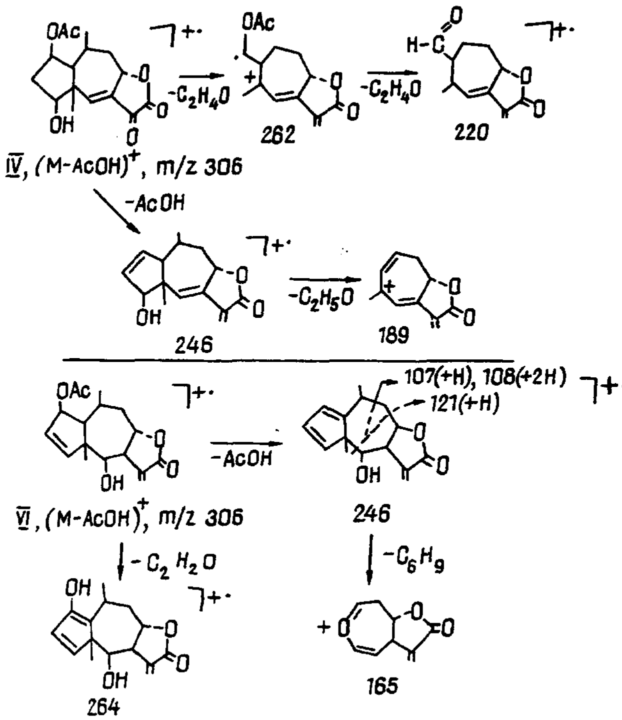
Using ergolide (II) as an example, it can be seen that ions containing the C_7-C_9 chain are predominantly hydrocarbon ions, while for the C_{10} and C_{11} ions the hydrocarbon component competes with an oxygen-containing component (Table 2). This means that the oxygen-free ions with m/z 97, 105, 119, 133, and 145 arise from the $(M - AcOH)^+$ ions after the elimination of CO from C-4 and of the elements of the lactone ring. However, it is likely that more complex fragmentation processes are also characteristic of ergolide and dihydroergolide. This is shown, for example, by the difference between the compositions of the ions with m/z 246 and 173 from ergolide, which are linked by a metastable transition, — $C_3H_5O_2$ (Tables 2 and 3). Such a particle can hardly be split out by the cleavage of the C-7–C-11 and C-8–O bonds. On the other hand, it can be seen from the general spectrum of dihydroergolide (III) (Table 1) that many ions are shifted partly or completely in the direction of high mass numbers by 2 m.u. as compared with (II). This means that the C-11 and C-13 atoms are included in their composition (m/z 107, 121, 147, 175). Therefore, in particular, the $246^+ \rightarrow 173^+$ transition of ergolide can be realized by the cleavage of the C-9–C-10, C-7–C-8, and C-1-C-12 bond with the migration of 2 H to the neutral fragment.

The hydrogenation of the C-11–C-13 π-bond leads to the appearance in the spectrum of (III) of ions having their analogues in the spectrum of (II) — for example, ions with m/z 167 ($C_{10}H_{15}O_2$) amd 178 ($C_{11}H_{14}O_2$ and $C_{12}H_{18}O$). Without going into details of the mechanism of the formation of these fragments, we may note that among their precursors in the MD spectra ions with m/z 248 are also recorded which, most probably, in the absence of a π-bond, have a number of alternative structures giving rise to different directions of fragmentation.

Approximately the same differences as between the spectra of (II) and (III) exist between the spectra of another pair of compounds — britanin (IV) and its 11,13-dihydro derivative (V). At the same time, in the spectrum of dihydrobritanin the intensity of the peak of the ions with m/z 176 ($C_{12}H_{16}O$), which has numerous precursors, including an ion with m/z 248, from which it can be formed by the elimination of the elements of the lactone ring, is greatly increased. In addition to this, in the spectrum of (V) there is another odd-electron fragment with m/z 148 the main component of which, $C_{11}H_{16}$, is formed from an ion with m/z 204 by two eliminations of CO.

Another distinguishing feature of the spectrum of (V) consists in the fact that the ion with m/z 107 is exclusively oxygen-containing (C_7H_7O), while the ion with m/z 95 also has the component C_6H_7O (Table 2).

Let us now compare the spectra of isomers — britanin (V) and erigerolide (VI). The main structural relationship between them appears in the fragmentation of the $(M - AcOH)^+$ ions with m/z 306. Together with the elimination of a second AcOH molecule and a molecule of water, which is common for the two compounds, in the case of britanin the splitting out of a molecule of acetaldehyde takes place at the expense of the C-3–C-4 chain (ion with m/z 262), and in erigerolide a ketene molecule is split out from the acetoxy group at C-2 (ion with m/z 264) (Scheme). In the case of britanin, a similar particle is ejected from the m/z 262 ion, giving an ion with m/z 220. Other differences between the structures of the isomers are due to the alternative structures of the $(M - 2AcOH)^+$ ions with m/z 246 (Scheme).



More characteristic for britanin is the fragmentation of this ion with the ejection of C_3H_5O, which gives a fragment with m/z 189. The conjugated system of π-bonds in the five-membered ring A of the $(M - 2AcOH)^+$ ion from erigolide (VI) stimulates the cleavage of the bonds of the seven-membered ring, leading to hydrocarbon ions with m/z 107, 108, and 121 and, on the other hand, to a three-oxygen fragment with m/z 165 which is characteristic only of this compound.

The EI spectra of compounds (I)-(VI) proved to be the most informative. The performance of chemical ionization (methane) experiments with the recording of positive and negative ions revealed no characteristic features of the spectra. The peaks of the molecular ions did not stand out by their intensities in all the spectra. A similar situation exists on the use of the LSIMS(+) and LSIMS(-) method (with glycerol as the matrix). Only in the case of carpesiolin (I) and dihydroergolide (III) are intense peaks of the $(M + H)^+$ and $(M - H)^-$ ions observed. In the spectra of the other compounds the main ions recorded are the cluster ions $(M + \text{glycerol} + H)^+$ and $(M + \text{glycerol} - H)^-$.

EXPERIMENTAL

The ordinary EI and CI spectra were obtained on a MS 25RF chromato-mass spectrometer (Kratos) combined with a El/Cl ion source, using a direct sample-insertion system, an ionizing energy of 70 eV, a source temperature of 200°C, a sample-introduction temperature of 120-150°C, and a collector current of 100 μA, while the elementary compositions of the ions and the MD spectra were measured in a MKh 1310 mass spectrometer with a IE-24 EI source at an ionizing voltage of 70 V, a collector current of 80 μA, and an evaporator temperature of 80°C. The LSIMS spectra were obtained in the same instrument with a secondary ion source from the firm Analiticheskie Pribory [Analytical Instruments] (St. Petersburg) using bombardment with Cs^+ ions having an energy of 7 keV.

Carpesiolin (I) was obtained by the hydrolysis of ergolide (II) [8]. Dihydroergolide (III) and dihydrobritanin (V) were obtained by the sodium tetrahydroborate reduction of (II) and of britanin (IV) by a published method [9].

The authors thank E. G. Mil'grom for assistance in the performance of the experiments.

REFERENCES

1. U. A. Abdullaev, Ya. V. Rashkes, I. D. Sham'yanov, and G. P. Sidyakin, Khim. Prir. Soedin., No. 1, 56-63 (1982).
2. V. N. Plugar', Ya. V. Rashkes, I. M. Sotboeva, and A. Mallabaev, Khim. Prir. Soedin., No. 1, 96-101 (1987).
3. A. Ovezdurdyev, B. Akyev, and Sh. Z. Kasymov, Khim. Prir. Soedin., No. 3, 396-397 (1981).
4. M. K. Makhmudov, B. Toshkhodzhaev, F. B. Zhonkhodzhaeva, and I. D. Sham'yanov, Khim. Prir. Soedin., No. 2, 232 (1993).
5. P. I. Zhakharov, R. I. Evstratova, and K. S. Rybalko, Khim. Prir. Soedin., No. 5, 587 (1971).
6. S. Matsueda, Yakugaku Zasshi, **92**, 905 (1972); Chem. Abstr., **77**, 101921W (1972).
7. L. Tsai, R. J. Hignet, and W. Herz, J. Org. Chem., **34**, No. 4, 945-948 (1969).
8. A. Ovezdurdyev, N. D. Abdullaev, Sh. Z. Kasymov, and B. Akyev, Khim. Prir. Soedin., No. 5, 568-571 (1987).
9. I. D. Sham'yanov, A. Mallabaev, and G. P. Sidyakin, Khim. Prir. Soedin., No. 4, 442-445 (1978).