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MASS-SPECTROMETRIC STUDY OF ANTIBIOTICS OF THE PYRIMIDO[5,4-e]-asym-TRIAZINE SERIES

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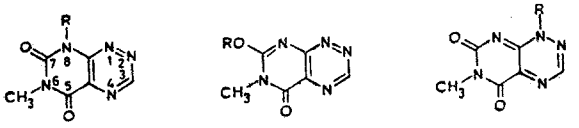
It has previously [1, 2] been reported that the methylation of rheumycin (Ia) by diazomethane yields three individual monomethylation products, which have been identified as 1,6-dimethylpyrimido[5,4-e] [1,2,4]triazine-5,7-dione (IIIa), which is known as the antibiotic xanthothricin [3] or toxoflavin, 6,8-dimethylpyrimido[5,4-e] [1,2,4]triazine-5,7-dione (Ic), which is known as the antibiotic fervenulin [5, 6] or planomycin [7], and 6-methyl-7-methoxypyrimido[5,4-e] [1,2,4]triazin-5-one (IIa), whose synonym is 7-methoxyrheumycin [2].



I a R=H; b R=D; c R=CH_3; d R=CH_2D; II a R=CH_3; b R=CH_2D; III a R=CH_3; b R=CH_2D

In order to further study the products of the chemical and biological conversion of antibiotics Ia, Ic, IIa, and IIIa, it is necessary to find analytical criteria, which would make it possible to identify compounds with very similar structures. This was the goal of the present investigation and presupposes the use of mass spectrometry [8].

Antibiotics Ia, Ic, IIa, and IIIa are distinguished by a low resistance to electron impact (W_M) (Table 1) in comparison to derivatives of uracil [9] and pyrimidine [10, 11]. This finding is evidence that the molecular ion (M^+) exists predominantly in the keto form, which is in complete agreement with the ground-state structure of the molecules under study. The appreciable decrease in the value of W_M in compound IIa is due to the appearance of addition fragmentation paths owing to the presence of the methoxy group in the uracil part of the molecule [12].

The directions for the fragmentation of M^+ for each antibiotic have been determined with the aid of an investigation of the mass spectra of metastable ions (the DADI technique) [13, 14] (Table 2). It was rigorously provided that the initial act in the fragmentation of M^+ is due to the loss of 28 amu (i.e., a CO or N_2 molecule). The elimination of a CO molecule is characteristic of most cyclic ketones of the hetaryl series. This is dictated not only by the predominant localization of the charge in M^+ on the more electronegative oxygen atom, but also to the formation of the energetically favorable pseudomolecular ion $[M-CO]^+$, which has the structure of a heteroaromatic five-membered ring. However, as the data from high-resolution mass spectrometry showed (Table 3), in the case of compounds Ia, Ic, and IIa, the triazine part of the molecule undergoes destruction with the elimination of an N_2 molecule, and the elimination of a CO molecule is characteristic only of compound IIIa.

In this connection it seemed of interest to compare the energetics of the two processes (Table 4). The value we determined for ΔE [the difference between the appearance potential (AP) of the fragment ion and the ionization potential (IP) of the molecule] for the process $M^+ \xrightarrow{-N_2} [M-N_2]^+$ in the case of compound Ia is small

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TABLE 1. Mass Spectra of Antibiotics Ia–Id, IIa, IIb, IIIa, and IIIb

Compound	Value of m/e (intensity of ion peaks in % of maximum)*
Ia	38 (17,8); 39 (36,0); 40 (7,2); 41 (8,2); 42 (53,1); 43 (14,6); 44 (4,6); 45 (16,1); 52 (4,6); 53 (17,8); 54 (14,8); 55 (3,9); 56 (13,7); 57 (3,0); 58 (16,2); 65 (12,7); 66 (22,8); 67 (100,0); 68 (39,4); 69 (5,9); 70 (3,4); 80 (3,2); 93 (5,4); 94 (15,3); 95 (19,4); 96 (4,5); 107 (7,4); 122 (5,5); 123 (76,5); 124 (3,7); 151 (58,1); 152 (3,9); 179 (66,5); 180 (5,4); W_M=8,2
Ib	39 (3,1); 40 (33,7); 41 (34,0); 42 (12,5); 43 (56,3); 44 (37,5); 53 (22,5); 54 (21,9); 55 (15,6); 56 (18,8); 57 (15,6); 58 (21,9); 59 (11,0); 65 (15,6); 66 (29,7); 67 (89,1); 68 (100,0); 69 (50,0); 81 (12,5); 93 (12,5); 94 (21,9); 95 (34,4); 96 (31,3); 97 (9,4); 107 (6,3); 108 (14,1); 109 (3,1); 122 (10,9); 123 (81,3); 124 (81,3); 125 (7,8); 151 (78,1); 152 (84,4); 153 (5,6); 179 (62,5); 180 (73,4); 181 (5,6)
Ic	40 (3,0); 41 (6,3); 42 (50,0); 43 (8,8); 51 (5,0); 52 (20,0); 53 (50,0); 54 (8,8); 55 (5,0); 56 (10,0); 57 (6,3); 58 (3,0); 65 (6,3); 66 (3,0); 67 (31,3); 68 (50,0); 69 (8,8); 70 (3,0); 79 (13,3); 80 (40,0); 81 (50,2); 82 (33,2); 83 (5,1); 93 (5,2); 94 (10,0); 96 (11,1); 108 (4,0); 109 (10,0); 110 (11,2); 111 (4,0); 121 (10,3); 122 (13,3); 135 (8,8); 136 (56,3); 137 (100,0); 138 (18,3); 165 (37,5); 193 (63,3); 194 (7,0); W_M=9,0
Id	42 (44,3); 43 (34,6); 44 (7,7); 52 (8,2); 53 (34,6); 54 (30,8); 55 (7,2); 56 (10,3); 57 (3,8); 58 (3,0); 65 (6,0); 66 (3,0); 67 (15,0); 68 (41,0); 69 (28,2); 70 (7,7); 79 (4,0); 80 (26,6); 81 (44,1); 82 (47,2); 83 (24,1); 84 (4,8); 95 (3,0); 96 (7,9); 97 (4,2); 107 (3,1); 108 (7,0); 109 (6,4); 110 (3,0); 122 (8,1); 123 (5,0); 136 (13,1); 137 (52,3); 138 (100,0); 139 (36,9); 140 (3,0); 165 (5,4); 166 (28,0); 167 (7,1); 193 (13,1); 194 (78,1); 195 (4,0)
IIa	42 (54,3); 43 (15,7); 44 (15,7); 45 (7,1); 51 (10,7); 52 (21,4); 53 (10,0); 54 (12,0); 55 (51,4); 57 (20,0); 58 (55,7); 59 (4,3); 65 (57,1); 66 (25,0); 67 (22,9); 68 (14,3); 69 (4,3); 72 (81,4); 73 (14,3); 79 (4,3); 80 (42,9); 81 (11,4); 82 (3,6); 92 (4,3); 93 (85,7); 94 (10,0); 95 (3,1); 106 (12,9); 107 (50,0); 109 (30,0); 110 (4,3); 120 (68,6); 121 (16,4); 122 (11,4); 134 (18,6); 135 (52,9); 136 (11,4); 150 (52,1); 151 (3,0); 165 (100,0); 166 (18,6); 193 (61,4); 194 (5,7); W_M=5,2
IIb	42 (28,3); 43 (15,2); 44 (6,3); 53 (8,2); 54 (4,3); 55 (4,3); 56 (15,2); 57 (8,5); 58 (28,9); 59 (13,1); 65 (20,1); 66 (3,0); 67 (7,2); 68 (13,3); 69 (7,2); 72 (8,2); 73 (41,3); 74 (4,4); 80 (53,4); 81 (7,2); 82 (4,3); 93 (63,1); 94 (10,2); 95 (4,4); 107 (16,8); 108 (8,2); 109 (11,0); 120 (26,5); 121 (20,3); 122 (6,3); 134 (14,0); 135 (22,1); 136 (13,1); 150 (25,4); 151 (3,1); 165 (20,3); 166 (100,0); 167 (33,6); 168 (6,6); 193 (10,2); 194 (55,1); 195 (15,1); 196 (3,3)
IIIa	43 (30,0); 44 (17,5); 55 (16,3); 56 (28,8); 57 (12,5); 58 (3,8); 65 (12,5); 66 (56,3); 67 (71,3); 68 (12,5); 69 (4,4); 81 (10,0); 82 (15,0); 83 (58,1); 84 (13,8); 93 (10,0); 94 (4,4); 108 (10,6); 109 (89,4); 110 (21,9); 111 (8,8); 135 (8,8); 136 (82,5); 137 (22,5); 138 (5,6); 150 (14,4); 164 (5,0); 165 (25,0); 166 (3,8); 193 (100,0); 194 (10,4); W_M=12,5
IIIb	42 (4,8); 43 (21,4); 44 (13,2); 53 (4,2); 54 (8,1); 55 (7,1); 56 (17,3); 57 (9,1); 58 (5,3); 65 (22,0); 66 (20,1); 67 (44,3); 68 (55,6); 69 (29,6); 70 (9,1); 82 (6,1); 83 (12,1); 84 (26,3); 85 (7,3); 109 (13,3); 110 (46,8); 111 (18,1); 136 (7,4); 137 (49,8); 138 (24,8); 139 (6,1); 150 (3,0); 151 (6,3); 165 (4,4); 166 (13,5); 167 (4,2); 193 (18,1); 194 (100,0); 195 (18,3); 196 (3,1)

*Peaks with intensities greater than 3% are listed.

(14.29 kcal/mole). In the case of the process $M^+ \xrightarrow{-CO} [M-CO]^+$, which is characteristic of compound IIIa, the value of ΔE is ~2 times higher.

The introduction of a methyl group at position 8 (Ic) or 1 (IIIa) to a nitrogen atom results in a slight decrease in the ionization potential (of only 0.2 eV). The introduction potential of IIb was 0.8 eV lower than that of compound Ia owing to the change in the electronic configuration in the uracil part of the molecule. Comparing the data in Tables 1 and 4, we may conclude that the value of W_M varies along with the value of the ionization potential.

The dissociative ionization of M^+ of compounds Ia and Ic follows a common pattern (Table 2) with a corresponding mass shift of the peaks of all the characteristic ions in the spectrum by 14 amu. This phenomenon is due to the fact that the addition of a weak electron-donor substituent, i.e., the methyl group, to the N_8 atom in the molecule of Ic cannot cause significant changes in the intramolecular distribution of the electron density; therefore, the site of the predominant localization of the positive charge in M^+ is maintained.

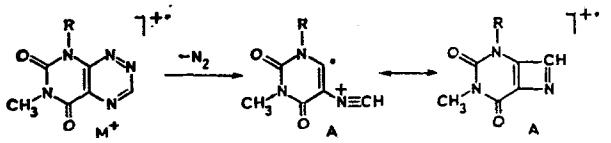
According to the peaks of the metastable ions (Table 2) and the elemental composition of the fragment ions (Table 3) observed in the mass spectra of compounds Ia and Ic, the ions of the type A successively split off two molecules of carbon monoxide to form ions of types B and C. In our opinion, these processes indicate that the ions of type A have a cyclic structure, since the localization of the charge on the exocyclic nitrogen atom should otherwise certainly result in the elimination of an HCN particle.

TABLE 2. Mass Spectra of Metastable Ions of Compounds Ia, Ic, IIa, and IIIa Obtained by the DADI Technique (the accuracy of the measurements of E_0 and E_i was 0.01 V)

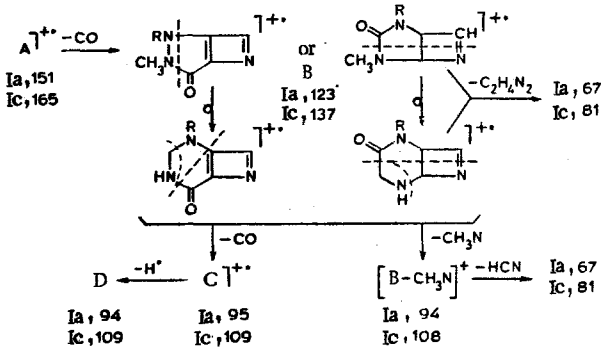
Value of m/e	Initial value of deflecting voltage (E_0, V)	Value of deflecting voltage at maximum of the peak of the metastable ion (E_i, V)	Metastable transition
		Compound Ia	
179	506,7	427,8	179 → 151
151	506,7	412,8	151 → 123
	506,7	358,7	151 → 107
	506,7	322,2	151 → 96
	506,7	228,1	151 → 68
123	506,7	391,2	123 → 95
	506,7	276,8	123 → 67
	506,7	173,1	123 → 43
107	506,7	378,8	107 → 80
	506,7	312,5	107 → 66
		Compound Ic	
193	509,1	436,3	193 → 165
165	509,1	423,3	165 → 137
	509,1	376,3	165 → 121
	509,1	339,7	165 → 110
	509,1	254,0	165 → 82
137	509,1	453,2	137 → 122
	509,1	402,6	137 → 109
	509,1	354,0	137 → 94
137	509,1	305,7	137 → 81
136	509,1	452,1	136 → 121
	509,1	416,7	136 → 109
121	509,1	338,3	121 → 81
		Compound IIa	
193	509,3	434,1	193 → 165
	509,3	193,5	193 → 72
165	508,7	462,1	165 → 150
	508,7	416,3	165 → 135
	508,7	376,5	165 → 122
	508,7	330,3	165 → 107
150	508,7	410,5	150 → 121
	508,7	315,3	150 → 93
135	508,7	452,3	135 → 120
		403,3	135 → 107
120	509,3	392,3	120 → 92
107	509,2	376,9	107 → 80
		Compound IIIa	
193	509,1	436,1	193 → 165
165	508,2	462,7	165 → 150
	508,2	424,2	165 → 137
	508,2	342,3	165 → 111
150	508,7	462,3	150 → 136
137	508,7	408,6	137 → 110
136	508,7	408,3	136 → 109
109	509,1	308,6	109 → 66

TABLE 3. High-Resolution Mass Spectra of Compounds Ia, Ic, IIa, and IIIa (M/△M = 25,000, the reference was perfluorokerosene)

Value of m/e	Ia		Ic		IIa		IIIa		Empirical formula of ion
	det.	calc.	det.	calc.	det.	calc.	det.	calc.	
193	—	—	,0590	,0599	,0603	,0588	,0599	,0599	$C_7H_7N_5O_2$
179	,0441	,0443	—	—	—	—	—	—	$C_6H_5N_5O_2$
165	—	—	,0536	,0537	,0534	,0537	—	—	$C_7H_7N_3O_2$
	—	—	—	—	—	—	,0658	,0649	$C_6H_7N_5O$
164	—	—	—	—	—	—	,0578	,0571	$C_6H_6N_5O$
151	,0367	,0381	—	—	—	—	—	—	$C_6H_5N_3O_2$
150	—	—	—	—	,0300	,0303	—	—	$C_6H_4N_3O_2$
	—	—	—	—	—	—	,0405	,0415	$C_5H_4N_5O$
137	—	—	,0579	,0588	—	—	—	—	$C_6H_7N_3O$
	—	—	—	—	—	—	,0486	,0463	$C_5H_5N_4O$
136	—	—	,0498	,0510	,0489	,0510	—	—	$C_6H_6N_3O$
	—	—	,0265	,0272	—	—	—	—	$C_6H_4N_2O_2$
	—	—	—	—	—	—	,0383	,0384	$C_5H_4N_4O$
135	—	—	—	—	,0427	,0432	—	—	$C_6H_5N_3O$
134	—	—	—	—	,0349	,0354	—	—	$C_6H_4N_3O$
123	,0429	,0432	—	—	—	—	—	—	$C_5H_5N_3O$ (91%)
	,0289	,0306	—	—	—	—	—	—	$C_4H_3N_4O$ (9%)
122	,0124	,0116	—	—	—	—	—	—	$C_5H_2N_2O_2$
	—	—	,0357	,0354	,0354	,0354	—	—	$C_5H_4N_3O$
121	—	—	,0645	,0639	—	—	—	—	$C_6H_7N_3$
120	—	—	—	—	,0195	,0197	—	—	$C_5H_2N_3O$
110	—	—	,0473	,0479	—	—	—	—	$C_5H_6N_2O$
	—	—	—	—	—	—	,0374	,0354	$C_4H_4N_3O$
109	—	—	,0638	,0639	—	—	—	—	$C_5H_7N_3$ (80%)
	—	—	,0401	,0401	—	—	—	—	$C_5H_5N_2O$ (20%)
	—	—	—	—	—	—	,0278	,0276	$C_4H_3N_3O$
108	,0176	,0197	—	—	—	—	—	—	$C_4H_2N_3O$
	—	—	,0573	,0561	—	—	—	—	$C_5H_6N_3$ (50%)
	—	—	,0322	,0323	,0310	,0323	—	—	$C_5H_4N_2O$ (50%)
	—	—	—	—	—	—	,0200	,0197	$C_4H_2N_3O$
107	,0502	,0483	—	—	,0472	,0483	—	—	$C_5H_5N_3$
	—	—	—	—	,0235	,0231	—	—	$C_5H_3N_2O$
96	,0333	,0323	,0323	,0323	—	—	—	—	$C_4H_4N_2O$
95	,0482	,0483	—	—	—	—	—	—	$C_4H_5N_3$ (90%)
	,0199	,0153	—	—	—	—	—	—	$C_4H_3N_2O$ (10%)
94	,0406	,0405	—	—	—	—	—	—	$C_4H_4N_3$ (45%)
	,0172	,0166	—	—	—	—	—	—	$C_4H_2N_2O$ (55%)
	—	—	,0538	,0530	—	—	—	—	$C_5H_6N_2$
93	—	—	,0096	,0088	—	—	,0089	,0088	C_4HN_2O
83	—	—	—	—	—	—	,0249	,0245	$C_3H_3N_2O$
82	—	—	,0532	,0530	—	—	—	—	$C_4H_6N_2$
	—	—	—	—	—	—	,0165	,0166	$C_3H_2N_2O$
81	—	—	,0439	,0452	—	—	—	—	$C_4H_5N_2$ (60%)
	—	—	,0212	,0214	—	—	—	—	C_4H_3NO (40%)
80	,0373	,0374	,0377	,0374	—	—	—	—	$C_4H_4N_2$
68	,0389	,0374	,0383	,0374	—	—	—	—	$C_3H_4N_2$
67	,0073	,0058	—	—	—	—	—	—	C_3HNO
	—	—	,0305	,0296	—	—	—	—	$C_3H_3N_2$
66	,0209	,0228	—	—	—	—	,0213	,0228	$C_3H_2N_2$



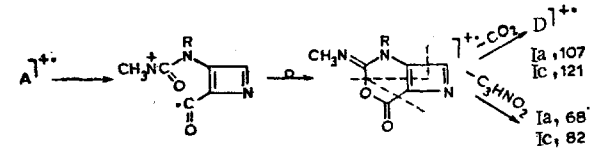
It has not been ruled out that the elimination of the first CO group to form an ion of type B is followed by the splitting of the ring owing to the methyl group in position 6. In this case, it is easy to account for the two successive competing processes involved in the fragmentation of the ion of type B, viz., the elimination of a second CO molecule (an ion of type C) or the removal of an H_3CN fragment (an ion of type D) (Table 3).



Ions 67 (compound Ia) and 81 (Ic) form either from the ions of type D as a result of the removal of HCN from the four-membered ring or from the ions of type B.

According to the mass spectra of the deuterated derivatives of xanthothricin (Ib) and fervenulin (Id), in which there is no methyl group in position 1 (see Table 1), both ions contain the label. However, in the case of compound Id, the enrichment percentage is significantly lower than in the case of Ib. This finding confirms (in the case of Ic) the alternative path involving the elimination of a $C_2H_4N_2$ particle from the ion of type B with the participation of the substituent R (Table 2).

The spectra of the metastable ions (Table 2) show that the further course of the fragmentation of the ion of type A involves the elimination of HC_2NO, C_3HNO_2, and CO_2 particles (Table 3). The elimination of the last two fragments suggests a skeletal rearrangement, which is realized by means of the cleavage of the labile amide bond in the uracil part of the molecules and subsequent recyclization to form a lactone group.



A similar process involving the splitting off of a CO_2 molecule has been observed in the case of cyclic imides and isoimides [15]. This rearrangement process is indirectly confirmed by the restraining of deuterium labeling in the fragment ions (Table 1). However, despite all the similarity in the nature of the fragmentation of M^+ in the cases of compounds Ia and Ic, the presence of the methyl group on the N_8 atom in compound Ic causes the appearance of new specific ions, which are characteristic only of this compound. For example, along with the elimination of a CO molecule of the ion of type A, the mass spectrum of fervenulin shows intense peaks for $[A-H]^+$ (56%) and $[A-CH_3]^+$ (13%) (Tables 2 and 3).

As we see from the mass spectrum of deuterated derivative Id, fragment ions $(B-H)^+$ and $(B-CH_3)^+$ contain a CH_2D group in position 8. On the basis of this finding it may be postulated that the elimination of hydrogen and the methyl group occurs mainly by virtue of the substitution in position 6 of the uracil ring. A process involving the elimination of an HNCO particle from the ion of type B, which is characteristic of uracils [9], is also observed.

The fragmentation of M^+ of 7-methoxyrheumycin (IIa), which, like compounds Ia and Ic, has an azo group in the triazine ring, also takes place with the elimination of a nitrogen molecule (Tables 2 and 3). The value

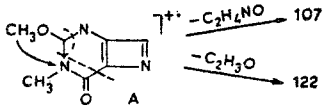
*Here and in the following the numbers characterizing an ion define the ratio of its mass to its charge.

TABLE 4. Ionization Potentials (IP) of Molecular Ions and Appearance Potentials (AP) of $[M-28]^+$ for Compound Ia and Methylated Isomers Ic, IIa, and IIIa in eV (±0.03)

Compound	IP	IP of $[M-28]^+$	$\Delta E = AP - IP$
Ia	9,24	9,86	0,62
Ic	9,03	10,09	1,06
IIa	8,43	9,47	1,01
IIIa	9,03	10,32	1,29

of ΔE for the process of the removal of an N_2 molecule from M^+ in this case is close to the value for fervenulin (Ic) and is equal to 1.01 eV (Table 4).

The further fragmentation of the ion of type A is determined by the presence of the methoxy group, causing the formation of ions 134 $[A-CH_3O]^+$, 135 $[A-CH_2O]^+$, 136 $[A-CHO]^+$, and 150 $[A-CH_3]^+$ (Tables 3 and 4). In addition, the elimination of C_2H_3O and C_2H_4NO particles is observed.

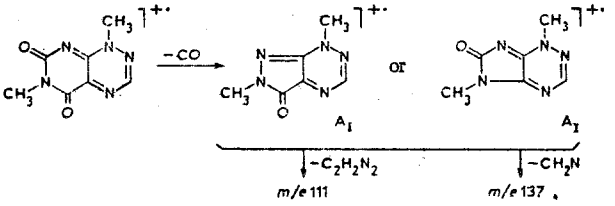


IIa, 165

The pattern of the fragmentation of M^+ of compound IIa just presented is supported by the mass spectrum of its deuterated analog (IIb) (Table 1), in which the bulk of the fragment ions observed do not contain the isotopic label. An exception is the 72 $(CH_3O\overset{+}{C}=N-CH_3)$, which forms directly from M^+ as a result of the synchronous cleavage of the C_5-N_6 and C_7-N_8 bonds in the pyrimidine ring. The shift of the value of m/e by 1 amu (IIb) indicates that a methoxy group is present in this ion.

The fragmentation of M^+ of xanthothricin (IIIa), which has a methyl group in the triazine ring differs appreciably from the fragmentation paths of compounds Ia, Ic, and IIa considered above. For example, in the case of compound IIIa, the $[M-28]^+$ ion forms, as we have already noted, as a result of the elimination of carbon monoxide (Tables 2 and 3), since the methyl group in position 1 presents the fragmentation of the triazine ring.

The loss of the CO molecule causes narrowing of the uracil ring of compound IIIa and results in the formation of a pseudomolecular ion of two possible structures (A_1 ion).



The formation of ion 136 in this case takes place in stages (Table 2), rather than as a result of the elimination of a CH_3NCO particle from the uracil part of the molecule [9]. The introduction of the label (compound IIIb) shifts the positions of the peaks of the principle fragment ions in the mass spectrum by 1 amu. This proves that the fragmentation of M^+ takes place without the participation of the methyl group in position 1, an exception being the process resulting in the formation of ion 111 (Table 1).

The fragmentation we have considered of M^+ of the antibiotic 1-dimethylxanthothricin (Ia) and its monoethyl derivatives, which differ with respect to the position of the methyl group in the pyrimido[5,4-e]-asym-triazine ring, shows that each of the compounds cited has a set of characteristic features (the ionization potential, the ΔE for the formation of the $[M-28]^+$ ions, and the specific peaks of the fragment ions), which make it possible to unequivocally identify them.

EXPERIMENTAL

Fervenulin (Ic), xanthothricin (IIIa), 7-methoxyrheumycin (IIa), and the derivative not containing a methyl group in position 1 were obtained by methylation with diazomethane in a 2:1 methanol–diethyl ether medium followed by the separation of the products formed by preparative thin-layer chromatography on Silica Gel KSK in

a 3:2 ethyl acetate–benzene system. Compound Ic was obtained with a 60–80% yield and Rf 0.67, compound IIIa was obtained with a 6–10% yield and Rf 0.09, and 7-methoxyrheumycin (IIa) was obtained with a 5–8% yield and Rf 0.38.

With respect to the deuterated analogs, compound Ib was obtained by isotope exchange of the hydrogen atom at N_8 in the presence of D_2O, and the introduction of a deuterium atom into the methyl groups in Id, IIb, and IIIb was achieved by the methylation of Ia with diazomethane in a medium of monodeuteromethanol.

The low-resolution mass spectra were recorded on an MS-1302 mass spectrometer with the use of a system for the direct introduction of the sample into the ion source with a temperature of the vaporizer equal to 100–150°C, and an ionization energy equal to 30–40 eV.

The ionization potentials of Ia, Ic, IIa, and IIIa, and the appearance potentials of their fragmentations were determined on this instrument, which was equipped with a vacuum monochromator and a gas-discharge hydrogen lamp.

The high-resolution mass spectra of compounds Ia, Ic, IIa, and IIIa were obtained on an MS-902 mass spectrometer. The mass spectra of the metastable ions were recorded by the DADI technique on a Varian MAT-311 instrument.

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