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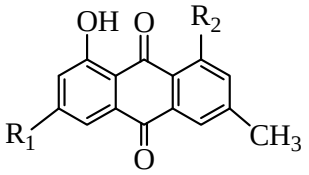
CHARACTERISTIC OF MASS-SPECTROMETRIC FRAGMENTATION MOLECULAR IONS OF EMODINE AND ITS METHYL ETHERS

Abstract. The work is devoted to the mass-spectrometric study and comparative analysis of mass-spectrometric fragmentation of molecular ions of 1,6,8-trihydroxy-3-methyl-9,10-anthraquinone (emodin) and its mono- and dimethyl ether. The influence of the substituent on the stability of molecular ions to ionization by electrons is considered, and schemes for their mass-spectrometric decay proposed. It is shown that the fragmentation of the derivatives depends on the location of the substituent in the anthraquinone system.

Key words: mass-spectrum, molecular ion, fragmentation, electron ionization, elimination, derivatives of 9,10-anthraquinone

Anthraquinones represent the most numerous group of natural quinones with diverse biological activity [1, 2]. Among them, one of the most common derivatives of 9,10-anthraquinone is emodin (1), which is identified not only in the free state, but in glycosidated, dimeric and condensed forms, in plants of such families as Rhamnaceae (Rhamnus, Maesopsis, Ventilage), Fabaceae (Cassia), Senna, Polygonaceae (Rheum, Rumex, Polygonum), Liliaceae (Aloe, Bulbine), Hypericaceae [3-8]. Modern studies have made it possible to establish, in addition to the laxative, also its antibacterial, vasorelaxant, cardiotonic, hepatoprotective and antitumor effects [9-12], and the ability of derivatives of emodin to inhibit the enzymatic activity of ATP-citrate lyase (ACL), a key player in the metabolism of cancer cells [13].

Considering the importance of the emodin derivatives (1) as biologically active compounds and continuing research into the mass spectrometric fragmentation of 9,10-anthraquinone derivatives [14-17]. This article is devoted to the analysis of the mass spectra of 1,6,8-trihydroxy-3 -methyl-9,10-anthraquinone (emodin) (1) and its methyl esters (2,3). The structure of the derivatives is presented below:



1-3

1 R_1, R_2-OH
2 R_1- OCH_3, R_2-OH
3 R_1, R_2-OCH_3

Table 1 shows the total mass spectra of emodin (1) and its methyl esters (2,3), and table 2 shows the data on the stability of MI (W_{mi}) for ionization by electrons (IE), as well as the characteristic ions (F_1-F_7) from of the total ion current. From the data in table 1, it can be seen that for the anthraquinones studied the MI peak in the spectra is the maximum (I = 100%), and the MI stability to the IE (W_{mi}) is in the range 11.9 ÷ 40.6% (table 2).

Table 1 – Mass spectra of 9,10-anthraquinone derivatives (1-3)

№	Compound	Mass spectrum: $M^{+\cdot}$, m/z ($I_{отс}$ в %)*
1	1,6,8-Trihydroxy-3-Methyl-9,10-anthraquinone (emodin)	271 (17), $M^{+\cdot}$ 270 (100), 269 (2), 255 (2), 254 (2), 253 (3), 243 (2), 242 (14), 241 (9), 227 (1), 226 (1), 225 (3), 224 (1), 215 (1), 214 (7), 213 (10), 200 (3), 199 (2), 197 (4), 196 (3), 195 (1), 186 (2), 185 (5), 172 (1), 171 (2), 169 (2), 168 (5), 167 (2), 158 (1), 157 (2), 155 (1), 145 (1), 141 (1), 140 (2), 139 (8), 137 (2), 136 (1), 135 (3), 129 (2), 128 (4), 127 (3), 126 (1), 121 (4), 116 (1), 115 (5), 114 (1), 108 (1), 107 (2), 106 (2), 105 (2), 102 (1), 101 (1), 92 (2), 91 (1), 90 (1), 84 (4), 79 (2), 78 (2), 77 (5), 76 (2), 75 (2), 74 (2), 70 (2), 69 (7), 65 (2), 64 (2), 63 (4), 62 (2), 53 (2), 52 (2), 51 (6), 50 (2), 39 (4).
2	1,8-Dihydroxy-6-Methoxy-3-methyl-9,10-anthraquinone (physcion) (emethine methyl ester)	286 (4), 285 (23), $M^{+\cdot}$ 284 (100), 283 (5), 269 (1), 267 (8), 257 (1), 256 (7), 255 (13), 254 (9), 253 (1), 242 (2), 241 (10), 239 (1), 237 (1), 228 (2), 227 (6), 226 (7), 225 (6), 214 (1), 213 (7), 212 (1), 211 (1), 210 (1), 199 (2), 198 (5), 197 (2), 195 (2), 185 (4), 184 (2), 167 (2), 139 (4), 129 (2), 128 (7), 127 (2), 115 (3), 106 (2), 105 (2), 79 (2), 78 (1), 77 (3), 76 (2), 75 (2), 63 (2), 51 (2), 28 (4).
3	1-Hydroxy-6,8-dimethoxy-3-methyl-9,10-anthraquinone (emodin dimethyl ether)	300 (4), 299 (21), $M^{+\cdot}$ 298 (100), 297 (8), 295 (2), 285 (2), 284 (5), 283 (5), 282 (5), 281 (22), 280 (49), 279 (3), 271 (2), 270 (7), 269 (26), 268 (10), 267 (5), 266 (3), 265 (15), 256 (3), 255 (9), 254 (6), 253 (19), 252 (70), 251 (6), 250 (3), 249 (2), 248 (2), 242 (1), 241 (4), 240 (5), 239 (10), 238 (11), 237 (27), 236 (2), 229 (3), 228 (8), 227 (6), 226 (10), 225 (7), 224 (7), 223 (7), 222 (3), 213 (3), 212 (7), 211 (10), 210 (12), 209 (13), 208 (3), 207 (3), 199 (4), 198 (5), 197 (13), 196 (6), 195 (5), 194 (4), 185 (3), 184 (10), 183 (7), 182 (11), 181 (15), 169 (12), 168 (8), 167 (4), 166 (4), 165 (6), 157 (4), 156 (8), 155 (8), 154 (5), 153 (11), 152 (10), 151 (7), 150 (5), 141 (12), 140 (9), 139 (20), 138 (4), 135 (24), 129 (5), 128 (17), 127 (13), 126 (7), 119 (7), 115 (17), 113 (7), 106 (7), 102 (7), 101 (6), 99 (6), 98 (6), 91 (9).

1,6,8-Trihydroxy-3-methyl-9,10-anthraquinone (1). In the mass spectrum of 1,6,8-trihydroxy-3-methyl-9,10-anthraquinone (emodin) (2), the peak of MI has a maximum intensity (I = 100%), whose stability is W_{mi} = 35.2% (table 2). The most intense peak of MI emodin (2) decays under the action of ionization by electrons (IE) along four directions and gives low-intensity ions (scheme 1).

Table 2 – Stability of molecular ions (W_{mi}) and characteristic ions (F_1-F_7) (W_f) from the total ion current of anthraquinone derivatives (1-3)

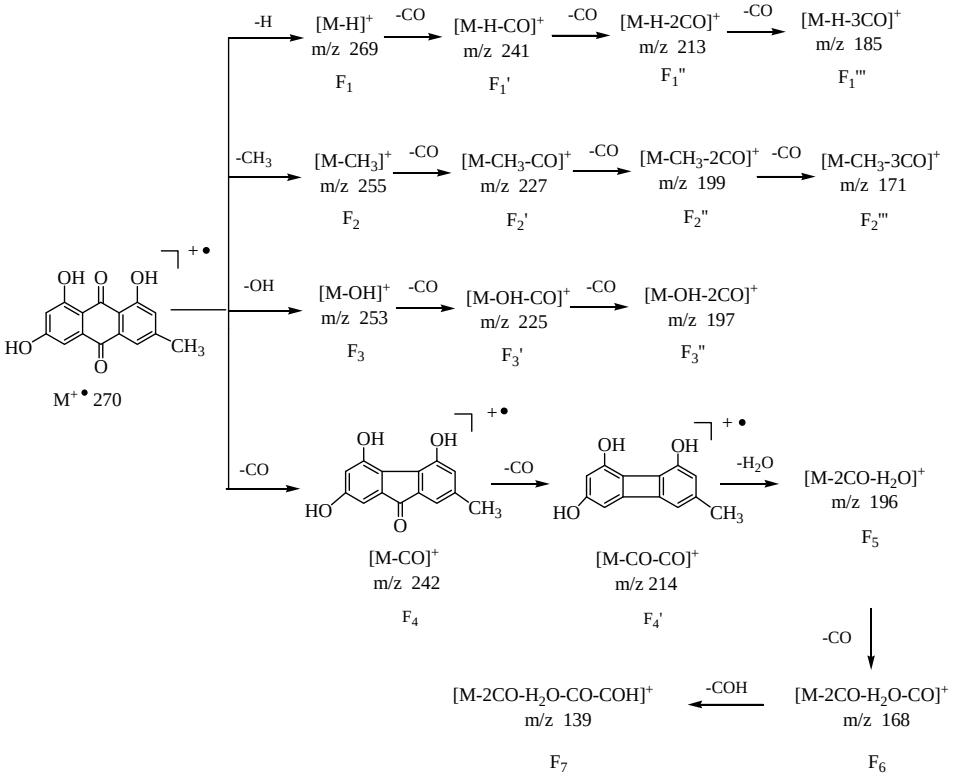
№	W_{mi}, %	m/z (W_f, %)						
		F_1 / F_1'- F_1'''	F_2 / F_2'-F_2'''	F_3 / F_3'-F_3'''	F_4 / F_4'-F_4'''	F_5 /F_5'	F_6/ F_6', F_6''	F_7
1	35,2	269 (0,6) 241 (2,7) 213 (3,0) 185 (1,5)	255 (0,6) 227 (0,3) 199 (0,6) 171 (0,6)	253 (0,9) 225 (0,9) 197 (1,2) 169 (0,6)	242 (4,1) 214 (2,0)	196 (0,9)	168 (1,5)	139 (2,4)
2	40,6	283 (1,6) 255 (4,2) 227 (1,9) 199 (0,65)	269 (0,3) 241 (3,2) 213 (2,2) 185 (1,3)	267 (0,65) 239 (0,3) 211 (0,3) 183 (0,3)	256 (2,3)	254 (3,0)	226 (2,3)	198 (1,6)
3	11,9	297 (0,8) 269 (2,5)	281 (2,1) 253 (1,8)	280 (4,7) 252 (6,7)	265 (1,4) 237 (2,6) 209 (1,2)	268 (0,9) 238 (1,0)	255 (0,9) 227 (0,6) 197 (1,2)	–

When hydrogen is lost, a peak of the ion F_1 $[M\text{-}H]^+$ with m/z 269 (I = 2%) is formed, which successively loses three molecules of carbon monoxide, which leads to the appearance of the ions F_1' $[M\text{-}H\text{-}CO]^+$ with m/z 241, F_1'' $[M\text{-}H\text{-}CO\text{-}CO]^+$ with m/z 213 and F_1''' $[M\text{-}H\text{-}CO\text{-}CO\text{-}CO]^+$ with m/z 185. The most intense, from the formed peaks, with I = 10% is the peak of the ion F_1'' $[M\text{-}H\text{-}CO\text{-}CO]^+$ with m/z 213 and with I = 9% - the peak of the ion F_1' $[M\text{-}H\text{-}CO]^+$ with m/z 241, and the intensity of the ion F1''' $[M\text{-}H\text{-}CO\text{-}CO\text{-}CO]^+$ is I = 5% (table 1).

The second direction of MI fragmentation occurs when a methyl radical is lost with the formation of the F_2 $[M\text{-}CH_3]^+$ ion with m/z 255. Further, the F_2 $[M\text{-}CH_3]^+$ ion sequentially eliminates three CO molecules to form F_2' $[M\text{-}CH_3\text{-}CO]^+$ with m/z 227, F_2'' $[M\text{-}CH_3\text{-}CO\text{-}CO]^+$ with m/z 199 and F_2''' $[M\text{-}CH_3\text{-}CO\text{-}CO\text{-}CO]^+$ with m/z 171, the intensity of the ions formed is I = 1-2%.

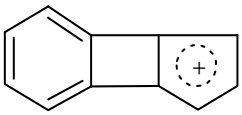
The third direction of fragmentation begins with the release of the OH group and the formation of the F_3 $[M\text{-}OH]^+$ ion with m/z 253, from which the CO molecules are eliminated, which leads to F_3' $[M\text{-}OH\text{-}CO]^+$ fragment ions with m/z 225, F_3'' $[M\text{-}OH\text{-}CO\text{-}CO]^+$ with m/z 197 and F_3'' $[M\text{-}OH\text{-}CO\text{-}CO\text{-}CO]^+$ with m/z 169, with intensity I = 2-4% .

The fourth direction of MI disintegration proceeds analogously to the decay of MI 9,10-anthraquinone and is associated with the sequential elimination of the carbon monoxide molecule. The ions of 1,6,8-trihydroxy-3-methylfluorenone F_4 $[M\text{-}CO]^{+\bullet}$ with m/z 242 (I = 14%) and 1,6,8-trihydroxy-3-methylbiphenylene are formed F_4' $[M\text{-}CO\text{-}CO]^{+\bullet}$ with m/z 214 (I = 7%). The formed ion F_4', in turn, can consecutively lose the water molecule (the ion F_5 $[M\text{-}2CO\text{-}H_2O]^+$, m/z 196), CO (ion F_6 $[M\text{-}2CO\text{-}H_2O\text{-}CO]^+$, m/z 168) and CHO (ion F_7 $[M\text{-}2CO\text{-}H_2O\text{-}COOH]^+$, m/z 139) due to reorganization processes, that is scrambling of hydrogen atoms due to migration and scrambling of carbon atoms as a result of valence isome-



Scheme 1 – Fragmentation of a molecular ion 1,6,8-trihydroxy-3-methyl-9,10-anthraquinone (1)

rism, as well as processes of randomization-displacement hydrogen atoms and carbon [18, 19]. Consequently, a significant peak with m/z 139 in the mass spectrum corresponds to the F_7 ion:

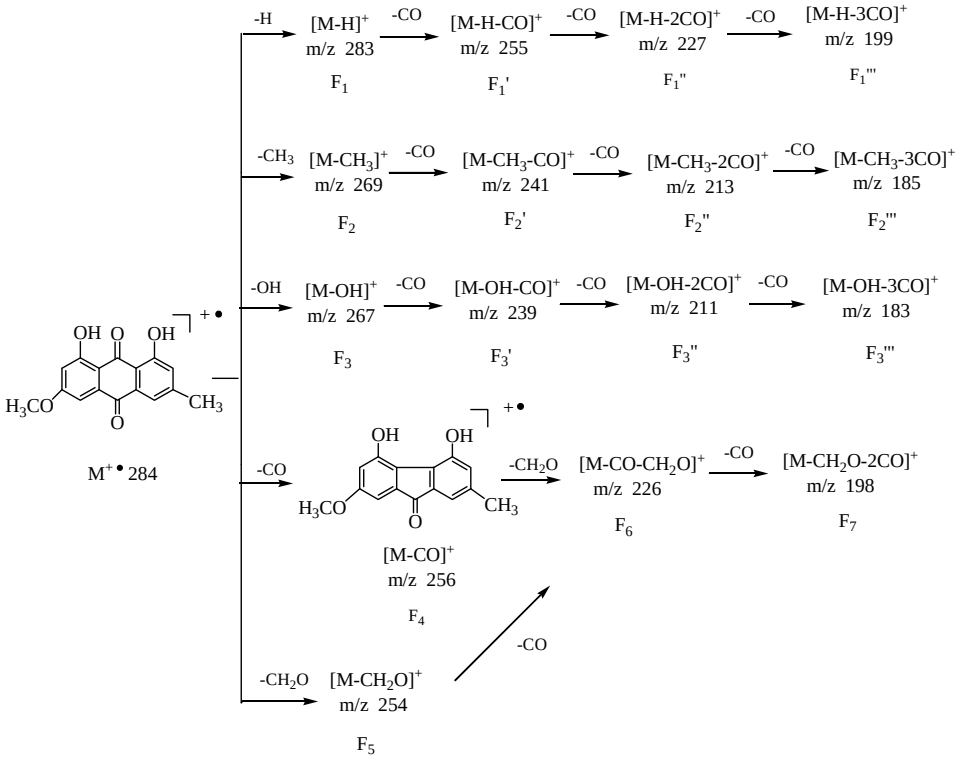


F_7 $[M\text{-}2CO\text{-}H_2O\text{-}COH]^+$, m/z 139

1,8-Dihydroxy-6-methoxy-3-methyl-9,10-anthraquinone (2). The substitution of the β-hydroxyl group for the methoxy group in the molecule of emodin (1) in the case of β-methoxyemodine (physcion) (2) practically does not affect the character of the initial MI decay in the mass spectrum, but increases the stability of MI (W_{mi} = 40.6%) (table 2).

For the mass-spectrometric decomposition of 1,8-dihydroxy-6-methoxy-3-methyl-9,10-anthraquinone (2), the original fragmentation of MI, as in the case of the emodin molecule (1), occurs as a result of the splitting off of the hydrogen

atom, OH and CO with the formation of primary fragment ions F_1 $[M-H]^+$ with m/z 283, F_2 $[M-CH_3]^+$ with m/z 269, F_3 $[M-OH]^+$ with m/z 267 and F_4 $[M–CO]^{+\bullet}$ with m/z 256 (scheme 2).



Scheme 2 – Fragmentation of a molecular ion
1,8-dihydroxy-6-methoxy-3-methyl-9,10-anthraquinone (2)

A distinctive feature of the mass-spectrometric decay of MI (2), in contrast to the emodin spectrum (1), is the elimination of the formyl radical CH_2O and the formation of the fragment ion F_5 $[M-CH_2O]^{+\bullet}$ with m/z 254 (scheme 2). The intensity of the formed F_1-F_5 ions is I = 5-9% (table 1). The further decay of the fragment ions F_1 $[M-H]^+$ with m/z 283, F_2 $[M-CH_3]^+$ with m/z 269 and F_3 $[M-OH]^+$ occurs by successive elimination of carbon monoxide molecules, which leads to the formation of ions F_1' $[M-H-CO]^+$ with m z 255, F_1'' $[M-H-CO-CO]^+$ with m/z 227, F_2' $[M-CH_3-CO]^+$ with m/z 241, F_3' $[M-OH-CO]^+$ with m/z 239, F_3'' $[M-OH-CO-CO]^+$ with m/z 211. The most intense of these are F_1' (I = 13%) and F_2 (I = 10%).

It is possible to eliminate the formyl radical CH_2O from the F_4 $[M-CO]^{+\bullet}$ m/z 256 fragment with the formation of the F_6 $[M-CO-CH_2O]^+$ ion with m/z 226 (I = 7%). The F_6 ion can also arise from the F_5 ion, after the elimination of the carbon monoxide molecule. The emission of a CO molecule from the F_6

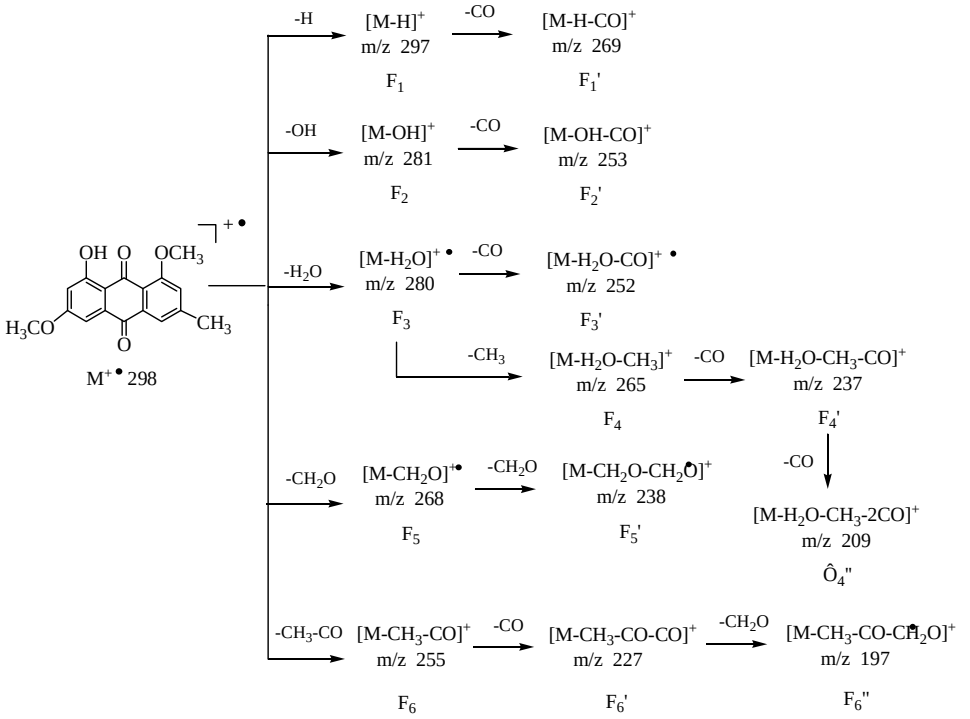
$[M\text{-}CO\text{-}CH_2O]^+$ ion with m/z 226 leads to the pairing of the F_7 $[M\text{-}CO\text{-}CH_2O\text{-}CO]^+$ ion with m/z 198 (I = 5%).

1-Hydroxy-6,8-dimethoxy-3-methyl-9,10-anthraquinone (3). The replacement of one α-hydroxyl group with an electron-donor methoxy group does not affect the intensity of MI of compound (3), which is I = 100% (table 1), but sharply decreases its stability - W_{mi} = 11.9% (table 2). Due to the diversity of the MI decay channels, in the mass spectrum, multiple peaks of fragment ions are observed.

For 1-methoxyanthraquinone, the main direction of the mass-spectral decomposition of MI is the elimination of the carbon monoxide molecule to form the ion fragment F_1 (m/z 210), from which the methyl radical and CO, as well as the separation of H, HCO and CH_2O, $[M\text{-}H]^+$, $[M\text{-}HCO]^+$ and $[M\text{-}CH_2O]^{+\bullet}$ respectively [14]. The replacement of one α-hydroxyl group with a methoxy group in the case of the derivative (3) sharply changes the picture of the MI decay, in comparison with the mass spectrum of the physcion (2). In the case of mass-spectrometric fragmentation of 1-hydroxy-6,8-dimethoxy-3-methyl-9,10-anthraquinone (3), primary MI decays occur as a result of the splitting off of the hydrogen atom, OH, H_2O, CH_2O and the group of $COCH_3$ atoms, of the primary fragment ions F_1 $[M\text{-}H]^+$ with m/z 297, F_2 $[M\text{-}OH]^+$ with m/z 281, F_3 $[M\text{-}H_2O]^{+\bullet}$ c m/z 280, F_5 $[M\text{-}CH_2O]^{+\bullet}$ with m/z 268, F_6 $[M\text{-}CO\text{-}CH_3]^+$ with m/z 255 (scheme 3). The most intense peaks in the spectrum are due to the release of the water molecule - F_3 $[M\text{-}H_2O]^{+\bullet}$ with m/z 280 (I = 49%) and OH- F_2 $[M\text{-}OH]^+$ with m/z 281 (I = 22 %) (table 1).

Further, the ions F_1-F_3 and F_6 eliminate the CO molecule, with the formation of the secondary fragment ions F_1' $[M\text{-}H\text{-}CO]^+$ with m/z 269, F_2' $[M\text{-}OH\text{-}CO]^+$ with m/z 253, F_3' $[M\text{-}H_2O\text{-}CO]^{+\bullet}$ with m/z 252 and F_6' $[M\text{-}CO\text{-}CH_3\text{-}CO]^+$ with m/z 227, and in the case of the F_5 ion $[M\text{-}CH_2O]^{+\bullet}$ c m/z 268, another formyl group of CH_2O eliminates to form the radical cation F_5' $[M\text{-}CH_2O\text{-}CH_2O]^{+\bullet}$ with m/z 238. The most intense peaks correspond to the ions F_1' $[M\text{-}H\text{-}CO]^+$ with m/z = 269 (I = 26%), F_2' $[M\text{-}OH\text{-}CO]^+$ with m/z 253 (I = 19%) and F_3' $[M\text{-}H_2O\text{-}CO]^{+\bullet}$ c m/z 252 (I = 70%) (table 1). The fragment ion F_3 can also consecutively lose the methyl group and carbon monoxide molecules to form the F_4 ion $[M\text{-}H_2O\text{-}CH_3]^+$ with m/z 265 (I=15%), F_4' $[M\text{-}H_2O\text{-}CH_3\text{-}CO]^{+\bullet}$ with m/z 237 (I = 27%) and F_4'' $[M\text{-}H_2O\text{-}CH_3\text{-}2CO]^{+\bullet}$ with m/z 209 (I = 13%). The secondary ion F_6' $[M\text{-}CO\text{-}CH_3\text{-}CO]^+$ with m/z 227 due to the loss of the formyl group CH_2O forms the fragment ion F_6'' $[M\text{-}CO\text{-}CH_3\text{-}CO\text{-}CH_2O]^+$ with m/z 197 (I = 13%).

Thus, an analysis of the mass-spectral decomposition of MI of the group of derivatives considered showed that if the decomposition of 1,8-dihydroxyanthraquinone (1) is associated with the successive elimination of two carbon monoxide molecules to form the cation of dihydroxyfluorenone with m/z 212 (I = 15%) and dihydroxybiphenylene F_2 $[M\text{-}CO\text{-}CO]^{+\bullet}$ with m/z 184 (I = 16%), the fragmentation of the derivatives (2,3) depends on the position of the substituent in the anthraquinone system. In the case of mass-spectrometric decomposition of emodin (1), in the region of high mass numbers, several low-intensity peaks of the



Scheme 3 – Fragmentation of a molecular ion
1-hydroxy-6,8-dimethoxy-3-methyl-9,10-anthraquinone (3)

characteristic ions associated with the initial decay of MI can be identified as a result of the splitting off of the hydrogen atom, CH_3, OH and CO with formation of primary fragment ions F_1 $[M-H]^+$, F_2 $[M-CH_3]^+$, F_3 $[M-OH]^+$ and F_4 $[M-CO]^{+\bullet}$. The main direction of the decomposition of stable MI of emodin (1) (I = 100%, W_{mi} = 35.2%) is the consecutive elimination of CO molecules by the "anthraquinone" type with the formation of the radical cation 1,6,8-trihydroxy-3-methylfluorenone F_4 $[M-CO]^{+\bullet}$ with m/z 242 (I = 14%) and 1,6,8-trihydroxy-3-methylbiphenylene F_4' $[M-CO-CO]^{+\bullet}$ with m/z 214 (I = 7%). MI physcion (2) decays with EI mainly by sequential ejection from MI of a hydrogen atom and two CO molecules, and for a dimethoxy derivative (3), the underlying direction of decomposition is the consecutive loss of H_2O and CO molecules. The replacement of one or two hydroxyl groups by the methoxy group in compounds (2,3) causes the appearance of yet another direction of fragmentation associated with the elimination of the formyl radical CH_2O. As in the case of the previously considered methoxy derivatives of 9,10-anthraquinone [14, 17], substitution of the α-hydroxyl group by the methoxy group reduces the stability of MI to ionization by electrons. So, if the stability of the MI physcion (2) is W_{mi} = 40.6%, then its α-methyl ester (3) - W_{mi} = 11.9% (Table 2). The low stability of the MI compound (3) promotes the diversity of the MI decay channels, which is reflected in the mass

spectrum of the derivative by the presence of a large number of peaks of fragment ions.

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Резюме

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ЭМОДИН ЖӘНЕ ОНЫҢ МЕТИЛ ЭФИРЛЕРІНІҢ МОЛЕКУЛАЛЫҚ ИОНДАРЫНЫҢ МАСС-СПЕКТРОМЕТРИЯЛЫҚ ФРАГМЕНТАЦИЯСЫНЫҢ СИПАТТАМАСЫ

Зерттеу жұмыс 1,6,8-үшгидрокси-3-метил-9,10-антрахинонның (эмодиннің) және оның кейбір метил эфирлерінің масс-спектрометрияы зерттеуіне және молекулярлық иондарының масс-спектрометралды фрагментациясының салыстырмалы талдауына арналған. Қарастырылған қосылыстар топтарына МИ қарқынды шыңы сипатты және оның тұрақтылығы $W_{ми}$=11,9÷40,6% құбылту мөлшерінде екені көрсетілген. Молекулярлық иондардың (МИ) ионизациялау электрондармен (ИЭ) мықтылығына орынбасардың әсері қаралған және олардың масс-спектрометралды ыдырау кестесі ұсынылған. Туындылардың фрагментациясы орынбасардың антрахинон ситемасында орналасқан орнына тәуелділігі көргелтілген. Эмодин молекуласының МИ бастапқы фрагментациясы сутегі атомы, CH_3, OH және CO бөліну нәтижесінде жүреді, ал оның метокситуындылары және формил радикалының CH_2O элиминирленуі сипатты.

Түйін сөздер: масс-спектр, молекулярлық ион, фрагментациялау, электрондық ионизациялау, элиминирлеу, 9,10-антрахинон туындылары.

Резюме

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ХАРАКТЕРИСТИКА МАСС-СПЕКТРОМЕТРИЧЕСКОЙ ФРАГМЕНТАЦИИ МОЛЕКУЛЯРНЫХ ИОНОВ ЭМОДИНА И ЕГО МЕТИЛОВЫХ ЭФИРОВ

Работа посвящена масс-спектральному исследованию и сравнительному анализу масс-спектральной фрагментации молекулярных ионов 1,6,8-дигидрокси-3-метил-9,10-антрахинона (эмодина) и его метиловых эфиров. Показано, что для рассматриваемой группы соединений характерен интенсивный пик МИ, а его стабильность варьируется в пределах 11,9÷40,6 %. Рассмотрено влияние заместителя на устойчивость молекулярных ионов к ионизации электронами и предложены схемы их масс-спектрального распада. Показано, что фрагментация производных зависит от расположения заместителя в антрахиноновой системе. Первоначальная фрагментация МИ молекулы эмодина происходит в результате отщепления атома водорода, CH_3, OH и CO, а для его метоксипроизводных характерно также элиминирование формильного радикала CH_2O.

Ключевые слова: масс-спектр, молекулярный ион, фрагментация, электронная ионизация, элиминирование, производные 9,10-антрахинона.