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## The Study of the Composition of High-Molecular Fatty Acids of the Tyulgan Brown Coal Bitumen

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### Abstract

Bitumen extraction is a promising project of brown coal processing. It raises the task of identifying and quantifying the components of recoverable bitumen. In this paper, the method of gas chromatography–mass spectrometry is used to solve this problem. The composition of high-molecular fatty acids of brown coal bitumen from the Tyulgan deposit was studied taking into account the patterns of molecular ion fragmentation for the butyl esters of fatty carboxylic acids under ionization by electron impact. The ethanol extract fraction was investigated. The NIST-11 Database and ChemStation D.01.02 software were used to identify the butyl esters of fatty carboxylic acids.

**Keywords:** gas chromatography–mass spectrometry, recoverable bitumen, butyl esters of carboxylic acids

### INTRODUCTION

Development of the methods for isolation of the components of bitumen extracts [1] implied identification of the composition and determination of the quantitative content of all components in a complex mixture of organic substances many of which have not been studied yet. The formulated problem may be solved by means of gas chromatography – mass spectrometry. However, the presence of non-investigated substances hinders the identification of the complete composition of extractable components because the corresponding information is absent from the databases of mass spectra [2]. In this connection, to carry out successful identification, it is necessary to reveal the general regularities of fragmentation of separate classes of compounds extracted from bitumen, which will allow us to establish the chemical nature of non-identified substances from the mass spectra. The substances assigned to the group of carboxylic acids and alkanes may

be related to the most representative fraction of the components of bitumen extracts [1]. Carboxylic acids extracted from bitumen are the products of decomposition of natural esters and may be used to obtain both technical and biologically active components. The presence of the free carboxyl group in carboxylic acids defines their high polarity, and in the gas chromatographic analysis this feature promotes the sorption of the substances at the inter-phase boundary, the formation of associates in the gas phase, which causes asymmetry of chromatographic peaks, strong and often irreversible adsorption of acids [3]. In this connection, it is usual to determine carboxylic acids in the form of derivatives – esters. For this purpose, esterification is carried out using different methods [4] obtaining esters based on different alcohols [2].

The goal of the present work was to reveal the regularities of fragmentation of the butyl esters of high-molecular fatty acids to identify butylated components of bitumen extracts on the basis of their mass spectra.

## EXPERIMENTAL

Investigation of the regularities of fragmentation of butyl esters of high-molecular fatty acids was carried out using the samples of the extracts of brown coal bitumen esterified with butyl alcohol. Brown coal from the Tyulgan deposit of the South Ural basin was involved. Fraction separation was carried out by means of adsorption column chromatography on silica gel [1]. The choice of butanol as the reagent for esterification of high-molecular carboxylic acids was made by the authors of [1] and is associated with its better extracting properties. In addition, with butanol as an esterifying agent, the probability of the losses of solvent and low-molecular components of the extract decreases due to the lower volatility of butyl esters [5]. The procedure of obtaining extracts was described in [1]. Analysis of the component composition of butylated extracts was carried out by means of gas chromatography – mass spectrometry using an Agilent 6890N chromatograph (USA) with a capillary column HP-5ms under programmable rise of column temperature from 50 to 280 °C at a rate of 5 °C/min. Exposure at 50 °C lasted for 3 min, at 280 °C for 60 min. Evaporator temperature was 290 °C, flow partition ratio was 50 : 1, the flow rate of helium as the carrier gas was 1 mL/min, the sample volume was 5.0 mm. The content of individual compounds was determined from the full ion current of the mass-selective detector Agilent 5973 (USA). The temperature of the ion source of the mass detector was 230 °C, the range of molecular mass (MM) scanning was from 15 to 550 Da, with the accuracy of 0.1 Da, at the scanning frequency of 2.76 scans/s. Identification of the component composition of the samples under investigation was carried out using the electronic spectral library NIST-11 and ChemStation D.01.02 software. Analysis of the structure of non-identified components related to butyl esters was carried out over the experimental mass spectra. Only chromatographic peaks that had passed the test for homogeneity were considered.

## RESULTS AND DISCUSSION

Identification of the components of butanol-esterified fractions of the extracts of brown coal bitumen with the help of the library of mass spectra allowed us to determine only some esters, such as butyl myristate, butyl oleate and butyl

esters of pentadecanoic, hexadecanoic, octadecanoic acids. The mass spectrum of the butyl ester of hexadecanoic acid is shown in Fig. 1, c in comparison with the mass spectrum of the component of ethanol extract. The high degree of coincidence of these mass spectra allows us to state that esterification of the acids according to the chosen procedure took place successfully. However, identification of a substantial part of chromatographic peaks is impossible because the entire diversity of structural isomers of the substances under investigation is not present in the library. In addition, butyl alcohol as esterifying reagent is used not frequently because of the opinion that the spectra of ethyl and other esters are more complicated than the spectra of methyl esters [7]. For this reason, the majority of esters present in the library are methyl esters. However, as we will demonstrate below, the mass spectra of the butyl esters of higher carboxylic acids not only possess a set of characteristic peaks distinguishing them from other classes of compounds and from the esters of other alkoxides but also allow determination of the molecular masses of carboxylic acids comprising them, on the basis of a characteristic peak of the ion of protonated carboxylic acid.

To establish the regularities of fragmentation of butyl esters of fatty acids with the general formula  $\text{RCOOBu}$  (here  $\text{Bu} = \text{C}_4\text{H}_9$ ), we analyzed their known mass spectra [9] and the data of the electronic library NIST-11. The mass spectra of butyl esters of decanoic and hexadecanoic acids are presented in Fig. 1, a, b as examples. As expected, one can see that the intensities of the peaks of molecular ions  $[\text{RCOOBu}]^{+\bullet}$  are not high, but they are necessarily present in the mass spectra; their fragmentation occurs independently of the length of the hydrocarbon part (R) of the acid, with the generation of the fragment with mass  $m = 55$  Da. The highest intensity in the mass spectra of butyl esters is that of the ion with  $m/z = 56$ . The presence of a long hydrocarbon chain (with more than 10 carbon atoms) in the acid residue of the esters under study is indicated by the peaks of homologous ions in the mass spectra. Two series of peaks corresponding to the rupture of C–C bonds in the middle of the hydrocarbon chain are clearly detected: at  $m/z = 29, 43, 57, \dots$  – alkane series, and at  $m/z = 27, 41, 55, \dots$  – a less intensive alkene series. If an acid comprising an ester under investigation is unsaturated, the intensity of alkene series exceeds the intensity of the alkane series [8]. Significant and

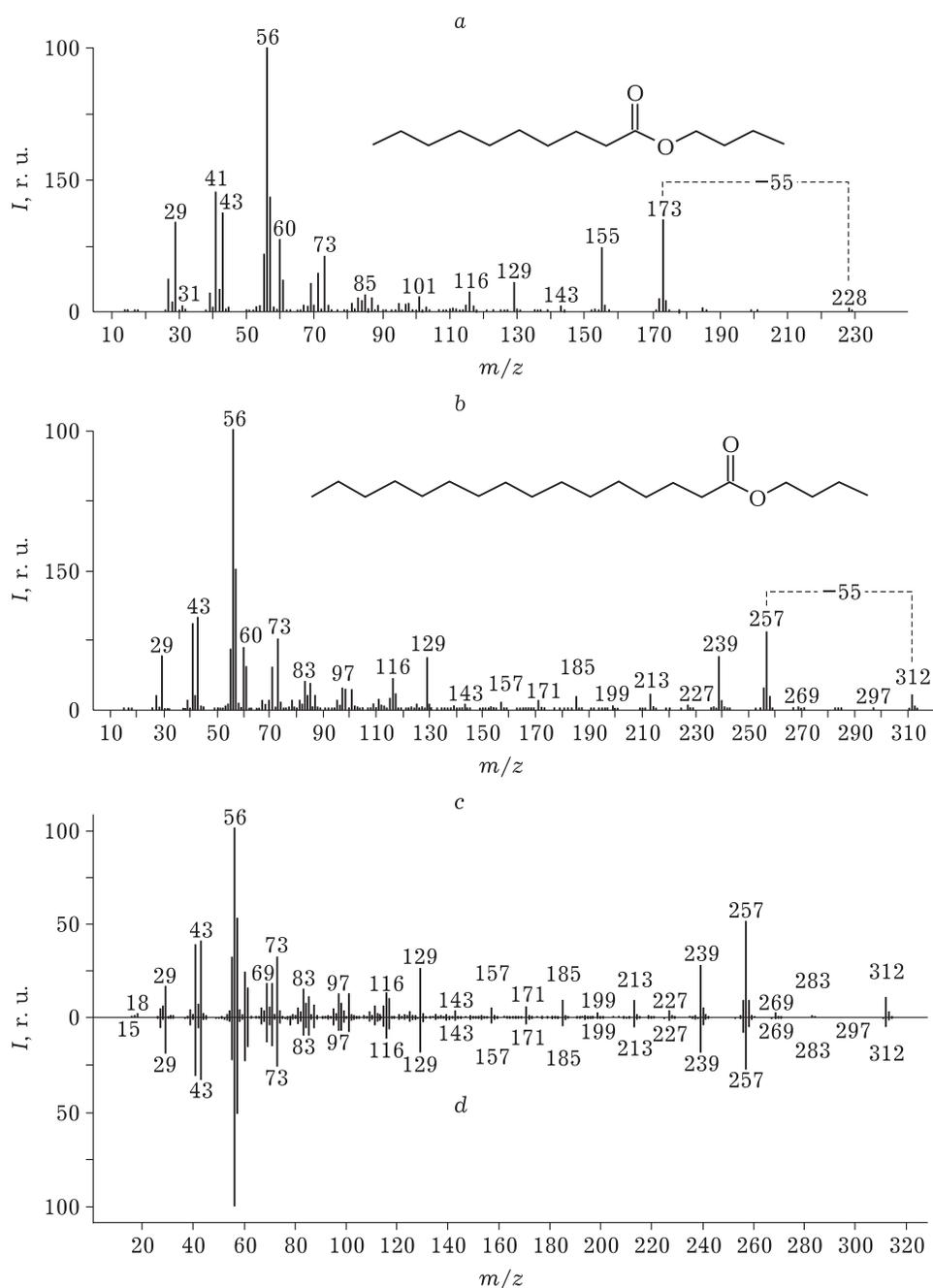


Fig. 1. Mass spectra of butyl esters of: decanoic (a) and hexadecanoic (b) acids according to the library of mass spectra NIST-11, and a comparison of the mass spectrum of the component with  $t_R = 38.23$  min (c) with the spectrum of the butyl ester of hexadecanoic acid from the Database (d). Here and in Fig. 2:  $t_R$  is retention time.

common for butyl esters are peaks with  $m/z = 60$  and  $73$ . The mass spectra of butyl esters are distinguished by the positions of molecular ions (MI) and ions formed as a result of MI fragmentation.

The revealed regularities were used to identify unknown components of butylated extracts. For this purpose, we considered the experimental spectra meeting two requirements at the same time: the most intensive peak in the mass spectrum

is detected at  $m/z = 56$ , and there is a peak pointing to the decomposition of MI with the elimination of a fragment, with  $m = 55$  Da. Characteristic spectra meeting the chosen requirements are shown in Fig. 2. The regions of chromatogram illustrating the homogeneity of the peaks of components under analysis are shown in the same Figure, too.

Relying on the literature data on the directions of fragmentation of the esters of carboxylic

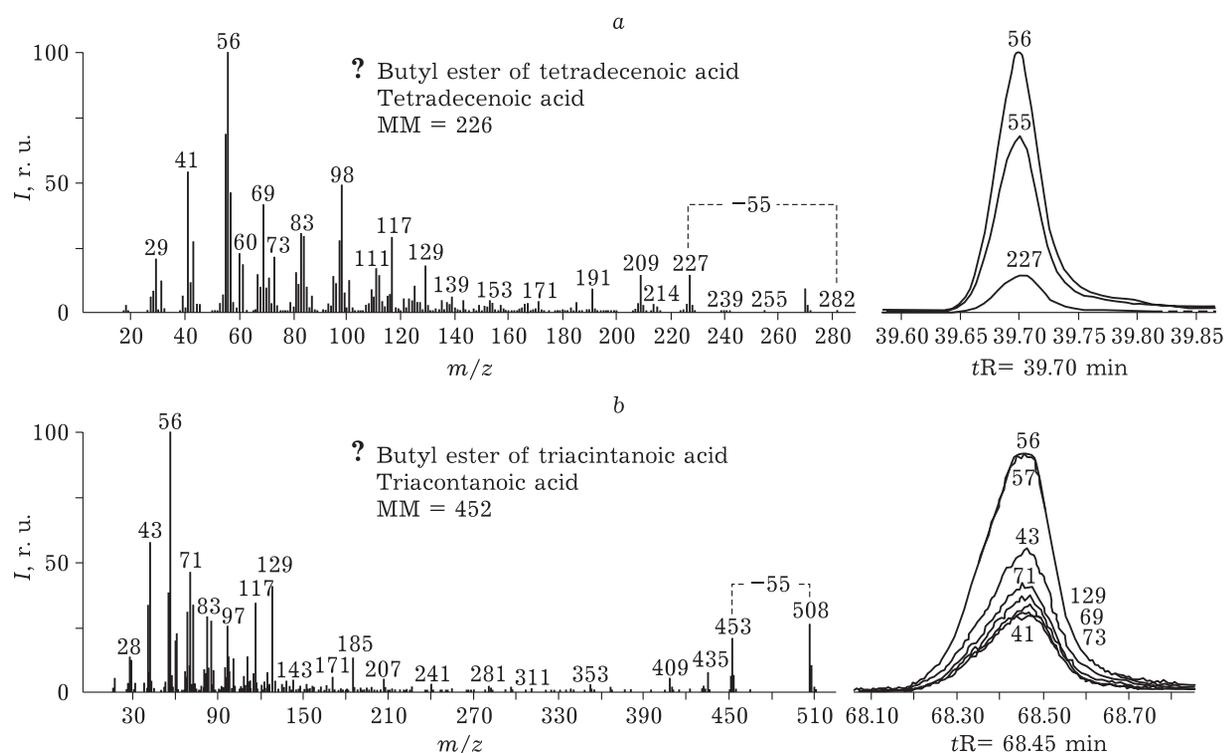


Fig. 2. Mass spectra of non-identified components with  $tR = 39.70$  (a) and  $68.45$  min (b) and the corresponding regions of the chromatogram (experimental data). For designations, see Fig. 1.

acids [7] and the analysis of the known mass spectra and those recorded in the present work, we may describe the major directions followed by the fragmentation of MI of the butyl esters of high-molecular carboxylic acids with the scheme shown in Fig. 3.

Taking into account this fragmentation scheme, one may conclude that the most probable direction of the decomposition of MI of butyl esters is  $\alpha$ - and  $\beta$ -decomposition at C–O and O–C bonds, which is exhibited in mass spectra as an intense peak at  $m/z = 56$  and the peak of  $[\text{BuO}]^+$  with  $m/z = 73$ . Additional decomposition participated by the alkoxide group, involving the detachment of alkyl from the alcohol part of the molecule [6, 7], manifests itself in the mass spectra under investigation in the products of  $\beta$ -decomposition of the MI of the ester with the elimination of alkyl  $\text{C}_4\text{H}_7^+$  with a mass of  $m = 55$  Da and the  $[\text{RCOOH}_2]^+$  ion, which is the ion of protonated carboxylic acid. The result of McLafferty rearrangement is the ion with  $m/z = 116$ . The ion of protonated acid  $[\text{RCOOH}_2]^+$  undergoes similar rearrangement with the generation of the ion with  $m/z = 60$ , which is characteristic of the mass spectra of all carboxylic acids [8]. The observed alkane series of ions with  $m/z = 29, 43,$

$57, \dots$  is due to the rupture of C–C bonds in the alkyl chain of the acid residue. The mass spectra of butyl esters contain a series of homologous ions ( $m/z = 129, 143, 157, 171, 185, 199, 213, \dots$ ) connected with the products of nonspecific migrations of H atoms, as described for the methyl esters [2]. In the case of butyl esters of unsaturated fatty acids (see Fig. 2, a), all above-described fragmentary ions are present in the mass spectra, which is the evidence of the general regularities of fragmentation of the esters of saturated and unsaturated fatty acids. The difference of the mass spectra of the esters of unsaturated acids manifests itself in the higher intensity of the peaks of alkene series.

For comparison, the normalized intensities of ion peaks in mass spectra of known butyl esters and those under investigation are presented in Table 1.

One can see that the MM of the acid comprising an ester may be determined from the  $m/z$  value of the MI, which is equal to the MM of the ester and the mass of the ion of protonated carboxylic acid, detected after the decomposition of the MI of butyl ester with the elimination of alkyl  $\text{C}_4\text{H}_7^+$  with  $m = 55$  Da. For this purpose, it is sufficient to reduce the  $m/z$  value of the ion of protonated carboxylic acid by 1. A comparison of



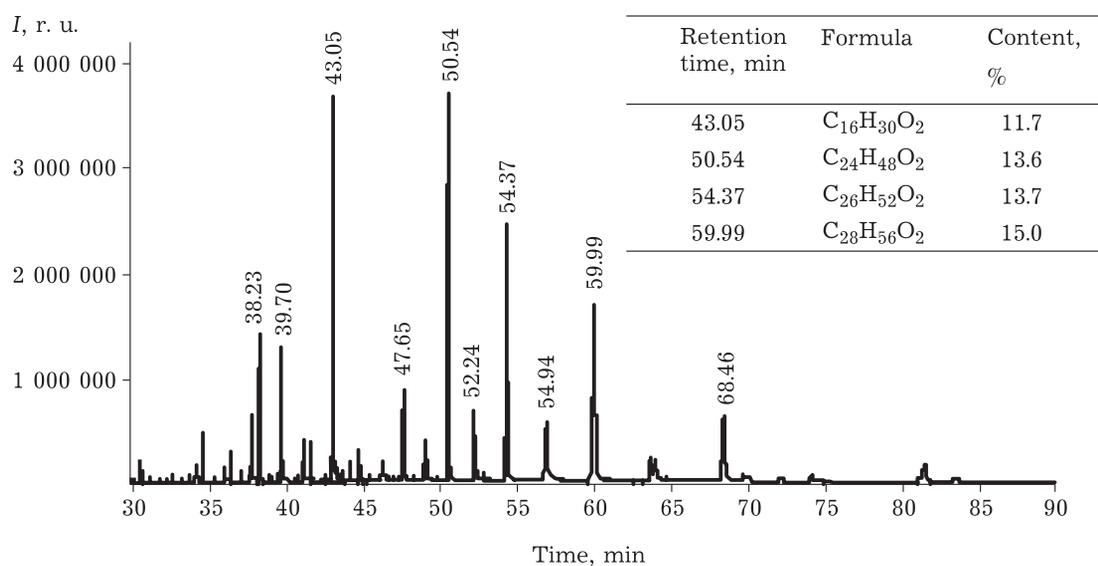


Fig. 4. Chromatogram of the butylated fraction of the ethanol extract of bitumen.

TABLE 2

Chromatographic characteristics and result of identification of the components of ethanol extract of bitumen

Retention time (t <sub>R</sub> ), min	Component	Formula	Content in ethanol extract, %	Calculated MM of acid	MI in mass spectrum, Da
34.56	Butyl ester of tetradecanoic (myristinic) acid <sup>a</sup>	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	1.51	—	—
36.42	Butyl ester of pentadecanoic acid <sup>a</sup>	C <sub>19</sub> H <sub>38</sub> O <sub>2</sub>	0.87	—	—
37.75	Butyl ester of hexadecenoic acid 16:9 <sup>a</sup>	C <sub>20</sub> H <sub>38</sub> O <sub>2</sub>	1.75	—	—
38.23	Butyl ester of hexadecanoic acid <sup>a</sup>	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	3.59	—	—
39.70	Butyl ester of tetradecenoic acid <sup>b</sup>	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	3.87	226	282
41.61	Butyl ester of octadecenoic (palmitic) acid <sup>a</sup>	C <sub>22</sub> H <sub>44</sub> O <sub>2</sub>	0.98	—	—
43.05	Butyl ester of hexadecenoic acid <sup>b</sup>	C <sub>20</sub> H <sub>38</sub> O <sub>2</sub>	11.72	254	310
44.74	Butyl ester of eicosanoic acid <sup>b</sup>	C <sub>24</sub> H <sub>48</sub> O <sub>2</sub>	0.81	312	368
47.65	Butyl ester of docosanoic acid <sup>b</sup>	C <sub>26</sub> H <sub>52</sub> O <sub>2</sub>	2.42	340	396
49.03	Butyl ester of tricosanoic acid <sup>b</sup>	C <sub>27</sub> H <sub>54</sub> O <sub>2</sub>	0.01	354	410
50.54	Butyl ester of tetracosanoic <sup>b</sup>	C <sub>28</sub> H <sub>56</sub> O <sub>2</sub>	13.65	368	424
52.25	Butyl ester of pentacosanoic acid <sup>b</sup>	C <sub>29</sub> H <sub>58</sub> O <sub>2</sub>	2.88	382	438
54.37	Butyl ester of hexacosanoic acid <sup>b</sup>	C <sub>30</sub> H <sub>60</sub> O <sub>2</sub>	13.67	396	452
56.94	Butyl ester of heptacosanoic acid <sup>b</sup>	C <sub>31</sub> H <sub>62</sub> O <sub>2</sub>	5.77	410	466
59.99	Butyl ester of octacosanoic acid <sup>b</sup>	C <sub>32</sub> H <sub>64</sub> O <sub>2</sub>	15.03	424	480
63.71	Butyl ester of nonacosanoic acid <sup>b</sup>	C <sub>33</sub> H <sub>66</sub> O <sub>2</sub>	2.06	438	494
63.97	Butyl ester of nonacosanoic acid <sup>b</sup>	C <sub>33</sub> H <sub>66</sub> O <sub>2</sub>	1.51	438	494
68.46	Butyl ester of triacontanoic acid	C <sub>34</sub> H <sub>68</sub> O <sub>2</sub>	7.93	452	508
74.18	Butyl ester of tetracontanoic acid <sup>b</sup>	C <sub>35</sub> H <sub>70</sub> O <sub>2</sub>	0.86	466	522
81.42	Butyl ester of pentacontanoic acid <sup>b</sup>	C <sub>36</sub> H <sub>72</sub> O <sub>2</sub>	2.85	480	536

<sup>a</sup> Identification in ChemStation software over the NIST-11 Database of mass spectra.<sup>b</sup> Identification on the basis of MM determined from the mass spectrum.

the known mass spectra of butyl esters and the chosen mass spectra, according to the formulated requirements, allowed us to identify unknown mass spectra of butyl esters relying on the MM of carboxylic acids, the latter values being determined from the mass spectra.

A characteristic chromatogram of the butylated fraction of bitumen extract is shown in Fig. 4, with the indication of retention times (*t*R) for the peaks of components identified as butyl esters of fatty acids (Table 2), with the data on the content of the most representative components.

It follows from the data presented in Fig. 4 and in Table 2 that the most intensive peaks belong to butyl esters of carboxylic acids with the number of carbon atoms C<sub>16</sub>, C<sub>24</sub>, C<sub>26</sub>, C<sub>28</sub>. The absence of a regularity for *t*R in the sequence C<sub>24</sub>, C<sub>26</sub>, C<sub>28</sub> points to the fact that acids are not homologous representatives of a series with the same type of structure. The studies aimed at the establishment of the structure of carboxylic acids under investigation will be continued.

## CONCLUSION

A number of fatty carboxylic acids (including tetradecenoic, octadecenoic, hexadecenoic, eicosanoic, docosanoic, tricosanoic, tetracosanoic, pentacosanoic, hexacosanoic, heptacosanoic, octacosanoic, nonacosanoic, triacontanoic, tetracontanoic, pentacontanoic) in the form of their butyl esters were identified in the ethyl extract of the bitumen of brown coal from the Tyulgan deposit. Taking into account the regularities of fragmentation of the butyl esters of fatty acids, we may conclude that along with fragmentation mechanisms common for the esters of carboxylic acids, the mass spectra of butyl esters contain the peaks that are characteristic only of these esters. The major peak belongs to the fragment C<sub>4</sub>H<sub>8</sub> with *m/z* = 56. The molecular ion of the ester decomposes with the elimination of alkyl C<sub>4</sub>H<sub>7</sub><sup>•</sup> with mass 55 Da, and the mass spectrum contains the ion of protonated carboxylic acid [RCOOH<sub>2</sub>]<sup>+</sup>, which is convenient for acid identification to be carried out. The formation of the protonated ion

of carboxylic acid during fragmentation under the electron impact is characteristic of butyl and propyl esters. To identify the structure, it is necessary to decrease *m/z* of the fragment [RCOOH<sub>2</sub>]<sup>+</sup> by 1, which results in the value equal to the MM of the carboxylic acid.

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