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ANALYSIS OF SOME β -BRANCHED PRIMARY ALCOHOLS AND α -BRANCHED CARBOXYLIC ACIDS BY COMBINED CAPILLARY GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

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SUMMARY

The application of a combined system of capillary chromatography and mass spectrometry for the separation and identification of C_6 - C_{10} β -branched primary alcohols and C_{11} - C_{17} and C_{19} α -branched carboxylic acids as their methyl esters is described.

The retention indices were measured of α -branched carboxylic acid methyl esters and β -branched alcohols on polyphenyl ether and polypropylene glycol, respectively.

INTRODUCTION

The coupling of gas chromatography (GC) with mass spectrometry (MS) provides a sensitive and convenient tool for the separation and identification of complex mixtures¹. The use of a light carrier gas (hydrogen or helium) on a capillary column excludes the need for a separator in the GC-MS system for the analysis of complex organic mixtures.

The GC-MS system was used in this work for the analysis of C_6 - C_{10} β -branched primary alcohols. Mass spectra of certain representatives of this class of compounds (2-methylpentan-1-ol; 2-ethylbutan-1-ol and 2-ethylhexan-1-ol) were reported by Friedel *et al.*².

C_{11} - C_{17} and C_{19} α -branched carboxylic acids containing tertiary and quaternary carbon atoms occur as complex mixtures or isomers the complete compositions of which have not previously been investigated.

The separation and analysis of C_6 - C_{11} α -branched carboxylic acids by capillary chromatography have been described elsewhere^{3,4}.

* Translated by A. Kofman, Kiev, U.S.S.R.

The purpose of this work was the separation and identification of C_{11} - C_{17} and C_{19} α -branched acids as their methyl esters by capillary chromatography.

EXPERIMENTAL AND RESULTS

Carboxylic acids synthesized according to Koch contain tertiary and quaternary carbon atoms in the α -position to the carboxylic group^{5,6}. The reaction is accompanied by the isomerization of the carbon skeleton, which gives rise to a complex mixture of isomeric acids, the number of which depends upon the number of carbon atoms in the α -olefin used⁶.

By the reduction of α -branched carboxylic acid methyl esters with lithium aluminium hydride, β -branched primary alcohols were prepared with an isomeric composition identical with that of the parent acids, as expected.

The work has been carried out with a Tsvet-4 gas chromatograph equipped with a flame ionization detector. A capillary column (50 m \times 0.2 mm I.D.) was coated by the dynamic method with polypropylene glycol (PPG) and polyphenyl ether (PPE) for the separation of iso-alcohols and iso-acids, respectively. The number

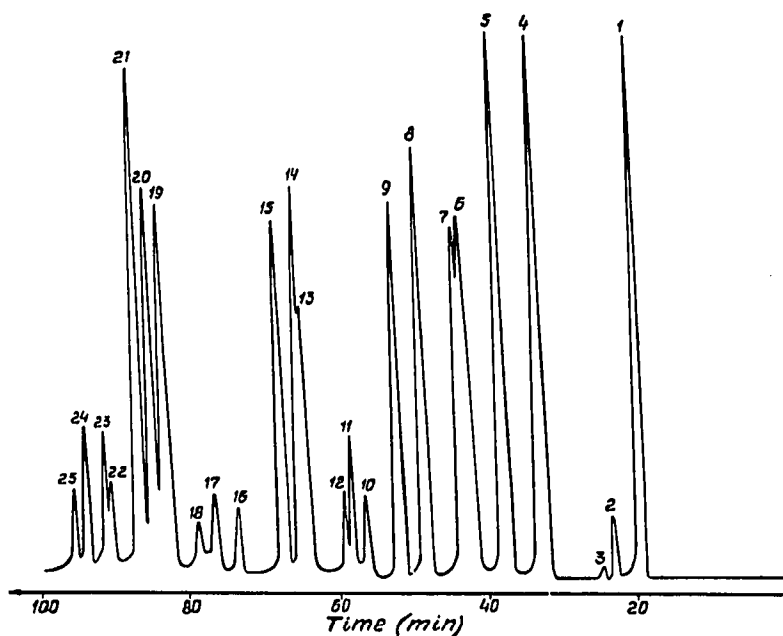


Fig. 1. Chromatogram of C_6 - C_{10} β -branched primary alcohols. 1 = 2,2-Dimethylbutan-1-ol; 2 = 2-ethylbutan-1-ol; 3 = 2-methylpentan-1-ol; 4 = 2,2-dimethylpentan-1-ol; 5 = 2-methyl-2-ethylbutan-1-ol; 6 = 2-ethylpentan-1-ol; 7 = 2-methylhexan-1-ol; 8 = 2,2-dimethylhexan-1-ol; 9 = 2-methyl-2-ethylpentan-1-ol; 10 = 2-propylpentan-1-ol; 11 = 2-ethylhexan-1-ol; 12 = 2-methylheptan-1-ol; 13 = 2-methyl-2-propylpentan-1-ol; 14 = 2,2-dimethylheptan-1-ol; 15 = 2-methyl-2-ethylhexan-1-ol; 16 = 2-propylhexan-1-ol; 17 = 2-ethylhexan-1-ol; 18 = 2-methyloctan-1-ol; 19 = 2-methyl-2-propylhexan-1-ol; 20 = 2,2-dimethyloctan-1-ol; 21 = 2-methyl-2-ethylheptan-1-ol; 22 = 2-butylhexan-1-ol; 23 = 2-propylheptan-1-ol; 24 = 2-ethyloctan-1-ol; 25 = 2-methylnonan-1-ol.

of theoretical plates for 2,2-dimethylhexan-1-ol on PPG and the methyl ester of 4-methyldodecane-4-carboxylic acid on PPE was 40,000 in both instances.

β -Branched alcohols were identified using a combined Tsvet-4 gas chromatograph-MI-1305 mass spectrometer system⁷. The composition of α -branched acids was determined chromatographically.

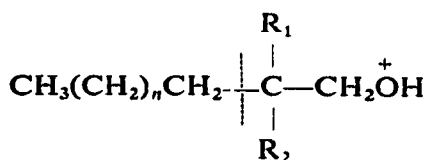
The chromatographic separation of the alcohols was performed on a capillary column with PPG at 115° and 130° for C₆-C₇ and C₈-C₁₀ iso-alcohols, respectively, with pressure programming from 0.28 to 0.55 atm (Fig. 1). Retention indices were measured at 130° and a flow-rate of carrier gas (nitrogen) of 1 ml/min. α -Branched C₁₁-C₁₅ carboxylic acids were separated at 160° and a nitrogen flow-rate of 2.5 ml/min. Acids with 16, 17 and 19 carbons were prepared as separate fractions from individual α -olefins. Their chromatographic separation was performed at 180° and 200° for the C₁₆ and C₁₇ acids, respectively, and a nitrogen flow-rate of 1.3 ml/min.

Separation and identification of β -branched primary alcohols

The chromatogram of C₆-C₁₀ β -branched primary alcohols is shown in Fig. 1. The components were identified by full mass spectra recorded by introducing the substance into the ion source at its maximum concentration during the peak elution.

Chromatographic peak identification was based on general rules of dissociative ionization of linear and branched alcohols^{8,9}. The most characteristic regularities relating mass spectra to the structure of corresponding isomers were used. Molecular weight (molecular ion peaks are not found in the mass spectra of C₆-C₁₀ alcohols) was determined by the peaks of (M+18)⁺ ions resulting from the removal of a water molecule from the molecular ion.

The presence of branching in the β -position as well as the types of alkyl substituents were determined by the peaks of oxygen-containing ions, which are due to the rupture of a C-C bond in a position β to the hydroxyl group:



In analyzing the fractions of iso-alcohols with the same number of carbon atoms, the composition of oxygen-containing ions and the type of alkyl substituent were determined by characteristic peaks in the mass spectrum corresponding to each type of isomers.

As an example, Table I shows the types of isomers of C₇ β -branched alcohols and their mass spectral characteristics.

When the mass spectral characteristics of isomers of a certain molecular weight were identical, the chromatographic peaks were identified with regard to the order of elution of isomers, this being related to the branching in a molecule. For this purpose, a standard 2,2-dimethylpentan-1-ol was synthesized which has been found to elute prior to 2-ethylpentan-1-ol (oxygen-containing ions with mass assignment 73 are characteristic in the mass spectra of both isomers).

TABLE I

TYPES OF ISOMERS OF C_7 β -BRANCHED ALCOHOLS AND THEIR MASS SPECTRAL CHARACTERISTICS

Characteristic ion	Mass number	Structural formula of isomer
C_3H_9O	73	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-(\text{CH}_2)_2-\text{C}-\text{CH}_2\text{OH} \end{array}$
$C_5H_{11}O$	87	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \\ \\ \text{CH}_3-(\text{CH}_2)-\text{C}-\text{CH}_2\text{OH} \end{array}$
C_4H_9O	73	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{CH}_3-(\text{CH}_2)_2-\text{CH}-\text{CH}_2\text{OH} \end{array}$
C_3H_7O	59	$\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{CH}_3-(\text{CH}_2)-\text{CH}-\text{CH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$

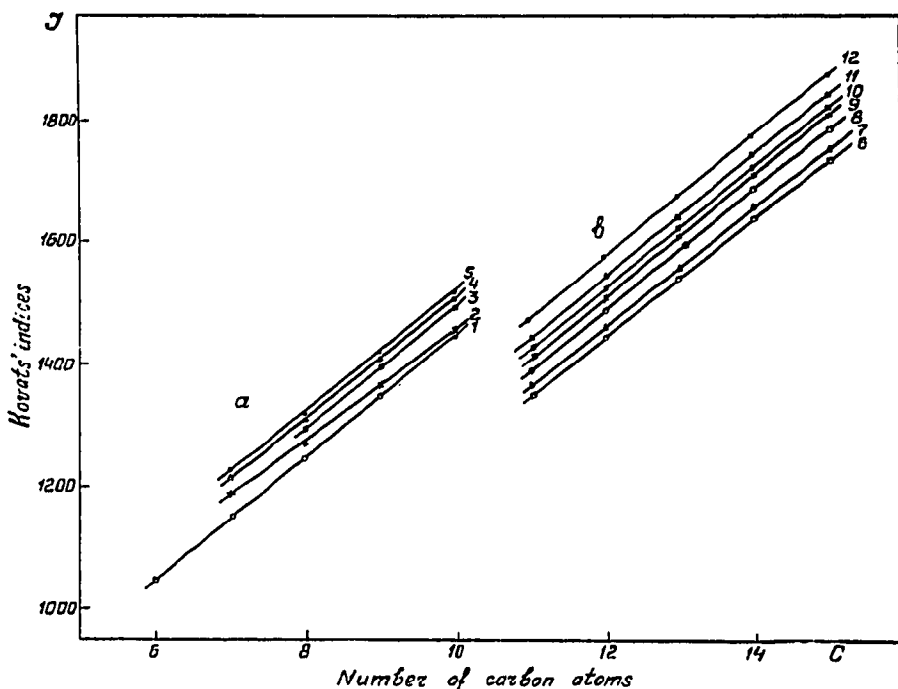


Fig. 2. Relationship between Kovats' retention indices and number of carbon atoms for homologous series of (a) alcohols and (b) acids. Alcohols: 1 = 2,2-dimethyl-; 2 = 2-methyl-2-ethyl-; 3 = 2-propyl-; 4 = 2-ethyl-; 5 = 2-methylalkan-1-ol. Acids: 6 = α -methyl- α -butyl-; 7 = α -methyl- α -propyl-; 8 = α,α -dimethyl-; 9 = α -butyl-; 10 = α -propyl-; 11 = α -ethyl-; 12 = α -methylalkanoic acid.

TABLE II

RETENTION INDICES OF C₆-C₁₀ β -BRANCHED PRIMARY ALCOHOLS ON POLY-PROPYLENE GLYCOL AT 130°

Isomer	Number of carbons in alcohol molecule				
	6	7	8	9	10
2-Methyl-2-propyl				1346	1439
2,2-Dimethyl	1040	1153	1247	1349	1448
2-Methyl-2-ethyl		1167	1269	1364	1460
2-Butyl					1487
2-Propyl			1299	1397	1493
2-Ethyl		1208	1309	1411	1510
2-Methylalkan-1-ol		1210	1316	1421	1521

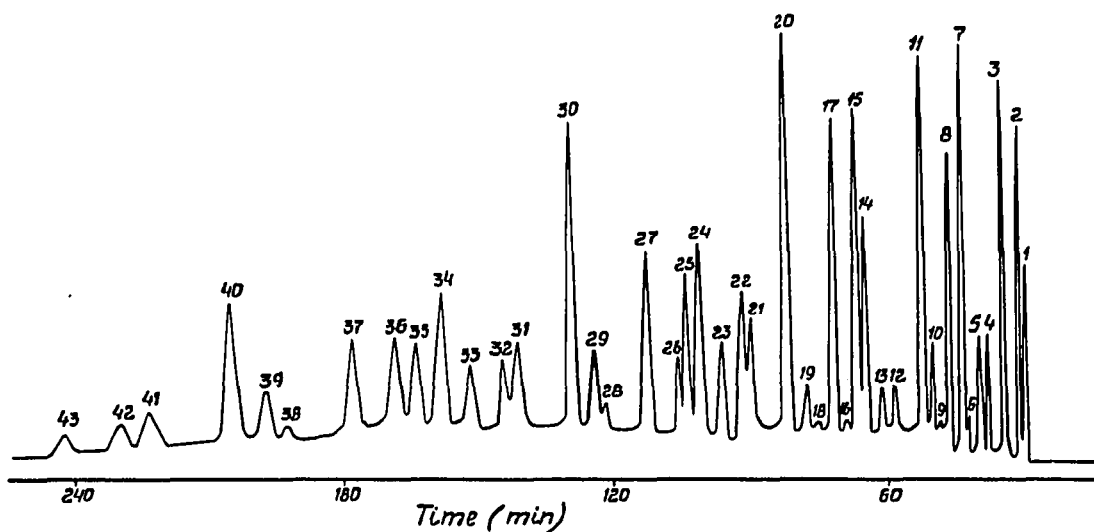


Fig. 3. Chromatogram of methyl esters of C₁₁-C₁₅ α -branched acids. 1 = 5-Methylnonane-5-carboxylic acid; 2 = 4-methylnonane-4-carboxylic acid; 3 = 2-methylnonane-2-carboxylic acid + 3-methylnonane-3-carboxylic acid; 4 = decane-5-carboxylic acid; 5 = decane-4-carboxylic acid; 6 = decane-3-carboxylic acid; 7 = 5-methyldecane-5-carboxylic acid; 8 = 4-methyldecane-4-carboxylic acid; 9 = decane-2-carboxylic acid; 10 = not identified; 11 = 2-methyldecane-2-carboxylic acid + 3-methyldecane-3-carboxylic acid; 12 = undecane-5-carboxylic acid; 13 = undecane-4-carboxylic acid; 14 = 6-methylundecane-6-carboxylic acid; 15 = 5-methylundecane-5-carboxylic acid; 16 = undecane-3-carboxylic acid; 17 = 4-methylundecane-4-carboxylic acid; 18 = undecane-2-carboxylic acid; 19 = not identified; 20 = 2-methylundecane-2-carboxylic acid + 3-methylundecane-3-carboxylic acid; 21 = dodecane-6-carboxylic acid; 22 = dodecane-5-carboxylic acid; 23 = dodecane-4-carboxylic acid; 24 = 6-methyldodecane-6-carboxylic acid; 25 = 5-methyldodecane-5-carboxylic acid; 26 = dodecane-3-carboxylic acid; 27 = 4-methyldodecane-4-carboxylic acid; 28 = dodecane-2-carboxylic acid; 29 = not identified; 30 = 2-methyldodecane-2-carboxylic acid + 3-methyldodecane-3-carboxylic acid; 31 = tridecane-6-carboxylic acid; 32 = tridecane-5-carboxylic acid; 33 = tridecane-4-carboxylic acid; 34 = 6-methyltridecane-6-carboxylic acid; 35 = 5-methyltridecane-5-carboxylic acid; 36 = tridecane-3-carboxylic acid; 37 = 4-methyltridecane-4-carboxylic acid; 38 = tridecane-2-carboxylic acid; 39 = not identified; 40 = 2-methyltridecane-2-carboxylic acid + 3-methyltridecane-3-carboxylic acid; 41 = tetradecane-6-carboxylic acid; 42 = tetradecane-5-carboxylic acid; 43 = tetradecane-4-carboxylic acid.

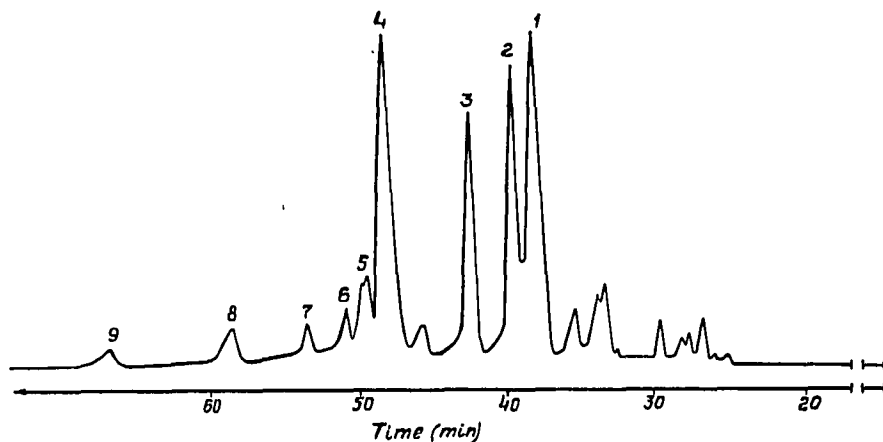


Fig. 4. Chromatogram of methyl esters of C_{17} α -branched carboxylic acids. 1 = 7-Methylpentadecane-7-carboxylic acid + 6-methylpentadecane-6-carboxylic acid; 2 = 5-methylpentadecane-5-carboxylic acid; 3 = 4-methylpentadecane-4-carboxylic acid; 4 = 2-methylpentadecane-2-carboxylic acid + 3-methylpentadecane-3-carboxylic acid; 5 = hexadecane-7-carboxylic acid + hexadecane-6-carboxylic acid; 6 = hexadecane-5-carboxylic acid; 7 = hexadecane-4-carboxylic acid; 8 = hexadecane-3-carboxylic acid; 9 = hexadecane-2-carboxylic acid.

In order to confirm the unambiguous identification of the whole mixture of C_6 - C_{10} β -branched alcohols, retention indices were plotted against the number of carbon atoms in the molecule of alcohol (Fig. 2a).

Retention indices are presented in Table II.

Separation and identification of methyl esters of α -branched carboxylic acids

The chromatogram of the methyl esters of C_{11} - C_{15} α -branched acids is shown in Fig. 3.

Acid fractions with an equal number of carbon atoms were prepared from individual α -olefins and used for the identification of the acids together with such standards as 2-methylundecane-2-carboxylic acid, 3-methylundecane-3-carboxylic acid and dodecane-2-carboxylic acid synthesized in this laboratory.

The knowledge of the retention pattern of C_7 - C_{10} acid isomers⁴ and the availability of the above standards made possible the identification of C_{13} acid isomers. The mixture of C_{11} - C_{15} acids, except for some components the identity of which was not established (Fig. 3), was identified by the relationship between retention indices and number of carbon atoms in the molecules of the acids (Fig. 2b). In addition, the isomers 2-methylalkane-2-carboxylic acid and 2-methylalkane-3-carboxylic acid had equal retention times and did not separate.

Acids with 16, 17 and 19 carbon atoms have an even greater number of isomers and their complete separation on this column could not be achieved. As an example, Fig. 4 represents a chromatogram of the C_{17} acids fraction. The identification of these acid isomers was based on the general retention trend found, *viz.*, that a more branched isomer is eluted before a less branched isomer with the same number of carbon atoms. For all C_{11} - C_{17} and C_{19} acid isomers identified as their methyl esters, retention indices on polyphenyl ether were determined (Table III).

TABLE III

RETENTION INDICES OF α -BRANCHED ACID METHYL ESTERS: C₁₁-C₁₅ AT 160°, C₁₆ AT 180° AND C₁₇ AND C₁₉ AT 200°

Isomer of acid	Number of carbons in a molecule of acid							
	11	12	13	14	15	16	17	19
7-Methylalkane-7-carboxylic acid*							1917	2116
6-Methylalkane-6-carboxylic acid			1535	1634	1733	1747	1919	2119
5-Methylalkane-5-carboxylic acid	1347	1441	1541	1641	1740	1830	1928	2130
4-Methylalkane-4-carboxylic acid	1357	1456	1557	1658	1757	1848	1947	2150
3-Methylalkane-3-carboxylic acid + 2-methylalkane-2-carboxylic acid	1387	1488	1588	1689	1789	1880	1982	2185
Alkane-7-carboxylic acid							1989	
Alkane-6-carboxylic acid			1607	1706	1804	1892	1994	
Alkane-5-carboxylic acid	1412	1510	1611	1711	1811	1898	1999	
Alkane-4-carboxylic acid	1422	1522	1622	1722	1822	1910	2012	
Alkane-3-carboxylic acid	1444	1543	1643	1744	1843	1936	2038	
Alkane-2-carboxylic acid**	1479	1580	1679	1777	1879	1978		

* 7-Methylalkane-7-carboxylic acid = α -methyl- α -hexylalkanoic acid.** Alkane-2-carboxylic acid = α -methylalkanoic acid.

It can be seen from Table III that at one of the temperatures used (160°) there exists a certain regularity in the retention indices of the isomers of a homologous series: the retention indices increase with the number of carbon atoms by approximately 100 units between adjacent components.

Gas chromatographic methods for the determination of β -branched alcohols and α -branched acids were employed for the investigation of the process for the synthesis of these products, which are used in the manufacture of synthetic and alkyd resins and plasticizers and in perfumery.

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