Study of the Properties of Ethyl Isothiocyanatocarboxylates by Means of Gas Chromatography and Mass Spectroscopy

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Received 13 November 1991

Retention indices of the aliphatic isothiocyanates as well as of the alkyl isothiocyanatocarboxylates on the stationary phases of different polarities have been measured and interpreted. The mass spectra of the title compounds have been measured and discussed as well.

Our previous papers have dealt with the preparation of esters of isothiocyanatocarboxylic acids [1] and with the investigation of their physicochemical properties by means of IR and ^{1}H NMR spectroscopy [2]. The title compounds show prominent biological activity, especially the yeast growth inhibiting one [3]. This fact led to an intensive investigation of the possibilities of their utilization for preservation of the beverages, especially of wine [4].

A detailed study of their properties by means of gas chromatography and mass spectroscopy contributes to our knowledge of the physicochemical properties of the title compounds and enables their qualitative and quantitative analyses.

For the analysis of the mixture of isothiocyanates prepared from the protein hydrolyzates a combination of chromatography with mass spectroscopy has been used [5]. Isothiocyanates of the alkyl and aryl types have been already chromatographically studied [6—8].

Table 1. Retention Indices I_x of Ethyl Isothiocyanatocarboxylates on the Phases UCW-98 and OV-17 at 160 °C

Compound	R	UCW-98 I_x	OV-17 I_x	ΔI_x
I	$SCNCH_2$	1149.3	1395.0	245.7
II	$SCNCH_2CH_2$	1229.3	1479.7	250.4
III	$CH_3CH(NCS)$	1141.8	1351.0	209.2
IV	$SCNCH_2CH_2CH_2$	1346.8	1622.4	275.4
V	$CH_3CH_2CH(NCS)$	1217.6	1438.0	220.4
VI	$(CH_3)_2C(NCS)$	1132.0	1313.0	181.0
VII	$(CH_3)_2CHCH(NCS)$	1271.0	1473.0	202.0
VIII	$CH_3(CH_2)_3CH(NCS)$	1401.2	1607.2	206.0
IX	$SCNCH_2(CH_2)_3CH$	1574.3	1841.0	266.7
X	$CH_3CH_2CH(CH_3)CH(NCS)$	1381.4	1564.4	183.0
XI	$(CH_3)_2CHCH_2CH(NCS)$	1355.4	1547.8	192.4
XII	$SCNCH_2(CH_2)_3CH(NCS)$	1847.1	–	–
XIII	$CH_3SCH_2CH(NCS)$	1609.2	1858.8	249.6
XIV	$H_5C_2OOCCH_2CH(NCS)$	1527.6	1716.6	257.0
XV	$H_5C_2OOCCH_2CH_2CH(NCS)$	1659.6	1916.6	253.0
XVI	$C_6H_5CH_2CH(NCS)$	1733.3	–	–

Retention indices are significant chromatographic parameters that describe chromatographic behaviour of the investigated substances in dependence on their structure [7]. For this reason measurements of the indices for the series of ethyl esters of isothiocyanatocarboxylic acids (Table 1) have been carried out. For the comparative purposes indices were measured also for the linear and isocyclic aliphatic isothiocyanates that do not contain other polar functional group (Table 2). Measurements have been performed on the stationary phases of different polarities (UCW-98, OV-17). For nonbranched alkyl isothiocyanates on both stationary phases a linear dependence between the retention index I_x and the number of carbon atoms in the molecule has been found (for UCW-98 the correlation coefficient $r = 0.998$, while for OV-17 $r = 0.997$). Branching of the carbon chain on the α-carbon atom relative to —NCS group causes a decrease of I_x values (for OV-17) approximately by 80 index units, which is in accordance with the change of polarity of the molecule and from this resulting interaction with the stationary phase.

Presence of the two polar groups in the molecules of isothiocyanatocarboxylates affects the I_x values

Table 2. Retention Indices I_x of the Alkyl Isothiocyanates RNCS on the Phases UCW-98 and OV-17 at 120 °C

R	UCW-98 I_x	OV-17 I_x	ΔI_x
CH_3	725.6	929.9	204.3
CH_3CH_2	786.2	979.9	193.1
$CH_3CH_2CH_2$	880.9	1068.3	187.3
$(CH_3)_2CH$	817.9	986.4	168.5
$CH_3CH_2CH_2CH_2$	979.3	1162.8	183.5
$CH_3CH_2CH(CH_3)$	913.0	1083.1	170.1
$CH_3CH_2CH_2CH_2CH_2$	1079.4	1262.9	183.5
$(CH_3)_2CHCH_2CH_2$	1040.7	1214.9	174.2
$CH_3(CH_2)_4CH_2$	1181.2	1358.7	171.5
$CH_3(CH_2)_5CH_2$	1228.9	1462.0	172.1

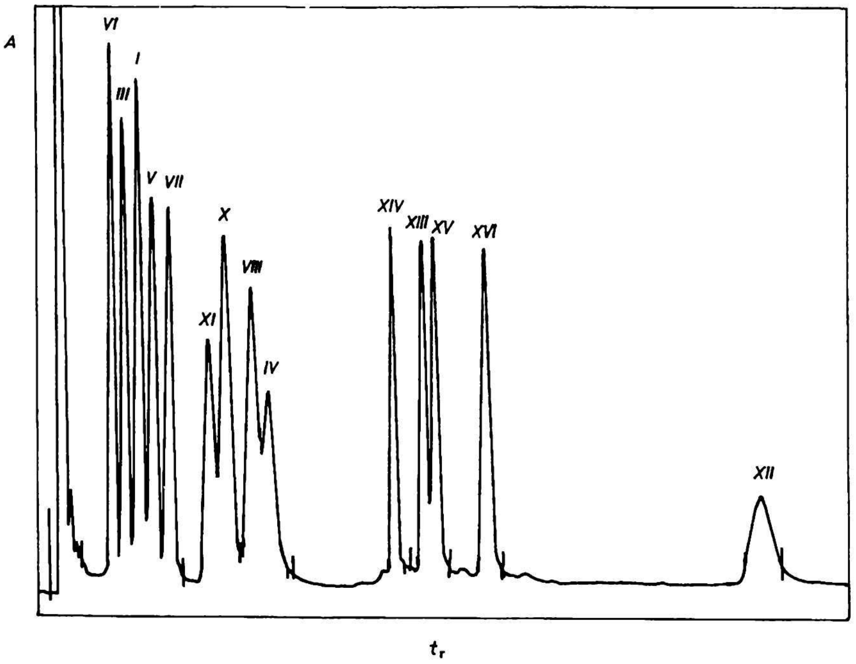

Fig. 1. Chromatogram of the multicomponent mixture of ethyl isothiocyanatocarboxylates on a column containing 10 % OV-17 on Chromosorb WAW DMCS (159—178 μm). (160 °C for 15 min isothermally, temperature gradient 30 °C min^{-1} to 230 °C.) Designation of the components of the mixture as in Table 1.

depending on the relative location of these groups (Table 1). With the elongation of the carbon chain and with the increased distance between the polar groups, the difference between the retention indices increases as a result of the interaction of these substances with the more polar stationary phase (OV-17). Branching of the carbon chain on C_α carrying —NCS group leads similarly as with alkyl isothiocyanates to the decrease of the I_x values. A semipolar phase OV-17 is suitable not only for estimation of the dependence of I_x values on the structure of the substances under investigation, but also in respect to the possibility of the separation of the multicomponent mixtures of these compounds (Fig. 1).

From the study of the mass spectra of ethyl isothiocyanatocarboxylates listed in Table 3, the presence of the corresponding molecular ions is evident. By losing 73 a.m.u. from $M^{+\bullet}$ fragments $M^{+\bullet} - {}^\bullet COOC_2H_5$ are formed. Fragmentation of the ions with $m/z = (M^{+\bullet} - 73)$ depends on the structure of the alkyl residue R, which in the case of branching enables splitting off of the propene molecule (compounds *VII*, *VIII*), which results in the formation of the ions with $m/z = 72$ or $m/z = 86$. In the spectrum of the compound *VIII* a metastable transition $m/z = 201 \rightarrow m/z = 128$ has been observed accompanied by a metastable ion with $m^*/z = 81.5$ (calculated 81.5). With elongation and branching of the substituent R other fragment ions are observed in the mass spectra. Splitting off of the molecule HNCS ($M^{+\bullet} - 59$) that is typical for the fragmentation of the aliphatic isothiocyanates [9] was observed only with compound *I*.

By McLafferty's rearrangement (splitting off of propene) of compound *VII* an ion with $m/z = 145$ appears that after splitting off of HNCS yields an ion with $m/z = 86$. Similarly, by splitting off of ethylene molecule from an ethoxycarbonyl group an ion with $m/z = 117$ is produced that upon the loss of water molecule produces an ion with $m/z = 99$. By McLafferty's rearrangement of compound *VIII* (splitting off of butane) an ion with $m/z = 145$ is formed from a molecular ion, similarly as with compound *VII*.

Compound *XVI* is represented by a basic peak of a tropylium ion $C_7H_7^{+\bullet}$ with $m/z = 91$. Ions with $m/z = 65$ and $m/z = 39$ that are formed from the tropylium ion are present in the mass spectrum as well [10].

Mass spectra of the measured compounds (Table 3) contain a fragment ion $CH_2{=}\overset{+}{N}CS$ with $m/z = 72$ which is produced directly from a molecular ion only in the case of compound *I* where suitable conditions for its formation exist.

EXPERIMENTAL

Ethyl esters of the isothiocyanatocarboxylic acids were prepared according to Ref. [1].

Chromatographic data of the studied compounds have been measured using a gas chromatograph 7620 A (Hewlett—Packard) equipped with a dual

Table 3. Mass Spectral Data of Ethyl Isothiocyanatocarboxylates

Compound	Molecular and fragment ions *m/z* (I_r/%)
I	146 (4), 145 ($M^{+\bullet}$, 74), 86 (7), 74 (5), 73 (20), 72 (100), 45 (13), 44 (5), 43 (5), 42 (9)
II	161 ($M^{+\bullet}$ + 2) (4), 160 (7), 159 ($M^{+\bullet}$, 91), 116 (7), 115 (17), 114 (60), 88 (20), 87 (11), 86 (19), 85 (100), 82 (15), 74 (4), 73 (14), 72 (80), 71 (19), 60 (13), 59 (15), 58 (6), 56 (6), 55 (26), 54 (9), 45 (9), 44 (19), 43 (13), 42 (5)
III	160 (4), 159 ($M^{+\bullet}$, 55), 88 (5), 87 (9), 86 (100), 60 (9), 59 (5), 44 (29), 42 (8), 41 (27)
IV	174 (6), 173 ($M^{+\bullet}$, 36), 130 (9), 129 (43), 127 (38), 101 (4), 100 (45), 99 (4), 98 (13), 96 (8), 88 (63), 87 (11), 86 (17), 85 (71), 83 (100), 73 (7), 72 (45), 70 (33), 69 (23), 68 (6), 67 (5), 61 (45), 60 (62), 59 (7), 55 (8), 49 (8), 48 (10), 47 (23), 45 (28), 44 (45), 43 (18), 42 (13), 41 (62)
V	174 (5), 173 ($M^{+\bullet}$, 56), 101 (10), 100 (100), 72 (22), 41 (47)
VI	173 ($M^{+\bullet}$, 22), 102 (6), 101 (9), 100 (100), 72 (6), 69 (6)
VII	189 ($M^{+\bullet}$ + 2) (4), 188 (7), 187 ($M^{+\bullet}$, 71), 145 (10), 117 (18), 116 (6), 115 (11), 114 (100), 100 (6), 99 (27), 86 (5), 72 (12), 71 (4), 69 (5), 56 (8), 55 (71), 42 (10), 41 (14)
VIII	202 (5), 201 ($M^{+\bullet}$, 33), 145 (6), 129 (7), 128 (93), 100 (4), 99 (5), 96 (4), 86 (7), 82 (5), 73 (4), 72 (33), 70 (8), 69 (100), 60 (4), 56 (4), 55 (10), 54 (4), 44 (11), 43 (10), 41 (6)
XI	202 (4), 201 ($M^{+\bullet}$, 41), 186 (14), 145 (10), 130 (5), 129 (9), 128 (100), 114 (6), 113 (11), 99 (8), 96 (6), 88 (97), 87 (13), 72 (6), 71 (18), 70 (6), 69 (72), 60 (5), 59 (5), 57 (8), 56 (9), 55 (16), 54 (23), 53 (4), 43 (61), 41 (40)
XII	260 ($M^{+\bullet}$ + 2) (7), 259 (13), 258 ($M^{+\bullet}$, 100), 212 (24), 200 (19), 187 (5), 186 (11), 185 (50), 184 (32), 158 (5), 154 (8), 152 (6), 151 (5), 127 (8), 126 (71), 125 (8), 124 (22), 109 (10), 108 (4), 100 (7), 99 (11), 98 (70), 94 (5), 93 (21), 92 (15), 86 (8), 85 (23), 82 (19), 74 (7), 72 (9), 69 (8), 68 (7), 67 (73), 65 (7), 60 (7), 59 (8), 58 (5), 45 (5), 41 (73)
XIV	233 ($M^{+\bullet}$ + 2) (4), 232 (9), 231 ($M^{+\bullet}$, 83), 187 (7), 186 (40), 185 (71), 159 (29), 158 (100), 130 (6), 128 (11), 127 (39), 126 (7), 117 (7), 116 (89), 114 (5), 113 (5), 112 (7), 101 (5), 100 (9), 99 (28), 88 (21), 87 (7), 86 (76), 85 (48), 84 (7), 82 (5), 73 (7), 72 (9), 71 (20), 69 (7), 60 (13), 59 (15), 58 (9), 55 (30), 54 (5), 45 (9), 44 (11), 42 (5), 41 (9)
XVI	235 ($M^{+\bullet}$, 4), 177 (9), 176 (30), 162 (7), 131 (8), 128 (22), 104 (9), 103 (10), 92 (8), 91 (100), 65 (12), 60 (6), 51 (10), 43 (5), 41 (4)

Peaks with intensities ≥ 4 % only are listed.

flame ionization detector FID and the stainless steel columns (180 cm × 0.2 cm). For the determination of the retention indices the following matrices have been used: 10 % UCW-98 on Chromosorb WAW DMCS (159—178 μm),10 % OV-17 on Chromosorb WAW DMCS (159—178 μm). Injection and FID temperature 250 °C, column temperature 120 °C for alkyl isothiocyanates, 160 °C for esters of isothiocyanatocarboxylic acids, 160 °C for 15 min isothermally, then heating to 230 °C at 30 °C min^{-1} gradient for separation of the mixture of esters of isothiocyanatocarboxylic acids.

Carrier gas (nitrogen) flow 35 cm^3 min^{-1}.

Mass spectra have been measured with an instrument MS 902S (AEI, Manchester) using all glass heated inlet system with a temperature of an ion source 90—120 °C. Electron energy was 70 eV, trap current 100 μA.

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Translated by G. Kogan