ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 3, pp. 449–456. © Pleiades Publishing, Ltd., 2014.
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Chromatographic Characteristics of α-Alkynols

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Received September 5, 2013

Abstract—Chromatographic retention indices on a standard nonpolar poly(dimethylsiloxane) phase were determined for 33 α-alkynols and their 27 dehydration products (conjugated alkenynes). The resulting data are proposed to be verified using the retention indices of acetylenic alcohols estimated by the additive scheme from the retention indices of isostructural alkynes with the inclusion of increments for secondary and tertiary hydroxy groups. The analogous approach to data the verification of data for alkenynes is based on correlation of their retention indices with normal boiling points.

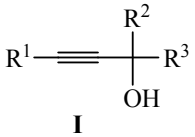
DOI: 10.1134/S1070363214030074

Gas chromatography–mass spectrometry (GCMS) identification of traces of organic compounds in mixtures suggests joint use of standard mass spectra and chromatographic retention parameters. The most informative of such parameters are retention indices (RI) on standard nonpolar stationary phases, which feature the highest interlaboratory reproducibility [1]. Furthermore, the efficiency of identification is determined by the number of compounds contained in the used databases. At present the number of compounds characterized by mass spectra is much higher than number of known retention indices. Thus, the most recent version of the NIST/EPA/NIH Mass Spectral Library (2011) [2] includes 243893 mass spectra for 212961 compounds and 346757 retention indices for 70835 compounds. Therewith, the set of objects characterized by mass spectra and chromatographic parameters overlap only partially.

The main predestination of databases is not only to systematize reference information (for known compounds), but also to provide the possibility to reveal insufficiently characterized classes of compounds that deserve primary attention. One of such classes includes aliphatic alcohols containing the C≡C bond α to the carbinol carbon atom, specifically α-alkynols **I** (Scheme 1).

Such α-alkynols and their transformation products have been extensively studied as far back as 1950s [3–5], but, paradoxically though it may seem, they have never been systematically studied by chromatography. This is not an infrequent situation in organic chemistry; some reasons for that are considered in [6]. The mass spectra of 27 α-alkynol homologs and isomers C_3H_4O–$C_{10}H_{18}O$ are available in the database [2]. At the same time, RIs were reported for as little as 7 compounds of this class. As would be expected, RIs on standard nonpolar stationary phases are known for the simplest homolog of the α-alkynol series: propargyl alcohol (546–576) [7–10]. Sufficient information is available for 2-methylbut-3-yn-2-ol (condensation product of acetylene with acetone) [11] and 3-methylpent-1-yn-3-ol (690, 695, 715) [11–13]. As to other compounds of this series, RIs are known for hex-2-yn-1-ol (820, 847) [14, 15] and dec-3-yn-2-ol (1101) [16].

Scheme 1.



I

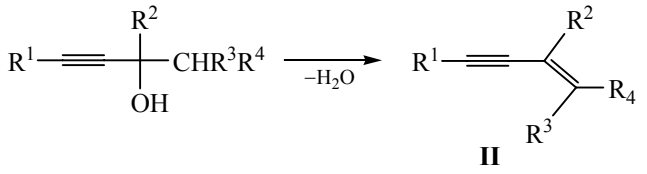
$R^1 = R^2 = R^3 = H, C_nH_{2n+1}$.

α-Alkynols are synthetic precursors of such unsaturated hydrocarbons as conjugated alkenynes **II** which, too, are poorly characterized by chromatography (Scheme 2).

The database [2] contains 31 mass spectra for compounds **II,** whereas RIs are presented for as little

† Deceased.

Scheme 2.



II

as 8 compounds of this series: but-1-en-3-yne (404 ± 1) [17], pent-3-en-1-yne (525) [18], as well as a number of higher homologs C_9–C_{13} (components of essential oils of certain plants), including 2-methyloct-1-en-3-yne (981) [19], *E* and *Z* isomers of dec-4-en-6-yne (1244, 1235) [20], undec-5-en-3-yne (1161) [21], 4-ethylnon-3-en-5-yne (1321) [22], and (*E*)-tridec-4-en-6-yne (1607) [23].

The present work is devoted to chromatographic characteristization of a series of α-alkynols **I,** which includes determination of their RIs on the standard nonpolar stationary phase OV-101, assessment of the possibility to predict the RIs of these compounds from data for compounds of other classes, as well as identification and determination of RIs of vinylacetylenes **II** as major impurities in compounds **I**. Approaches to verifying experimental data for mixture components without their preparative isolation are discussed.

Table 1 lists the experimental RIs of 33 α-alkynols C_3–C_{11} in the range 570–1200. For the simplest five representatives of this class (printed italic), the experimental RIs are averaged with published data (interlaboratory randomization).

Even though compounds **I** have a fairly simple structure, their RTs vary over a wide range, which depends on a number of factors: type of carbinol carbon (primary, secondary, or tertiary), position of the C≡C bonds in the hydrocarbon skeleton (terminal or disubstituted) [24], as well as intramolecular steric interactions which are difficult to account for. Provided the dependence of RIs from the number of carbon atoms in the molecule is compensated for by the recalculation of RIs [Eq. (1)] into their homological increments (i_{RI}) [25], the effect of other factors on RIs can be reflected by the function $i_{RI}(N)$ [Eq. (2)], where *N* is the total number of branchings in the hydrocarbon skeleton. Therewith, the increments for quaternary fragments of the hydrocarbon or carbinol carbon atoms of tertiary alcohols are taken to be 2.

$$i_{RI} = RI - 100x. \quad (1)$$

Here x = int (M/14), where M is the molecular weight of the compound.

$$i_{RI} = aN + b. \quad (2)$$

The plot corresponding to the linear regression equation (2) is shown in the figure (the equation parameters are given in the figure legend). It is readily seen even visually that the scatter of i_{RI} values at $N = 2$ is about 100 and $N = 3$, about 150. Consequently, this dependence allows reliable differentiation of compounds with $N = 0$, 1, whereas at $N = 1$, 2, not to mention higher N values, the results become ambiguous.

Nevertheless, there is a fairly simple method both to independently verify the RIs of α-alkynols and to, is necessary, to estimate RIs for still uncharacterized homologs or isomers. This method involves calculation of RIs by an additive scheme, using data for isostructural alkynes and increments for the primary, secondary, or tertiary hydroxy groups. Such increments were previously calculated for alkanols [26].

OH group	primary	secondary	tertiary
ΔRI	282 ± 32	208 ± 24	155 ± 23

The RIs of alkynes, used to estimate the RIs of α-alkynols, and the resulting values are listed in Table 1. Such estimates are slightly "shifted:" The (RI_{exp} – RI_{calc}) values for secondary and tertiary α-alkynols are 19 ± 17 and 18 ± 4, respectively. Such a satisfactory agreement between experiment and additive estimates provides evidence for the correctness of structural assignment of the α-alkynol samples and correctness their estimated RIs. The fact that the estimates are slightly higher than the experimental RIs (the deviation being compared with the average accuracy of additive schemes [26]) can be considered to imply weak interactions of OH groups with C≡C bonds [27]. If this variant of the additive scheme is needed to be used, previously estimated ΔRI values [26] can be refined specially for α-alkynols. However, the potential of this approach is limited in principle by the lack of reference information on RIs for higher alkyne homologs, which reveals itself in empty lines at the bottom of Table 1.

Chromatographic analysis of α-alkynols can also provide information of the RIs of conjugated alkenynes **II**; the data for 27 compounds of this class,

Table 1. Gas chromatographic retention indices of α-alkynols and their dehydration products (alkenynes) and isostructural alkynes

Alkynols **I**			Alkynes			Alkenynes		
M	Compound	RI[a]	Compound	RI	Additive RI(**I**)	*M*	Compound	*RI*
56	Prop-2-yn-1-ol	*566±8*	Propyne	330±13	612	–	–	–
70	But-2-yn-1-ol	*695±21*	But-2-yne	466±11	748	–	–	–
70	But-3-yn-2-ol	*608±12*	But-1-yne	416±9	624	52	But-1-en-3-yne	<500
84	Pent-1-yn-3-ol	675±3	Pent-1-yne	515±10	723	66	Pent-3-en-1-yne	578±6 (*E*); 537±7 (*Z*)
84	Pent-3-yn-2-ol	754±3	Pent-2-yne	575±8	783	66	Pent-1-en-3-yne	595±6
84	2-Methylbut-3-yn-2-ol	*610±22*	3-Methylbut-1-yne	477±6	632	66	2-Methylbut-1-en-3-yne	504±7
98	3-Methylpent-1-yn-3-ol	*704±23*	3-Methylpent-1-yne	569±13	724	80	3-Methylpent-3-en-1-yne	622±4 (*E*)
							2-Ethylbut-1-en-3-yne	586±6
98	4-Methylpent-1-yn-3-ol	797±5	4-Methylpent-1-yne	572±9	780	80	4-Methylpent-3-en-1-yne	654±6
98	2-Methylpent-3-yn-2-ol	752±3	2-Methylpent-3-yne	615±15	770	80	2-Methylpent-1-en-3-yne	674±4
98	Hex-1-yn-3-ol	813±5	Hex-1-yne	611±11	819	80	Hex-3-en-1-yne	675±7 (*E*)
98	Hex-3-yn-2-ol	833±3	Hex-3-yne	640±14	848	80	Hex-1-en-3-yne	677±6
112	3-Ethylpent-1-yn-3-ol	806±4	3-Ethylpent-1-yne	673±10	828	94	3-Ethylpent-3-en-1-yne[b]	719±6 (*E*)
112	3-Methylhex-4-yn-3-ol	858±3	4-Methylhex-2-yne	717±11	872	94	3-Methylhex-2-en-4-yne	756±3 (*E*)
112	Hept-2-yn-4-ol	939±2	Hept-2-yne	754±11	962	94	Hept-4-en-2-yne	772±5 (*E*)
112	3-Methylhex-1-yn-3-ol	810±5	3-Methylhex-1-yne	666±11	821	94	3-Methylhex-3-en-1-yne	710±5 (*E*)
112	4-Methylhex-1-yn-3-ol	874±5	4-Methylhex-1-yne	675±12	883	94	4-Methylhex-3-en-1-yne	769±8
112	Hept-3-yn-2-ol	920±5	Hept-3-yne	727±9	935	94	Hept-1-en-3-yne	766±4
126	Oct-3-yn-2-ol	1008±2	Oct-3-yne	833±11	1041	108	Oct-1-en-3-yne	848±4
126	3-Ethylhex-1-yn-3-ol	950±9	–	–	–	108	3-Ethylhex-3-en-1-yne	788±6 (*E*)
126	3,4,4-Trimethylpent-1-yn-3-ol	835±4	–	–	–	108	4,4-Dimethyl-3-methylidenepent-1-yne	728±4
140	2-Methyloct-3-yn-2-ol	1010±3	–	–	–	122	2-Methyloct-1-en-3-yne	919±3
140	4-Methyl-3-(1-methylethyl)-pent-1-yn-3-ol	952±7	–	–	–	122	4-Methyl-3-(1-methyl-ethyl)pent-2-en-1-yne	865±2
140	4,4-Dimethyl-3-ethylpent-1-yn-3-ol	935±3	–	–	–	122	3-(1,1-Dimethylethyl)-pent-3-en-1-yne	842±3
140	4-Ethylheprtane-4-ol	987±2	–	–	–	–	–	–
140	2,2,3-Trimethylhex-4-yn-3-ol	1022±2	–	–	–	122	5,5-Dimethyl-4-methylidenehex-2-yne	856±3
154	2,2-Dimethyl-3-ethylhex-4-yn-3-ol	1065±2	–	–	–	136	3-(1,1-Dimethylethyl) hex-2-en-4-yne	937±2 (*Z*); 946±2 (*E*)
154	Dec-3-yn-2-ol	1201±3	Dec-3-yne	1026±12	1234	136	Dec-1-en-3-yne	1040±3
154	2-Methyl-3-(1-methylethyl)-hex-4-yn-3-ol	1090±3	–	–	–	–	–	–

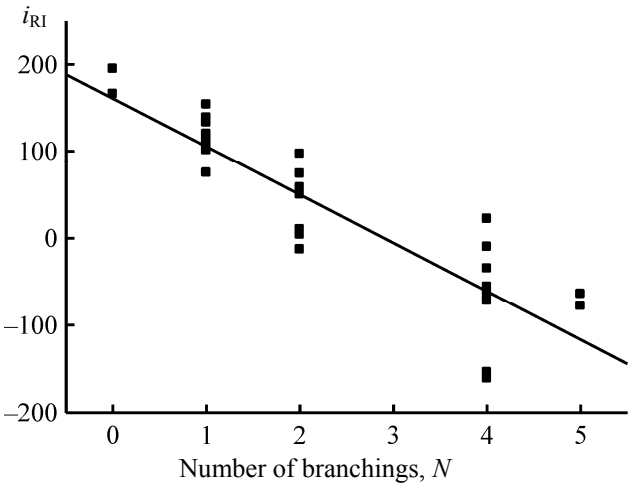
Table 1. (Contd.)

Alkynols **I**			Alkynes			Alkenynes		
M	Compound	RI[a]	Compound	RI	Additive RI (**I**)	*M*	Compound	*RI*
154	4,4-Dimethyl-3-(1-methylethyl)-pent-1-yn-3-ol	1022±2	–	–	–	–	–	–
154	2,6,6-Trimethylhept-4-yn-3-ol	1028±3	–	–	–	136	2,6,6-Trimethylhept-2-en-4-yne	869±3
168	2,2-Dimethyl-3-(1-methylethyl)-hex-4-yn-3-ol	1136±3	–	–	–	150	2-Methyl-3-(1,1-dimethylethyl)hex-2-en-4-yne	1079±2
168	4,7,7-Trimethyloct-5-yn-4-ol	1039±4	–	–	–	–	–	–
168	6,6-Dimethyl-3-ethylhept-4-yn-3-ol	1046±5	–	–	–	–	–	–

[a] Interlaboratory average RIs on standard nonpolar phases are printed italic. [b] The sample contains dimeric hydrocarbons $C_{14}H_{20}$; the most abundant of them has RI 1338±3.

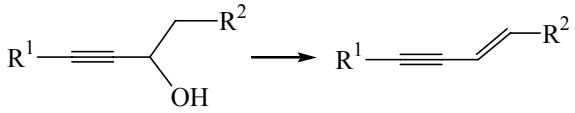
corresponding to α-alkynols **I**, are listed in Table 1. Since the intensities of chromatographic peaks of compounds **II**, detected in the most part of α-alkynol **I** samples in the temperature range of GC injector (200–230°C), we consider it as evidence that compounds **II** are present as impurities in the specific samples of α-alkynols **I** and are not formed as a result of dehydration of the latter in the injector. Further raise of the injector temperature leads to increase of the peak areas of the dehydration products of compounds **I**.

The lack of RI values for certain alkenynes **II** in Table 1 suggests that these compounds are impossible to be formed (for primary α-alkynols), or do not present as impurities in certain samples, or that we detected several (more than two) components with RIs lower than those of compounds **I** by 75–170, which makes the expected alkenynes **II** impossible to identify. The appearance of several compounds can be associated, for example, with the retropinacoline rearrangement that occur during dehydration of α-acetylenic alcohols [5]. In certain cases, *Z*- and *E*-alkenynes could be detected and identified. They were identified by analogy with *Z*- and *E*-pent-3-en-1-ynes, whose normal boiling points [44 (*Z*) and 53°C (*E*)] and, consequently, chromatographic elution order are known.



Homological RI increments vs. number of branchings in the hydrocarbon skeleton of α-alkynols. Linear regression parameters: $a = -55.5 \pm 5.2$, $b = 161 \pm 14$, $r = -0.888$, $S_0 = 42$.

The possibility to estimate RIs for alkenynes **II** by additive schemes seems quite limited, because there are some factors which are difficult to account for, such as position of each of C≡C and C=C bonds in the hydrocarbon skeleton, number of substituents at the C=C bond, and intramolecular steric interactions. The differences of the RIs of α-alkynols **I** and alkenynes **II**, which formally relate to the same dehydration process, vary over a wide range (78–167). However, even having such a great scatter in ΔRI values, we can recognize a cluster of well-reproduced values relating to dehydration of alk-3-yn-2-ols, alk-2-yn-4-ols, alk-4-yn-3-ols, and other secondary α-alkynols.



The average ΔRI for all such compounds is 160±5.

Table 2. Verification of experimental retention indices of the simplest C_5–C_8 alkenynes by the reference values of normal boiling points[a]

Compound	*M*	bp, °C	RI_{exp}	RI_{approx}	ΔRI
(*E*)-Pent-3-en-1-yne	66	53	578±6	570	–8
(*Z*)-Pent-3-en-1-yne	66	44	537±7	541	+4
Pent-1-en-3-yne	66	59.5	595±6	591	–4
2-Methylbut-1-en-3-yne	66	33	504±7	507	+3
(*E*)-3-Methylpent-3-en-1-yne	80	69	622±4	624	+2
4-Methylpent-3-en-1-yne	80	78.5	654±6	656	+2
2-Methylpent-1-en-3-yne	80	83	674±4	672	–2
Hex-1-en-3-yne	80	85	677±6	679	+2
(*E*)-3-Ethylpent-3-en-1-yne	94	96.5	719±6	721	+2
3-Methylhex-2-en-4-yne	94	107–108	756±3	761	+5
3-Methylhex-3-en-1-yne	94	95	710±5	715	+5
4-Methylhex-3-en-1-yne	94	107–108	769±8	761	–8
Hept-1-en-3-yne	94	110	766±4	770	+4
4,4-Dimethyl-3-methylidenepent-1-yne	108	96–97	728±4	721	–7
Average ΔRI, index units					4±2

[a] Coefficients of Eq. (3): *a* 1.8637, *b* 0.41777×10^{-5}, *c* –4.4429.

The use of this information can be illustrated by the identification of a component with RI 869 ± 3 in the 2,6,6-trimethylhept-4-yn-3-ol sample (RI 1028 ± 3). The ΔRI is 1028 – 869 = 159, which, provided no other components are detected in this RI range, allows its unequivocal identification as 2,6,6-trimethylhept-2-en-4-yne.

Thus, alkenynes **II** were all identified as impurities in the parent α-alkynols, i.e. they were not isolated individually, and their structure was not confirmed by independent methods. This circumstance places stringent requirements upon substantiation of correct identification. By this reason, it is quite desirable to use additional methods for structure confirmation. As one of them we could recommend Eq. (3) for correlation of RI values with reference normal boiling points (bp, K) [1].

$$\log (RI) = a\log (bp) + bA + c. \quad (3)$$

Here *A* is a parameter which characterizes the position of a concrete compound in the corresponding taxonomic group [1]; in our case, an expedient choice is *A* = *M* (molecular weight); the coefficients *a, b*, and *c* are calculated by the least squares method.

The "only" limitation of the described approach is that reference normal boiling points are available only for relatively simple homologs. Table 2 lists the boiling points of 14 C_5–C_8 alkenynes and the RIs approximated by Eq. (3), in comparison with experimental data. The absolute $RI_{exp} - RI_{calc}$ deviation is 2–8 at the average RI value of 4 ± 2. This fact implies that the selected set of fourteen RI_{exp} values contains no outliers, and all values seem to be fairly reliable.

The same approach to verification of experimental data can be applied to the RIs of α-alkynols, even so its efficiency is slightly lower because of the more limited range of available reference normal boiling points. Moreover, Eq. (3) has different parameters for secondary and tertiary alcohols, and, consequently, secondary and tertiary α-alkynols should be considered separately. Table 3 lists boiling points for 7 tertiary C_5–C_8, α-alkynols, experimental RIs, as well as RI values approximated by Eq. (3). The absolute $RI_{exp} - RI_{calc}$ deviation varies from 0 to 11 at the average RI value of 6 ± 5, which is slightly larger than for alkenynes but, too, is evidence for the reliability of the estimated values.

The samples of α-alkynols **I**, even though they were purified by distillation [5], may contain, along with alkenynes **II,** contain a lot of other impurities, whose concentrations could not be estimated at the time when

Table 3. Verification of experimental retention indices of tertiary C_5–C_8 alkynols by the reference values of normal boiling points[a]

Compound	*M*	bp, °C	RI_{exp}	RI_{approx}	ΔRI
2-Methylbut-3-yn-2-ol	84	103	610±22	609	–1
3-Methylpent-1-yn-3-ol	98	121.5	704±23	704	0
2-Methylpent-3-yn-2-ol	98	134	752±3	762	+10
3-Ethylpent-1-yn-3-ol	112	138	806±4	799	–7
3-Methylhex-4-yn-3-ol	112	149.5	858±3	857	–1
3-Methylhex-1-yn-3-ol	112	138	810±5	799	–11
3,4,4-Trimethylpent-1-yn-3-ol	126	143	835±4	844	+9
Average ΔRI, index units					6±5

[a] Coefficients of Eq. (3): *a* 2.5189, *b* 1.6934×10^{-3}, *c* –8.6665.

Table 4. Mass spectra of impurities in the 2,6,6-trimethylhept-4-yn-3-ol sample and results of their identification

RI	$m/z \geq 45$ ($I_{rel} \geq 2$ %)	Assignment
978±5	154 (5) $[M]^+$, 139(7), 121(2), 112(9), 111(100) $[M - C_3H_7]$, 97(8), 96(2), 95(3), 93(9), 91(4), 83(6), 81(4), 79(2), 77(3), 71(3), 69(9), 68(2), 67(7), 65(2), 57(4), 56(3), 55(51) $[M - C_3H_7 - C_4H_8]$, 53(8), 51(2)	2,6,6-Trimethylhept-4-en-3-one, *Z* isomer
1028±3	154(0) $[M]^+$, 140(2), 139(2), 121(4), 112(9), 111(100) $[M - C_3H_7]$, 109(2), 107(2), 105(3), 98(3), 97(38) $[M - C_4H_9]$, 96(5), 95(6), 94(2), 93(15), 91(13), 83(8), 81(8), 79(9), 78(3), 77(17), 71(3), 70(2), 69(21), 68(2), 67(15), 66(2), 65(8), 63(2), 57(18), 56(4), 55(70) $[M - C_4H_9 - C_3H_6]$ and $[M - C_3H_7 - C_4H_8]$, 53(13), 52(3), 51(8), 50(3), 45(4)	Major component: 2,6,6-trimethylhept-4-yn-3-ol
1033±4	152(0) $[M]^+$, 137(2), 124(2), 110(8), 109(100) $[M - C_3H_7]$, 95(3), 93(3), 82(3), 81(39) $[M - C_3H_7 - CO]$, 79(32), 77(5), 67(13), 66(4), 65(7), 63(2), 57(3), 53(7), 53(24) $[M - C_3H_7 - C_4H_8]$, 51(5), 50(3)	2,6,6-Trimethylhept-4-yn-3-one
1051±3	156(0) $[M]^+$, 141(10), 123(7), 114(8), 113(99) $[M - C_3H_7]$, 112(8), 100(3), 99(2), 86(2), 85(33) $[M - C_3H_7 - CO]$, 83(2), 81(2), 72(3), 71(46) $[C_3H_7CO]$, 70(4), 69(8), 67(2), 58(5), 57(100) $[C_4H_9]$, 56(9), 55(14), 53(4)	2,6,6-Trimethylheptan-3-one
1068±3	154(4) $[M]^+$, 139(6), 112(8), 111(100) $[M - C_3H_7]$, 99(2), 96(2), 95(2), 93(7), 91(3), 83(4), 81(3), 77(3), 71(2), 69(9), 67(6), 57(3), 56(2), 55(43) $[M - C_3H_7 - C_4H_8]$, 53(6), 51(2)	2,6,6-Trimethylhept-4-en-3-one, *E* isomer

alkynols **I** were synthesized (end of 1950s) because of the absence of capillary chromatography. Almost all samples contained traces of the starting carbonyl compounds or vinylacetylenes (in certain samples), which is consistent with the chemical properties of enynes [4]. Moreover, there are peaks of a number of minor components with retention parameters close to those of α-alkynols **I**. To identify these components, we performed GCMS analysis of the 2,6,6-trimethylhept-4-yn-3-ol sample (Table 4).

The mass spectrum of the major component (RI 1028 ± 3) is illustrative of the fragmentation regularities of α-alkynols [28]. The intensities of molecular ion (*m*/*z* 154) are close to zero, the base peaks belong to $[M - C_3H_7]^+$ ions, *m*/*z* 111 (α-cleavage to the carbinol carbon atom), and the secondary $[M - C_4H_9 - C_3H_6]^+ \equiv [M - C_3H_7 - C_4H_8]^+$ ion peaks (*m*/*z* 55) are next in intensity. Another component, whose RI differs by as little as 5 (RI 1033 ± 4), is lower by 2 Da in molecular weight from the major component and analogous mass spectrum (major signals: *m*/*z* 109 and 83), which allows us to assign this component the structure of a carbonyl compound corresponding to α-alkynols: 2,6,6-trimethylhept-4-yn-3-one. The component with RI 1051 ± 3 (major signals: *m*/*z* 113, 85, 71, and 57; they all belong to the homologous series $y = 1$ [25]) was assigned the structure of a saturated analog

of the carbonyl compound: 2,6,6-trimethylheptan-3-one. And, finally, the two peaks with RI 978 ± 5 and 1068 ± 3 and completely identical mass spectra can be assigned to the *Z* and *E* isomers of 2,6,6-trimethylhept-4-en-3-ones. In agreement with the conclusions in [29], the *Z* isomer of this compound should be eluted first. Unlike other impurities, this unsaturated ketone has the conjugation system CH=CH–CO, and, as a result, the mass spectra of its isomers show molecular ion signals (I_{rel} 4–5 %).

We are the first to detect such impurities in α-alkynol samples. Their formation can be associated with the disproportionation of α-alkynols in strongly basic conditions (in the presence of alkali metal acetylides and, consequently, corresponding alkoxides).

EXPERIMENTAL

All α-alkynols **I** were synthesized by a common procedure from the corresponding carbonyl compounds and alk-1-ynes which were reacted as acetylenides (most frequently, potassium acetylenides) [3]. The physicochemical characteristics of characterized compounds are reports in [3–5] and references therein. The normal boiling points of alkenynes and α-alkynols are listed in Tables 2 and 3.

The GC analysis of α-alkynols dissolved in methylene chloride (RI 515 ± 7) was performed on a Biokhrom-1 chromatograph with FID and an OV-1 WCOT quartz capillary column (25 m × 0.25 mm i.d.; film thickness 0.25 μm), linear temperature programming from 40 to 220°C at a rate of 6 deg/min, injector temperature 220°C, detector temperature 250°C, carrier gas nitrogen at a linear rate of 21 cm/s. The samples were injected with a Gazokhrom-101 syringe, sample volume 0.2–0.3 μL, split ratio 1 : 30. The GC peaks were registered on a TR 2213 integrator. To measure retention indices, a mixture of the reference *n*-alkanes C_5–C_{14} was added to the solutions. The linear logarithmic indices were calculated using QBasic software [30].

The GCMS analysis of impurities in the 2,6,6-trimethylhept-4-yn-3-ol sample was performed on a Shimadzu QP 2010+ instrument; separations were performed on an HP-5 MS WCOT column (25 m × 0.20 mm i.d.; film thickness 0.33 μm) at linear temperature programming from 45 (hold 1 min) to 280°C (2 min) at a rate of 5 deg/min; carrier gas helium, volume rate 1.0 mL/min; injector temperature 250°C, interface temperature 280°C, ion source temperature 200°C; ionization energy 70 eV, solvent delay time 4 min. The mass spectra, RI values, and results of identification of the components of the 2,6,6-trimethylhept-4-yn-3-one sample are presented in Table 4.

ACNOWLEDGMENTS

The author is grateful to I.A. Balova for providing a few α-alkynols.

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