ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 6, pp. 1106–1114. © Pleiades Publishing, Ltd., 2014. Original Russian Text © I.G. Zenkevich, A.V. Ul'yanov, S.L. Golub, A.K. Buryak, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 6, pp. 923–931.

Chromatographic Component of Identification of the Transformation Products of 1,1-Dimethylhydrazine in the Presence of Sulfur

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Received November 18, 2013

Abstract—The gas-chromatographic retention indices of the products of 1,1-dimethylhydrazine transformations in the presence of sulfur allows one to confirm and, in ceratin cases, make more exact the results of their gas chromatography–mass spectrometry identification. Features of identification of new compounds, including 1,1-dimethyl-2-thioxohydrazine are discussed.

Keywords: dialkyl polysulfides, 1,1-dimethylhydrazine, gas chromatography-mass spectrometry, retention index

DOI: 10.1134/S1070363214060097

1,1-Dimethylhydrazine (unsymmetrical dimethylhydrazine) (I) is a widely used component of rocket fuels [1]. Like other hydrazine derivatives, this compound is highly reactive toward a great variety of reagents [2], which predetermines its diverse transformations in the environment, in particular in soil. In this connection, much effort has been devoted to detailed research of the products of transformations of compound I in natural media by means of gas chromatography-mass spectrometry [1, 3, 4], and high-performance liquid chromatography (HPLC), and ionic chromatography [5-9]. As a result, a series of previously unknown compounds were identified, including formic 2,2dimethylhydrazide [(CH₃)₂NNHCHO] [5], substituted triazoles [9], etc. A contact of unsymmetrical hydazine with sulfur and sulfur-enriched soils (shungites) 10] leads to formation of previously uncharacterized compounds containing N-S bonds. They include methyl (dimethylamino) polysulfides $(CH_3)_2NS_nCH_3$ 4) and bis(dimethylamino) polysulfides (n < $(CH_3)_2NS_nN(CH_3)_2$ ($n \le 4$). Moreover, 1,1-dimethyl-2thioxohydrazine (a thio analog of N-nitrosamines) was identified for the first time in natural objects [1, 3, 4]. The mentioned compounds were initially identified exclusively by mass spectra. Therefore, we found it necessary to cofirm this identification by chromatographic data, of which the best interlaboratory reproducibility is characteristic of retention indices (*RI*) on standard nonpolar polydimethylsiloxane phases [11].

In the present work we determined the RIs of the transformation products of compound **I**, formed by its reactions with elemental sulfur and sulfur-containing soils and used the resulting RIs for a more detailed identification of these compounds.

Even though a great number of compounds with N-S and N=S bonds have been characterized by the present time [12-14], they are fairly rarely used in practical synthetic organic and analytical chemistry and are considered quite "exotic" compounds. In most major reference databases [15], no reliable estimates for the N-S and N=S bond energies are available, and the information on the physicochemical characteristics of such compounds is fragmentary, not to speak of chromatographic retention indices. The most known compounds containing N-S bonds are heteroaromatic isothiazoles, whose simplest homologs are among components that impart odor to food products [16-20] and are also comprised in essential oils of certain plants. For example, 4,5-dimethylisothiazole was found in the essential oil of Azadirachta indica A. juss seeds [21]. The unusual properties of isothiazoles can

be illustrated by their normal boiling points: If the boiling point of isoxazole is higher compared to oxazole (95 and 68–70°C, respectively), with isothiazol and thiazol we deal with the reverse situation (114 and 116.8°C). Bis(dimethylamino) sulfide $[(CH_3)_2N]_2S$ (bp 127–130°C) was characterized by RIs on standard nonpolar stationary phases (811 ± 15); mass spectral data were reported for bis(dimethylamino) disulfide $[(CH_3)_2N]_2S$ [22].

Aliphatic amines and hydrazines catalyze certain reactions of elemental sulfur, including the transformations of sulfides or disulfides to polysulfides [23–27].

$$\mathbf{R}_2\mathbf{S} + \mathbf{S}_8 \rightarrow \mathbf{R}_2\mathbf{S}_x \ (x \ge 2).$$

Sulfur, too, activates certain reactions of hydrazines, for example, the condensation with aldehydes to form both hydrazones and azines [28]. Secondary aliphatic amines react with diaryl disulfides to form sulfenamides [29] (the role of oxidant in this reaction appears to belong to air oxygen).

$$Ar_2S_2 + R_2NH \rightarrow ArSNR_2$$

The reaction mixtures of elemental sulfur with hydrazine hydrate solutions [25] and substituted hydrazines (the most characterized of the latter are 1,1-disubstituted hydrazines) acquire intense colors (from red orange to purple); thioxohydrazines are suggested as primary reaction products [15].

$$R_2NNH_2 + 1/4S_8 \rightarrow R_2N-N=S + H_2S.$$

The color of compounds of this class is provided by the N=S chromophore which is similar to the C=S chromophore. Thioxohydrazines are unstable when stored in solutions at room temperature, still less on when distilled; the main reason for this feature is their tendency for polymerization, probably, due to a considerable contribution of bipolar structures [14].

$$R_2N-N=S \leftrightarrow R_2N^+=N-S-.$$

The same reason explains the high reactivity of thioxohydrazines as dienophiles in Diels–Alder reactions [14]. As little as three thioxihydrazines were isolated in the free state: 1,1-dimethyl-2-thioxohydrazine, *N*thioxopiperidine, and *N*-thioxoazepan-1-amines [30]. 1,1-Dimethyl-2-thioxohydrazine forms low-melting purple crystals. A lot of complexes of 1,1-dimethyland 1,1-diphenylthioxohydrazines with such compounds as Pt(II) and Pd(II) dichlorides, triphenylphosphine [31–34], and chromium pentacarbonyl, for example, [(CH₃)₂NNS]Cr(CO)₅ [35, 36], have been characterized.

Determination of chromatographic retention indices of analytes suggests additional determination of retention times of reference *n*-alkanes either in mixtures with the analytes or in separate chromatographic runs but in absolutely identical separation conditions [11]. The second approach is commonly used in the analysis of complex mixtures or unknown samples to exclude possible overlaps of analyte and reference peaks. If, by one or another reason, the mixture of reference *n*-alkanes was not analyzed, all detected compounds remain to be characterized exclusively by retention times; the latter are not infrequently considered impossible to recalculate into retention indices. The results of gas chromatography-mass spectrometry (GCMS) identification of the reaction products of compound I with sulfur-containing materials were presented just in this form [1, 3, 4]. The data set for each compound includes retention time, mass spectral information [molecular masses and mass numbers of the base peaks in the mass spectra $(m/z)^{100}$], and identification result.

Nevertheless, even in such cases there is a way to find retention index for each component. To this end one can make use of the following approach: retention indices can be calculated not only by the retention indices of *n*-alkanes $C_n H_{2n+2}$ (their retention indices are postulated to be 100n), but also with the retention indices of any components, provided these values are determined with a sufficient level of reliability. To minimize the so-called interpolation errors associated with the nonlinearity of the dependence of retention index on retention time for chosen reference components, this approach is expedient to apply to calculate linear logarithmic rather than linear retention indices [37, 38]. In view of the fact that the calculation formula for RI_x [Eq. (1)] contains a variable coefficient q, such dependences can be linearized at any reference components. The nonlinearity of $RI(t_R)$ can be compensated for by varying q.

$$RI_{x} = RI_{n} + (RI_{n+k} - RI_{n}) \left[f(t_{R,x}) - f(t_{R,n}) \right] / \left[f(t_{R,n+k}) - f(t_{R,n}) \right].$$
(1)

Here $t_{R,x}$, $t_{R,n}$, and $t_{R,n+k}$ are the retention times of the analyte and reference components with the retention indices RI_n and RI_{n+k} , $f(t_R) = t_R + q \log t_R$. The parameter q is calculated from the retention times of three reference compound; to this end, it is more convenient to use the simplest software (QBasic) [39].

As an example, we would like to describe the recalculation of the retention times (Table 1) of the reaction products of unsymmetrical dimethylhydrazine

$t_{\rm R}$, min	$M/(m/z)^{100}$	Reaction product	$RI^{\rm b}(q - 2.71)$
5.9	94/94	Dimethyl disulfide	730±9 (730±9)
9.4	120/76	Bis(dimethylamino) sulfide	815(811±15)
11.3	115/44	1,1,4,4-Tetramethylamidrazone	868 (868±2)
12.5	123/76	(Dimethylamino) methyl sulfide	904
14.1	126/126	Dimethyl trisulfide	952±10 (952±10)
15.6	90/90	1,1-Dimethyl-2-thioxohydrazine	999
15.9	89/89	N,N-Dimethylthioformamide	1008 (1004±7)
18.6	152/44	Bis(dimethylamino) disulfide	1095
19.6	155/76	(Dimethylamino) methyl trisulfide	1127
20.6	136/136	Naphthalene-d ₈	1160 (1160)
21.6	158/79	Dimethyl tetrasulfide	1193 (1191±6)
23.7	184/42	Bis(dimethylamino) trisulfide	1264
24.3	129/129	Dimethylaminoacetaldehyde dimethylhydrazone	1284
25.9	187/76	(Dimethylamino) methy tetrasulfide	1338

Table 1. Recalculation of retention times to retention indices for the reaction products of 1,1-dimethylhydrazine with sulfur (aqueous extract)^a

^a The data for compounds chosen as reference components for calculation of the retention indices of the other components (no less than three) are printed bold. ^bParenthesized are the reference *RI* values.

with sulfur (wiping with water followed by dichloromethane extraction. Of 14 components one have to choose those that are unambiguously identified by mass spectra. This relates first of all to such wellknown compounds as dimethyl disulfide (the mean RI on standard nonpolar polydimethylsiloxane phases is 730 ± 9) and dimethyl trisulfide (*RI* 952 \pm 10). As the third component we can choose the next polymer homolog in this series (dimethyl tetrasulfide). For quantitative analysis we added to this sample such a readily detectable internal standard as naphthalene- d_8 which could also be used as the reference component. The mean retention index of naphthalene is 1163 ± 11 . Then for naphthalene- d_8 we can take RI 1160, and the RI of $(CH_3)_2S_4$ (1191 ± 6) can be used for independent control of the resulting data. The q value of -2.71, calculated with the retention times of the reference components, was used to calculate retention indices for other components by Eq. (1).

For each component in Table 1 we put retention time, $M/(m/z)^{100}$, and known reference retention indices. Retention indices for seven identified compounds are determined for the first time. The *RI* value of dimethyl tetrasulfide was estimated at 1193,

which coincides, within error, with the reference RI1191 ± 6 and provides evidence for the correctness of the chosen algorithm of data treatment. The other important issue to be commented upon is the extrapolation of retention indices to the retention times larger than the retention time of the last of the reference components. Thus, the t_R of naphthalene- d_8 is 20.6 min (RI 1160) and the t_R of (dimethylamino) methyl tetrasulfide is 25.9 min, which corresponds to RI 1338. The most reliable evidence for the reliability of such data is the coincidence of the RIs of the same components in different samples analyzed in different conditions.

Table 2 shows analogous results of the recalculation of retention times to retention indices for the reaction products of compound **I** with sulfur in an acetone solution, as well as the results of identification of the products. For the reference compounds we chose three dimethyl polysulfides $(CH_3)_2S_n$, $2 \le n \le 4$ (q –2.89). The main reference compound is acetone dimethylhydrazone (RI 696 ± 4) formed by condensation of 1,1-dimethylhydrazine with acetone. The table only shows the components with larger RI values. Like in the previous case, the retention indices of

$t_{\rm R}, \min$	$M/(m/z)^{100}$	Reaction product	$RI^{b}(q - 2.89)$
_	100/56	Acetone dimethylhydrazone	(696±4)
5.8	94/94	Dimethyl disulfide	730±9 (730±9)
6.8	92/91	Toluene ^c	751 (760±8)
7.9	98/55	4-Methylpent-3-en-2-one ^c	777 (783±11)
9.3	120/76	Bis(dimethylamino) sulfide	814 (811±15)
9.6	116/43	4-Hydroxy-4-methylpentan-2-one ^c	822 (820±7)
11.0	115/44	1,1,4,4-Tetramethylamidrazone	862 (868±2)
12.3	123/76	(Dimethylamino) methyl trisulfide	900
14.0	126/126	Dimethyl trisulfide	952±10 (952±10)
15.5	90/90	1,1-Dimethyl-2-thioxohydrazine	999
15.8	89/89	Dimethylthioformamide	1009 (1004±7)
18.3	152/44	Bis(dimethylamino) disulfide	1090
19.4	155/76	(Dimethylamino) methyl trisulfide	1127
21.3	158/79	Dimethyl tetrasulfide	1191±6 (1191±6)
23.5	184/42	Bis(dimethylamino) trisulfide	1266
25.6	187/76	Dimethylaminoacetaldehyde dimethylhydrazone	1339
29.4	184/42	(Dimethylamino) methy tetrasulfide	1472

Table 2. Recalculation of retention times to retention indices for the reaction products of 1,1-dimethylhydrazine with sulfur (acetone extract)^a

^a The data for compounds chosen as reference components for calculation of the retention indices of the other components (no less than three) are printed bold. ^b Parenthesized are the reference *RI* values. ^c Solvent admixtures and products of acetone condensation in the presence of bases.

seven compounds are determined for the first time; note that the resulting values are well consistent with those in Table 1. Moreover, the results can be checked out using the retention indices of admixtures, specifically the products of intermolecular condensation of acetone in the presence of bases: 4-hydroxy-4-methylpentan-2-one (diacetone alcohol, *RI* 822, reference *RI* 820 \pm 7) and 4-methylpent-3-en-2-one (mesityl oxide, *RI* 777 and 783 \pm 11, respectively). It is noteworthy that the retention indices for 1,1-dimethyl-2-thioxohydrazine in Tables 1 and 2 coincide with each other (*RI* 999).

The transformation products of unsymmetrical dimethylhydrazine, extracted from the shungite surface with acetone (Table 3) are more diverse. In this case to recalculate the retention times varying over a fairly broad range (from 4.6 to 25.0 min) to retention

induces, we need not three but four reference components and use in the calculations two triads of reference compounds (Table 3).

The first set of references includes acetaldehyde dimethylhydrazone ($RI 675 \pm 9$), mesityl oxide ($RI 783 \pm 11$), and tetramethyltetrazene ($RI 831 \pm 4$), which correspond to q 10.98. The second set includes two last components of the first set and naphthalene- d_8 (RI 1160, q -5.62). Such different q values (including their different signs), do not, however, only slightly affect RIs. As seen in the middle part of Table 3, the RI values calculated with two different sets of reference compounds differ from each other by as little as 1–2.

The resulting data allowed us to exclude wrong variants of mass spectral identification and to correct the other data. Thus, for example, the component with t_R 18.1 min (*RI* 990) was identified as acetaldehyde

			RI^{b}		
$t_{\rm R}$, min $M/(m/z)$	Reaction product	<i>q</i> 10.98	<i>q</i> –5.62	Reference <i>RI</i>	
4.6	88/88	Tetramethylhydrazine	627	_	614±21
6.0	86/42	Acetaldehyde dimethylhydrazone	675±9	_	675±9
6.7	100/56	Acetone dimethylhydrazone	696	_	696±4
7.8	74/74	Dimethyl-N-nitrosamine	726	_	708±5
9.5	73/73	Dimethylformamide	769	_	749±16
9.7	-/43	Not identified	774	_	_
10.1	98/83	4-Methyl-3-penten-2-one ^c	783±11	783±11	783±11
10.4	97/97	$C_5H_7N_3$	790	789	_
10.8	96/96	1,3-Dmethyl-1 <i>H</i> -pyrazole, C ₄ H ₈ N ₂	799	797	805±6
11.2	97/96	$C_5H_7N_3$	808	806	_
11.6	96/96	Dimethylpyrazole, C ₄ H ₈ N ₂	816	815	_
11.9	116/43	4-Hydroxy-4-methylpentan-2-one ^c	823	822	820±7
12.0	112/56	Acetone azine	825	824	828±7
12.3	116/116	Tetramethyltetrazene	831±4	831±4	831±4
13.7	115/44	Tetramethylamidrazone	_	866	868±2
18.1	-/99	Not identified	_	990	_
18.7	-/59	The same	_	1009	_
19.2	-/43	"	_	1024	_
19.6	-/43	"	_	1037	_
21.4	-/43	"	_	1094	_
22.2	-/58	"	_	1120	_
23.4	136/136	Naphthalene- <i>d</i> 8	_	1160	1160
24.8	142/44	Ethanedial bis(dimethylhydrazone)	_	1207	-
25.0	-/97	Not identified	-	1214	-

Table 3. Recalculation of retention times to retention indices for the transformation products of 1,1-dimethylhydrazine on the surface of shungite (acetone extract)^a

^a The data for compounds chosen as reference components for calculation of the retention indices of the other components (no less than three) are printed bold. ^b Calculated by two sets of reference compounds. ^c Solvent admixtures.

diethylhydrazone [4]. However, taking account of the chromatographic invariants, we cannot accept this assignment, because the reference *RI* of this compound is 822 ± 5. The three components with $t_{\rm R}$ 10.4–11.6 min (*RI* 790–816) have molecular masses of 96 and 97, which allows these compounds to be assigned the structures of dimethylpyrazoles and dimethyltriazoles (the latter of these components was identified as 1,3-dimethyl-1*H*-pyrazole). However, the reference *RI* 805 ± 6 is better consistent with 1,3-dimethylpyrazole (*RI* 799, $t_{\rm R}$ 10.8 min), whereas the peak at $t_{\rm R}$ 11.6 min probably belongs to 1,5-dimethylpyrazole. In view of

the lack of reference retention indices for dimethyltriazoles, we can do nothing more than specify their molecular formulas $C_4H_7N_3$.

The use of retention indices not only allows them to be compared with reference data, but also makes possible "secondary" control of the results, which is especially important with new compounds. Among the transformation products of unsymmetrical dimethylhydrazine in the presence of sulfur we found three series of compounds: dimethyl polysulfides $CH_3S_nCH_3$, (dimethylamino) methyl polysulfides $(CH_3)_2NS_nCH_3$,

п	CH ₃ S _n CH ₃		$(CH_3)_2NS_nCH_3$		$(CH_3)_2NS_nN(CH_3)_2$	
	RI	$\Delta RI(S)$	RI	$\Delta RI(S)$	RI	$\Delta RI(S)$
1	506±14 ^a		661±12 ^a		814±1	
2	730±9	224	902±3	241	1092±4	279
3	952±10	222	1127	225	1265±2	173
4	1191±6	239	1338	211	1472	207
5	1408±11	217	_	_	_	-
Average $\Delta RI(S)$		226±9	226±15		220±54	

Table 4. Comparison of the increments to retention indices $\Delta RI(S)$ for dialkyl polysulfides CH₃SnCH₃, (dimethylamino) methyl polysulfides (CH₃)₂NSnCH₃, and bis (dimethylamino) polysulfides (CH₃)₂NSn(CH₃)₂

^a Not detected in the samples. The data are given to calculate $\Delta RI(S)$.

and bis(dimethylamino) polysulfides $(CH_3)_2NS_nN(CH_3)_2$ with $2 \le n \le 4$. Previously [40] such polysulfides were identified among the products of chemical destruction of *O*-isobutyl *S*-(2-diethylaminoethyl)phosphonothioate. In all analogous cases, further evidence for the correctness of structural assessment of analytes should be provided. In our example, the variable structural characteristic is the number of sulfur atoms in the polysulfide bridge S_n ; consequently, as the criterion of correct structural assessment of such homologous polymers we can take the increments of retention indices, corresponding to one sulfur atom. As a result, we obtain a data set (Table 4).

The mean increment $\Delta RI(S)$ for the series of dimethyl polysulfides is 226 ± 9 , which ideally coincides with the value (226 ± 8) estimated previously for any dialkyl polysulfide [41]. The value of this increment for (dimethylamino) methyl polysulfides is the same but its standard deviation is larger (226 ± 15) . And, finally, bis(dimethylamino) polysulfides naturally have close $\Delta RI(S)$ values but the scatter of data is even larger (220 ± 54) . The coincidence of $\Delta RI(S)$ implies that the three series of compounds all correspond to the same type of structural transformations of the molecules, namely $-S_2 - \rightarrow -S_3 - \rightarrow -S_4 - \rightarrow \dots$

The above reasoning concerning the necessity of providing further evidence for the structure of new compounds relates in full measure to such transformation product of unsymmetrical hydrazine in the presence of sulfur and sulfur-containing materials as 1,1-dimethyl-2-thioxohydrazine. The mean retention index of this compound on standard nonpolar

polydimethylsoloxane stationary phases is 998 ± 2 ; the base peak in its mass spectrum belong to the molecular ion $[(m/z)^{100}$ 90], which allows fairly reliable interpretation of the isotope signals m/z 91 and 92 and thus confirm the presence of sulfur in the molecule. The fragment ions $[M - (CH_3)_2N]$, $m/z \ 90-44 = 46$, are assignable to the fragment [NS]⁺, which is evidence for the presence of the dimethylamino group. Consequently, the molecular formula $C_2H_6N_2S$ can be considered established even without resorting to highresolution mass spectrometry. However, all the above could be considered sufficient for reasoning unambiguous structural assessment, provided among the whole set of possible C₂H₆N₂S isomers no other structure meeting the same criteria is found. Therefore, it is necessary to compare the characteristics of $C_2H_6N_2S$ isomers, ten of which are presented in Table 5.

CAS numbers are known for six $C_2H_6N_2S$ isomers. This fact implies not a high degree of knowledge of these compounds but the research interest in them. Four compounds (including dimethylthioxohydrazine) are characterized by mass spectra. Some physicochemical characteristics are known for only one $C_2H_6N_2S$ isomer: *N*-methylthiourea. However, only four of the ten isomers contain N–N or N=N bonds, and the (CH₃)₂N fragment is present in dimethylthioxohydrazine and absent from the other isomers.

The retention index of dimethylthioxohydrazine is impossible to estimate using additive schemes, because until now no retention indices have been reported for N=S compounds. However, to confirm the assignment to the compound with *RI* 998 ± 2 and $M/(m/z)^{100} =$ 90/90 of the (CH₃)₂NNS structure, we can consider

C ₂ H ₆ N ₂ S isomer	CAS number	Mass spectrum; $m/z (I_{rel}, \%)$	Other data	Presence of fragment	
				N–N	$(CH_3)_2N$
N-Methylthiourea	598-52-7	90(100), 30	mp 118–121°C; p <i>K</i> _a 0.83	_	_
Methyl carbamidothioate	2986-19-8	43(100), 90	_	_	_
<i>N,N'</i> -Dimethylsulfur diimide	13849-02-0	28(100), 61, 30, 62	_	—	_
Methyl(methylsulfanyl)diimide	_	_	_	+	_
(2-Aminoethane)thioamide	105301-27-7	_	-	_	_
(2-Sulfanylethane)imidate	50433-21-1	_	_	-	_
1,3,4-Thiadiazoline	39517-32-3	_	-	+	_
1,2,4-Thiadiazoline	36712-81-9	_	-	_	_
1,1-Dimethyl-2-thioxohydrazine ^a	_	90(100), 46, 42		+	+
Dimethyldiazene thioxide	_	_	_	+	_

Table 5. Comparison of the availability of data for certain possible $C_2H_6N_2S$ isomers and presence of N–N and $(CH_3)_2N$ structural fragments in the molecules

^a The melting point is higher than room temperature.

Table 6. Comparison of the retention indices of compounds with varied N-CH fragment

Structure	RI	Structure	RI	$\Delta RI(O \rightarrow S)$
$(CH_3)_2N-N=S$	998±2 ^a	$(CH_3)_2N-N=O$	708±5	+290
$(CH_3)_2N$ -CH=S	1004±7	$(CH_3)_2N$ – $CH=O$	749±16	+255
$\Delta RI(N \rightarrow CH)$	+6		+41	

^a Checked value.

how the retention indices vary in going from dimethylthioxohydrazine to dimethylthioformamide, dimethyl-*N*-nitrosamine, and dimethylformamide. One can see without calculations that the retention indices of compounds with varied CH–N fragment are fairly close to each other (Table 6).

Such analogy allows the retention index of dimethylthionitrosamine to be estimated by the following scheme.

$$(CH_3)_2N-N=O + (CH_3)_2N-CH=S - (CH_3)_2N-CH=O$$

= $(CH_3)_2N-N=S$,
 $(708 \pm 5) + (1004 \pm 7) - (749 \pm 16) = 963 \pm 18$.

This estimate coincides, even though not very exactly (within two standard deviations), with the experimental *RI* value of 998 \pm 2, which is quite acceptable for previously unknown compounds.

The chromatographic retention indices of new compounds, determined for the first time, can be included into the corresponding databases and used for identification of these compounds.

EXPERIMENTAL

Spiking soils with unsymmetrical dimethylhydrazine, preparation of the reaction mixtures, and sample preparation for analysis were performed as described in [1, 3, 4]. The GCMS analysis was performed on a JMS-D300 mass spectrometer coupled with a HP 5890 gas chromatograph. Chromatography conditions: DB-5 quartz capillary column (30 m × 0.5 mm × 0.25 μ m); temperature program: initial 30°C (hold 4 min), ramp rate 5–12 deg/min, final 300°C (hold 5–10 min); injector temperature 280°C, split ratio 1 : 6, carrier gas helium (5 mL/min). Mass spectrometry conditions: ionizing energy 70 eV, accelerating voltage 3 kV, mass range from m/z 10–40 to 450–650, ion source temperature 130–170°C. Identification was performed using WILEY275, NBS75K, and NIST98 databases or considering the principal regularities of mass spectral fragmentation of organic compounds [42].

1,1-Dimethyl-2-thioxohydrazine. Mass spectrum, $m/z > 40 \ (I_{rel} \ge 2\%): 92 \ (6), 91 \ (3), 90 \ (100) \ [M]^+, 75 \ (30) \ [M - CH_3]^+, 58 \ (4), 56 \ (6), 47 \ (4), 46 \ (16) \ [M - (CH_3)_2N]^+, 44 \ (10) \ [C_2H_6N]^+, 43 \ (25), 42 \ (39), 41 \ (6).$ The intensity of the m/z 44 signal is variable, because it overlaps with the background signal of CO₂.

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