Chromatographic and IR characteristics of methyl-, formyl-, and acetyl-substituted furans and thiophenes

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The GC and FTIR spectral characteristics of methyl-, formyl-, and acetyl-substituted furans and thiophenes were determined. The substituent contributions to the retention indices were calculated. It was found that contributions of identical substituents differ according to the nature of the heterocycle, their position relative to the heteroatom and other neighboring groups. The contributions of CH_3-, CHO-, and $COCH_3$-groups in the β-position of the cycle for monosubstituted substances were equal to the contributions of these groups in monosubstituted benzenes. The contributions of carbonyl groups in the α-position were greater than in the β-position for the same groups. The contributions were found to be non-additive for disubstituted methyl and carbonyl-containing thiophenes and furans. The presence of two carbonyl groups as substituents in furans and thiophenes results in reduction of the sorption energy of the latter, which is known as «negative» α-effect. The scheme for *a priori* calculation of retention indices taking into account the non-uniformity of the contributions of methyl and carbonyl substituents in thiophenes and furans was suggested. The indices of 12 unknown substances of these classes were calculated.

Key words: capillary gas chromatography; FTIR spectroscopy; methyl-, formyl-, and acetyl-substituted furans and thiophenes; scheme for prediction of retention indices.

The gas chromatography methods for the identification of trace amounts of organic compounds in complex mixtures are based on making a comparison between experimental values of retention indices for a number of various sorbents. A study of the correlation between structure and sorption ability allows the number of available retention indices to be extended considerably, because on the basis of this correlation the indices of compounds that are difficult to obtain and isomeric compounds can be calculated. Previously we have studied the structure—sorption ability correlation of thienyl and furfuryl alkyl sulfides; IR and mass spectral characteristics of these compounds have also been obtained.[1,2] Thiophene and furan derivatives are the most important components of food aroma,[3,4] model systems,[5—9] and fragrance volatiles.[10—13] As a rule isomers of alkyl-, formyl-, and acetyl-substituted furans and thiophenes are present in mixtures. The mass spectra of these isomers are practically identical, therefore the most important characteristics, which make it possible to identify these compounds, are their retention indices on columns of various polarity.

The purposes of this study are to investigate the sorption parameters of methyl-, formyl-, and acetyl-substituted furans and thiophenes on polar and nonpolar columns; to determine the spectral characteristics of these compounds by FTIR spectroscopy; to evaluate the sorption contributions of substituents on the basis of GC data, and to apply these values in schemes for predicting the retention indices of substituted furans and thiophenes.

Experimental

GC analysis of furans and thiophenes, shown in Table 1, was carried out on a 5710-A «Hewlett Packard» chromatograph with a flame-ionization detector and a capillary quartz column with immobilized methyl-silicon SPB-1 from Supelco (60 m × 0.32 mm; d_f = 0.25 μm), a capillary glass column with SP-2300 phase (50 m × 0.32 mm; d_f = 0.25 μm), and a packed column with ~5 % OV-210 on Chromosorb W-AW (210 × 0.4 cm). The temperature of the evaporator and detector was 200 °C. The ratio of the division of gas flow at the entrance to the capillary column was 1:40, and *V* of the samples analyzed were 0.5 μL of 1 % solutions of the compounds or their mixtures with *n*-alkanes in pentane. Kovac indices (*I*) were measured at 100 °C and are given in Table 1 as the average of 4—5 measurements. When the temperature of the analysis was programmed to go from 50 to 200 °C at a rate of 8 deg min^{-1}, the indices (I_{pr}) were calculated by the Van den Dool and Kratz[14] formula using the retention times of the compound and *n*-alkanes.

The GC and IR spectral analyses of thiophenes and furans were performed on a «Bruker IFS-88» FTIR-spectrometer, connected to a Mega-5300 (Carlo-Erba) chromatograph with a quartz capillary column SE-52 (60 m × 0.32 mm; d_f = 2 μm). The temperature was programmed to go from 50 to 250 °C at a rate of 8 deg min^{-1}. The helium flow rate was

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Table 1. Retention indices of methyl-, formyl-, and acetyl-substituted furans and thiophenes for chromatographic columns with various polarity

Compound	SPB-1		OV-210	SP-2300
	I_l	I_{pr}	I_l	I_l
Furan	500	—	611	—
2-Methylfuran	594	585	722	—
2,5-Dimethylfuran	696	685	831	—
2-Formylfuran	805	800	1195	—
2-Formyl-5-methylfuran	934	927	1360	—
3-Formyl-2-methylfuran	936	931	1355	—
2-Acetylfuran	886	881	1277	1453
2-Acetyl-5-methylfuran	1010	1007	1426	1586
2-Acetyl-5-formylfuran	1118	1116	—	—
Thiophene	668	658	804	974
2-Methylthiophene	770	761	908	1077
3-Methylthiophene	776	768	928	1102
2,5-Dimethylthiophene	864	855	1020	—
2-Formylthiophene	974	963	1356	1610
3-Formylthiophene	960	950	1327	1579
2-Formyl-5-methylthiophene	1088	1082	1497	1712
3-Formyl-2-methylthiophene	1091	1086	1495	1714
2-Acetylthiophene	1061	1055	1467	1696
3-Acetylthiophene	1053	1048	1445	1674

Note. I_l — retention indices at 100 °C, I_{pr} — temperature programmed at 8 deg min^{-1}.

1.5 mL min^{-1}. The temperature of the evaporator, detector, transfer line and flow cuvette of the light guide (20 × 0.1 cm) was 200 °C. Additional helium was introduced into the cuvette at a rate of 8 mL min^{-1}. A mercury-cadmium-tellurium detector registered absorption in the 600—4000 cm^{-1} wave number region.

Results and Discussion

Furans and thiophenes with methyl-, formyl-, and acetyl-substituents in different positions of the heterocycle were analyzed on columns of various polarity. OV-210 and SP-2300 phases were selected as the polar phases. These phases contain trifluoropropyl and cyanoethoxypropyl groups capable of specific donor-acceptor interactions with non-polar compounds. It is shown in Table 1 that the isothermal indices of the non-polar SPB-1 column are several units higher than those in the cases where the temperature was programmed (I_{pr}). At 100 °C the vapors of isomeric methylformylfurans and -thiophenes are not separated on practically all the columns. In the case of programmed temperature these isomers are separated on SPB-1. Usually GC analysis of natural mixtures is carried out on immobilized non-polar columns with programmed temperature, especially if IR or mass spectral methods are additionally used. I_{pr} indices of SPB-1 can be used for identification of substituted thiophenes and furans.

Table 2. The contributions of methyl, formyl, and acetyl groups to the retention indices of substituted furans and thiophenes for capillary columns of different polarity at 100 °C

Compared compounds	Substituent (surroundings)	δI (i. u.)		
		SPB-1	OV-210	SP-2300
2-Methylthiophene — thiophene	α-CH_3	102	104	103
3-Methylthiophene — thiophene	β-CH_3	108	124	128
2-Methylfuran — furan	α-CH_3	94	111	—
2,5-Dimethylthiophene — 2-methylthiophene	α-CH_3 (α'-CH_3)	96	112	—
2,5-Dimethylfuran — 2-methylfuran	α-CH_3 (α'-CH_3)	102	109	—
5-Formyl-2-methylthiophene — 2-formylthiophene	α-CH_3 (α'-CHO)	114	141	102
2-Formyl-3-methylthiophene — 3-formylthiophene	β-CH_3 (α'-CHO)	117	139	104
5-Formyl-2-methylfuran — 2-formylfuran	α-CH_3 (α'-CHO)	129	165	—
2-Formyl-3-methylfuran — 2-formylfuran	β-CH_3 (α'-CHO)	131	160	—
5-Acetyl-2-methylfuran — 2-acetylfuran	α-CH_3 (α'-$COCH_3$)	124	149	—
2-Formylthiophene — thiophene	α-CHO	303	552	636
3-Formylthiophene — thiophene	β-CHO	288	523	605
2-Formylfuran — furan	α-CHO	305	584	—
5-Formyl-2-methylthiophene — 2-methylthiophene	α-CHO (α'-CH_3)	315	589	635
2-Formyl-3-methylthiophene — 3-methylthiophene	α-CHO (β-CH_3)	311	567	612
5-Formyl-2-methylfuran — 2-methylfuran	α-CHO (α'-CH_3)	339	638	—
5-Formyl-2,4-dimethylfuran — 2,4-dimethylfuran	α-CHO (β'-CH_3)	316	572	—
2-Acetylthiophene — thiophene	α-$COCH_3$	390	663	722
3-Acetylthiophene — thiophene	β-$COCH_3$	382	641	705
2-Acetylfuran — furan	α-$COCH_3$	386	663	—
5-Acetyl-2-methylfuran — 2-methylfuran	α-$COCH_3$ (α'-CH_3)	416	704	—
5-Acetyl-2-formylfuran — 2-acetylfuran	α-CHO (α'-$COCH_3$)	232	—	—
5-Acetyl-2-formylfuran — 2-formylfuran	α-$COCH_3$ (α'-CHO)	313	—	—

Table 3. The contributions of methyl groups to the retention indices of aromatic and heterocyclic compounds for non-polar phases (OV-101, SE-30, SPB-1)

Compared compounds	Substituent (surroundings)	$\delta I(CH_3)$
Toluol — benzene	CH_3	105
p-Methyltoluol — toluol	γ-CH_3 (CH_3)	101
m-Methyltoluol — toluol	β-CH_3 (CH_3)	101
o-Methyltoluol — toluol	α-CH_3 (CH_3)*	126
p-Methylbenzaldehyde — benzaldehyde	γ-CH_3 (CHO)	120
m-Methylbenzaldehyde — benzaldehyde	β-CH_3 (CHO)	106
o-Methylbenzaldehyde — benzaldehyde	α-CH_3 (CHO)*	107
p-Methylacetophenone — acetophenone	γ-CH_3 ($COCH_3$)	118
m-Methylacetophenone — acetophenone	β-CH_3 ($COCH_3$)	108
o-Methylacetophenone — acetophenone	α-CH_3 ($COCH_3$)*	70
Methylpyrazine — pyrazine	α-CH_3	91
2,3-Dimethylpyrazine — pyrazine	α-CH_3 (α-CH_3)*	96
2,5-Dimethylpyrazine — pyrazine	α-CH_3 (CH_3)	88
2,6-Dimethylpyrazine — pyrazine	α-CH_3 (CH_3)	88
3-Acetyl-2-methylpyrazine — acetylpyrazine	α-CH_3 ($COCH_3$)*	68
5-Acetyl-2-methylpyrazine — acetylpyrazine	α-CH_3 ($COCH_3$)	100
6-Acetyl-2-methylpyrazine — acetylpyrazine	α-CH_3 (α-$COCH_3$)	95
2-Methylpyridine — pyridine	α-CH_3	69
3-Methylpyridine — pyridine	β-CH_3	114
4-Methylpyridine — pyridine	γ-CH_3	118
5-Methyloxazole — oxazole	α_O-CH_3	103
5-Methylthiazole — thiazole	α_S-CH_3	105
4-Methylthiazole — thiazole	α_N-CH_3	71
Benzaldehyde — benzene	CHO	285
p-Methylbenzaldehyde — toluol	γ-CHO (CH_3)	300
m-Methylbenzaldehyde — toluol	β-CHO (CH_3)	287
o-Methylbenzaldehyde — toluol	α-CHO (CH_3)*	288
Acetophenone — benzene	$COCH_3$	386
p-Methylacetophenone — acetophenone	γ-$COCH_3$ (α'-CH_3)	391
m-Methylacetophenone — acetophenone	β-$COCH_3$ (α'-CH_3)	389
o-Methylacetophenone — acetophenone	α-$COCH_3$ (α'-CH_3)*	350
Acetylpyrazine — pyrazine	$COCH_3$	283
3-Acetyl-2-methylpyrazine — methylpyrazine	α-$COCH_3$ (α-CH_3)*	260
5-Acetyl-2-methylpyrazine — methylpyrazine	α-$COCH_3$ (α-CH_3)	292
6-Acetyl-2-methylpyrazine — methylpyrazine	α-$COCH_3$ (α'-CH_3)	277

* Compounds with the substituents in the *ortho*-position.

The position of substituents in furans and thiophenes affects their retention ability (see Table 1). We have calculated the contributions of methyl, formyl, and acetyl groups to quantitatively estimate the influence of the position and structure of substituents on the retention indices (Table 2). Thiophene, 2- and 3-methylthiophenes, 2- and 3-formyl-, acetylthiophenes, and furans with analogous substituents were used as the initial compounds to determine the contributions of the substituents. It is clear from Table 2 that the contributions of substituents vary according to their position in the cycle, the structure of other substituents, and the polarity of the stationary phase. In addition the $\delta I(CH_3)$ value of a β-position substituent in thiophene is similar to that of methylbenzene[13—17] (Table 3). The contribution of the CH_3 group in the α-position is 6 i. u. lower than the contribution of this group in the β-position, *i.e.*, there is a weak α-effect in α-methylthiophene. In 2-methylfuran $\delta I(CH_3)$ is 94 i. u. for SPB-1 and 111 i. u. for OV-210. The CH_3 group of 5-methyloxazole and 5-methylthiazole makes similar contributions, which were calculated by us according to the literature data[16] (see Table 3). However the contribution of the α-CH_3 group, which is adjacent to the nitrogen atom, is lower, *e.g.*, in a non-polar phase the value $\delta I(CH_3)$ for α-methylpyrazine is 91 i. u. (Ref. 18), and for α-methylpyridine and 4-methylthiazole — only 69—71 i. u. (see Table 3). Methyl groups in β- and γ-methylpyridine make contributions similar to those of isolated CH_3 groups, *i.e.*, 114—118 i. u. (see Table 3). Thus, the α-CH_3 group contribution is noted to be lower in α-methylthiophene, -furan, as well as in nitrogen heterocyclic compounds than in β-isomers.

In the cases of the OV-210 and SP-2300 polar phases used in this work, an unusual effect is observed, *i.e.*, an increase in the CH_3 group contribution compared with that on a non-polar phase. Previously it was pointed out that on the polar phase CW-40M, the β-CH_3 group of 3-methylthiophene makes a contribution[19] of 97 i. u., which is lower than that on methylsilicon phases, and in the case of OV-210 and SP-2300 stationary polar phases the β-CH_3 group contribution is 124—128 i. u. In comparison with the α-CH_3 group, the β-CH_3 group contribution to the retention indices of these phases is 20—25 i. u. greater. This fact indicates the existence of weak donor-acceptor interactions between the β-methylthiophene and -furan CH_3 groups with the trifluoropropyl groups of OV-210.

The introduction of a second CH_3 group to the α'-position of furan and thiophene results in non-additive increases in the retention indices by 102 i. u. and 96 i. u., respectively. In *p*- and *m*-xylenes these contributions are 101 i. u., and in 2,5- and 2,6-dimethylpyrazines — 88 i. u., which means that they are also different (see Table 3). Therefore, the contributions of the CH_3 group to the retention indices of aromatic heterocyclic compounds (including those of the thiophenes and furans studied in our work) differ according

Table 4. IR spectra of substituted thiophenes in the gas phase at 200 °C

Compound	ν/cm^{-1} (I (%))
Thiophene	694 (61), 710 (100), 729 (67), 837 (35), 848 (32), 1080 (11), 1265 (16), 1408 (20), 1568 (11), 1778 (4), 3097 (14)
3-Methylthiophene	679 (13), 759 (100), 848 (26), 922 (6), 1396 (14), 1446 (17), 1539 (14), 2889 (21), 2939 (36), 3062 (11),
2,5-Dimethylthiophene	663 (6), 791 (100), 953 (9), 1041 (13), 1161 (22), 1234 (34), 1338 (8), 1450 (25), 1570 (12), 1720 (7), 2750 (6), 2881 (57), 2939 (100), 3078 (40)
3-Formylthiophene	729 (13), 783 (26), 1080 (4), 1153 (14), 1238 (16), 1404 (14), 1516 (14), 1720 (100), 2800 (15)
2-Formylthiophene	667 (15), 717 (38), 818 (8), 1041 (10), 1207 (29), 1361 (5), 1423 (23), 1524 (10), 1709 (100), 2808 (13), 3089 (2)
2-Acetylthiophene	714 (51), 852 (14), 933 (10), 1057 (11), 1257 (81), 1365 (31), 1419 (47), 1520 (23), 1697 (100), 3020 (4), 3089 (5)
3-Acetylthiophene	644 (18), 783 (31), 867 (25), 1084 (8), 1196 (18), 1253 (69), 1361 (16), 1408 (37), 1516 (28), 1705 (100),
2-Formyl-3-methylthiophene	664 (10), 729 (24), 779 (8), 1199 (15), 1419 (20), 1531 (10), 1697 (100), 2727 (11), 2824 (11), 2939 (6)
2-Formyl-5-methylthiophene	675 (11), 799 (16), 1045 (9), 1215 (25), 1642 (36), 1705 (100), 2724 (8), 2800 (16), 2935 (7), 3078 (3)

to the substituent position. In addition, the longer the distance between the CH_3 group and the heteroatom, the greater this group's contribution to the retention index.

In contrast to 2- and 3-methylthiophenes, the retention times of α-substituted formyl- and acetylthiophenes are longer than those of the β-isomers, and this difference between the retention indices increases with the increase in the phase polarity, *i.e.*, from 15 i. u. on SPB-1 to 31 i. u. on SP-2300 (in the case of formylthiophenes) (see Table 2). This difference is smaller for acetylthiophenes. Contrary to 2-acetyl-substituted thiophene and furan, in acetylpyrazine the acetyl group contribution is almost 100 i. u. lower (see Table 3). Thus, when a nitrogen atom is present in the cycle, the α-effect appears to give a non-additive decrease in the retention indices of substituted nitrogen compounds. We have named this phenomenon the «negative» α-effect, and that of α- and β-formylthiophenes the «positive» α-effect, the latter giving an increase in the contribution of the α-substituent.

The contributions of the CHO and $COCH_3$ groups in 3-substituted thiophenes are equal to those of phenylaldehide and acetophenone (see Table 3), because these groups are in a position remote from the heteroatom, and it is possible to consider them as isolated beyond heteroatom influence. On the other hand, a substituent in the α-position to the heteroatom changes the contribution of the latter to the retention time of the compound.

The non-equivalence of the formyl and acetyl groups in the α- and β-positions of thiophene can also be concluded from a comparison of the IR spectra of thiophene, 2- and 3-formylthiophenes, and 2- and 3-acetylthiophenes (Table 4). Thiophenes have a specific absorption band with ν = 1265 cm^{-1} (for thiophene), which is shifted to ν = 1238 cm^{-1} for 3-formylthiophene, and to ν = 1207 cm^{-1} for 2-formylthiophene. These facts confirm the existence of conjugation of the cycle bonds with the C=O bond of the formyl group. In 2- and 3-acetylthiophenes the above-mentioned band is only insignificantly shifted (ν = 1254—1257 cm^{-1}), but the band intensity is very high, which also indicates conjugation between the cycle and the C=O bonds. The absorption bands of the carbonyl groups of the 2-isomers are also shifted to lower frequencies than those of the 3-isomers, indicating a difference between the α- and β-carbonyl groups and the conjugation of the cycle bonds with the C=O bond in the α-substituted isomers. As a result, the retention times of α-isomers are greater than the retention times of β-isomers.

When furans and thiophenes have two substituents, *i.e.*, polar and non-polar substituents, the contributions of the CH_3, CHO, and $COCH_3$ groups to the retention indices are greater than in the case of the analogous monosubstituted compounds. Thus, the contribution of the CH_3 group in 5-formyl-2-methylthiophene is 114 i. u. (on SPB-1), and it is 12 i. u. greater than in 2-methylthiophene. In 5-formyl-2-methylfuran the contribution of the CH_3 group is 129 i. u., and in 2-methylfuran it is only 94 i. u. A similar effect has also been found for 5-acetyl-2-methylfuran (see Table 2). On the polar phase OV-210 the contribution of the CH_3 group in these compounds is much greater than in 2-methylfuran and thiophene, *i.e.*, 165 i. u. for 5-formyl-2-methylfuran and 141 r. u. for 5-formyl-2-methylthiophene. Therefore, it is evident that the introduction of a formyl or acetyl group to 2-methylthiophene and furan results in a dramatic increase in the contributions of the substituents. The results collected in Table 3 allow the contributions of these groups in other aromatic and heterocyclic compounds to be compared. The introduction of CH_3 group to the *m*- and *o*-positions of benzaldehyde gives a 1—2 i. u. increase in $\delta I(CH_3)$; in the *p*-position it is 15 i. u. In the case of acetophenone the same tendency has been found: a CH_3 group in the *p*-position has the maximum contribution (13 i. u.), for the *m*-position $\delta I(CH_3)$ is only 3 i. u., and for the *o*-position the value of $\delta(CH_3)$ decreases by 35 i. u., *i.e.*, in this case the «negative» *ortho*-effect takes place for CH_3 and $COCH_3$ neighbouring groups (a decrease in the contributions of these two groups when they are drawn together), whereas the «positive» *ortho*-effect is observed in the presence of two methyl groups, *e.g.*, in *o*-xylol (see Table 3).

Thus, the contributions of all of the aromatic and heterocyclic compounds are affected by the substituents. As a result, the retention indices of disubstituted derivatives increase non-additively, and it is impossible to apply additive schemes based on the equivalence of contributions for substituted carbonyl-containing compounds.

The considerable difference between the IR spectrum of 5-formyl-2-methylthiophene and the IR spectra of 2-formylthiophene and 2,5-dimethylthiophene (see Table 4) also gives evidence for the reciprocal influences of the CH_3 and CHO groups, which leads to a shift of the carbonyl absorption band and to changes of the thiophene ring characteristic frequencies (ν/cm^{-1}: 1215, 1207, 1234 and 1462, 1423, 1450, respectively). The intensity of these bands increases in 5-formyl-2-methylthiophene in comparison with 2-formylthiophene. These differences in the IR spectra confirm the non-equivalence of the substituents in 5-formyl-2-methylthiophenes and those in 2,5-dimethyl- or 2-formylthiophenes. As a result, the substituent contributions in 2,5-disubstituted thiophene are greater than the contributions of the isolated substituents.

The contributions of the methyl and formyl groups in 2-formyl-3-methylthiophene and furan are not additive either. The contributions of the neigbouring CH_3 and CHO groups are greater than those in 3-methylthiophene, 2-formylthiophene, and in the corresponding substituted furans. On the other hand, when there are two carbonyl substituents in the α- and α'-positions of a heterocycle, a different effect arises. For example, the contribution of the CHO group in 2-formylfuran is 305 i. u. (SPB-1), and the contribution of the $COCH_3$ group in 2-acetylfuran is 386 i. u., whereas the contributions of the same groups in 5-acetyl-2-formylfuran are 232 i. u. and 313 i. u., respectively. Thus, the sorption energy of this compound decreases (see Table 2), and a «negative» α-effect is observed.

For calculations of the retention indices of monosubstituted thiophenes and furans the contributions of the substituents, given in Table 2, can be used. In the case of disubstituted thiophenes and furans it is possible to sum the index values of unsubstituted furan and thiophene, the corresponding contributions of CH_3, CHO, and $COCH_3$ groups (see Table 2), and the increments δI, which take into account the deviations from additivity and reciprocal influences of the substituents under consideration. In Table 5 the increment values calculated for an SPB-1 column are given.

Table 5. Increments for calculation of the retention indices (δI) of disubstituted furans and thiophenes, allowing for reciprocal influences of the substituents (SPB-1, 100 °C)

Substituent (surroundings)	δI	
	Furan	Thiophene
α-CH_3(α'-CH_3)	9	−6
α-CH_3(α'-CHO)	35	12
α-CH_3(β-CHO)	37	13
α-CH_3(α'-$COCH_3$)	30	12
α-CHO(α'-$COCH_3$)	−73	−73
α-CH_3(α'-CH_3, β-CH_3)	12	—

In Table 6 the predicted values of the retention indices for 12 substituted furans and thiophenes that were not studied are given, calculated according to the following scheme. For example, the retention index for 2,3,5-trimethylfuran is calculated as follows:

$$I = I_f + 2\delta I(\alpha\text{-}CH_3) + \delta I(\beta\text{-}CH_3) + \delta I(\alpha\text{-}CH_3,\ \alpha'\text{-}CH_3), \quad (1)$$

where I_f is the retention index of unsubstituted furan, $\delta I(\alpha\text{-}CH_3)$ and $\delta I(\beta\text{-}CH_3)$ are the contributions of the α-CH_3 and β-CH_3 groups to the retention indices of 2- and 3-methylfurans (see Table 2), $\delta I(\alpha\text{-}CH_3,\ \alpha'\text{-}CH_3)$ is an increment accounting for the mutual influences of the methyl groups and the cycle heteroatom.

$$I = 500 + 2 \cdot 94 + 112 + 9 = 809 \text{ i. u.}$$

According to the results of experimental examination, the retention index of 2,3,5-trimethylfuran on SPB-1 is 810 i. u., *i.e.*, the deviation from the calcu-

Table 6. Predicted retention indices of substituted furans and thiophenes, according to Eq. (1) (SPB-1, 100 °C)

Compound	Retention index
3-Methylfuran	602
2,3,5-Trimethylfuran	809*
3-Formylfuran	790
2-Formyl-4-methylfuran	917
3-Acetylfuran	878
3-Formyl-2-methylfuran	921
2,4-Dimethylfuran	877
2,3,5-Trimethylthiophene	974
2-Formyl-4-methylthiophene	1082
5-Formyl-2,4-dimethylthiophene	1196
5-Acetyl-2-methylthiophene	1175
3-Formyl-2-methylthiophene	1086

* Experimental value is 810 i. u.

lated value is 1 i. u. In Table 6 the values of retention indices are given, which are applicable for the identification of substituted furans and thiophenes in various objects. Experimental (see Table 1) and predicted (see Table 6) indices of furans and thiophenes can be used for extension of the data base for computer identification of the components of complex mixtures.

Thus, GC and IR spectral data have demonstrated that the contributions of methyl, formyl, and acetyl groups to the retention indices of substituted furans and thiophenes are not equal. The contributions of CH_3, CHO, and $COCH_3$ groups in the β-position of monosubstituted compounds are equal to the contributions of these groups in substituted benzenes. In α-methylsubstituted furan and thiophene the «negative» α-effect is observed, whereas α-formyl and acetylthiophenes have the «positive» α-effect, unlike the same groups in the β-position. The contributions in disubstituted methyl and carbonyl-containing thiophenes and furans were noted to be greater than in monosubstituted compounds. At the same time, for compounds with two carbonyl groups in the α- and α'-positions, their contributions were much lower as a result of a strong «negative» α-effect. A scheme for predicting the retention indices of substituted furans and thiophenes was suggested. The indices of 12 non-studied substances of these classes were calculated.

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