

CHROM. 14,592

PREDICTION OF MOLECULAR STRUCTURES OF THIOLS AND SULPHIDES BY RETENTION INDICES

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SUMMARY

A method is discussed, in which the presence of thiols and sulphides is confirmed by combination of a post-column reaction and flame photometric detection. The molecular structures are determined by comparing the calculated and the observed retention indices. The retention indices of these compounds can be given in terms of the increment due to a mercapto group or a thio group and the correction values for the shielding effect of these groups by neighbouring carbon atoms.

INTRODUCTION

Recent advances in high-resolution capillary gas chromatography have made it possible to separate peaks whose retention values lie close together, thus increasing the amount of information which retention values can supply. The retention index (I) defined by Kováts¹ has a linear relationship with the free energy of solution and may be closely related to the molecular structure of the solute. It has been shown that the retention indices for several types of compounds can be accurately calculated from their molecular structures. It is, however, difficult to predict the molecular structure of compound by comparison of observed and calculated retention indices, without prior information on the type of compound or elements contained within it. In other words, if information is obtained about the unknown compound by means of a selective detector or by reaction gas chromatography, the retention index will become more useful for identification purposes. Sulphur-containing compounds are readily detected by a flame photometric detector without serious interference from coexistent substances. Furthermore, selective reactions of particular functional groups would afford information on the functional group to which the sulphur atom belongs. Fujii² utilized fractional extraction of sulphur-containing compounds in gasoline by silver nitrate and mercuric cyanide. Several earlier investigators³⁻⁵ have discussed the retention index of sulphur-containing compounds. Golovnya and Garbuzov⁵ have described the similarities observed in the retention behaviour of sulphur- and oxygen-containing compounds and have presented equations for estimating the retention index of the former from the latter.

In this paper, a method is reported by which (i) the presence of aliphatic thiols

and sulphides is confirmed by using a combination of a post-column reaction [with silver nitrate or mercury(II) chloride] and flame photometric detection and (ii) the molecular structures are determined by comparing the calculated and the observed retention indices.

EXPERIMENTAL

The gas chromatographic separations were carried out on a Shimadzu 6A gas chromatograph equipped with a flame-ionization detector (FID) and a flame photometric detector (FPD). Three open-tubular columns were prepared. Pyrex glass capillary tubes (0.25 mm I.D.), drawn with a Shimadzu GDM-1B glass-drawing machine and on the inner wall of which was formed a layer of fine particles of barium carbonate⁶, were coated with polyethylene glycol 20M (50 m length) and silicone oil DC 550 (70 m) by a dynamic technique. Glass capillary tubes of the same inner diameter were coated with silver nitrate or mercuric chloride together with polyethylene glycol 600 by a dynamic technique and were used as post-column reactors. When used for differentiation of compound types, these reactors were connected to the outlet of a separation column by a piece of thermally shrinkable PTFE and placed in the column bath. The chromatographic conditions were as follows: carrier gas, nitrogen, 1.0 ml/min; splitting ratio, 1:90; make-up gas, nitrogen, 50 ml/min; column temperature, 80°C (polyethylene glycol 20M), 70°C (silicone oil DC 550); temperatures of injection port and detector, 120 and 130°C, respectively; flow-rates of other gases, hydrogen 50 ml/min (FID) and 40 ml/min (FPD), air, 850 ml/min (FID) and 40 ml/min (FPD).

Some of the thiols and sulphides were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan) and Wako (Osaka, Japan). Other thiols were prepared from the corresponding alkyl bromides and sodium hydrosulphide⁷ and other sulphides were prepared from alkyl bromides and methanethiol⁸ or by addition of thiols to alkenes⁹. Products were identified by their mass spectra, obtained with a Hitachi RM-50 GC gas chromatograph-mass spectrometer. Identification was also supported by the results obtained with the above-mentioned reactor.

RESULTS AND DISCUSSION

Confirmation of the presence of aliphatic thiols and sulphides by use of a combination of post-column reaction and flame photometric detection

Fig. 1 shows chromatograms obtained by use of different detection systems. Chromatograms (a) and (b) are recorded by FID and FPD, respectively. In this case, the eluted substances from the column were injected directly into the detector. Chromatograms (c), (d) and (e) were recorded by FPD after the eluted substances had been forced through 3.4 and 35 cm of silver nitrate-coated and 2 cm of mercury(II) chloride-coated reactors, respectively. All reactors captured the thiols completely and no peaks ascribed to them were obtained. Thiols are converted into non-volatile metal mercaptides within the reactors. The peaks due to aliphatic sulphides are shifted by the silver nitrate, possibly because of formation of a sulphide complex with this salt. The shorter silver nitrate reactor had little influence on the retention values of sulphides but the longer one retained these and gave broadened peaks. Thus, the silver

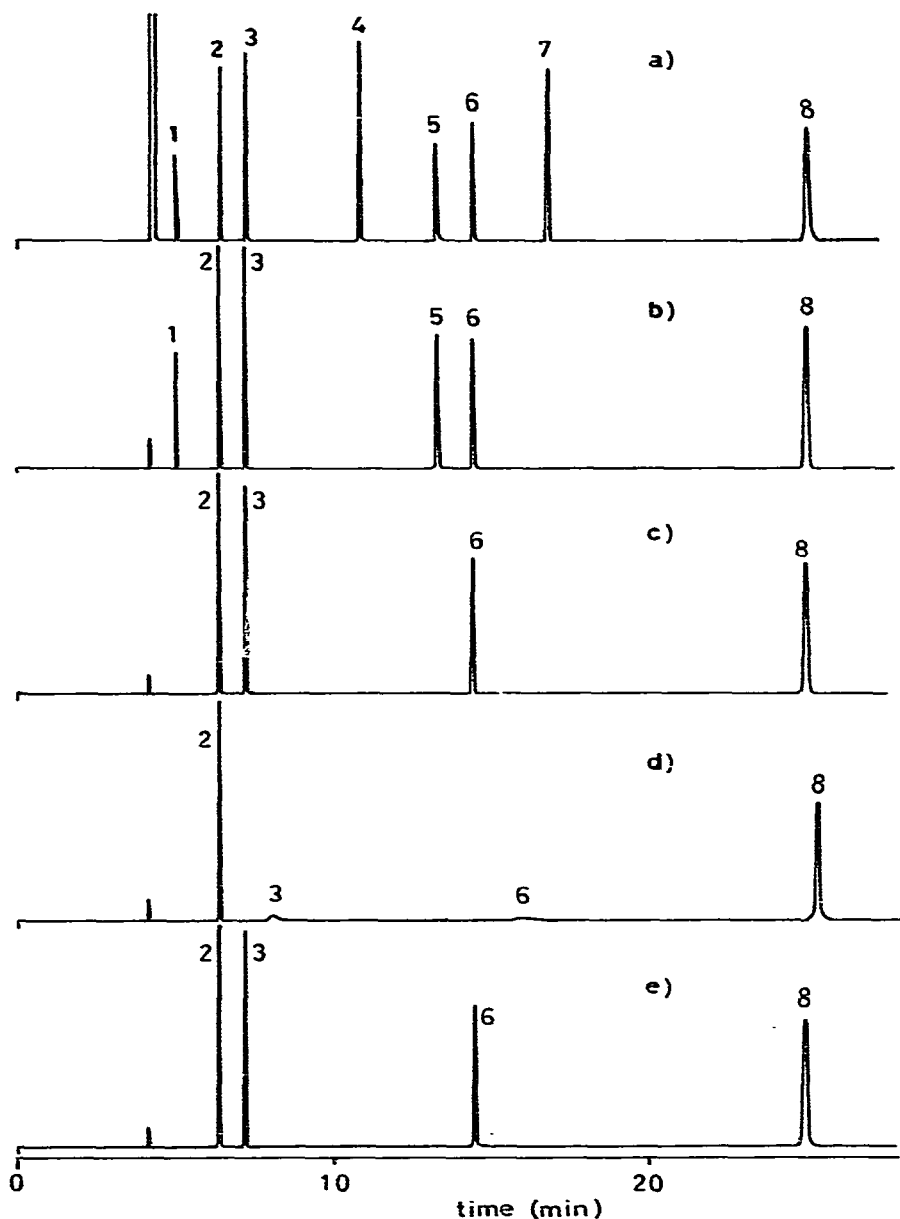
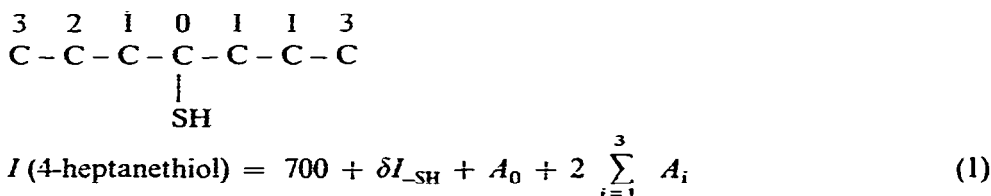


Fig. 1. Gas chromatograms obtained with different systems. (a), FID; (b) FPD; (c), post-column reactor (AgNO_3 -PEG 600, 3.4 cm) + FPD; (d), post-column reactor (AgNO_3 -PEG 600, 35 cm) + FPD; (e), post-column reactor (HgCl_2 -PEG 600, 2.0 cm) + FPD. Stationary phase: polyethylene glycol 20M, 80°C . Peaks: 1 = 2-methyl-2-butanethiol; 2 = thiophene; 3 = dipropyl sulfide; 4 = *n*-dodecane; 5 = 1-heptanethiol; 6 = dibutyl sulfide; 7 = *n*-tridecane; 8 = dipropyl disulfide.

nitrate reactor may be useful for the confirmation of not only thiols but also sulfides. A longer mercury(II) chloride reactor (*ca.* 100 cm) does not retain sulfides. This reactor is useful as a thiol-specific subtractor.

Prediction of retention indices of aliphatic thiols

Table I shows the retention indices of straight-chain thiols. I^{PEG} and I^{DC550} indicate the indices on polyethylene glycol 20M and silicone oil DC 550, respectively, ΔI being the difference between them. As shown in Table I, not all the increments of I corresponding to insertion of a methylene group in a homologous series are equal to 100. The retention index is apparently affected by the length of the alkyl chain, which possibly reflects that alkyl chains hinder a mercapto group from coming close to the polar site of the solvent molecule in the stationary phase. Thus the retention index of a thiol can be represented as the sum of the increment for a mercapto group, the correction values for the shielding effect by alkyl chains and $100 \times$ the carbon number, similar to that for a haloalkane¹⁰. As an example, the I value of 4-heptanethiol may be represented by the following equation:



where $\delta I_{\text{-SH}}$ is the increment of I for a mercapto group and A_i is the correction value for the shielding effect by each carbon atom; the sum of A_i therefore means the shielding effect of an alkyl chain. For all the other thiols, the additive structural

TABLE I

RETENTION INDICES OF STRAIGHT-CHAIN THIOLS ON POLYETHYLENE GLYCOL 20M AND SILICONE OIL DC 550

I^{PEG} = retention index on polyethylene glycol 20M at 80°C, I^{DC550} = retention index on silicone oil DC550 at 70°C, $\Delta I = I^{\text{PEG}} - I^{\text{DC550}}$, $D_1: I_{\text{calcd.}}^{\text{PEG}} - I_{\text{obsd.}}^{\text{PEG}}$, $D_2: \Delta I_{\text{calcd.}} - \Delta I_{\text{obsd.}}$.

Compound	Observed			Calculated			
	I^{PEG}	I^{DC550}	ΔI	I^{PEG}	D_1	ΔI	D_2
1C ₅ SH*	1047.9	866.1	181.8	1048.1	+0.2	181.1	-0.7
1C ₆ SH	1148.0	967.2	180.8	1147.8	-0.2	181.5	+0.7
1C ₇ SH	1248.7	1068.7	180.0	1248.7	0.0	180.0	0.0
2C ₅ SH	964.9	806.3	158.6	962.8	-2.1	155.6	-3.0
2C ₆ SH	1062.1	907.8	154.3	1060.4	-1.7	154.4	+0.1
2C ₇ SH	1160.0	1004.4	155.6	1160.2	+0.2	154.9	-0.7
3C ₅ SH	973.9	815.5	158.4	971.7	-2.2	155.8	-2.6
3C ₆ SH	1058.0	906.0	152.0	1057.1	-0.9	152.5	+0.5
3C ₇ SH	1153.2	1002.5	150.7	1154.8	+1.6	151.4	+0.7
4C ₇ SH	1140.9	993.0	147.9	1142.5	+1.6	149.2	+1.3

* For example, 1C₅SH indicates 1-pentanethiol.

TABLE II

INCREMENTS OF I AND ΔI FOR A MERCAPTO GROUP [δI_{-SH} , $\delta(\Delta I)_{-SH}$] AND THE CORRECTION VALUES FOR HINDRANCE BY METHYLENES (A_i)

$\delta I_{-SH} = \delta I_{-SH} + A_0(I)$, $\delta I_{-SH} = \delta(\Delta I)_{-SH} + A_0(\Delta I)$, δI_{-SH} (PEG 20M) = 658.3, δI_{-SH} (DC 550) = 443.1, $\delta(\Delta I)_{-SH} = 215.2$.

Parameter	$i = 1$	2	3	4	5	6
A_i (PEG 20M)	-87.7	-5.6	-14.6	-2.3	-0.2	+0.5
A_i (DC550)	-61.0	-2.6	-11.3	-1.2	-0.7	+2.4
(ΔI)	-26.7	-3.0	-3.3	-1.1	+0.5	-1.5

influence can be represented by a similar formula. The increments and the correction values were determined by the least-squares method from the observed I values and the above relationships. The values assigned are shown in Table II. As δI_{-SH} and the correction value for the carbon atom bonded to the mercapto group (A_0) cannot be determined independently, the sum of them ($\delta I'_{-SH}$) is given in Table II. In Table I, the calculated I and ΔI values are compared with the corresponding observed values.

Table III shows the retention indices of branched-chain thiols on silicone oil DC 550. The I values of these compounds cannot be predicted by using only the increment and the correction values in Table II; the effect of methyl branching must additionally be evaluated. This may be divided into two terms. (i) one is the contribution of methyl branching itself. This can be evaluated from the I value of the corresponding branched-chain alkane. It can be calculated as above by regarding a methyl branching as a functional group. Table IV shows the increment (δI_{Me}) for a methyl branching and the correction values (B_i) for the steric situation around it. As δI_{Me} , B_0 and B_1 cannot be determined independently, the sum of them is given in Table IV; $\delta I_{Me} = \delta I_{Me} + B_0 + 2B_1$. They were determined as follows; first, a linear plot was obtained between the observed I values on silicone oil DC 550 and the published I values on squalane¹¹. Secondly, I^{DC550} values for many branched-chain alkanes were evaluated from this plot. Finally, the values in Table IV were determined by expressing the structure of methyl-branched alkanes in the same way as that of linear thiols and by applying the least-squares method to the evaluated I^{DC550} values. (ii) The other term is the effect due to the positional relationship between methyl branching and a mercapto group. The calculated I^{DC550} values are shown in Table III and are obtained by taking into account only the individual contributions of a methyl branching and a mercapto group. The difference between the observed and the calculated values seems to correspond to the increment based on the positional relationship.

Prediction of retention indices of aliphatic sulphides

Table V shows the retention indices of straight-chain sulphides. The retention index of a sulphide can be represented as being based on incremental structural contributions. For example, the I value of propyl butyl sulphide is represented as follows:



$$I(C_3SC_4) = \delta I_{-S} + \sum_{i=1}^3 C_i + \sum_{i=1}^4 C_i + 700 \quad (2)$$

TABLE III

RETENTION INDICES OF BRANCHED-CHAIN THIOLS ON SILICONE OIL DC 550 AT 70°C

$$D: f_{\text{obsd.}}^{\text{DC550}} - f_{\text{calcd.}}^{\text{DC550}}$$

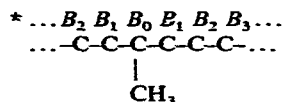
Compound	$f_{\text{obsd.}}^{\text{DC550}}$	$f_{\text{calcd.}}^{\text{DC550}}$	D
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{SH} \end{array}$	836.9	849.7	-12.8
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{SH} \end{array}$	928.0	938.3	-10.3
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{SH} \end{array}$	829.7	849.7	-20.0
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{SH} \end{array}$	937.2	954.0	-16.8
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{SH} \end{array}$	930.4	938.3	- 7.9
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{SH} \end{array}$	753.9	800.0	-46.1
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{SH} \end{array}$	838.9	878.5	-39.6
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{SH} \end{array}$	873.1	902.9	-29.8
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{SH} \end{array}$	811.6	800.0	+11.6
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{SH} \end{array}$	893.0	887.2	+ 5.8
$\begin{array}{c} \text{C} \\ \\ \text{C}-\text{C}-\text{C}-\text{C}-\text{C} \\ \\ \text{SH} \end{array}$	859.6	878.5	-18.9

TABLE IV

INCREMENT OF I^{PC550} FOR A METHYL BRANCHING (δI_{Mc}) AND CORRECTION VALUES FOR ITS STERIC SITUATION

$$\delta I_{Mc} = \delta I_{Mc} + B_0 + 2B_1^* = 76.0.$$

Parameter	$i = 2$	3	4	5	6
B_i	+5.5	-10.2	-4.5	-2.6	-0.7



where δI_{-S-} and C_i are the increment for a thiol group and the correction value for the shielding effect by each carbon atom, respectively. The values assigned to them are shown in Table VI. As δI_{-S-} and C_1 cannot be determined independently, the sum of them is given in Table VI; $\delta I'_{-S-} = \delta I_{-S-} + 2C_1$. The calculated I values are compared with the observed values in Table V. The good agreement between them indicate that the deviation from the regularities in I shown in Table VI is small. The retention index of branched-chain sulphides may be represented in the same way as that of branched-

TABLE V

RETENTION INDICES OF STRAIGHT-CHAIN SULPHIDES ON POLYETHYLENE GLYCOL 20M AND SILICONE OIL DC 55G

Symbols as in Table I.

Compound	Observed			Calculated			
	I^{PEG}	I^{PC550}	AI	I^{PEG}	D_1	AI	D_2
$C_4SC_1^*$	1029.3	860.8	168.5	1031.5	+2.2	167.9	-0.6
C_5SC_1	1128.1	963.0	165.1	1128.0	-0.1	165.0	-0.1
C_6SC_1	1227.0	1064.5	162.5	1226.1	-0.9	163.0	+0.5
C_7SC_1	1326.8	1164.9	161.9	1325.4	-1.4	162.0	+0.1
C_3SC_1	1426.3	1265.0	161.3	1426.3	0.0	161.3	0.0
C_5SC_1	1525.7	1364.9	160.8	1525.7	0.0	160.8	0.0
C_4SC_2	1091.1	939.7	151.4	1091.6	+0.5	151.7	+0.3
C_5SC_2	1188.6	1040.2	148.4	1188.1	-0.5	148.8	+0.4
C_6SC_2	1286.6	1139.2	147.4	1286.2	-0.4	146.8	-0.6
C_7SC_2	1385.3	1239.2	146.1	1385.5	+0.2	145.8	-0.3
C_3SC_3	1080.5	933.4	147.1	1080.6	+0.1	147.0	-0.1
C_4SC_3	1173.3	1031.2	142.1	1172.4	-0.9	142.6	+0.5
C_5SC_3	1269.7	1130.2	139.5	1268.9	-0.8	139.7	+0.2
C_6SC_5	1367.0	1228.9	138.1	1367.0	0.0	137.7	-0.4
C_7SC_3	1465.2	1328.6	136.6	1466.3	+1.1	136.7	+0.1
C_4SC_4	1265.6	1127.0	138.6	1264.2	-1.4	138.4	-0.2
C_5SC_4	1361.3	1225.6	135.7	1360.7	-0.6	135.5	-0.2
C_6SC_4	1457.8	1324.5	133.3	1458.8	+1.0	133.6	+0.3
C_5SC_5	1456.3	1323.5	132.8	1457.2	+0.9	132.6	-0.2

* For example, C_4SC_1 indicates methyl butyl sulphide.

TABLE VI

INCREMENTS OF I AND ΔI FOR A THIO GROUP [δI_{-S-} , $\delta(\Delta I)_{-S-}$] AND CORRECTION VALUES FOR HINDRANCE BY METHYLENES (C_i)

$\delta I_{-S-} = \delta I_{-S-} + 2C_1 (I)^*$, $\delta(\Delta I)_{-S-} = \delta(\Delta I)_{-S-} + 2C_1 (\Delta I)$, δI_{-S-} (PEG 20M) = 598.8, δI_{-S-} (DC 550) = 401.4, $\delta(\Delta I)_{-S-} = 197.4$.

Parameter	$i=2$	3	4	5	6	7	8	9
C_i (PEG 20M)	-39.9	-19.2	-8.2	-3.5	-1.9	-0.7	+0.9	-0.6
C_i (DC 550)	-23.7	-10.1	-4.0	-0.6	+0.1	+0.3	+1.6	-0.1
(ΔI)	-16.2	-9.1	-4.2	-2.9	-2.0	-1.0	-0.7	-0.5

* ... $C_2 C_1 C_1 C_2 C_3 \dots$
 $C-C-S-C-C-C$

TABLE VII

RETENTION INDICES OF BRANCHED-CHAIN SULPHIDES ON SILICONE OIL DC 550 AT 70°C

$D = j_{DC550}^{obsd.} - j_{DC550}^{calcd.}$

Compound	$j_{DC550}^{obsd.}$	$j_{DC550}^{calcd.}$	D
$\begin{array}{c} C \\ \\ C-S-C-C-C \end{array}$	912.9	940.4	-27.5
$\begin{array}{c} C \\ \\ C-C-S-C-C-C \end{array}$	892.9	920.7	-27.8
$\begin{array}{c} C \\ \\ C-C-C-S-C-C \end{array}$	883.4	910.7	-27.3
$\begin{array}{c} C \\ \\ C-S-C-C-C-C-C \end{array}$	1009.8	1035.3	-25.5
$\begin{array}{c} C \\ \\ C-C-S-C-C-C-C \end{array}$	981.0	1006.5	-25.5
$\begin{array}{c} C \\ \\ C-C-C-S-C-C-C \end{array}$	980.6	1006.1	-25.5
$\begin{array}{c} C \\ \\ C-C-C-C-S-C-C \end{array}$	980.6	1004.1	-23.5
$\begin{array}{c} C \\ \\ C-S-C-C-C-C \end{array}$	921.8	940.4	-18.6

TABLE VII (continued)

Compound	$I_{DC550}^{obsd.}$	$I_{DC550}^{calcd.}$	D
$\begin{array}{c} \text{C} \\ \\ \text{C-C-S-C-C-C} \end{array}$	893.6	910.7	-17.1
$\begin{array}{c} \text{C} \\ \\ \text{C-S-C-C-C-C} \end{array}$	1013.5	1029.6	-16.1
$\begin{array}{c} \text{C} \\ \\ \text{C-C-S-C-C-C} \end{array}$	996.7	1012.2	-15.5
$\begin{array}{c} \text{C} \\ \\ \text{C-C-C-S-C-C} \end{array}$	982.6	998.0	-15.4
$\begin{array}{c} \text{C} \\ \\ \text{C-S-C-C-C} \end{array}$	923.4	930.4	- 7.0
$\begin{array}{c} \text{C} \\ \\ \text{C-S-C-C-C-C} \end{array}$	1030.7	1035.3	- 4.6
$\begin{array}{c} \text{C} \\ \\ \text{C-C-S-C-C-C} \end{array}$	999.4	1004.1	- 4.7
$\begin{array}{c} \text{C} \\ \\ \text{C-S-C-C-C-C} \end{array}$	1023.7	1027.2	- 3.5

chain thiols, except that the contribution of methyl branching is evaluated from the I value of the branched-chain alkane whose carbon skeleton is depicted by substituting a methylene for the thio group of the original sulphide. Table VII shows the retention indices on silicone oil DC 550 for several branched-chain sulphides. The difference between the observed and the calculated values is considered to correspond to the increment based on the positional relationship between the thio group and the methyl branching, and seems to be determined by the distance between them.

CONCLUSION

The peaks due to aliphatic thiols and sulphides can be confirmed by combination of a silver nitrate or mercury(II) chloride reactor and an FPD. The retention indices of these compounds are represented in terms of the increment due to a mercapto group or a thio group and the correction values for the shielding effect of these groups by carbon atoms, and can be accurately predicted. It is suggested that the molecular structures of thiols or sulphides can be estimated by comparison of the observed I values with the values calculated for the expected structures.

REFERENCES

- 1 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
- 2 T. Fujii, *Bunseki Kagaku (Jap. Anal.)*, 25 (1976) 141.
- 3 V. Martinuú and J. Janák, *J. Chromatogr.*, 52 (1970) 69.
- 4 G. D. Gal'pern, N. T. Gollandskikh and G. N. Gordadze, *J. Chromatogr.*, 109 (1975) 119.
- 5 R. V. Golovnya and V. G. Garbuzov, *Chromatographia*, 8 (1975) 265.
- 6 K. Grob and G. Grob, *J. Chromatogr.*, 125 (1976) 471.
- 7 L. M. Ellis and E. E. Reid, *J. Amer. Chem. Soc.*, 54 (1932) 1674.
- 8 W. R. Kirner and G. H. Richter, *J. Amer. Chem. Soc.*, 51 (1929) 3135.
- 9 S. O. Jones and E. E. Reid, *J. Amer. Chem. Soc.*, 60 (1938) 2452.
- 10 F. Morishita, Y. Terashima and T. Kojima, *J. Chromatogr.*, submitted for publication.
- 11 R. A. Hivey and R. E. Hinton, *J. Gas Chromatogr.*, 6 (1968) 203.