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## SEPARATION OF MONOHYDRIC ALKYLPHENOLS BY GAS CHROMATOGRAPHY. II

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### SUMMARY

The separation of  $C_7$ - $C_{12}$  monohydric alkylphenols,  $C_7$ - $C_8$  methoxyphenols and  $C_9$ - $C_{10}$  indanols on a capillary column coated with 95% tri(2,4-xylene)l phosphate + 5% orthophosphoric acid was studied. The relative retention times ( $R_t$ ) for the individual homologous series were determined as a function of the number of carbon atoms in the molecule. It was found for the homologous series of alkylphenols that the function  $\log R_t = f(\text{carbon number})$  has an anomalous course characterized by a sudden change in slope for all derivatives containing an  $n$ -alkyl substituent longer than  $C_3$ .

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### INTRODUCTION

This is a continuation of Part I<sup>1</sup>, which dealt with the separation of  $C_7$ - $C_{12}$  monohydric alkylphenols on a capillary column coated with 95% tri(2,4-xylene)l phosphate (TXP) + 5% orthophosphoric acid. In this paper, relative retention times ( $R_t$ ), Kováts retention indices and their temperature dependence in the range 125-150° are reported.

The aim of the work was to ascertain the dependence of the relative retention times of phenols in different homologous series on the number of carbon atoms in the molecule using a capillary column coated with TXP. Eighty substances were examined, including  $C_{10}$ - $C_{12}$  monohydric alkylphenols and  $C_7$ - $C_8$  methoxyphenols.

### EXPERIMENTAL AND RESULTS

Experimental mixtures of known composition were prepared from available standard compounds and were repeatedly chromatographed under the operating conditions shown in Table I.

The chromatographic behaviour of individual phenols was studied for each

TABLE I

## OPERATING CONDITIONS FOR CAPILLARY COLUMN CHROMATOGRAPHY

An open stainless-steel capillary column was used with 95% TXP + 5% H<sub>3</sub>PO<sub>4</sub> as the stationary phase. It should be noted that this column is not the same as that used in Part I<sup>1</sup>.

Parameter	Value
Length	50 m
Inner diameter	0.25 mm
Column temperature	130.0°
Carrier gas	Nitrogen
Carrier gas pressure in front of the column	160 kPa
Bypass	1:100
Injection chamber temperature	300°
Amount injected	0.3–0.5 µl

TABLE II

## RELATIVE RETENTION TIMES OF MONOHYDRIC PHENOLS

Except for 2,4-dimethylphenol and 2-ethyl-5-methylphenol, all of the compounds were examined in only one of the possible homologous series. The relative retention times of 4-*sec.*-butylphenol and 4-*tert.*-butyl-2-methylphenol published in Part I<sup>1</sup> do not correspond to their chemical structures. During the experimental work, we found that the identities of these compounds, assumed from the supplier's data, were incorrect. We apologize for this error.

No.	Compound	R <sub>t</sub>	No. of carbon atoms	Correlation with Fig. 1
1	Phenol	1.00	6	Curve 1
2	2-Methylphenol	1.21	7	
3	2-Ethylphenol	1.91	8	
4	2- <i>n</i> -Propylphenol	3.02	9	
5	2- <i>n</i> -Butylphenol	5.31	10	
6	2- <i>n</i> -Pentylphenol	9.21	11	Curve 2
7	2- <i>n</i> -Hexylphenol	16.22	12	
8	3-Methylphenol	1.68	7	
9	3-Ethylphenol	2.82	8	
10	3- <i>n</i> -Propylphenol	4.63	9	
11	3- <i>n</i> -Butylphenol	8.32	10	Curve 3
12	4-Methylphenol	1.57	7	
13	4-Ethylphenol	2.63	8	
14	4- <i>n</i> -Propylphenol	4.48	9	
15	4- <i>n</i> -Butylphenol	7.85	10	
16	4- <i>n</i> -Pentylphenol	13.80	11	Straight line 4
17	4- <i>n</i> -Hexylphenol	24.30	12	
18	2,4-Dimethylphenol	1.87	8	
19	2-Methyl-4-ethylphenol	2.99	9	
20	2-Methyl-4- <i>n</i> -propylphenol	4.81	10	
21	2,6-Dimethylphenol	0.96	8	Straight line 5
22	2-Methyl-6-ethylphenol	1.41	9	
23	2-Methyl-6- <i>n</i> -propylphenol	2.12	10	
24	3,4-Dimethylphenol	3.12	8	
25	3-Methylphenol-4-ethylphenol	4.92	9	
26	3-Methyl-4- <i>n</i> -propylphenol	7.80	10	Straight line 6
27	2,4-Dimethylphenol	1.87	8	
28	2-Ethyl-4-methylphenol	2.79	9	
29	2- <i>n</i> -Propyl-4-methylphenol	4.26	10	

TABLE II (Continued)

No.	Compound	$R_t$	No. of carbon atoms	Correlation with Fig. 1
30	2,5-Dimethylphenol	2.00	8	Straight line 8
31	2-Ethyl-5-methylphenol	3.09	9	
32	2- <i>n</i> -Propyl-5-methylphenol	4.92	10	
33	2,5-Dimethylphenol	5.13	10	Straight line 9
34	2-Ethyl-5- <i>n</i> -propylphenol	8.44	11	
35	2-Ethyl-5- <i>n</i> -butylphenol	14.73	12	
36	2-Isopropylphenol	2.62	9	Dashed line 10
37	2-Isobutylphenol	3.93	10	
38	4-Isopropylphenol	3.58	9	Dashed line 11
39	4-Isobutylphenol	5.79	10	
40	4- <i>tert.</i> -Butylphenol	5.17	10	Dashed line 12
41	4- <i>tert.</i> -Pentylphenol	9.72	11	
42	2,5-Dimethylphenol	2.00	8	Dashed line 13
43	5-Ethyl-2-methylphenol	3.14	9	
44	3,5-Dimethylphenol	2.79	8	Dashed line 14
45	3-Ethyl-5-methylphenol	4.52	9	
46	2,4,5-Trimethylphenol	3.63	9	Dashed line 15
47	2-Ethyl-4,5-dimethylphenol	5.56	10	
48	2,3-Dimethylphenol	2.43	8	
49	3-Isopropylphenol	3.68	9	Point 17
50	2,4,6-Trimethylphenol	1.61	9	Point 18
51	2,3,6-Trimethylphenol	2.08	9	Point 19
52	2,3,5-Trimethylphenol	3.94	9	Point 20
53	2,3,4-Trimethylphenol	4.74	9	Point 21
54	3,4,5-Trimethylphenol	6.39	9	Point 22
55	2- <i>sec.</i> -Butylphenol	3.95	10	Point 23
56	4- <i>sec.</i> -Butylphenol	5.86	10	Point 24
57	2- <i>tert.</i> -Butylphenol	4.08	10	Point 25
58	3- <i>tert.</i> -Butylphenol	5.40	10	Point 26
59	2,4-Diethylphenol	4.32	10	Point 27
60	3,4-Diethylphenol	7.36	10	Point 28
61	2-Methyl-6-isopropylphenol	1.80	10	Point 29
62	3-Methyl-6-isopropylphenol	4.27	10	Point 30
63	2-Methyl-4-isopropylphenol	5.25	10	Point 31
64	2,3,5,6-Tetramethylphenol	3.56	10	Point 32
65	2,3,4,6-Tetramethylphenol	3.68	10	Point 33
66	2,3,4,5-Tetramethylphenol	7.14	10	Point 34
67	2- <i>tert.</i> -Butyl-6-methylphenol	2.16	11	Point 35
68	2- <i>tert.</i> -Butyl-4-methylphenol	5.46	11	Point 36
69	2- <i>tert.</i> -Butyl-5-methylphenol	6.06	11	Point 37
70	4- <i>tert.</i> -Butyl-2-methylphenol	3.42	11	Point 38
71	4- <i>tert.</i> -Butyl-3-methylphenol	11.90	11	Point 39
72	Pentamethylphenol	9.50	11	Point 40
73	2,6-Diisopropylphenol	2.34	12	Point 41
74	2-Methoxyphenol	0.57	7	Point 42
75	4-Methoxyphenol	5.30	7	Point 43
76	3-Methoxyphenol	6.35	7	Point 44
77	2-Methoxy-4-methylphenol	0.94	8	Point 45
78	4-Indanol	6.07	9	Point 46
79	5-Indanol	8.32	9	Point 47
80	5-Methyl-4-indanol	5.71	10	Point 48

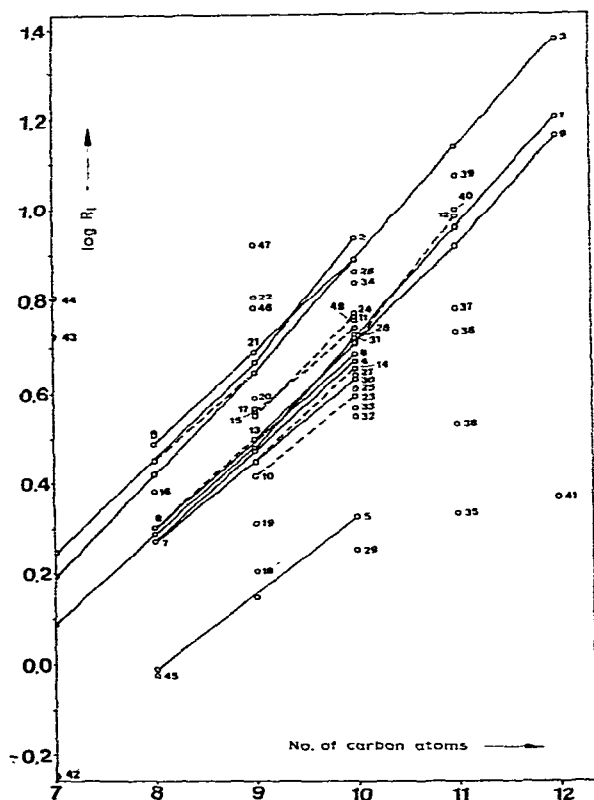


Fig. 1. Plot of  $\log R_t$  against number of carbon atoms. Capillary column coated with 95% TXP + 5%  $H_3PO_4$ , 130°.

homologous series according to the position and type of substituent on the benzene ring. The results are given in Table II and are represented graphically in Fig. 1 as a plot of  $\log R_t$  against number of carbon atoms in the molecule.

#### Results of resolution studies on the stationary phase 95% TXP + 5% $H_3PO_4$

Fig. 1 shows that the smallest relative retention times occur for alkylphenols with substituents in the 2,6-positions (straight line 5). This result could be explained by steric shielding of the hydroxy group of phenols by alkyl groups, which prevents the formation of hydrogen bonds between the polar stationary phase and the phenol being chromatographed.

Alkyl branching in the 2-position increases the steric hindrance of the phenolic hydroxy group, as shown from the comparison of  $\log R_t$  for 2-methyl-6-*n*-propylphenol (last point on straight line 5) and 2-methyl-6-isopropylphenol (point 29).

The greatest hindrance of the phenolic hydroxy group occurs with 2,6-diisopropylphenol (point 41). Its  $R_t$  is smaller than that of 2-isopropylphenol, in spite of having three carbon atoms more in its molecule.

The second and third fastest eluting homologous series of phenols, of which only the first members were available to us, are those with methyl groups in the

2,4,6- (point 18) and 2,3,6-positions (point 19). In both instances the homologous series contains alkyl groups in the 2,6-position also.

The second fastest eluting homologous series of phenols, beginning at C<sub>8</sub>, is that with alkyl groups in the 2,4-positions (straight line 7). The resolution of this homologous series of phenols with substituents in the 2,4-positions and alkyl groups of increasing length in the 2-position (straight line 7) improves with increasing carbon number in comparison with the homologous series with substituents in the 2,4-positions but with alkyl groups of increasing length in the 4-position (straight line 4).

The hindrance of the phenolic hydroxy group in homologous series with alkyl groups in the 2,4-positions with the length of the alkyl group in the 2-position increasing becomes greater and straight line 7 deviates from the other straight lines in Fig. 1 as the number of carbon atoms in the molecule increases. The slope of this line approaches that of straight line 5, relating to phenols with alkyl groups in the 2,6-positions.

For alkylphenols beginning with C<sub>9</sub> the third fastest eluting homologous series is that with an isoalkyl group in the 2-position (straight line 10). This effect could be also explained by steric hindrance of the hydroxy group.

For mono-*n*-alkylphenols the order of elution is *ortho*-isomers (curve 1) (steric shielding of hydroxy group); *para*-isomers (curve 3) and *meta*-isomers (curve 2).

There is a break in the straight lines of log *R<sub>t</sub>* against carbon number for propylphenols for all three homologous series of *n*-alkylphenols (2-, 3- and 4-substituted). The gradient is greater for phenols with an *n*-alkyl group longer than C<sub>3</sub> than for the C<sub>7</sub>-C<sub>9</sub> alkyl phenols. For example, there is a sudden change in slope for the homologous series of 2-ethyl-5-*n*-alkylphenols (straight line 9) on passing from 2-ethyl-5-*n*-butylphenol to 2-ethyl-5-*n*-propylphenol; this course is not corresponding with the original slope of straight line 9. From the comparison of courses of log *R<sub>t</sub>*, plotted against carbon number for alkylphenols and examined polar stationary phase it is now evident, that with the *n*-alkyl shift towards the phenolic hydroxy group, the change in gradient increases. The smallest change was observed for 4-*n*-alkylphenols, a greater change for 3-*n*-alkylphenols and the greatest change for 2-*n*-alkylphenols.

For 2-butylphenols, the order of elution is isobutylphenol, *sec*-butylphenol, *tert*-butylphenol, *n*-butylphenol, which could be explained by the steric influence of the geometry of such substituent on the formation of hydrogen bonds. For 4-butylphenols the sequence of elution is *tert*-butylphenol, *sec*-butylphenol, isobutylphenol, *n*-butylphenol, and here the dominant effect is probably the induction effect of alkyl groups on the polarizability of phenolic hydroxy groups, which affect the strength of the hydrogen bonds with the hydroxy group of the phenol.

Dimethylphenols are eluted in the order 2,6-, 2,4-, 2,5-, 2,3-, 3,5-, 3,4-, trimethylphenols in the order 2,4,6-, 2,3,6-, 2,4,5-, 2,3,4-, 2,3,5-, 3,4,5- and tetramethylphenols in the order 2,3,5,6-, 2,3,4,6-, 2,3,4,5-. In each instance the order of elution is affected by the number of substituents in positions 2- and 6- (steric hindrance) and by the overall induction effect of methyl groups in *meta*- and *para*-positions on the polarizability of the phenolic hydroxy group.

It can be seen from a comparison of the homologous series of 4-isoalkylphenols (straight line 11) with the 2-alkyl-4,5-dimethylphenols (straight line 15) that, with increasing number of carbon atoms in the molecule the order of elution changes. As the alkyl groups in the 2-position increase in length, greater steric shielding of the

hydroxy group occurs, which results in faster elution compared with 4-isoalkylphenols with the same number of carbon atoms in the molecule.

From a comparison of the elution of 2-methoxyphenol (point 42) and 2-methoxy-4-methylphenol (point 45) with that of 3- and 4-methoxyphenol (points 43 and 44), the existence of an intramolecular hydrogen bridge between the hydrogen atom of the hydroxy group and the oxygen atom of the methoxy group in the 2-position can be postulated. In spite of having one carbon atom more than 3- and 4-methoxyphenol, 2-methoxy-4-methylphenol is eluted faster. Both compounds examined with a methoxy group in the 2-position are eluted faster than phenol; hence intramolecular hydrogen bonds affect the strength of the intermolecular hydrogen bonds.

## CONCLUSION

In graphs of  $\log R_f$  against number of carbon atoms in the molecules of homologous series of monohydric *n*-alkylphenols, a sudden change of slope occurs for all derivatives that contain an *n*-alkyl substituent longer than  $C_3$ . This change becomes greater as the *n*-alkyl group shifts towards the phenolic hydroxy group. Therefore, when attempting to identify unknown phenols eluted from the polar stationary phase consisting of 95% TXP + 5%  $H_3PO_4$  on the basis of their gas chromatographic peaks with the aid of graphs of  $\log R_f$  against carbon number, it is necessary to know in advance if the compound contains an *n*-alkyl group longer than  $C_3$ . For  $C_7$ - $C_9$  alkylphenols, for which the necessary standards are usually available, it is possible to extrapolate or interpolate.

## REFERENCE

- 1 J. Macák, P. Buryan and J. Hrivňák, *J. Chromatogr.*, 89 (1974) 309.