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Note

Linear relationship between retention indices and chemical structure of phenols

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Gas–liquid chromatography has been employed successfully for the determination of a variety of compounds, and good results have been reported when the Kováts retention indices (I_K) were used[1]. However, the results revealed that (I_K) was ineffective as a function of the number of carbon atoms in a molecule (n_c) in structural studies. For this reason, a modification of the Kováts equation has been developed that provides a linear relationship between the retention indices and chemical structure of phenols.

EXPERIMENTAL

In addition to the retention indices and n_c, the number of oxygen atoms (n_o) in the molecule of a compound has been included in the Kováts equation. The modified equation can be written in the form

$$I_B = B_1 + (B_2 - B_1) \cdot \frac{\log t_{r(B)} - \log t_{r(B_1)}}{\log t_{r(B_2)} - \log t_{r(B_1)}}$$

where I_B is the retention index of a compound B, t_r (B) is its retention time and $t_{r(B_1)}$ and $t_{r(B_2)}$ are the retention times of the first and last compounds, respectively, eluted from the column (in this work, phenol and syringic acid); B_1 and B_2 are parameters calculated for compounds with the shortest and the longest retention times, respectively, in a given homologousseries. The parameters have been calculated from the equation

$$B_i = 10\, n_c n_o$$

where $i = 1,2,...,$ etc.

The modified equation has been verified using 23 phenols. Retention indices were measured on a Pye Unicam Series 104 chromatograph equipped with a flame-ionization detector and a glass column (2.1 m × 4 mm I.D.) packed with 3% OV-1 on Chromosorb W HMDS (100–120 mesh). The operating conditions of the chromatograph were identical for each compound [column temperature 180°, detector temperature 250°, carrier gas (argon) flow-rate 15 ml/min].

Table I gives the structural parameters and retention indices for the phenols. The numbers of the compounds correspond to those in the figures and the text.

TABLE I

STRUCTURAL PARAMETERS AND RETENTION INDICES FOR PHENOLS

No.	*Compound*	n_c	n_o	B_l	$\log t_{r(Bl)}$	I_K	I_B
1	Phenol	6	1	6	0.4771	905.1	60.0
2	*o*-Cresol	7	1	7	0.5911	978.1	87.6
3	*m*-Cresol	7	1	7	0.6021	985.1	90.3
4	*p*-Cresol	7	1	7	0.6128	991.9	92.8
5	Guaiacol	7	2	14	0.6990	1047.1	113.8
6	3,5-Xylenol	8	1	8	0.8195	1124.1	143.0
7	2,3-Xylenol	8	1	8	0.8325	1132.5	146.1
8	2,4,6-Trimethylphenol	9	1	9	0.8692	1155.9	155.0
9	Thymol	10	1	10	0.9823	1228.3	182.4
10	Hydroquinone	6	2	12	1.1367	1327.0	219.8
11	Eugenol	10	2	20	1.1553	1338.9	224.3
12	4-Propylguaiacol	10	2	20	1.1644	1344.8	226.5
13	2,6-Dimethoxyphenol	8	3	24	1.2148	1392.1	238.7
14	Resorcinol	6	2	12	1.2175	1378.7	239.4
15	BHT butylated hydroxytoluene)	15	1	15	1.3424	1458.6	269.7
16	BHA (3-*tert.*-butyl-4-hydroxyanisole)	11	2	22	1.3424	1458.6	269.7
17	4-Methyl-2,6-dimethoxyphenol	9	3	27	1.4043	1498.2	284.7
18	Acetovanillone	9	3	27	1.4116	1502.8	286.4
19	4-Ethyl-2,6-dimethoxyphenol	10	3	30	1.4969	1557.4	307.1
20	4-Propyl-2,6-dimethoxyphenol	11	3	33	1.5966	1621.2	331.3
21	Syringaldehyde	9	4	36	1.7810	1739.1	375.9
22	Acetosyringone	10	4	40	1.8745	1798.9	398.6
23	Syringic acid	9	5	45	2.0864	1934.4	450.0

RESULTS AND DISCUSSION

The relationship between the Kováts indices (I_K) and the number of carbon atoms in a molecule (n_c) is shown in Fig. 1. Only some of the phenols obey a straight-line relationship, and it can be seen that it is the 2-substitued methyl- and methoxy-

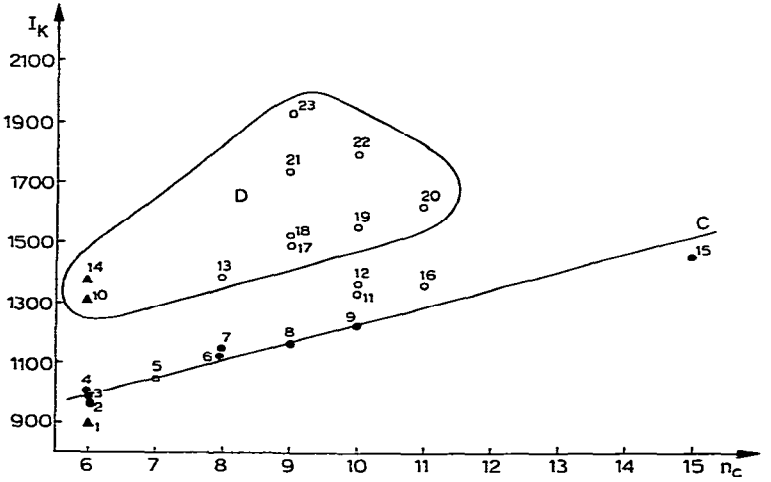

Fig. 1. Kováts indices (I_K) *versus* the number of carbon atoms in a molecule (n_c) for phenols. Numbers refer to Table I. ○, 2-Methoxy-substituted; ●, 2-methyl-substituted; ▲, no 2-substituents.

phenols that fall on the straight line C. Hence the relationship between I_K and n_c cannot be used for structural studies with phenolic compounds. On the other hand, an excellent correlation was obtained between I_B and B_i (Fig. 2). There are two straight lines, C and D, the former representing 2-methyl-substituted phenols and phenols with no substituent in position 2, and the latter 2-methoxyphenols.

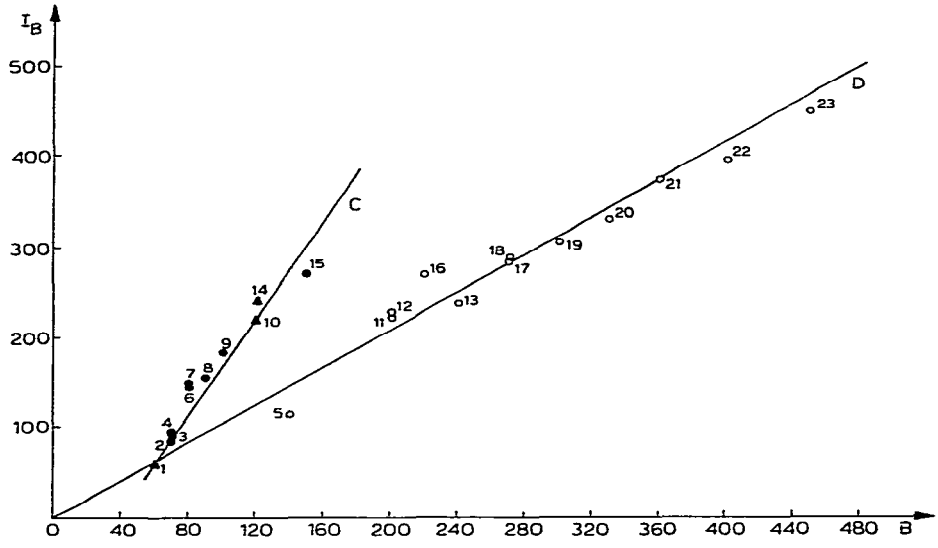

Fig. 2. Suggested indices (I_B) *versus* B_i values for phenols. Numbers and symbols as in Fig. 1.

The straight lines shown in Fig. 2 can be described by the general equation

$$I_B = aB + b$$

For the straight line C, $a = 25.56$ and $b = -75.24$, and for D $a = 10.31$ and $b = 20.49$. The correlation coefficients for lines C and D are 0.9750 and 0.9700, respectively.

Much lower correlation coefficients were obtained for the relationship between I_K and n_c (Fig. 1). For the straight line C in Fig. 1 the correlation coefficient was 0.9116 and for the population D 0.6224.

It should be noted that the function $I_B = f(B)$ clearly differentiates 2-substituted methyl- and methoxyphenols and for this reason it should be particularly useful in structural studies. This advantage has not been observed when using the Kováts equation.

REFERENCES

1 E. Kováts, *Helv. Chim. Acta.* 41 (1958) 1915.