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KOVÁTS RETENTION INDICES OF ALKYLQUINOLINES ON CAPILLARY COLUMNS

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SUMMARY

The retention indices of 25 alkylquinolines were measured at 140–160°C on glass capillary columns coated with OV-101, UCON LB-550-X and PEG-20M. The temperature and structure increments of the retention indices were determined and correlated with the molecular structure and physico-chemical parameters of the alkylquinolines (boiling points, number of carbon atoms, Taft and Palm steric constants and molecular connectivity).

INTRODUCTION

Heterocyclic nitrogen bases of the quinoline type are obtained mainly from coal tar and its fractions[1–8]. The determination of quinoline bases is difficult owing to the complex composition of the coal tar fractions and, therefore capillary gas chromatography[9,10] and its combination with mass spectrometry[11–13] have proved to be the most helpful methods for the analysis of these compounds.

The published retention parameters of alkylquinolines involve relative retention volumes for a limited number of compounds on packed columns[14–17] and retention indices on capillary columns[9] and columns packed with PEG-20M[11]. Linear retention indices of alkylquinolines on capillary columns with different stationary phases have been published[18–20].

In this work the Kováts retention indices of alkylquinolines on glass capillary columns with different stationary phases were determined. The relationship between the retention indices and the physico-chemical properties and the molecular structure of alkylquinolines was investigated.

EXPERIMENTAL

The measurements were carried out on Tswett-152 (Experimental Design Bureau of Automatics, Moscow, U.S.S.R.) and Chrom-41 (Laboratory Instruments,

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TABLE I

CHARACTERISTICS OF THE CAPILLARY COLUMNS USED

Parameter	*Stationary phase*		
	OV-101	*UCON-LB-550-X*	*PEG-20M*
Column length (m) and I.D. (mm)	50 × 0.22	17 × 0.30	30 × 0.25
Capacity ratio (k) at 100°C	2.9	2.6	2.3
Column efficiency with respect to n-dodecane (theoretical plates)	105 000	32 000	71 000

Prague, Czechoslovakia) gas chromatographs equipped with flame ionization detectors and Pyrex glass capillary columns (Table I). Nitrogen was used as the carrier gas at a flow-rate of 9–10 cm/s. The splitting ratio was 1:200. The samples (mixtures of alkylquinolines with n-alkanes) were injected with a 1-μl Hamilton microsyringe into the injector at 250–300°C. Methane was injected simultaneously in order to determine the gas hold-up time. The retention times were measured by a stop-watch with an accuracy of ±0.1 s. The Kováts retention indices were calculated from the retention times and were taken as averages of 3–5 determination for each compound. The accuracy of the determination of retention indices was ±1–3 i.u.

RESULTS AND DISCUSSION

The Kováts retention indices measured for the compounds investigated are shown in Table II. The retention indices of alkylquinolines are characterized by relatively high temperature coefficients, the magnitude of which increases in the stationary phases series OV-101 < Ucon LB-550-X < PEG-20M. The temperature coefficients within each stationary phase vary slightly: OV-101 6.3–9.3; UCON 6.5–11.0; PEG-20M 11.0–14.5 units.

The relationship between the retention indices of alkylquinolines on UCON and those on OV-101 and PEG-20M is linear and described by the following equations:

$$I_{160°C}^{UCON} = 0.871 I_{160°C}^{OV\text{-}101} + 395.8 \qquad (r = 0.992)$$

$$I_{160°C}^{PEG\text{-}20M} = 0.878 I_{160°C}^{UCON} + 618.3 \qquad (r = 0.981)$$

where r is the correlation coefficient.

The elution order of alkylquinolines generally corresponds to their boiling points and molecular masses, the values of which characterize the capacity of molecules for dispersive interactions. Although the dependence of the retention indices on the boiling points of alkylquinolines is linear, the correlation coefficients for the corresponding regression equations are too low in some instances (Table III). Thus, on OV-101 and PEG-20M a more strictly linear dependence is found for the series of methyl- and dimethylquinolines, and on UCON a more strictly linear correlation is observed for all of the alkylquinolines studied.

TABLE II

RETENTION INDICES OF ALKYLQUINOLINES AND THEIR TEMPERATURE COEFFICIENTS

*Compound**	*OV-101*			*UCON LB-550-X*			*PEG-20M*		
	140°C	*160°C*	*10 (δI/δT)*	*140°C*	*160°C*	*10 (δI/δT)*	*140°C*	*160°C*	*10 (δI/δT)*
Quinoline	1231	1246	7.7	1460	1478	9.3	1897	1924	13.5
Isoquinoline	1251	1269	8.8	1485	1503	9.5	1934	1958	12.0
2-MeQ	1294	1308	7.0	1512	1527	7.5	1924	1946	11.0
8-MeQ	1304	1319	7.5	1512	1527	7.5	1916	1943	13.5
7-MeQ	1338	1354	7.8	1563	1581	9.5	1995	2020	12.5
6-MeQ	1343	1358	7.3	1564	1582	9.5	1995	2020	12.5
3-MeQ	1346	1361	7.2	1572	1590	8.8	2014	2042	14.0
5-MeQ	1355	1375	9.3	1588	1609	9.5	2025	2054	14.5
4-MeQ	1357	1376	9.3	1593	1615	9.5	2037	2065	14.0
2-EtQ	1381	1388	7.0	1574	1587	8.3	1970	1993	12.0
2,8-Di-MeQ	1361	1374	6.5	1549	1563	7.3	1921	1945	12.0
2,7-Di-MeQ	1400	1415	7.5	1616	1628	7.3	2018	2044	13.0
2,6-Di-MeQ	1397	1413	8.0	1616	1631	7.8	2019	2044	12.5
6,8-Di-MeQ	1408	1422	7.0	1615	1630	8.3	2013	2037	12.0
5,8-Di-MeQ	1427	1442	7.8	1634	1651	8.8	2038	2065	13.5
2,4-Di-MeQ	1417	1434	8.3	1644	1660	8.3	2063	2088	12.5
2,3-Di-MeQ	1427	1443	7.8	1645	1666	9.5	2066	2090	12.0
4,6-Di-MeQ	1472	1487	7.5	1698	1712	8.3	2133	2159	13.0
2,6,8-Tri-MeQ	1461	1475	6.8	1653	1667	6.5	2018	2042	12.0
2,4,6-Tri-MeQ	1525	1539	7.0	1744	1758	7.3	2156	2180	12.0
2-*n*-PrQ	1458	1472	7.0	1653	1667	7.0	2040	2064	12.0
2-iso-BuQ	1501	1515	7.0	1683	1697	6.8	2048	2077	14.5
2-*n*-PeQ	1650	1664	7.0	1854	1873	9.5	2225	2249	12.0
8-Me-5-iso-PrQ	1560	1574	6.8	1764	1777	6.5	2135	2164	14.5
3-Et-2-*n*-PrQ	1644	1657	6.3	1851	1864	6.5	2208	2236	14.0
2-Me-3-*n*-BuQ	1695	1708	6.5	1899	1915	8.0	2282	2309	13.5
3-Pr-2-*n*-BuQ	1803	1816	6.7	1947	1964	8.5	2329	2357	14.0

* Me = Methyl; Et = ethyl; Pr = propyl; Bu = butyl; Pe = pentyl; Q = quinoline.

TABLE III

COEFFICIENTS IN THE REGRESSION EQUATION $I = at_b + b$ AT 160°C

Homologous series	*OV-101*			*UCON LB-550-X*			*PEG-20M*		
	a	*b*	*r**	*a*	*b*	*r**	*a*	*b*	*r**
Methylquinolines	3.997	323.3	0.997	5.374	195.2	0.996	7.407	110.0	0.991
Dimethylquinolines	3.998	353.3	0.989	5.242	232.4	0.987	7.443	56.8	0.979
All alkylquinolines	4.021	325.0	0.806	5.403	190.1	0.997	5.109	691.3	0.947

* r = Regression coefficient.

The studies carried out indicate that the Kováts isomer rule[21]:

$$\delta I \approx 5\delta t_b \tag{1}$$

(where t_b = boiling point) for alkylquinolines is not completely valid in all instances, *i.e.*, the proportionality factor, K_p, varies over a wider range. The mean proportionality factors on OV-101 and UCON were found to be 3.87 and 5.47, respectively, for methylquinolines and 4.22 and 5.27, respectively for dimethylquinolines.

The dependence of the retention indices on the number of carbon atoms in the molecules of the compounds (n_c) is described by the equation

$$I = an_c + b \tag{2}$$

where a and b are regression coefficients.

The dependence of the retention indices of 2-alkylquinolines on the number of carbon atoms in the alkyl groups (n_c) is described by the following equations:

$$I_{160°C}^{OV\text{-}101} = 89.4n_c + 1212.2 \qquad (r = 0.999)$$

$$I_{160°C}^{UCON} = 87.8n_c + 1422.0 \qquad (r = 0.996)$$

$$I_{160°C}^{PEG\text{-}20M} = 77.3n_c + 1850.5 \qquad (r = 0.991)$$

To verify the dependence of the retention indices on the number of carbon atoms in the molecules of alkylquinolines we calculated the middle retention indices (I_m) of alkylquinolines with different numbers of carbon atoms (Table IV). The dependence of the middle retention indices on the number of carbon atoms in the molecule of alkylquinolines is approximately linear and is described by the following equations:

$$I_m^{OV\text{-}101}(160°C) = 78.8n_c + 551.3 \qquad (r = 0.997)$$

$$I_m^{UCON}(160°C) = 68.5n_c + 880.3 \qquad (r = 0.990)$$

$$I_m^{PEG\text{-}20M}(160°C) = 59.1n_c + 1403.3 \qquad (r = 0.982)$$

TABLE IV

MIDDLE RETENTION INDICES OF ALKYLQUINOLINES AT 160°C

Stationary phase	*No. of carbon atoms in molecule*						
	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{16}
OV-101	1258	1350	1424	1495	1545	1673	1816
UCON LB-550-X	1491	1576	1636	1697	1737	1884	1964
PEG-20M	1941	2013	2051	2095	2121	2265	2357

These equations allow the group identification of alkylquinolines in composite industrial mixtures.

The specific interaction of alkylquinolines with the stationary phase may be calculated using the ΔI values[21]:

$$\Delta I = I^{\text{UCON}} - I^{\text{OV-101}} \quad \text{and} \quad \Delta I^{\text{PEG-20M}} - I^{\text{OV-101}} \tag{3}$$

as can be seen from Table II, the increment ΔI depends on the polarity of the stationary phase and the position, amount and chain length of the alkyl group. ΔI for methylquinolines decreases in the order 4- > 3- > 5- > 6- > 7- > 2- > 8-methylquinoline. The minimal ΔI values are observed for alkylquinolines with a screened nitrogen atom, *i.e.*, alkylquinolines with alkyl groups in the 2- and 8-positions. With increasing chain length of the alkyl substituent, the degree of screening of the nitrogen atom increases and ΔI decreases. Therefore, for 2-alkylquinolines ΔI decreases in the order $CH_3 > C_2H_5 > C_3H_7 > C_5H_{11}$.

The ΔI values are related linearly to the Taft induction constant, σ^* (Fig. 1) and the Taft (E_s) and Palm (E_s^0) steric constants (Fig. 2), which characterize the ability of a substituent to screen the reaction centre of the molecule[22–25].

The retention index increment δI represents the difference in retention indices of an alkylquinoline (I_{alq}) and quinoline (I_q) on the same stationary phase, *i.e.*,

$$\delta I = I_{alq} - I_q \tag{4}$$

The δI increments were used to characterize the interaction of the solute with the stationary phase (Table V).

The contribution of δI for an alkyl substituent is determined by the position of the group and the polarity of the stationary phase. Thus, the highest δI_{CH_3} value (130–140 i.u.) is achieved when the CH_3 group is introduced in 4- and 5-positions (the most remote from the nitrogen atom). As the nitrogen atom becomes closer (3-, 6- and 7-positions), the δI_{CH_3} value decreases to 96–118 i.u., and reaches minimal values for the 2- and 8-positions (19–73 i.u.).

The screening of the nitrogen atom by the methyl group interferes with the interaction forces between methylquinolines and the stationary phase molecules, which reduces the retention indices of 2- and 8-methylquinoline. The δI_{CH_3} value

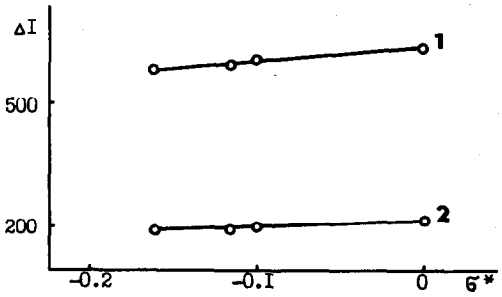

Fig. 1. Dependence of the ΔI values for 2-alkylquinolines at 160°C on the Taft induction constant. (1) $\Delta I = I^{\text{PEG-20M}} - I^{\text{OV-101}}$; (2) $\Delta I = I^{\text{UCON}} - I^{\text{OV-101}}$.

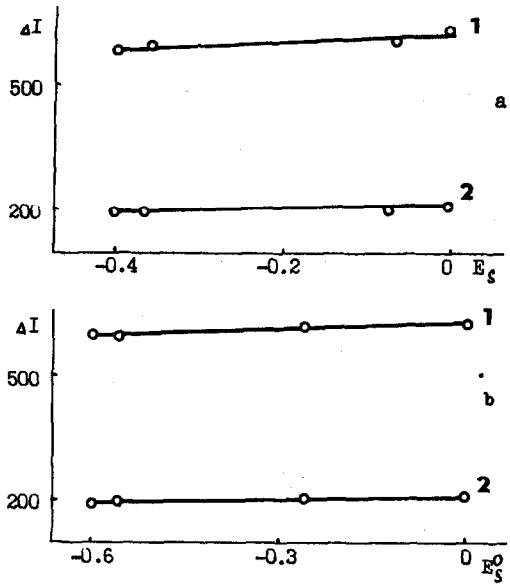

Fig. 2. Dependence of the ΔI values for 2-alkylquinolines at 160°C on (a) Taft and (b) Palm steric constants. (1) $\Delta I = I^{\text{PEG-20M}} - I^{\text{OV-101}}$; (2) $\Delta I = I^{\text{UCON}} - I^{\text{OV-101}}$.

decreases with increase in the polarity of the stationary phase. When the nitrogen atom is blocked by two methyl groups, the retention index of 2,8-dimethylquinoline on PEG-20M becomes comparable to those of 2- and 8-methylquinoline. With an increase in the polarity of the stationary phase (*e.g.*, diglycerol, polydiethylene glycol succinate and others[15,26]), 2- and 8-methyl- and 2,8-dimethylquinoline elute from the column before quinoline.

TABLE V

RETENTION INDEX INCREMENTS OF VARIOUS ALKYL SUBSTITUENTS AT 160°C

Compound	*Stationary phase*			*Compound*	*Stationary phase*		
	OV-101	*UCON LB-550-X*	*PEG-20M*		*OV-101*	*UCON-LB-550-X*	*PEG-20M*
2-MeQ	62	49	22	5,8-Di-MeQ	196	173	141
3-MeQ	115	112	118	6,8-Di-MeQ	176	152	113
4-MeQ	130	137	141	2,4,6-Tri-MeQ	293	280	256
5-MeQ	129	131	130	2,6,8-Tri-MeQ	229	189	118
6-MeQ	112	104	96	2-EtQ	142	109	69
7-MeQ	108	103	96	2-*n*-PrQ	226	189	140
8-MeQ	73	49	19	2-iso-BuQ	269	219	153
2,3-Di-MeQ	197	188	166	2-*n*-PeQ	418	376	325
2,4-Di-MeQ	188	182	161	8-Me-5-iso-PrQ	328	286	240
2,6-Di-MeQ	167	153	120	3-Et-2-*n*-PrQ	411	373	312
2,7-Di-MeQ	169	150	120	2-Me-3-*n*-BuQ	462	421	385
2,8-DI-MeQ	128	85	23	3-Pr-2-*n*-BuQ	570	469	433
4,6-Di-MeQ	241	234	235				

If the difference between the retention indices of 4- and 8-methylquinoline is taken as a quantitative measure of the screening effect of the methyl group, its values for the stationary phases studied were found to be OV-101 52, UCON 88 and PEG-20M 122 i.u., *i.e.*, the screening effect increases with increase in the polarity of the stationary phase.

The regularities considered are also valid for dimethylquinolines: the contribution of the methyl groups which are the most remote from the nitrogen atom (*e.g.*, 4,6-dimethylquinoline) markedly exceeds the contribution of the groups in 2- and 8-positions or located in close proximity (2,8-, 2,6- and 6,8-dimethylquinoline).

The same sequence is valid for trimethylquinolines and, therefore, the contribution of the methyl groups to the retention index of 2,4,6-trimethylquinoline is higher than that of 2,6,8-trimethylquinoline.

Recently, considerable attention has been devoted to the relationship between the chromatographic behaviour and molecular structure of compounds. The molecular connectivity (χ) has been used to correlate the molecular structure with the various physical properties and chromatographic retention[27–33]. It was introduced by Randić[34] and widely used by Kier and Hall[27]. The connectivity indices of alkylquinolines were calculated according to Kier and Hall[27]: first-order term $^1\chi$, second-order term $^2\chi$ and third-order term $^3\chi$. Further, we studied the relationship between the retention indices and connectivity indices:

$$I = a^{1-3}\chi_m + b \tag{5}$$

where $^{1-3}\chi_m$ is the middle connectivity index, which was calculated by means of the following equation:

$$^{1-3}\chi_m = \frac{^1\chi + ^2\chi + ^3\chi}{3} \tag{6}$$

The retention indices on OV-101 at 160°C were regressed against $^{1-3}\chi_m$. Eqn. 5 describe the dependence of $I^{OV\text{-}101}$ on the connectivity index $^{1-3}\chi_m$:

All alkylquinolines:

$$I = 222.2\ ^{1-3}\chi_m + 740.5 \qquad (n = 24;\ r = 0.981;\ s = 26.7) \tag{7}$$

2-Alkylquinolines:

$$I = 243.7\ ^{1-3}\chi_m + 650.6 \qquad (n = 5;\ r = 0.995;\ s = 17.4) \tag{8}$$

2-Methyl-, 2,6- dimethyl-, 2,4,6-trimethylquinoline:

$$I = 317.3\ ^{1-3}\chi_m + 443.1 \qquad (n = 3;\ r = 0.996;\ s = 10.5) \tag{9}$$

6-Methyl-, 2,6-dimethyl-, 2,6,8-trimethylquinoline:

$$I = 165.4\ ^{1-3}\chi_m + 908.1 \qquad (n = 3;\ r = 0.999;\ s = 2.6) \tag{10}$$

It may be concluded that the relationships between the retention and connectivity indices can be used for the prediction of the retention indices of alkylquinolines.

CONCLUSION

Measured Kováts retention indices of the alkylquinolines have been correlated with their main physico-chemical parameters and with the number of carbon atoms in alkylquinolines.

Considerable attention has been paid to the relationship between chromatographic behaviour and molecular structure and reactivity expressed as Taft induction constants and Taft and Palm steric constants. The relationship between the retention and connectivity indices can be used for the prediction of the retention indices of alkylquinolines.

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