Journal of Chromatography, 104 (1975) 337–349

CHROM. 7861

GAS CHROMATOGRAPHY OF ISOPRENOID ALKANES*

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(Received August 1st, 1974)

SUMMARY

The retention indices of ten isoprenoid alkanes on Apiezon L, SE-30 and diethylene glycol adipate polyester cross-linked with pentaerythritol at different temperatures have been determined. The regularities in the variation of the retention indices within homologous series are discussed.

A certain similarity in the structure of the compounds investigated enabled two methods to be developed for calculating retention indices based on retention increments and Wiener's structural constant. The Kováts retention indices of twelve compounds have been calculated. For 3,7,11-trimethyltridecane and 2,6,10,14-tetramethyloctadecane, the average divergences between the calculated and experimental retention indices were found to be ± 0.5 and ± 2.6 units, respectively. With the aid of the calculated retention indices, the presence of 3,7,11-trimethylalkanes and higher isoprenoids in a sample of Romashkino petroleum was demonstrated.

INTRODUCTION

Organic compounds with an isoprenoid carbon skeleton are synthesized by living organisms and are used as "biological markers". Data on isoprenoids in natural samples are of interest in organic geochemistry, and in petroleum geochemistry in particular.

The determination of isoprenoid alkanes in complex multicomponent mixtures is very difficult. Gas chromatography is used either as an independent analytical method or in combination with mass spectrometry[1–3]. The basic information on the nature of a substance is derived from mass spectra, in particular when the compounds have been detected for the first time[4–6]. Identifications made from mass spectra, however, are not always unequivocal for some isomers with similar structures, and cannot be achieved for diastereoisomers. In our opinion, a reasonable approach would be to collect isothermal retention data for saturated hydrocarbons that have been obtained sufficiently reproducibly by different investigators.

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[*] Translated into English by A. S. Brashnina.

Until now, no systematic studies have been carried out on the determination of the isothermal retention values of isoprenoid alkanes. Some data are recorded in the literature[4,7–12], and retention volumes of isoprenoids obtained on Apiezon L using temperature programming have been cited[13].

The object of this work was to determine the Kováts retention indices of isoprenoids and monomethylalkanes. Three stationary phases, *viz.*, Apiezon L, the methylsilicone rubber SE-30 and diethylene glycol adipate ester cross-linked with pentaerythritol (LAC 2-R-446) (DEGA-PE), having different selectivities with respect to isoprenoids, were used. Regularities in the variation of the retention indices depending on temperature would be useful for identification purposes. An attempt has been made to calculate the retention indices from the chemical structures of compounds. The possibility of calculating the retention indices of alkanes from retention increments and the structural constants of Wiener and Platt, making use of the physical properties of compounds, has drawn the attention of many investigators[14–23]. However, the methods developed have been found to be universal for low-molecular-weight alkanes only.

EXPERIMENTAL

The experimental studies were made on Tsvet-2 and LKhM-7a chromatographs fitted with a flame ionization detector. Copper and stainless-steel capillary columns of various lengths were used, with an efficiency of 20,000–90,000 theoretical plates. The separating ability of the column can be expressed more precisely by the $Z_{n,m}$ parameter[24]. For the columns used in this study, $Z_{C_{12},C_{18}}$ was about 120–180 under optimum conditions. The thickness of the stationary phase film was varied, depending on the column length. Short columns were coated with a thicker layer of the partition liquid, the most efficient method being the thermal coating procedure involving gradually moving the column into the heated oven, the column having been filled with a solution of the stationary phase. Capillary columns wetted with a layer of SE-30 were prepared following the thermal procedure.

The retention indices of isoprenoids were determined from chromatograms of some fractions of Romashkino petroleum, with the use of the data of Krasavchenko *et al.*[13] and with the aid of reference compounds. The average reproducibility of the Kováts retention indices obtained with different columns and instruments during a 4-year period was ± 1 unit.

RESULTS AND DISCUSSION

Retention indices of 2,6-dimethyl- and 2,6,10-trimethylalkanes, pristane and phytane

Fig. 1 shows chromatograms of methane–naphthenic fractions of Romashkino petroleum, and Table I gives the retention indices of isoprenoid alkanes and 2- and 3-methyltetradecanes and the temperature coefficients ($\Delta I/\Delta T$) calculated from the relationships between the retention indices and temperature (Fig. 2).

These results show that the retention indices of non-polar isoprenoid alkanes have substantially different values. The lowest retention indices are found on the polar DEGA-PE phase and the highest on the non-polar SE-30. Retention indices on Apiezon L occupy an intermediate position. The polarity of a phase, as seen from a

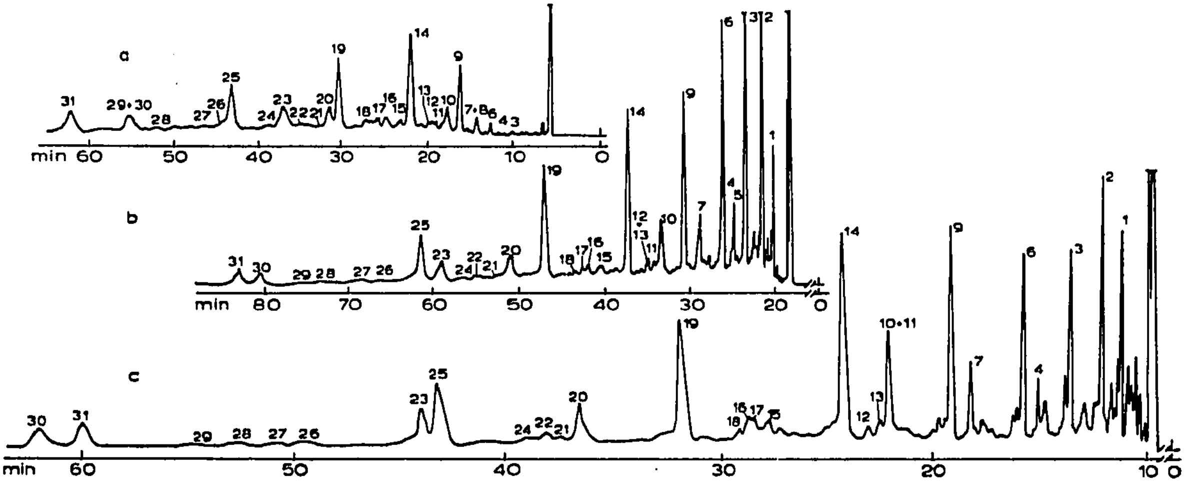


Fig. 1. Chromatograms of methane–naphthenic fractions of Romashkino petroleum. (a) DEGA-PE, 130°, 67 m × 0.3 mm, d = 21.3 cm/sec, (b) Apiezon L, 200°, 93 m × 0.3 mm, d = 8 cm/sec. (c) SE-30, 170°, 75 m × 0.3 mm, d = 12.9 cm/sec. Peaks: 1 = n-C_{10}; 2 = n-C_{11}; 3 = n-C_{12}; 4 = C_{14} (2,6,10); 5 = C_{13} (2); 6 = n-C_{13}; 7 = C_{15} (2,6,10); 8 = C_{14} (2); 9 = n-C_{14}; 10 = C_{16} (2,6,10); 11 = C_{15} (2); 12 = C_{16} (3,7,11); 13 = C_{15} (3); 14 = n-C_{15}; 15 = C_{17} (2,6,10); 16 = C_{17} (3,7,11); 17 = C_{16} (2); 18 = C_{16} (3); 19 = n-C_{16}; 20 = C_{18} (2,6,10); 21 = C_{18} (3,7,11); 22 = C_{17} (2); 23 = C_{19} (2,6,10,14); 24 = C_{17} (3); 25 = n-C_{17}; 26 = C_{19} (2,6,10); 27 = C_{19} (3,7,11); 28 = C_{18} (2); 29 = C_{18} (3); 30 = C_{20} (2,6,10,14); 31 = n-C_{18}.

TABLE I

RETENTION INDICES AT 200° AND TEMPERATURE COEFFICIENTS OF ISOPRENOIDS AND MONOMETHYLALKANES

Compound	*Apiezon L*		*SE-30*		*DEGA-PE*	
	I	$\frac{\Delta I}{\Delta T}$	*I*	$\frac{\Delta I}{\Delta T}$	*I*	$\frac{\Delta I}{\Delta T}$
2,6-Dimethylnonane [C_{11}(2,6)]	1018.5	+0.045	1026.0	+0.053	—	—
2,6-Dimethyldecane [C_{12}(2,6)]	1112.0	+0.070	1119.1	+0.058	—	—
2,6-Dimethylundecane [C_{13}(2,6)]	1207.0	+0.041	1215.5	+0.049	—	—
2,6,10-Trimethylundecane [C_{14}(2,6,10)]	1260.4	+0.013	1274.8	+0.039	1231.2	−0.070
2,6,10-Trimethyldodecane [C_{15}(2,6,10)]	1366.3	+0.030	1378.9	+0.050	1346.7	−0.049
2,6,10-Trimethyltridecane [C_{16}(2,6,10)]	1448.8	+0.011	1462.8	+0.031	1422.8	−0.079
2,6,10-Trimethyltetradecane [C_{17}(2,6,10)]	1540.0	+0.013	1554.6	+0.044	1509.9	−0.103
2,6,10-Trimethylpentadecane [C_{18}(2,6,10)]	1632.7	0.0	1650.2	+0.052	1602.5	−0.112
2,6,10,14-Tetramethylpentadecane [C_{19}(2,6,10,14)]	1686.6	0.0	1709.4	+0.028	1645.9	−0.137
2,6,10,14-Tetramethylhexadecane [C_{20}(2,6,10,14)]	1790.9	+0.014	1813.6	+0.052	1759.3	−0.121
2-Methyltetradecane [C_{15}(2)]	1461.0	—	1461.8	—	1451.9	—
3-Methyltetradecane [C_{15}(3)]	1469.3	—	1469.2	—	1469.6	—

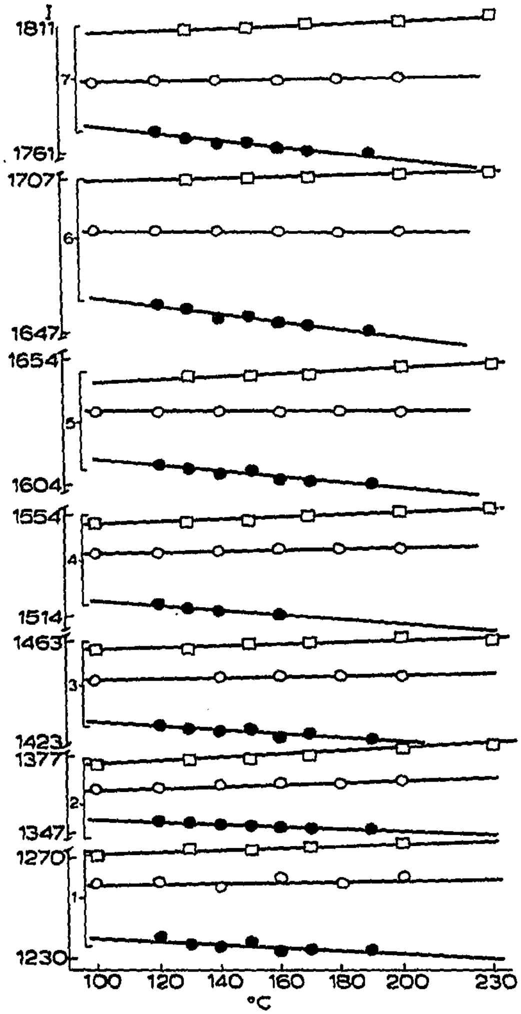


Fig. 2. Dependence of retention indices on temperature. ●, DEGA-PE; ○, Apiezon L; □, SE-30. 1 = C_{14} (2,6,10); 2 = C_{15} (2,6,10); 3 = C_{16} (2,6,10); 4 = C_{17} (2,6,10); 5 = C_{18} (2,6,10); 6 = C_{19} (2,6,10,14); 7 = C_{20} (2,6,10,14).

comparison of data obtained on SE-30 and Apiezon L, which have about the same polarities, is not a critical characteristic. Considerable influence on the retention indices of isoprenoid alkanes is exercised by the chemical nature of the stationary phase.

As seen from Fig. 2, the Kováts indices vary with temperature in a linear manner on all of the stationary phases investigated. This relationship is displayed most markedly in the case of non-polar phases. With DEGA-PE, a polar phase, when measurements are made over a wide temperature range a non-linear relationship would probably be observed, characterized by an increase in the $\Delta I/\Delta T$ ratio as the separation temperature is lowered. A distinguishing feature of this phase is a linear dependence of the $\Delta I/\Delta T$ ratio of 2,6,10-trimethyl- and 2,6,10,14-tetramethylalkanes on difference in the retention indices of an n-alkane and of an isoprenoid with the same number of carbon atoms in the molecule (Fig. 3). On DEGA-PE, a polar phase, the retention indices decrease with increase in temperature, whereas on non-polar phases the retention indices increase. Retention indices on Apiezon L vary with temperature less markedly than on SE-30. On decreasing the separation temperature, the difference between the retention indices of isoprenoid alkanes on any two of the stationary phases investigated decreases, and the difference in selectivity between the stationary phases diminishes. The different nature of the dependence of retention indices on temperature on the stationary phases studied offers the possibility of using this parameter for identification purposes.

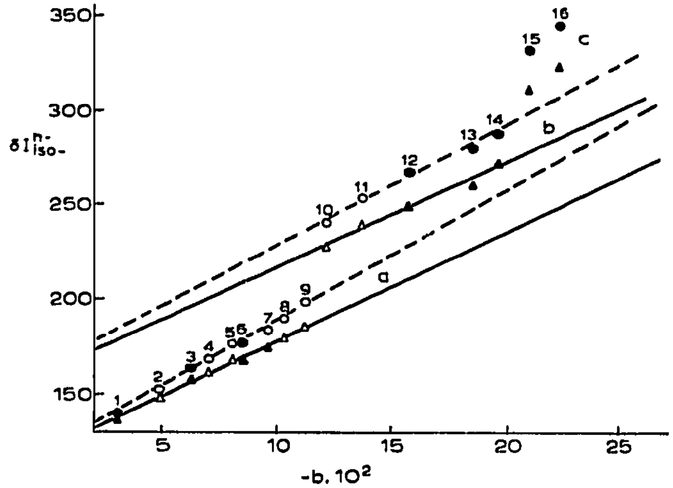


Fig. 3. Dependence of the temperature coefficient of Kováts retention indices of isoprenoids on DEGA-PE upon the retention index difference between an *n*-alkane and an isoprenoid with the same carbon number; $b = \Delta I/\Delta T$. (a) Trimethylalkanes; (b) tetramethylalkanes; (c) pentamethylalkanes. 1 = C_{16} (3,7,11); 2 = C_{15} (2,6,10); 3 = C_{17} (3,7,11); 4 = C_{14} (2,6,10); 5 = C_{16} (2,6,10); 6 = C_{18} (3,7,11); 7 = C_{19} (3,7,11); 8 = C_{17} (2,6,10); 9 = C_{18} (2,6,10); 10 = C_{20} (2,6,10,14); 11 = C_{19} (2,6,10,14); 12 = C_{21} (2,6,10,14); 13 = C_{22} (2,6,10,14); 14 = C_{23} (2,6,10,14); 15 = C_{25} (2,6,10,14,18); 16 = C_{24} (2,6,10,14,18). Open symbols, experimental values; ○, 200°; △, 100°. closed symbols, calculated values; ●, 200°; ▲, 100°.

Isoprenoid 2,6-dimethyl-, 2,6,10-trimethyl- and 2,6,10,14-tetramethylalkanes form three homologous series. However, the difference in retention indices between neighbouring homologues is not equal to 100 units (Fig. 4, Table I): for the first two members of the series it is over 100 units and for subsequent members it is less than 100 units, asymptotically approaching 100 as the straight carbon chain is increased in length. An analogous relationship has also been found for other classes of hydrocarbons[25,26]. Accordingly, there is no strict linear relationship between the retention index and the number of carbon atoms in an isoprenoid molecule. The largest deviations are found with 2,6,10-trimethyldodecane and 2,6,10,14-tetramethylhexadecane. The plot in Fig. 4 permits extrapolated values of the Kováts retention indices of 2,6,10-trimethylhexadecane and 2,6,10,14-tetramethylheptadecane to be obtained (Table II).

TABLE II

KOVÁTS RETENTION INDICES DETERMINED BY THE GRAPHICAL TECHNIQUE

Compound	*Apiezon L*		*SE-30*		*DEGA-PE*	
	100°	*200°*	*100°*	*200°*	*100°*	*200°*
C_{19}(2,6,10)	1729.2	1729.2	1742.2	1747.4	1709.7	1698.0
C_{21}(2,6,10,14)	1872.0	1871.6	1893.5	1898.3	1849.1	1833.3

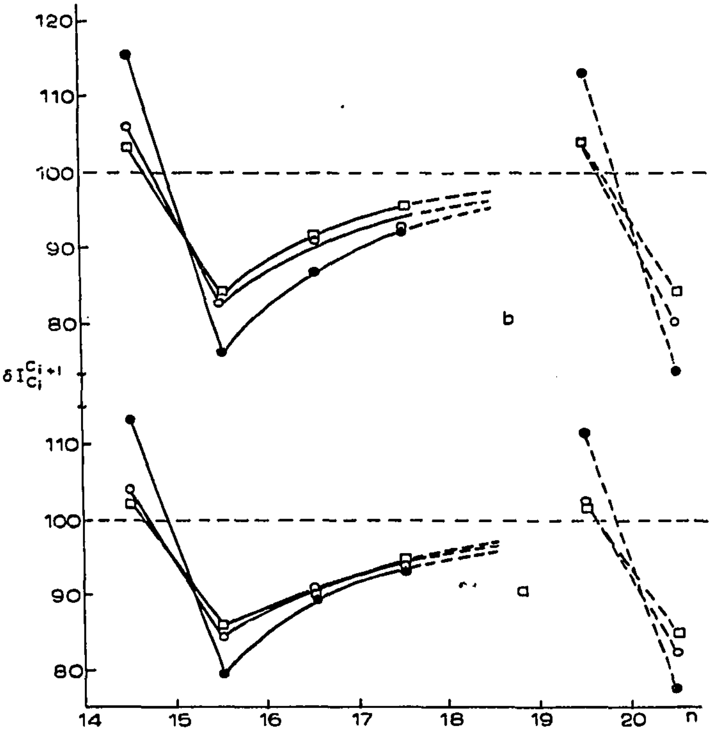


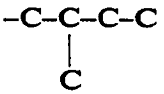
Fig. 4. Variation of the retention index difference between homologues in the 2,6,10-trimethyl- and 2,6,10,14-tetramethylalkane homologous series at (a) 100° and (b) 200°. ○, Apiezon L; □, SE-30; ●, DEGA-PE.

Calculation of retention indices of polymethylalkanes from structural increments of retention

There are other compounds, in addition to those mentioned above, that are of considerable interest in organic geochemistry, such as 2,6,10,14-tetramethylalkanes, 2,6,10,14,18-pentamethylalkanes detected in some petroleums[6,27] and 3,7,11-trimethylalkanes, which, in the authors' opinion, can be formed during the thermocatalytic destruction of phytol. All of these compounds are polymethylalkanes with similar structures, so that the prediction of their retention indices from retention increments, determined from the known retention indices of 2,6-dimethyl-, 2,6,10-trimethyl- and 2,6,10,14-tetramethylalkanes, should not show any significant divergence from the true values.

A retention index is considered to be made up of additive components corresponding to different carbon atoms (primary, secondary and tertiary). Each retention increment involves the characteristic of a particular carbon atom, as well as of the neighbouring carbon atoms, and the characteristic of carbon atoms directly bound to these neighbouring atoms. In this way, in the limiting case, it is the effect of the three nearest carbon atoms that is taken into consideration for the primary carbon atom, and the effect of five carbon atoms is considered for the secondary and the tertiary carbon atoms. For the ten retention indices known, ten equations can be derived, which include seventeen unknowns. Calculation of the retention indices of isoprenoids of interest in the present study can be made by a comparative method, since the following equations are valid:

$$\begin{aligned} IC_n(2,6,10) - IC_{n-5}(2,6) &= IC_{n+5}(2,6,10,14) - IC_n(2,6,10) \\ &= IC_{n+10}(2,6,10,14,18) - IC_{n+5}(2,6,10,14) \\ &= \ldots \text{ etc.} \\ &= 1\,[3(2,2)] + 2\,[2(3) - 2(3)] + 2\cdot 2\,[2(2) - 3(1,2)] \\ &\quad + 3\,[1 - 2(2) - 2(2)] \\ &= \text{increment of the isoprenoid link, } \text{-C-}\underset{\displaystyle C}{\underset{|}{C}}\text{-C-C} \qquad (1) \end{aligned}$$



$$\text{-C-}\underset{\displaystyle C}{\underset{|}{C}}\text{-C-C}$$

where $n = 14,15\ldots.$ Experimental studies have shown that the isoprenoid link increment is not constant but depends on molecular size. The use of more subtle differences in retention increments does not afford any better agreement with experimental data. Even if the effect of eleven neighbouring carbon atoms on the characteristics of the secondary and tertiary carbon atoms is taken into account, the following equations hold:

$$\begin{aligned} IC_{n+5}(2,6,10,14) - IC_n(2,6,10) &= IC_{n+10}(2,6,10,14,18) - IC_{n+5}(2,6,10,14) \\ &= \ldots \text{ etc.} \end{aligned}$$

It would seem that to a certain extent the "non-calculability" principle[28] is true when developing universal systems of calculation. In order to take into account the effect of molecular size, we extrapolated the dependence of the retention increment of the isoprenoid link on the number of carbon atoms in a molecule of the heavier compound used in the calculations to the range of higher-molecular-weight compounds (Fig. 5). The results of calculations are summarized in Table III (column 1). In order to calculate the retention indices of 3,7,11-trimethylalkanes, the following equations can be used without any corrections:

$$IC_{20}\,(2,6,10,14) - IC_n\,(2,6,10) = IC_{19}\,(2,6,10,14) - IC_{n+1}\,(3,7,11) \qquad (2)$$

where $n = 15, 16\ldots.$

The use of Wiener's structural constant[29] and of the correction coefficients determined by the number of methyl groups in position 2 (k) and 3 (l) enabled us to derive empirical equations for calculating the retention indices of polymethylalkanes:

Apiezon L, 100°:

$$\delta I^n_{iso} = 4.638\left(\frac{100\,\Delta W_i}{N^2} + 4.57\,k - 0.3\,\;l\right) - 39.4$$

TABLE III

RETENTION INDICES OF POLYMETHYLALKANES CALCULATED BY THE INCREMENT TECHNIQUE (COLUMN 1) AND BY THE AID OF THE EMPIRICAL EQUATIONS (COLUMN 2)

Compound	*Apiezon L*				*SE-30*				*DEGA-PE*			
	100°		*200°*		*100°*		*200°*		*100°*		*200°*	
	1	*2*	*1*	*2*	*1*	*2*	*1*	*2*	*1*	*2*	*1*	*2*
C_{16} (3,7,11)	1466.3	1466.4	1470.6	1470.1	1475.9	1475.9	1483.1	1483.0	1463.2	1462.8	1460.1	1459.8
C_{17} (3,7,11)	1550.6	1551.4	1553.1	1553.9	1562.0	1561.3	1567.0	1566.5	1542.5	1542.7	1536.2	1535.4
C_{18} (3,7,11)	1641.6	1641.8	1643.0	1644.1	1652.3	1652.8	1658.8	1657.9	1631.9	1632.3	1623.3	1624.1
C_{19} (3,7,11)	1735.6	1735.2	1737.0	1737.4	1747.3	1746.9	1754.5	1752.0	1725.5	1725.2	1715.9	1716.3
C_{19} (2,10,14)	–	1770.6	–	1773.2	–	1780.3	–	1786.0	–	1759.0	–	1754.9
C_{19} (2,6,14)	–	1775.7	–	1778.4	–	1784.9	–	1790.6	–	1764.6	–	1761.0
C_{19} (2,6,10)	–	1728.0	–	1728.9	–	1741.2	–	1744.9	–	1709.1	–	1698.0
C_{21} (2,6,10,14)	1872.0	1874.2	1872.2	1874.1	1894.3	1893.2	1896.8	1896.7	1849.6	1850.7	1833.9	1834.2
C_{22} (2,6,10,14)	1961.7	1963.3	1962.5	1963.0	1984.4	1983.5	1988.6	1987.0	1938.1	1938.9	1919.8	1921.3
C_{23} (2,6,10,14)	2054.7	2055.2	2054.4	2054.7	2079.3	2076.2	2076.2	2079.7	2031.0	2030.1	2011.4	2011.7
C_{24} (2,6,10,14,18)	2107.8	2111.2	2107.6	2109.6	2140.3	2139.0	2143.3	2142.8	2076.4	2077.8	2054.1	2056.3
C_{25} (2,6,10,14,18)	2210.2	2215.3	2211.4	2215.0	2242.3	2242.0	2247.5	2247.2	2187.8	2190.7	2166.8	2171.1

Apiezon L, 200°:

$$\delta I^{n}_{iso} = 4.724\left(\frac{100\,\Delta W_i}{N^2} + 4.62\,k - 0.5\;l\right) - 44.4$$

SE-30, 100°:

$$\delta I^{n}_{iso} = 4.1335\left(\frac{100\,\Delta W_i}{N^2} + 4.10\,k - 0.6\;l\right) - 27.6$$

SE-30, 200°:

$$\delta I^{n}_{iso} = 4.145\left(\frac{100\,\Delta W_i}{N^2} + 4.00\,k - 1.05\,l\right) - 31.4$$

DEGA-PE, 100°:

$$\delta I^{n}_{iso} = 5.03\left(\frac{100\,\Delta W_i}{N^2} + 5.47\,k - 1.05\,l\right) - 42.8$$

DEGA-PE, 200°:

$$\delta I^{n}_{iso} = 5.494\left(\frac{100\,\Delta W_i}{N^2} + 5.15\,k - 1.5\;l\right) - 51.5$$

where $\Delta W_i = W_n - W_{iso}$; W is the sum of the products of the number of carbon atoms on one side of each C–C bond of the molecule multiplied by those on the other side; N is the number of carbon atoms in the molecule. These equations are presented in graphical form in Fig. 6.

The average divergence between the experimental values of the retention in-

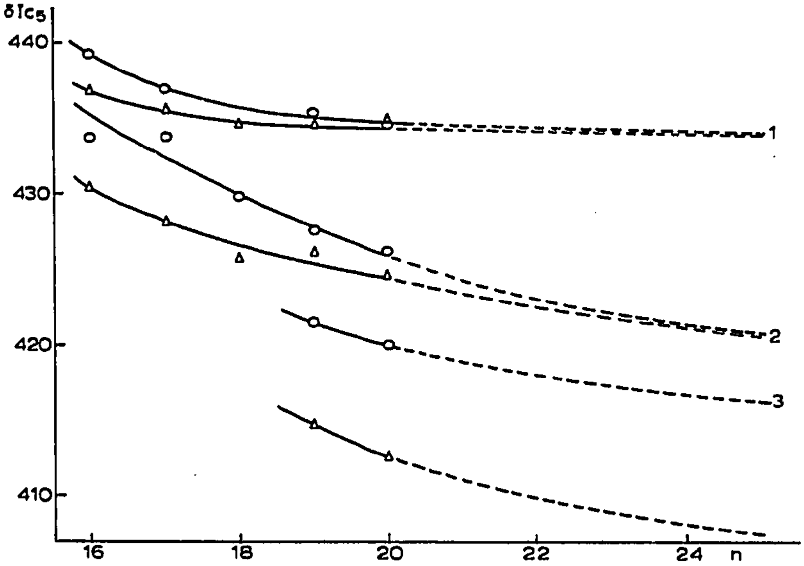


Fig. 5. Dependence of the retention increment of the isoprenoid link on the size of molecules. 1, SE-30; 2, Apiezon L; 3, DEGA-PE. ○, 100°; △, 200°.

TABLE IV

COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF RETENTION INDICES OF ISOPRENOIDS BY THE INCREMENT TECHNIQUE (COLUMN 1) AND BY THE STRUCTURAL CONSTANTS TECHNIQUE (COLUMN 2)

Compound	*Apiezon L*				*SE-30*				*DEGA-PE*			
	Temperature (°C)	*Experimental*	*Calculated*		*Temperature (°C)*	*Experimental*	*Calculated*		*Temperature (°C)*	*Experimental*	*Calculated*	
			1	*2*			*1*	*2*			*1*	*2*
C_{16} (3,7,11)	180	1469.8	1469.7	1469.4	170	1480.4	1480.9	1480.9	160	1460.7	1461.3	1461.0
C_{17} (3,7,11)		1552.8	1552.6	1553.4		1565.8	1565.5	1564.9		1539.6	1538.7	1538.3
C_{18} (3,7,11)		1641.7	1642.7	1643.6		1657.6	1656.9	1656.4		1630.6	1626.7	1627.4
C_{19} (3,7,11)		1735.8	1736.7	1737.0		1751.5	1752.3	1750.5		1718.6	1719.7	1719.9
C_{19} (2,6,10)		1726.9	1729.2	1728.7		1743.7	1746.1	1743.8		1700.0	1702.7	1702.4
C_{21} (2,6,10,14)	200	1871.5	1872.2	1874.1	200	1893.3	1896.8	1896.7	160	1839.3	1840.2	1840.8
C_{22} (2,6,10,14)		1959.2	1962.5	1963.0		1984.1	1988.6	1987.0		1928.4	1927.1	1928.3
C_{23} (2,6,10,14)		2052.8	2054.4	2054.7		2076.5	2084.2	2079.7		2018.0	2019.2	2019.1
C_{24} (2,6,10,14,18)		2113.4	2107.6	2109.6		2141.0	2143.3	2142.8				
C_{25} (2,6,10,14,18)		2214.2	2211.4	2215.0								

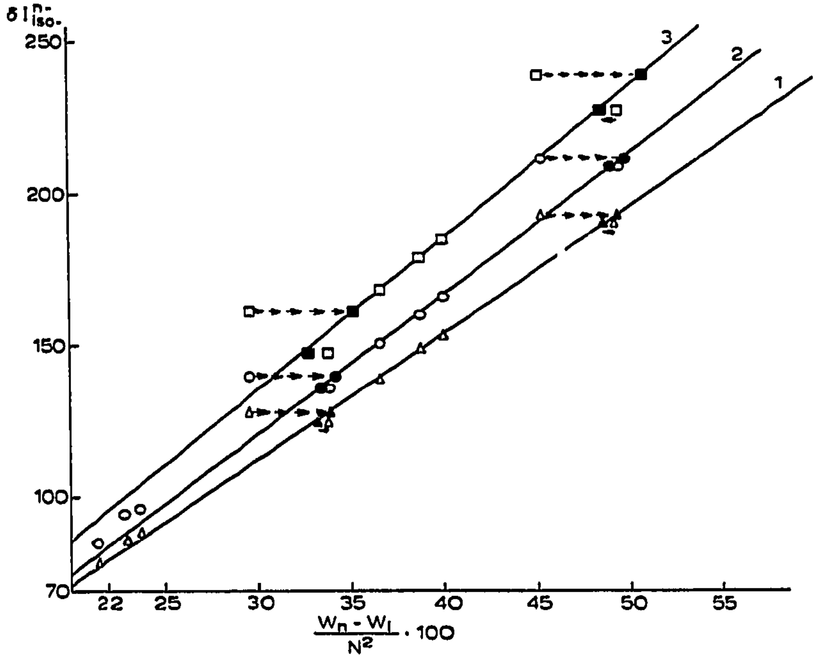


Fig. 6. Relation between the difference in retention indices of an alkane and an isoprenoid with the same carbon number and Wiener's structure constant at 100°. 1, SE-30; 2, Apiezon L; 3, DEGA-PE. Arrows show the values of correction coefficients referring to the excess methyl group in position 2 [C_{14} (2,6,10) and C_{19} (2,6,10,14) isoprenoids], and to the methyl group in position 3 [C_{15} (2,6,10) and C_{20} (2.6, 10,14) isoprenoids].

dices of 2,6,10-trimethyl- and 2,6,10,14-tetramethylalkanes that were used in determining the parameters in these equations, and the data calculated from the equations, was ± 0.4–0.8 unit. The results of the calculations are given in Table III (column 2). From the data in Table III, it can be seen that, in general, there is good agreement between the retention indices calculated by the two methods. The divergence increases for high-molecular-weight compounds, the retention indices of which were calculated in a more remote extrapolation range. The retention indices calculated for DEGA-PE show a good fit with the straight lines in Fig. 3.

Identification of C_{21}–C_{25} isoprenoids and 3,7,11-trimethylalkanes in the Romashkino petroleum

Experimental verification of the proposed calculation methods was carried out using reference compounds, C_{16} (3,7,11) and C_{22} (2,6,10,14). In addition, chromatograms of a sample of Romashkino petroleum were obtained at different temperatures on the three stationary phases investigated (Fig. 1); according to the data of Petrov *et al.*[27], this petroleum contains C_{16}(3,7,11) and higher isoprenoids (C_{21}–C_{25}). The retention indices of the peaks emerging in the chromatograms were calculated. Table IV shows some results of the measurement of Kováts retention indices of the components of Romashkino petroleum, the values of which are the closest to the calculated values. In order to secure greater certainty of identification, the relative peak size of the component to be identified in the n-C_i–n-C_{i+1} range and the retention indices of 2- and 3-methylalkanes were taken into account. The presence of C_{16} (3,7,11) and C_{22} (2,6,10,14) in Romashkino petroleum was demonstrated by adding reference compounds to the mixture under study. The average divergence between the experimental and calculated values of the Kováts retention indices is ± 0.5 unit for C_{16} (3,7,11) and ± 2.6 units for C_{22} (2,6,10,14). On the basis of the above results, it can be concluded that C_{16} (3,7,11), C_{17} (3,7,11) and C_{19} (3,7,11) isoprenoids and higher (C_{21}–C_{25}) isoprenoids are present in Romashkino petroleum. The concentration of these components in this petroleum is about ten times less than that of 2,6,10-trimethylalkanes, pristane and phytane, and is comparable to the 2- and 3-monomethylalkanes concentration. The presence of C_{18} (3,7,11) and C_{19} (2,6,10) is possible but in substantially lower concentrations. No C_{19} (2,6,14) and C_{19} (2,10,14) isoalkanes were detected.

The identification of new compounds in complex multicomponent mixtures is generally considered to have been established after a comparison of the mass spectra of reference compounds with those of the compounds separated from the mixture has been made. We consider the study we have performed as an attempt to achieve a practical application of calculated retention indices and to ascertain the possibilities offered by isothermal gas chromatography as an independent method of identification. In our opinion, the data obtained will also be useful for combined gas chromatography–mass spectrometry.

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