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GAS CHROMATOGRAPHY OF ALL C₁₅-C₁₈ LINEAR ALKENES ON CAPILLARY COLUMNS WITH VERY HIGH RESOLUTION POWER

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SUMMARY

Conditions were studied for the separation of mixtures of all the 60 isomers of C₁₅-C₁₈ *n*-alkenes in the presence of the corresponding *n*-alkanes in highly efficient glass capillary columns ($N \approx 0.5 \cdot 10^6$ effective plates for *n*-alkenes with $k \approx 3$), coated with C₈₇ hydrocarbon, Apiezon L or Carbowax 20M as stationary phase.

The separation of *cis*- and *trans*-isomers of *n*-alkenes is made possible at a sufficiently high column efficiency by the different dependences of their retentions on temperature. The separation of positional isomers of *n*-alkenes having even carbon numbers for the pairs with the most centrally situated double bonds can be achieved only by use of highly efficient columns with polar or non-polar stationary phases ($n_{\text{req}} \approx 10^6$ plates). Correlations between the structure and increments H , δI , dI/dT and ΔI , derived from retention indices of *n*-alkenes, were used for identification as they reflect the position of the double bond, the geometrical arrangement and the length of the carbon chain in various isomers. The so-called propyl effect was confirmed for *trans*-4-alkenes, disturbing the regularity of all correlations between structure and retention.

The influence of adsorption of *n*-alkanes and *n*-alkenes at the polar phase-carrier gas interface on the retention characteristics is discussed. Reproducibility of retention indices of *n*-alkene isomers is a function of their capacity ratios (thickness of the stationary phase film in the column), decreases with polarity of the stationary phase and the isomer under analysis and with the difference between a reference standard and the *n*-alkene in question. These effects are so significant for the columns with Carbowax 20M that a different retention sequence was found for some *n*-alkene isomers in columns with relatively small differences in the thickness of the stationary phase.

INTRODUCTION

The separation of all positional and geometrical isomers of linear alkenes, even in the range up to C_{15} , can only be achieved by using highly efficient capillary columns for both non-polar^{1,2} and polar³ stationary phases. The conditions for the separation of *n*-alkenes higher than C_{15} are even more exacting⁴⁻⁶, and the separation of all the isomers has not yet been effected.

The analysis of isomers of linear C_{18} alkenes in the products from the isomerization of 1-octadecene was described by Chapman and Keummel⁴. The isomerization products were first separated into *cis*- and *trans*-fractions by gas-solid chromatography on alumina impregnated with $AgNO_3$; 1-octadecene was eluted together with the *cis*-isomers. The fractions obtained were then analyzed in a 50-m capillary column with polyphenyl ether stationary phase at 125°C. Despite the fact that simplified mixtures of *n*-octadecene isomers were analyzed, the separation of internal positional isomers was not achieved; 1-octadecene, which was eluted together with *cis*-3-octadecene on a capillary column coated with polyphenyl ether, was partly separated on a capillary column with butanediol succinate stationary phase.

Falconer and Walker⁵ analyzed *n*-hexadecenes in the products from the radiolysis of *n*-hexadecane. They found that the separation of linear hexadecenes on highly efficient capillary columns was not successful owing to some peak overlapping caused by a large excess of *n*-hexadecane. Fourteen liquid phases coated in packed columns were tested and 5% Carbowax 20M treated with terephthalic acid in a 12-m packed column was found to be the most suitable. Five partly separated peaks were obtained for fifteen possible *n*-hexadecene isomers on this column at 155°C.

We have previously shown⁶ that all the isomers of *n*-pentadecenes and *n*-hexadecenes in the products from catalytic dehydrogenation of *n*-alkanes can be resolved by using very highly efficient squalane stainless-steel capillary columns (500,000 effective plates). However, very long analysis times, even at 130°C (24 h), make it unsuitable to apply this separation system to the analysis of still higher *n*-alkenes. The analysis of *n*-pentadecene isomers has recently been speeded up by using a 200-m glass capillary column coated with C_{27} hydrocarbon stationary phase².

The present paper considers the possibilities of separating mixtures of the 60 isomers of C_{15} - C_{18} *n*-alkenes and the corresponding *n*-alkanes in glass capillary columns coated with C_{27} hydrocarbon, Apiezon L and Carbowax 20M stationary phases, with the aim of optimizing working conditions (efficiency, selectivity, temperature) and investigating the problems associated with the reproducibility of the retention data. Relationships between the structure of *n*-alkene isomers and their retention behaviour were applied to the identification of the isomers.

EXPERIMENTAL

Mixtures of the isomers of *n*-pentadecenes, *n*-hexadecenes, *n*-heptadecenes and *n*-octadecenes were prepared by catalytic dehydrogenation of the corresponding individual C_{15} - C_{18} *n*-alkanes¹. *n*-Alkenes from the reaction products were concentrated in a silica gel column with Fluorescent Indicator Adsorption indicator by displacement chromatography with the aid of isopropanol.

Glass capillary columns were prepared of soft soda-lime glass (Unihost type;

Jablonec Glassworks, Jablonec, Czechoslovakia)⁷. The inner walls were roughened with HCl and deactivated with trimethylchlorosilane⁸ (columns coated with C₈₇ hydrocarbon and Apiezon L) or with methyl trifluoroethyl ether⁹ (columns coated with Carbowax 20M stationary phase). The stationary phases were applied by the dynamic method with the aid of a mercury piston^{10,11}. Capillary columns (200–300 m × 0.25 mm I.D.) were obtained by coupling two to four shorter coated columns by means of tubes made of thermoplastic polytetrafluoroethylene.

The gas chromatographic analysis was performed on a Carlo Erba apparatus, Model GI 452, equipped with a flame ionization detector. Nitrogen and hydrogen at an inlet pressure of up to 0.3 MPa were used as carrier gases. The retention data, measured as distances in the chromatogram, were expressed as retention indices; the average repeatability of the measurements was 0.2 index unit (I.U.) (standard deviation).

RESULTS AND DISCUSSION

The product from the catalytic dehydrogenation of *n*-alkanes contains all the isomers of the *n*-alkenes corresponding to the carbon numbers of the initial *n*-alkanes. Other by-products, particularly alkylaromatics and alkadienes, are, however, formed. Mixtures of *n*-alkenes, containing a small amount of the parent *n*-alkanes, were obtained sufficiently pure by concentration in a column with silica gel and were used as model mixtures.

Figs. 1–4 show chromatograms of the separation of isomers of *n*-pentadecenes, *n*-hexadecenes, *n*-heptadecenes and *n*-octadecenes on capillary columns coated with C₈₇ hydrocarbon (HC), Apiezon L (AL) and Carbowax 20 M (CW), respectively. Table I gives the corresponding values of the retention indices and their temperature increments dI/dT . The problems associated with the separation and identification of *n*-alkene isomers are now discussed.

Separation

The difficulties in separating mixtures of higher *n*-alkene isomers can be demonstrated for *n*-hexadecenes, the fifteen possible isomers of which boil in the range 282.2–287.4°C, or the thirteen isomers (excluding 2-alkenes) which have a range of 2.9°C⁶ corresponding to a retention interval of 21.1 I.U. on squalane at 130°C. The peaks are, however, irregularly spaced in this interval since with the shift of the double bond towards the centre of the molecule the properties of the two neighbouring positional isomers become more similar and their separation is more difficult. This behaviour was demonstrated for the separation of *n*-pentadecenes and *n*-hexadecenes on a 200-m squalane capillary column⁶. At a temperature of 130°C and carrier gas (hydrogen) inlet pressure of 0.3 MPa, the analysis time was 24 h for *n*-hexadecenes, and problems occurred with the separation of the pairs of *trans*-5/*cis*-4- and *trans*-3-/1-pentadecenes and analogous pairs of hexadecenes. In order to separate these pairs, a lower temperature had to be used which prolonged the analysis time. Thus a search was made for more suitable separation systems for higher *n*-alkenes.

For the separation of C₁₅-C₁₈ *n*-alkenes, stationary phases were selected so that highly efficient glass capillary columns could be prepared which were sufficiently

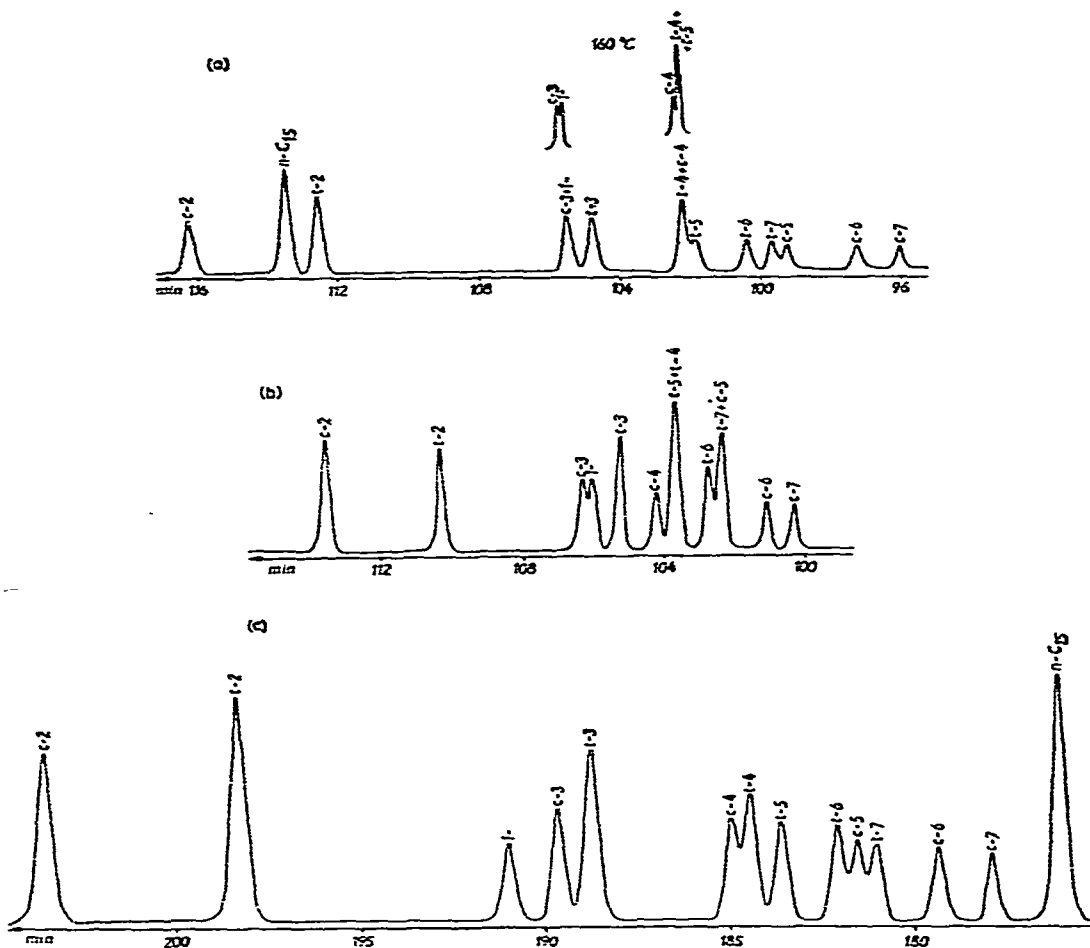


Fig. 1. Chromatograms of the separation of *n*-pentadecene isomers in the following columns: (a) 200 m with C_{37} hydrocarbon at 130°C and 0.3 MPa H_2 ; (b) 220 m with Apiezon L at 154°C and 0.3 MPa N_2 ; (c) 300 m with Carbowax 20M at 96°C and 0.15 MPa N_2 ; *t* = *trans*-, *c* = *cis*-isomer; *n*- C_{15} = *n*-pentadecane.

stable at higher operation temperatures. C_{37} hydrocarbon and Apiezon L were used to advantage as non-polar stationary phases, bearing in mind the experience gained in analysing *n*-alkenes up to C_{16} on squalane^{1,6}. Since the preceding work⁶ demonstrated that, for *n*-decene isomers, the retention interval expands with increasing polarity of the stationary phase, the separation of higher *n*-alkenes was also studied on the polar stationary phase Carbowax 20M.

The requirement for highly efficient columns for the separation of isomers of *n*-alkenes up to C_{18} as well as for a more reasonable analysis time was solved by the preparation of long glass capillary columns (up to 300 m) having thin films of the stationary phase. The characteristics of the columns prepared, expressed as the dependences of the number of theoretical plates, *n*, and the number of effective

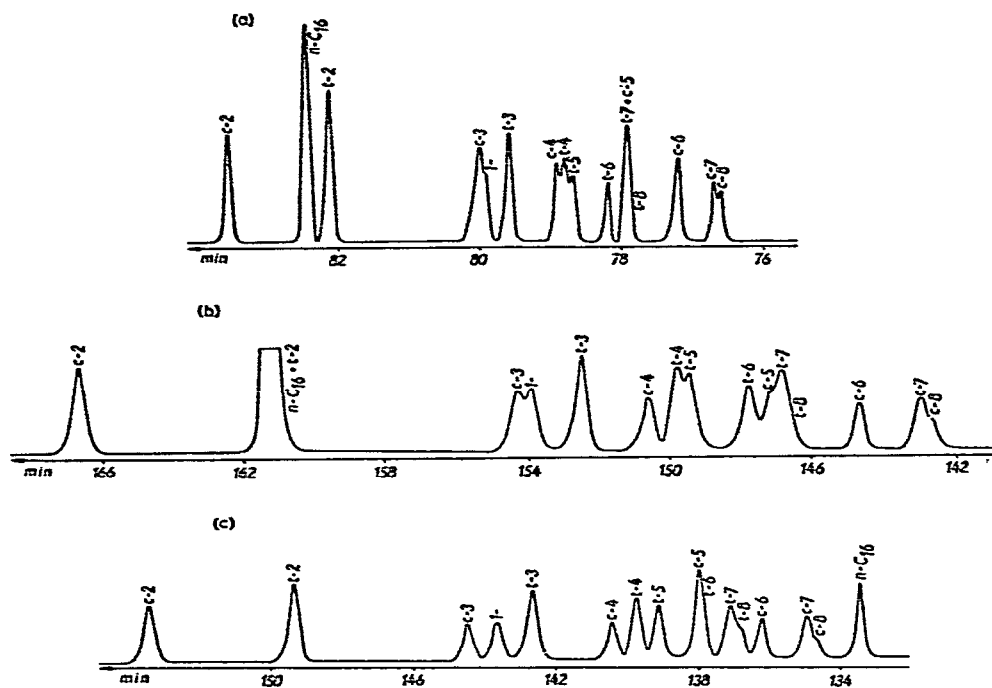


Fig. 2. Chromatograms of the separation of *n*-hexadecene isomers in the following columns: (a) 200 m with C₃₇ hydrocarbon at 150°C and 0.3 MPa H₂; (b) 220 m with Apiezon L at 154°C and 0.3 MPa N₂; (c) 300 m with Carbowax 20M at 110°C and 0.3 MPa N₂; *t* and *c* as in Fig. 1; *n*-C₁₆ = *n*-hexadecane.

plates, N , on the capacity ratio, k , of the isomers, are illustrated in Fig. 5. Such characteristics had previously been obtained² for a column of C₃₇ hydrocarbon (a value of $N = 670,000$ effective plates was measured for *n*-pentadecane with $k = 11.8$ at 110°C). These dependences indicate the very high efficiencies of the glass capillary columns prepared, e.g., for isomers with $k \approx 3$ the value of N is ca. $0.5 \cdot 10^6$ plates.

Tables II and III give the efficiencies calculated for the mixtures under analysis, expressed as the theoretical plate number, n_{req} , required for the separation of the critical pairs of positional isomers of *n*-alkenes up to the baseline (resolution $R = 1.5$). The values of n_{req} obtained on C₃₇ hydrocarbon, Apiezon L and Carbowax 20M lie in the range $0.4 \cdot 10^5$ – $10 \cdot 10^6$ plates from which it follows that the separation is very exacting on both polar and non-polar liquid phases. The values of n_{req} are greater for the *trans*-pairs than for the corresponding *cis*-isomers, and decrease with increasing carbon number in *n*-alkenes for the neighbouring positional isomers.

The most serious difficulties were found for the separation of *n*-alkenes with even carbon numbers and with the double bond position in the centre of the carbon chain, i.e., for "new" positional structural features: for the pair of *trans*-7-/*trans*-8- or *cis*-7/*cis*-8-*n*-hexadecene isomers, or for the pair of *trans*-8-/*trans*-9- or *cis*-8-/*cis*-9-*n*-octadecene isomers. The retention interval of *trans*-isomers is by 35% shorter than for *cis*-isomers with C₁₅–C₁₈ *n*-alkenes (Table IV) and hence the separation is more difficult for *trans*- than for *cis*-isomers. The separation of the pairs of the

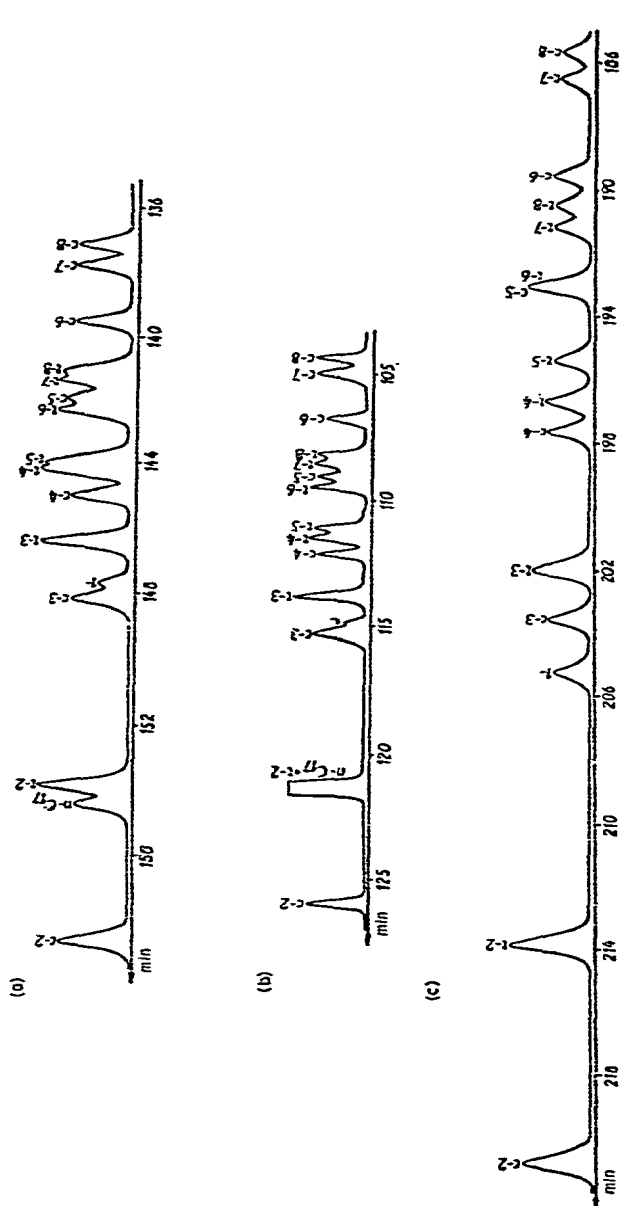


Fig. 3. Chromatograms of the separation of *n*-heptadecene isomers in the following columns: (a) 200 m with Carbowax 20M at 168°C and 0.3 MPa N₂; (b) 220 m with Apiezon L at 154°C and 0.3 MPa N₂; (c) 300 m with Carbowax 20M at 110°C and 0.3 MPa N₂; r and c as in Fig. 1; n-C₁₇ = *n*-heptadecane.

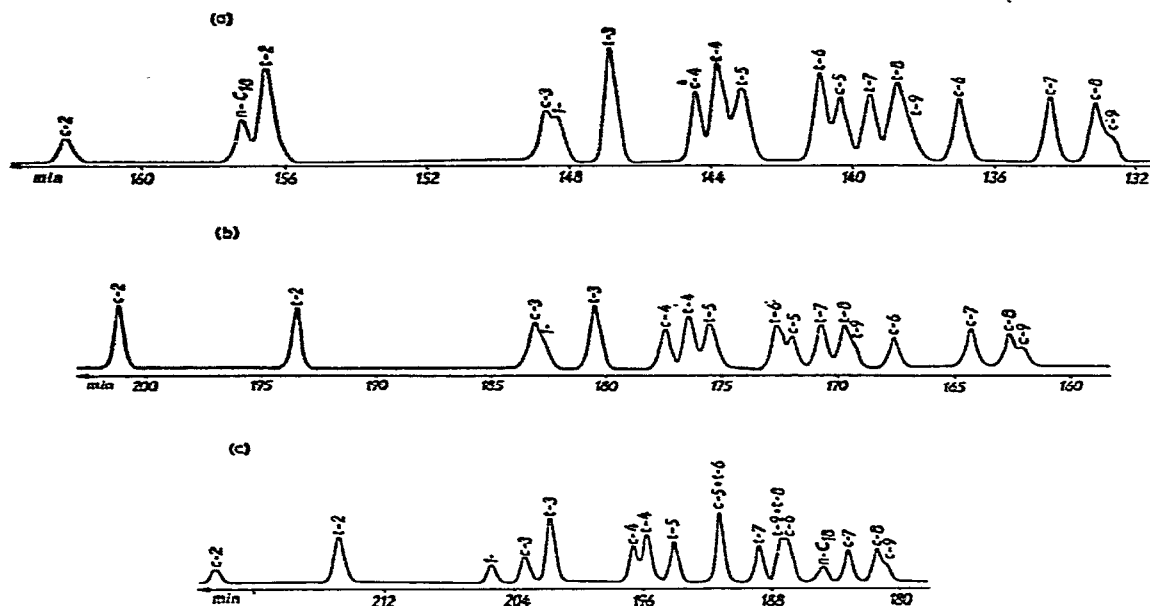


Fig. 4. Chromatograms of the separation of *n*-octadecene isomers in the following columns: (a) 200 m with C₆₇ hydrocarbon at 160°C and 0.3 MPa H₂; (b) 220 m with Apiezon L at 154°C and 0.3 MPa N₂; (c) 300 m with Carbowax 20M at 110°C and 0.3 MPa N₂; *t*, *c* as in Fig. 1; *n*-C₁₈ = *n*-octadecene.

TABLE I

RETENTION INDICES OF C₁₅-C₁₈ *n*-ALKENES ON C₆₇ HYDROCARBON, APIEZON L AND CARBOWAX 20M AND THEIR TEMPERATURE INCREMENTS

<i>n</i> -Alkene	I_{160}^{HC}	dI^{HC}/dT	I_{154}^L	dI^{AL}/dT	I_{110}^{CW}	dI^{CW}/dT
Pentadecenes						
<i>cis</i> -7-	1469.8	0.11	1470.9	0.09	1506.6	0.25
<i>cis</i> -6-	1472.2	0.10	1473.3	0.08	1508.9	0.25
<i>trans</i> -7-	1476.3	0.07	1477.2	0.06	1511.0	0.18
<i>cis</i> -5-	1476.3	0.09	1477.2	0.07	1512.7	0.24
<i>trans</i> -6-	1477.4	0.06	1478.3	0.05	1512.4	0.17
<i>trans</i> -5-	1480.3	0.05	1481.2	0.03	1515.4	0.16
<i>trans</i> -4-	1480.3	0.04	1481.2	0.03	1516.2	0.13
<i>cis</i> -4-	1481.7	0.08	1482.8	0.07	1518.2	0.23
<i>trans</i> -3-	1484.6	0.02	1485.7	0.00	1522.8	0.13
1-	1486.7	0.04	1488.0	0.03	1526.7	0.16
<i>cis</i> -3-	1487.6	0.07	1488.8	0.06	1525.0	0.22
<i>trans</i> -2-	1498.8	0.01	1500.0	0.00	1537.4	0.17
<i>cis</i> -2-	1506.8	0.06	1508.3	0.05	1546.0	0.27
Hexadecenes						
<i>cis</i> -8-	1567.2	0.11	1568.1	0.09	1602.6	0.25
<i>cis</i> -7-	1567.5	0.11	1568.3	0.09	1603.3	0.25
<i>cis</i> -6-	1570.8	0.10	1571.9	0.08	1606.6	0.25
<i>trans</i> -8-	1574.7	0.08	1575.3	0.07	1608.1	0.18

(Continued on p. 50)

TABLE I (continued)

<i>n</i> -Alkene	I_{15}^{HC}	dI^{HC}/dT	I_{14}^{LC}	dI^{LC}/dT	I_{15}^{CW}	dI^{CW}/dT
<i>trans</i> -7-	1574.7	0.08	1575.7	0.07	1608.6	0.17
<i>cis</i> -5-	1575.2	0.09	1576.6	0.08	1610.9	0.24
<i>trans</i> -6-	1576.6	0.06	1577.5	0.06	1610.7	0.17
<i>trans</i> -5-	1579.3	0.05	1580.5	0.05	1613.5	0.15
<i>trans</i> -4-	1579.9	0.04	1581.1	0.03	1615.0	0.12
<i>cis</i> -4-	1581.2	0.08	1582.5	0.07	1616.6	0.23
<i>trans</i> -3-	1584.6	0.02	1585.7	0.00	1621.8	0.13
1-	1586.8	0.04	1588.1	0.03	1625.7	0.16
<i>cis</i> -3-	1587.4	0.07	1588.8	0.06	1624.0	0.22
<i>trans</i> -2-	1598.8	0.01	1600.0	0.00	1636.2	0.17
<i>cis</i> -2-	1606.7	0.06	1608.5	0.06	1644.5	0.27
<i>Heptadecenes</i>						
<i>cis</i> -8-	1664.4	0.12	1665.6	0.10	1699.2	0.27
<i>cis</i> -7-	1665.9	0.11	1667.0	0.10	1700.9	0.26
<i>cis</i> -6-	1669.6	0.11	1670.9	0.09	1704.2	0.25
<i>trans</i> -8-	1673.0	0.09	1674.0	0.06	1705.3	0.18
<i>trans</i> -7-	1673.6	0.08	1674.8	0.06	1706.3	0.17
<i>cis</i> -5-	1674.9	0.09	1676.0	0.08	1709.1	0.24
<i>trans</i> -6-	1675.9	0.07	1676.8	0.05	1708.9	0.17
<i>trans</i> -5-	1679.2	0.05	1680.1	0.04	1712.0	0.16
<i>trans</i> -4-	1680.0	0.04	1681.0	0.03	1713.7	0.13
<i>cis</i> -4-	1681.2	0.08	1682.3	0.07	1715.0	0.23
<i>trans</i> -3-	1684.6	0.02	1685.7	0.00	1720.5	0.12
1-	1686.8	0.04	1687.6	0.04	1724.6	0.15
<i>cis</i> -3-	1687.4	0.07	1688.7	0.06	1722.6	0.21
<i>trans</i> -2-	1698.8	0.01	1700.0	0.00	1735.0	0.16
<i>cis</i> -2-	1706.9	0.07	1708.6	0.06	1742.8	0.26
<i>Octadecenes</i>						
<i>cis</i> -9-	1761.5	0.12	1762.4	0.11	1795.0	0.27
<i>cis</i> -8-	1762.4	0.12	1763.1	0.11	1795.8	0.26
<i>cis</i> -7-	1764.6	0.11	1765.3	0.10	1798.1	0.25
<i>cis</i> -6-	1769.0	0.10	1769.6	0.09	1802.5	0.24
<i>trans</i> -9-	1771.3	0.09	1771.7	0.08	1803.3	0.18
<i>trans</i> -8-	1771.8	0.08	1772.2	0.08	1803.3	0.18
<i>trans</i> -7-	1773.1	0.08	1773.6	0.07	1805.0	0.16
<i>cis</i> -5-	1774.4	0.09	1775.2	0.08	1807.2	0.23
<i>trans</i> -6-	1775.4	0.07	1775.9	0.06	1807.6	0.15
<i>trans</i> -5-	1778.9	0.05	1779.5	0.05	1811.2	0.14
<i>trans</i> -4-	1780.0	0.04	1780.6	0.03	1813.2	0.12
<i>cis</i> -4-	1781.0	0.08	1781.8	0.07	1814.2	0.21
<i>trans</i> -3-	1784.7	0.02	1785.3	0.01	1820.1	0.12
1-	1786.8	0.04	1787.8	0.04	1824.0	0.15
<i>cis</i> -3-	1787.5	0.07	1788.4	0.06	1821.8	0.20
<i>trans</i> -2-	1798.9	0.01	1800.0	0.00	1834.1	0.16
<i>cis</i> -2-	1807.0	0.07	1808.6	0.06	1841.7	0.26

positional 7-/8-isomers is easier for *n*-heptadecenes than for the corresponding *n*-hexadecenes and a similar situation may also be expected for the separation of the pairs of 8-/9-isomers of *n*-nonadecenes. These conclusions are in accord with the rules for separation of isomeric pairs which were published earlier¹².

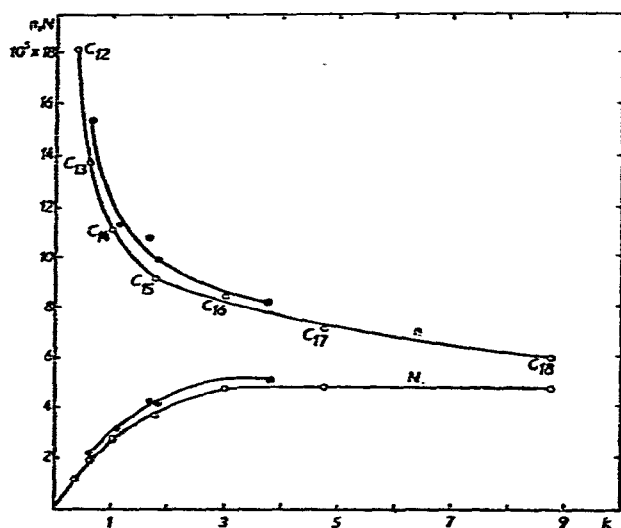


Fig. 5. Dependence of the theoretical plate number, n , and the effective plate number, N , on the capacity ratio, k , of the components under analysis, on Apiezon L at 154°C and Carbowax 20M at 115°C. Columns: Apiezon L, 220 m \times 0.25 mm I.D., inlet pressure 0.3 MPa N₂, N₂ flow-rate 8.7 cm/sec (○); Carbowax 20M, 300 m \times 0.25 mm I.D., 0.3 MPa N₂, flow-rate 7.7 cm/sec (●).

TABLE II

VALUES OF n_{req} FOR *cis*-8-/cis-9-OCTADECENE PAIR ON C₆₇ HYDROCARBON, APIEZON L AND CARBOWAX 20M

$n_{\text{req}} = 16 R^2 \left(\frac{\alpha}{\alpha - 1} \right)^2 \left(\frac{k_2 + 1}{k_2} \right)^2$, where α is the relative retention and k_2 is the capacity ratio for *cis*-8-octadecene. For baseline separation resolution, $R = 1.5$.

Stationary phase	Temperature (°C)	Capacity ratio, k_2	Rel. retention, α	$n_{\text{req}} \cdot 10^6$
C ₆₇ Hydrocarbon	160	5.27	1.0042	3.2
Apiezon L	154	6.77	1.0041	2.9
Carbowax 20M	110	3.18	1.0048	2.7

TABLE III

VALUES OF n_{req} FOR 7-/8-POSITIONAL C₁₅-C₁₈ *cis*- AND *trans*-ALKENES ON APIEZON L AT 154°C

Pair of isomers	k_2	α	$n_{\text{req}} \cdot 10^6$
<i>cis</i> -7-/cis-8-Hexadecene	2.40	1.0031	7.4
<i>cis</i> -7-/cis-8-Heptadecene	4.05	1.0075	1.0
<i>cis</i> -7-/cis-8-Octadecene	6.85	1.0117	0.4
<i>trans</i> -7-/trans-8-Hexadecene	2.49	1.0027	10.1
<i>trans</i> -7-/trans-8-Heptadecene	4.23	1.0040	3.4
<i>trans</i> -7-/trans-8-Octadecene	7.16	1.0071	0.9

TABLE IV

RETENTION INTERVALS OF POSITIONAL C₁₅-C₁₈ *trans*- AND *cis*-ALKENES ON C₃₇ HYDROCARBON, APIEZON L AND CARBOWAX 20M AT 130°CHC = C₃₇ hydrocarbon; AL = Apiezon L; CW = Carbowax 20M.

No. of carbon atoms	<i>trans</i> -Isomers			<i>cis</i> -Isomers		
	HC	AL	CW	HC	AL	CW
C ₁₅	24.3	24.3	26.2	38.5	39.4	39.8
C ₁₆	26.2	26.4	27.9	41.0	41.1	42.3
C ₁₇	28.2	27.5	29.3	44.0	44.0	43.4
C ₁₈	30.0	30.2	30.4	47.0	47.5	46.5

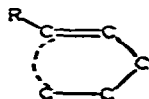
Another problem is the separation of C₁₅-C₁₈ *trans*-4-/*trans*-5-alkenes. In contrast to the regularities found in the separation of neighbouring positional isomers of *n*-alkenes, the separation of this pair is more difficult than that of the pair of *trans*-5-/*trans*-6-isomers or that of pairs having more centrally situated double bonds (Table V). *trans*-4-Isomers of *n*-alkenes exhibit lower retentions, owing to the

TABLE V

δI VALUES OF NEIGHBOURING POSITIONAL *trans*- AND *cis*-ISOMERS OF C₁₅-C₁₈ *n*-ALKENES ON C₃₇ HYDROCARBON, APIEZON L AND CARBOWAX 20M AT 130°CHC = C₃₇ hydrocarbon; AL = Apiezon L; CW = Carbowax 20M.

Isomers compared	C ₁₅			C ₁₆			C ₁₇			C ₁₈		
	HC	AL	CW	HC	AL	CW	HC	AL	CW	HC	AL	CW
<i>trans</i> -2-/ <i>trans</i> -3-	14.5	14.3	15.4	14.5	14.3	15.2	14.5	14.3	15.3	14.5	14.9	14.8
<i>trans</i> -3-/ <i>trans</i> -4-	4.9	5.2	6.6	5.3	5.4	7.0	5.2	5.4	6.6	5.3	5.2	7.1
<i>trans</i> -4-/ <i>trans</i> -5-	0.3	0.0	0.2	0.9	1.0	0.9	1.1	1.2	1.1	1.4	1.5	1.4
<i>trans</i> -5-/ <i>trans</i> -6-	3.2	3.4	2.8	3.0	3.3	2.4	3.9	3.5	2.9	4.1	3.8	3.4
<i>trans</i> -6-/ <i>trans</i> -7-	1.4	1.4	1.2	2.5	1.9	2.1	2.6	2.2	2.6	2.6	2.6	2.4
<i>trans</i> -7-/ <i>trans</i> -8-	—	—	—	0.0	0.5	0.3	0.9	0.9	0.8	1.3	1.6	1.3
<i>trans</i> -8-/ <i>trans</i> -9-	—	—	—	—	—	—	—	—	—	0.8	0.5	0.0
<i>cis</i> -2-/ <i>cis</i> -3-	19.5	19.8	22.0	19.6	19.7	21.5	19.5	19.9	21.2	19.5	20.3	21.1
<i>cis</i> -3-/ <i>cis</i> -4-	6.3	6.2	6.6	6.5	6.5	7.2	6.5	6.7	7.2	6.8	6.8	7.4
<i>cis</i> -4-/ <i>cis</i> -5-	6.0	5.6	5.3	6.3	6.1	5.5	6.6	6.5	5.9	6.6	6.8	6.6
<i>cis</i> -5-/ <i>cis</i> -6-	4.1	4.1	3.6	4.7	4.8	4.1	5.9	5.4	4.5	5.7	5.9	4.5
<i>cis</i> -6-/ <i>cis</i> -7-	2.7	2.3	2.3	3.6	3.8	3.3	3.7	4.1	3.1	4.7	4.5	4.2
<i>cis</i> -7-/ <i>cis</i> -8-	—	—	—	0.5	0.2	0.6	1.8	1.4	1.5	2.5	2.0	2.1
<i>cis</i> -8-/ <i>cis</i> -9-	—	—	—	—	—	—	—	—	—	0.9	1.2	0.6

possibility of cyclization of the propyl group with the π-electron system of the molecule



which is why they are eluted closer to *trans*-5-isomers¹³. As the carbon number of *n*-alkenes increases, the separation of *trans*-4/*trans*-5-isomers improved slightly, again in agreement with the rules for retention behaviour of isomers¹².

The separation of geometrical isomers is somewhat easier than that of positional isomers since the dependence of their retention on temperature is different. The vapour pressure of more asymmetric *cis*-isomers has a greater dependence on temperature than that of the corresponding more symmetric *trans*-isomers and therefore the temperature increments of the retention indices are of the *cis*-isomers larger¹. It follows from the values of dI/dT in Table I that the separation of the critical pairs of positional isomers will improve if the temperature is reduced. More central positional isomers of *n*-alkenes are eluted earlier than isomers in which the double bond is shifted towards the ends of the chain, and also possess somewhat greater values of dI/dT ; hence their separation slightly improves with temperature decrease.

This is another reason why the separation of positional isomers of *n*-alkenes is more advantageous at lower column temperatures. To prevent long analysis times at these temperatures it is necessary to use capillary columns with thinner films of the stationary phase and with hydrogen as carrier gas. Such conditions may not necessarily be the most convenient for the separation of some pairs of *cis*/*trans*-alkenes having the double bond in different positions, therefore the column temperature should be optimized (Figs. 1-4).

By comparing the separations of *n*-alkenes on C₈₇ hydrocarbon, Apiezon L and Carbowax 20M (Figs. 1-4), it is possible to determine the changes in the retention sequence of some isomers with change in polarity of the stationary phase. As shown above, a similar effect—mutual shift *cis*- and *trans*-isomers—may also partially be achieved by changing the column temperature. The retention interval of positional *trans*- and *cis*-isomers of *n*-alkenes slightly expands with increasing polarity of the stationary phase (Table IV), but with increasing carbon number this expansion in retention interval becomes smaller and for C₁₇-C₁₈ *cis*-isomers there may even be a contraction (this unexpected result will be discussed later). The application of more polar phases is advantageous since the retention of *n*-alkenes decreases enabling analyses at lower column temperatures. Another advantage of the application of polar phases is the fact that the *cis*-isomers yield greater dI/dT values than the *trans*-isomers, which makes easier the optimization of temperature during the separation of some isomers having more centrally situated double bonds.

Reproducibility of retention indices. Problems may arise in the use of retention indices or optimal temperatures, based on the data of Table I, for the separation and the identification of *n*-alkene isomers, particularly if a polar stationary phase is used.

Fig. 6 shows the dependence of the retention index of 1-pentadecene on its capacity ratio, obtained from measurements performed in seven different glass capillary columns coated with Carbowax 20M at 110°C; the point corresponding to the value $k = 5$ was obtained on a column the surface of which was first coated with BaCO₃ (ref. 14). It can be seen that the retention index of 1-pentadecene obviously increases with its capacity ratio, *i.e.*, with the thickness of the film of the stationary phase in the column.

A linear dependence of $I^{CW} = f(k)$ was obtained (Fig. 7) for all *n*-pentadecene isomers from measurements in three Carbowax columns within a relatively

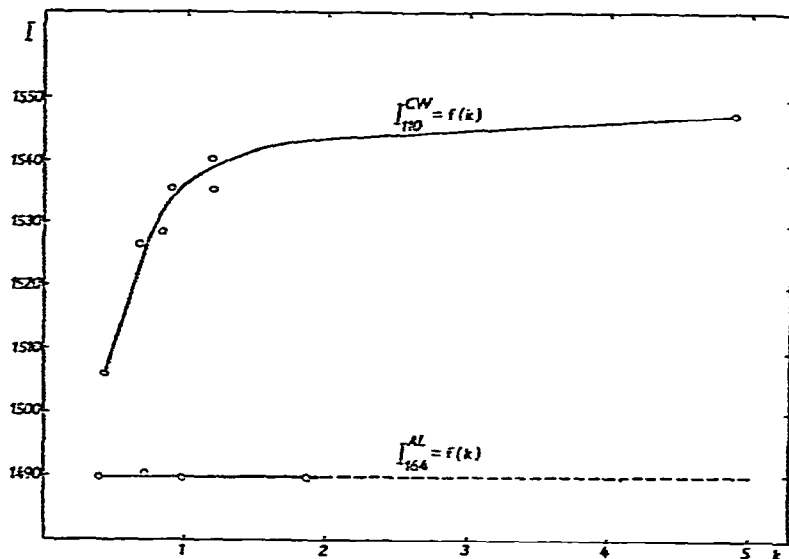


Fig. 6. Dependence of retention index of 1-pentadecene on its capacity ratio of Carbowax 20M obtained from measurements in seven columns at 110°C, and on Apiezon L in four columns at 164°C.

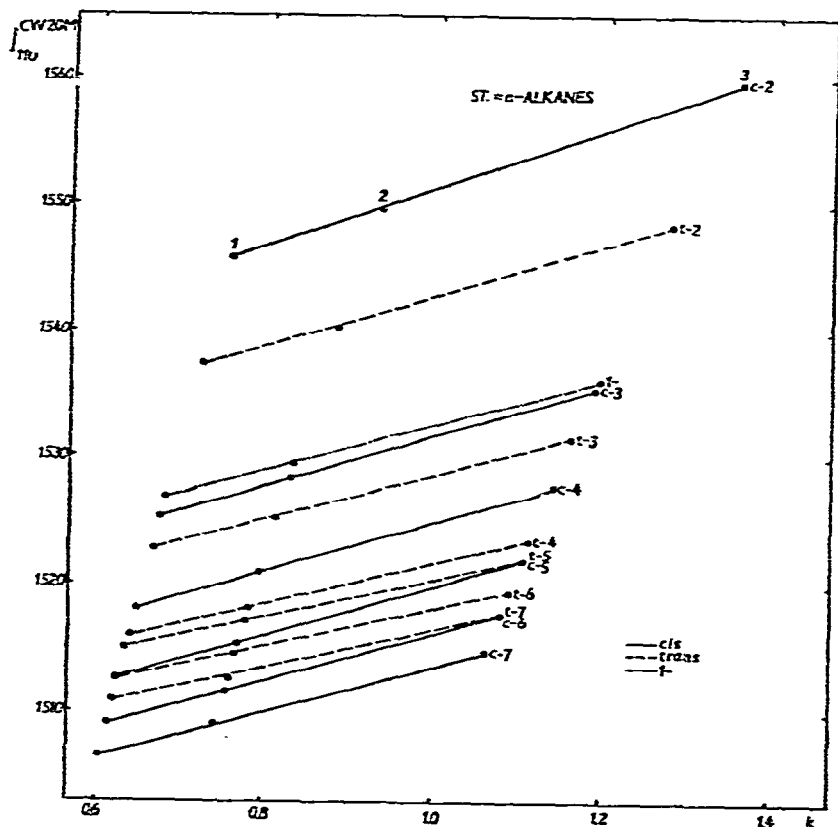


Fig. 7. Dependence of retention indices of *n*-pentadecene isomers on their capacity ratios obtained from measurements in three columns with Carbowax 20M at 110°C.

narrow range of k values. It can be seen from this figure that the slopes of the straight lines differ for individual *n*-pentadecenes, being greater for *cis*- than for *trans*-alkenes, are close for *cis*-isomers to 1-alkene and greater for 2-alkenes than for the other positional isomers. In agreement with the above, the differences in the properties of individual columns during the separation appear as a shift of *cis*- towards *trans*-isomers or of 1- towards *trans*-isomers, while the mutual retention of positional isomers changes negligibly. This shift (change in selectivity), depending on the thickness of the film of the stationary phase, was observed, e.g., in the separation of isomers on two different Carbowax columns under the same experimental conditions, in that a reversed retention sequence was obtained for *trans*-6- and *cis*-5-pentadecenes (Fig. 8). Another important aspect of this result is that, by changing the stationary phase film thickness, the optimal selectivity of the capillary column may be adjusted for the separation of the mixture under analysis.

The different slopes of the function $I^{CW} = f(k)$ for individual isomers agree well with the values of $\Delta I = I^{\text{polar}} - I^{\text{non-polar}}$ for *n*-alkenes, discussed below. Based on these relationships the smaller retention indices of *n*-alkenes measured on Carbowax columns with thinner layers of the stationary phase could be explained by partial orientation of hydroxyl groups of the stationary phase towards the surface of the glass capillary. However, it is also necessary to consider the contribution of the adsorption of *n*-alkanes and *n*-alkenes at the polar stationary phase-carrier gas interface. In these separation systems in which retention results from both solution and adsorption, the ratio of the two contributions changes with change in the amount of stationary phase in the column, which leads to changes in the retention indices^{15,16}.

As can be seen from Fig. 9, the replacement of *n*-alkanes by 1-alkenes as the internal standard improves significantly the reproducibility of the retention indices of *n*-alkenes on Carbowax columns.

In accord with the preceding conclusions, the reproducibility of retention indices of *n*-alkenes in glass capillary columns with non-polar stationary phases is substantially better than with polar phases. Retention indices of *n*-alkenes also changed on Apiezon L with the thickness of the film of the stationary phase, however to substantially smaller extent than on Carbowax 20M. Table VI gives retention indices of 1-pentadecene measured in four different glass capillary columns with Apiezon L at 164°C. In spite of significant differences in the capacity ratios, comparable with k values for Carbowax 20M (Fig. 6), the retention indices of 1-pentadecene change only slightly with the thickness of the film of stationary phase. Retention indices of *n*-alkenes appear to increase slightly with their capacity ratios even on Apiezon L. Column 2 is an exception since the retention index is somewhat greater than that corresponding to the capacity ratio measured, probably as a consequence of a more active glass surface. As can be seen from Fig. 10, greater retention of *n*-alkenes, in comparison with *n*-alkanes, appears on this Apiezon column, and *trans*-2-alkenes and the corresponding C₁₅-C₁₈ *n*-alkanes ($I_{164}^{\text{AL}} = 1702.1$ for *trans*-2-heptadecene) can be resolved.

Identification

The position of the double bond in alkenes is at present determined by derivatization and subsequent gas chromatographic-mass spectrometric (GC-MS) analysis. However, the precision of such determinations is limited by difficulties in the interpretation of mass spectra¹⁷.

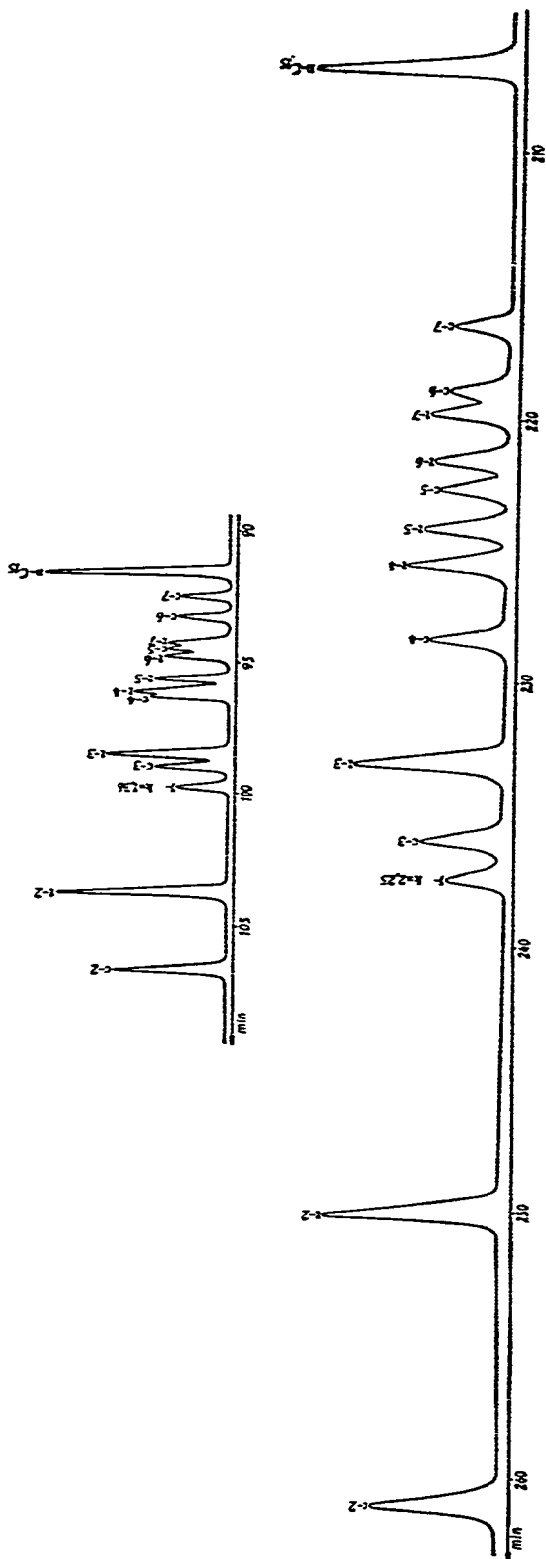


Fig. 8. Chromatograms of the separation of *n*-pentadecene isomers in two 300-m columns with Carbowax 20M (columns 1 and 3 in Fig. 7) at 95°C and inlet pressure 0.3 MPa N₂; the capacity ratios for 1-pentadecene in these columns are 1.36 and 2.25, respectively.

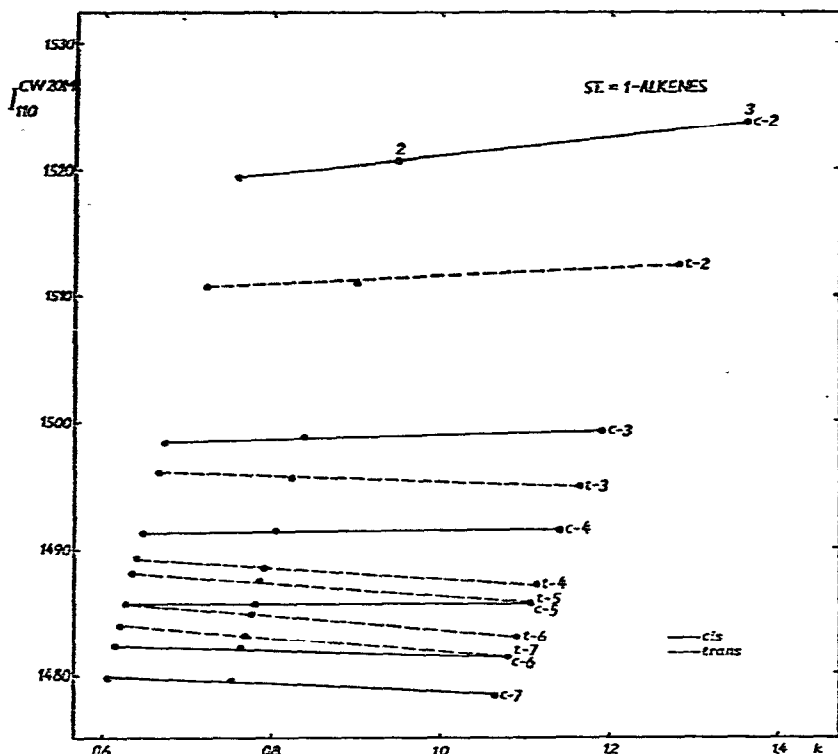


Fig. 9. Dependence of retention indices of *n*-pentadecene isomers on their capacity ratios on Carbowax 20M at 110°C; conditions as in Fig. 7, except an homologous series of 1-alkenes is used as the internal standard in place of *n*-alkanes.

TABLE VI

CAPACITY RATIOS AND RETENTION INDICES OF 1-PENTADECENE ON APIEZON L COLUMNS AT 164°C

Column No.	Capacity ratio, <i>k</i>	I_{164}^L
1	0.40	1488.0
2	0.76	1491.3
3	0.98	1488.2
4	1.87	1488.3

Despite the lack of standards and retention data, the use of identification procedures for C₁₅-C₁₈ *n*-alkenes which we had previously given¹ for the identification of lower *n*-alkenes on a squalane phase led to positive results. The correlation used was that between the structure and the gas chromatographic behaviour of *n*-alkenes. The parameters were as follows structural increments of retention indices, *H*; the difference in the retention indices of the two neighbouring positional and geometrical isomers, δI ; the temperature increment of the retention indices, dI/dT ; the difference in the retention indices of *n*-alkenes on two stationary phases of different polarities, ΔI .

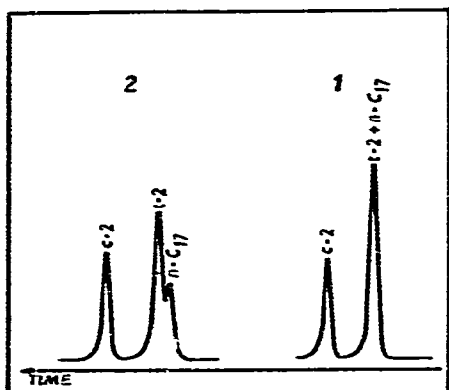


Fig. 10. Separation of *n*-heptadecane (*n*-C₁₇) and *trans*-2-heptadecene (*t*-2) in two 100-m columns with Apiezon L (Nos. 1 and 2 in Table VI) at 164°C and inlet pressure 0.3 MPa N₂; *c*-2 = *cis*-2-heptadecene.

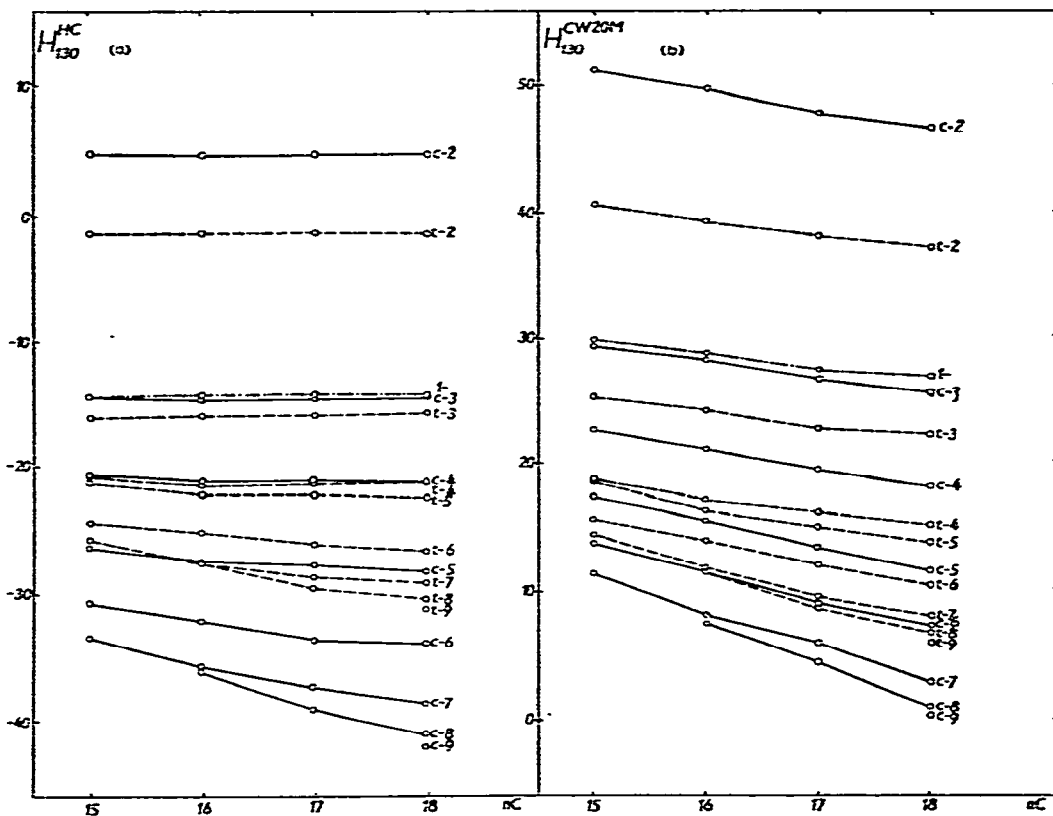


Fig. 11. Dependence of structural increments, H , on carbon number in C₁₅-C₁₈ *n*-alkenes at 130°C: (a) on C₆₇ hydrocarbon; (b) on Carbowax 20M. *t*, *c* as in Fig. 1.

Structural increment, H . This characterizes the position of the double bond and of any isomerization, as well as the dependence on the length of the carbon chain. The dependence

$$H^{\text{HC}} = I^{\text{HC}}(n\text{-alkene}) - I^{\text{HC}}(n\text{-alkane})$$

on the carbon number of n -alkenes separated on C₈₇ hydrocarbon at 130°C is illustrated in Fig. 11a. It can be seen that the dependences are characteristic for various homologous series of n -alkenes and that their slopes decrease as the double bond shifts towards the centre of the molecule. A similar dependence was found on Apiezon L.

For the polar stationary phase Carbowax 20M the character of the above dependence is different: the values of H^{CW} decrease more rapidly with the carbon number (Fig. 11b). This difference for polar and non-polar stationary phases may be associated with the reduction of the relative contribution of the double bond to the intermolecular interaction as the length of the alkyl chain in the n -alkene molecule increases. It may also be associated with the effect of increasing adsorption of n -alkanes (used as reference standards in the retention index system) with increasing number of their carbon atoms at the polar phase-carrier gas interface^{15,16} and with the different adsorptions of various n -alkenes at this interface.

Difference in retention indices, δI . This parameter shows characteristic regularities (Table V). Thus with the shift of the double bond towards the centre of n -alkene

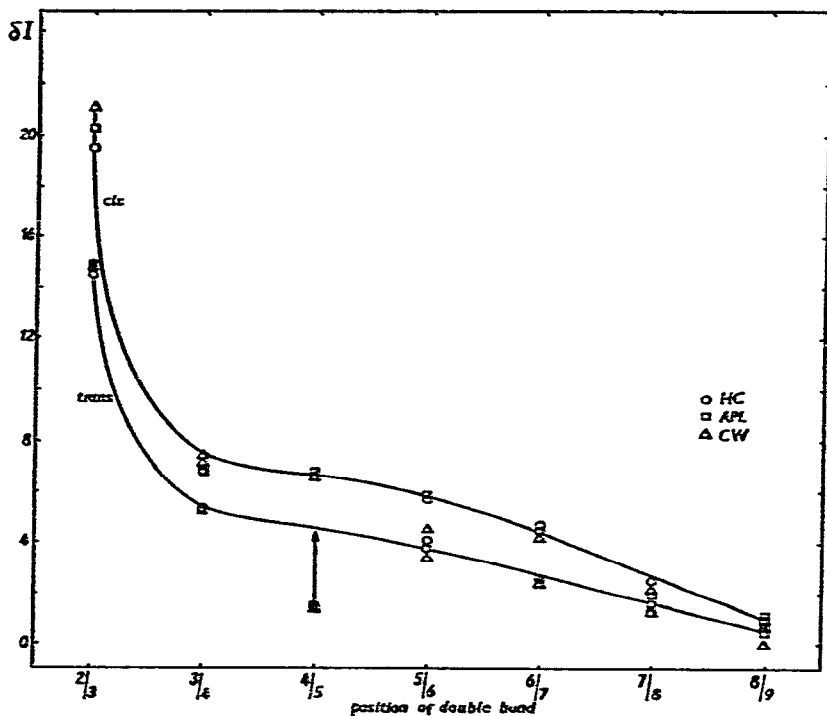


Fig. 12. Dependence of the values of δI of the neighbouring positional *cis*- and *trans*-isomers on the position of the double bond for n -octadecenes on C₈₇ hydrocarbon, Apiezon L and Carbowax 20M at 130°C.

TABLE VII

δI VALUES OF GEOMETRICAL *cis*-/*trans*-ISOMERS OF C₁₅-C₁₉ *n*-ALKENES ON C₄₇ HYDROCARBON, APIEZON L AND CARBOWAX 20M AT 130°C

Isomers compared	C ₁₅			C ₁₆			C ₁₇			C ₁₈		
	HC	AL	CW	HC	AL	CW	HC	AL	CW	HC	AL	CW
<i>cis</i> -2-/ <i>trans</i> -2-	6.5	7.1	10.6	6.4	7.0	10.3	6.3	7.2	9.8	6.3	7.2	9.6
<i>cis</i> -3-/ <i>trans</i> -3-	1.5	1.6	4.0	1.3	1.6	4.0	1.3	1.6	3.9	1.3	1.9	3.3
<i>cis</i> -4-/ <i>trans</i> -4-	0.2	0.6	4.0	0.1	0.5	3.8	0.0	0.3	3.3	-0.2	0.3	3.0
<i>cis</i> -5-/ <i>trans</i> -5-	-5.2	-5.0	-1.1	-5.3	-4.6	-0.8	-5.2	-5.0	-1.5	-5.7	-5.0	-2.2
<i>cis</i> -6-/ <i>trans</i> -6-	-6.4	-5.7	-1.9	-7.0	-6.1	-2.5	-7.5	-6.9	-3.1	-7.3	-7.1	-3.3
<i>cis</i> -7-/ <i>trans</i> -7-	-7.7	-7.0	-3.0	-8.1	-8.0	-3.7	-8.6	-8.8	-3.6	-9.4	-9.0	-5.1
<i>cis</i> -8-/ <i>trans</i> -8-	-	-	-	-8.4	-7.7	-4.1	-9.5	-9.3	-4.3	-10.6	-9.4	-5.9
<i>cis</i> -9-/ <i>trans</i> -9-	-	-	-	-	-	-	-	-	-	-10.7	-10.1	-6.5

molecules the values of δI decrease (Fig. 12). The regularity of this dependence is significantly disturbed for all the pairs of C₁₅-C₁₈ *trans*-4-/*trans*-5-alkenes, and always towards lower values of δI , because of the so-called propyl effect of *trans*-4-isomers. With increasing carbon number in *n*-alkenes, the values of δI are almost identical for 2- to 4-alkenes and increase slightly for more central positional isomers.

For the corresponding geometrical *cis*-/*trans*-isomers, δI decreases gradually from positive to negative values with the shift of the double bond position towards the centre of the molecule. Also a change in the retention sequence occurs: up to the 4-position of the double bond the *trans*-isomers are eluted first, but starting from the 5-position, it is the corresponding *cis*-isomers (Table VII).

Temperature increments of the retention index, dI/dT. The dependence of the temperature increments of the retention indices on the position and the geometry of the double bond in C₁₅-C₁₈ *n*-alkenes on C₈₇ hydrocarbon and Carbowax 20M is shown in Fig. 13. On the non-polar phases (C₈₇ hydrocarbon and Apiezon L) the values of dI/dT of *n*-alkenes are similar; however, in contrast to expectation, they are slightly greater on C₈₇ hydrocarbon than on Apiezon L. On the non-polar phases the values of dI/dT are greater for *cis*- than for *trans*-isomers of *n*-alkenes for the same position of the double bond. The sequence of dI/dT values for 1-alkenes eluting in the critical range of 3-alkenes is: *trans*-3- < 1- < *cis*-3-isomer. With the shift of the position of the double bond from the 2-position towards the centre of the *n*-alkene molecule dI/dT increases slightly.

The dI/dT values are greater on more polar Carbowax 20M than on non-polar phases; they are also generally greater for *cis*- than for *trans*-alkenes because of a stronger hindering effect of more symmetric *trans*-alkenes on the interactions of the double bond with the stationary phase. Characteristically large dI/dT values of 2-alkenes on the polar phase can be explained by a hyperconjugation effect (greater electron polarizability of the molecule resulting from the presence of an electron-donating methyl group in a neighbouring position to the double bond). For other isomers with centrally situated double bonds, the values of dI/dT on Carbowax 20M slightly increase with the shift of the double bond towards the centre of the molecule and are close to those for the most central positional isomers of 2-alkenes.

In homologous series of *n*-alkene isomers the values of dI/dT are almost identical, or they seem to be slightly greater on the non-polar phase and to decrease slightly on the polar phase with the carbon number in *n*-alkenes.

The difference in dI/dT values of corresponding *cis*-/*trans*-isomers rises with the polarity of the stationary phase: it is on average 0.05 I.U./°C for non-polar C₈₇ hydrocarbon and Apiezon L phases and 0.08 I.U./°C for Carbowax 20M, which suggests important possibilities of separating *n*-alkanes from *n*-alkenes. The separation of *n*-alkanes from *trans*-2-alkenes is a problem on Apiezon L columns since these compounds possess almost identical retention indices and dI/dT values (however, their separation was obtained by using a more active glass surface). These pairs are separated on C₈₇ hydrocarbon, which is less polar than Apiezon L, *trans*-2-alkenes being eluted before the corresponding *n*-alkanes (as on squalane).

Difference in retention indices, ΔI . The values of $\Delta I = I^{CW} - I^{HC}$ also show regularities depending on the carbon number and the position of the double bond in *n*-alkenes (Table VIII). It can be seen from Fig. 14 that ΔI values decrease with the

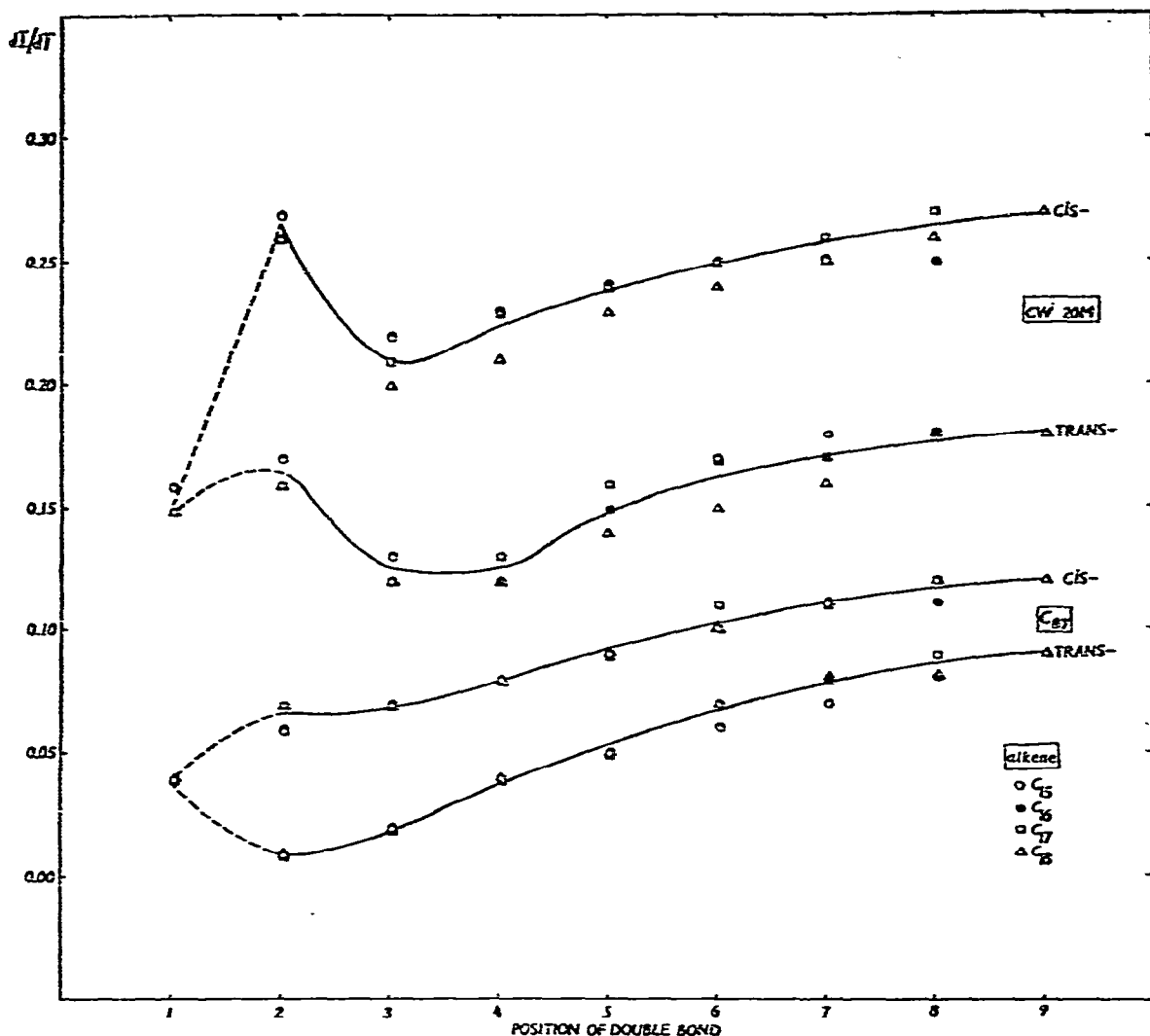


Fig. 13. Dependence of temperature increments of retention indices on the position of the double bond in C₁₅-C₁₈ *n*-alkenes on C₆₇ hydrocarbon and Carbowax 20M, respectively.

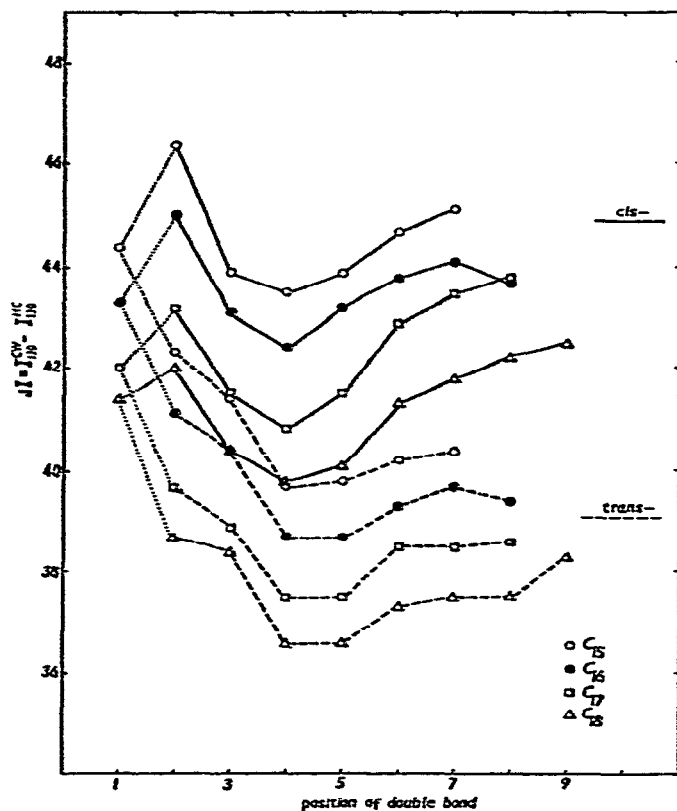
carbon number in various homologous series of *n*-alkenes. It can be assumed that, except for a growing hindering effect on the double bond with the expansion of the carbon chain, described for *H* values, the dependence is due to the adsorption of *n*-alkanes at the polar phase-carrier gas interface and is proportional to their number of carbon atoms.

The ΔI values of the positional *cis*- and *trans*-isomers decrease with the shift of the double bond from the 2- to the 4-position and then, unexpectedly, slightly increase with further shift towards the centre of the molecule. Large ΔI values for 2- and partly also for 3-alkenes can be explained by the hyperconjugation effect. Relatively large ΔI values for 1-alkenes is in agreement with the interaction of the acidic hydrogen atom of the most electronegative carbon atom in the 1-position with proton-acceptor oxygen atoms of Carbowax 20M. For *trans*-4-isomers, showing the propyl effect, ΔI values are somewhat lower than those expected on the basis of a similar dependence for *cis*-4-isomers (Fig. 14), and result from a relatively smaller

TABLE VIII

VALUES OF $\Delta I = I_{130}^{CN} - I_{130}^{HC}$ OF C₁₅-C₁₈ n-ALKENE ISOMERS AT 130°C

n-Alkene	C ₁₅	C ₁₆	C ₁₇	C ₁₈
trans-2-	42.3	41.1	39.7	38.7
trans-3-	41.4	40.4	38.9	38.4
trans-4-	39.7	38.7	37.5	36.6
trans-5-	39.8	38.7	37.5	36.6
trans-6-	40.2	39.3	38.5	37.3
trans-7-	40.4	39.7	38.5	37.5
trans-8-	—	39.4	38.6	37.5
trans-9-	—	—	—	38.3
cis-2-	46.4	45.0	43.2	42.0
cis-3-	43.9	43.1	41.5	40.4
cis-4-	43.5	42.4	40.8	39.8
cis-5-	43.9	43.2	41.5	40.1
cis-6-	44.7	43.8	42.9	41.3
cis-7-	45.1	44.1	43.5	41.8
cis-8-	—	43.7	43.8	42.2
cis-9-	—	—	—	42.5
1-	44.4	43.3	42.0	41.4

Fig. 14. Dependence of the values of $\Delta I = I_{130}^{CN} - I_{130}^{HC}$ on the position of the double bond in C₁₅-C₁₈ n-alkenes.

interaction of the anomalous structure of *trans*-4-isomers with the polar stationary phase. The increase in ΔI values with the shift of the double bond from the 4- or 5-position towards the centre of the molecule may be associated with the different adsorptions of *n*-alkene isomer¹⁶. As the double bond shifts towards the centre of the molecule, the polarity of the *n*-alkene falls and therefore its adsorption at the polar phase-carrier gas interface rises. This conclusion is in accord with the fact that ΔI values for 5- to 9-positional isomers are somewhat smaller on Carbowax 20M than those on C₃₇ hydrocarbon or Apiezon L (Table V), and also with the trends in retention intervals of *trans*- and *cis*-isomers of C₁₅-C₁₈ *n*-alkenes on polar and non-polar phases (Table IV). Comparison of ΔI values for the corresponding *cis*- and *trans*-isomers shows that all the *cis*-isomers have greater ΔI values than their corresponding *trans*-isomers.

CONCLUSIONS

The high resolution capacity of the columns used ($N \approx 0.5 \cdot 10^6$ for $k \approx 3$) and the good repeatability of the measurements of the retention indices ($s \approx 0.2$ I.U.) on both polar and non-polar stationary phase in a single column made possible correlations between the fine structure and the retention of isomers of C₁₅-C₁₈ *n*-alkenes. The structure-retention correlations reflect fine differences in the stereochemistry and electronic configuration of the isomers. The position of the double bond in the carbon chain, stereochemistry and the length of carbon chain are reflected in different values of H , δI , dI/dT and ΔI as a consequence of the changes in the contributions of stereochemical and charge effects or of the effects on the retention index of the adsorption of *n*-alkanes and *n*-alkenes at the polar stationary phase-carrier gas interface. These correlations appear to be a good means of identifying components of mixtures of isomers of C₁₅-C₁₈ *n*-alkenes without the need for internal standards.

On the other hand, for slightly polarizable substances, separated on the polar phase, the precise measurements illustrate how much the column parameters (*e.g.*, capacity ratio) influence the values of the retention indices. This fact must be considered seriously when using any compilation of GC retention data, particularly those measured in capillary columns.

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