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CAPILLARY GAS CHROMATOGRAPHY OF LINEAR ALKENES ON SQUALANE

SEPARATION AND IDENTIFICATION OF *n*-PENTADECENES AND *n*-HEXADECENES

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SUMMARY

All positional and spatial isomers of straight-chain C_{15} and C_{16} alkenes (except both pairs of *trans*-5- and *cis*-4-isomers) were separated on an efficient squalane capillary column at 130°. The identification of the isomers was achieved with sufficient certainty only by means of gas chromatography. Retention data are given and unknown boiling points were derived from them.

INTRODUCTION

We have recently defined useful correlations between the structures and chromatographic behaviour of linear alkenes on squalane[1], based on precise measurements on C_6–C_{14} linear monoolefins. Similar work has been carried out by other workers[2–4]. In our earlier paper[1], we demonstrated the possibility of estimating the retention behaviour of typical isomers of higher alkenes. Of higher *n*-alkenes, Falconer and Walker[5] studied the separation of hexadecenes on Carbowax using packed columns, and Chapman and Kuemmel[6] the separation of octadecenes on a poly-(phenyl ether) capillary column. Falconer and Walker separated 15 possible isomers of *n*-hexadecene in five peaks, while Chapman and Kuemmel did not succeed in separating isomers with internal positions of the double bond.

In this paper, we describe gas chromatographic studies on pentadecenes and hexadecenes and compare the results with theoretical data. Unknown boiling points of all of the linear C_{15} and C_{16} alkene isomers are also correlated.

EXPERIMENTAL

Mixtures of *n*-pentadecene and *n*-hexadecene isomers were prepared by the catalytic dehydrogenation of *n*-pentadecane and *n*-hexadecane. The *n*-alkene contents

in the reaction products were concentrated by means of a silica gel column. Chromatographic separations were carried out on a Carlo Erba (Milan, Italy) GI 450 gas chromatograph, equipped with stainless-steel capillary column, 200 m in length, I.D. 0.2 mm, coated with squalane. The column temperature was 130° and the carrier gas was hydrogen (inlet pressure 3.0 kg/cm^2). The sample size was 0.5 μl, with a splitting ratio of 1:100. The column efficiency for the components to be separated was about 500,000 theoretical plates. The separation time was about 24 h.

The retention data are expressed as retention indices; the repeatability of their measurements was 0.1–0.2 index units (standard deviation from 4–6 measurements).

RESULTS AND DISCUSSION

Identification

The only standards available were n-alkanes and 1-alkenes. The identification of the n-hexadecene and n-pentadecene isomers with an internal position of the double bond was based on the estimated dependences of the structural increments, H, on the number of carbon atoms in the individual homologous series of n-alkenes[1]: the structural increment of any n-alkene in squalane, $H^{Sq} = I^{Sq}_{n\text{-alkene}} - I^{Sq}_{n\text{-alkene}}$, is dependent on the number of carbon atoms in the molecule, on the position of the double bond and its spatial isomerism, and on the column temperature. The H^{Sq}-values for the individual homologous series of n-alkenes decrease characteristically with the number of carbon atoms in the molecule and the decrease can still be measured even seven carbon atoms from the beginning of a given point in the structure. The decrease in the structural increments between the first member of the series and the members with closely similar H^{Sq} is greater for the *cis*- than for the *trans*-isomers.

The retention measurements of n-pentadecenes and n-hexadecenes were performed on the same squalane column as used previously[1], but at a higher temperature and after about two yaars. Preliminary experiments with n-dodecenes, n-tri-decenes and n-tetradecenes showed some systematic positive error, which was 0.7 index unit for *cis*-alkenes, 0.5 index unit for *trans*-alkenes and 0.6 index unit for 1-alkenes, as compared with the results published earlier[1]. For comparison with earlier material, the new results must be carefully corrected. Therefore, also all n-dodecenes, n-tridecenes and n-tetra-decenes were analyzed together with n-pentadecenes and n-hexadecenes. The values of the H^{Sq}_{130} structural increments calculated from the retention data are listed in Table I. It can be seen that the values of the structural increments for n-alkenes correspond well with the rules described previously[1]. Thus, all isomers of n-penta-decenes and n-hexadecenes with the double bond in positions 2 to 7 were identified.

Another correlation of the structural increment was used for the identification of new structural isomers of n-hexadecenes with the double bond in position 8. This dependence is illustrated in Fig. 1 as the relationship between the H^{Sq}_{130} structural increment and the number of carbon atoms for the first members of the homologous series with a particular molecular arrangement (*cis*- or *trans*-2-butene, -3-hexene, -4-octene, -5-decene, -6-dodecene, -7-tetradecene and -8-hexadecene). The peaks of *trans*-8- and *cis*-8-hexadecene, measured experimentally, correspond with this dependence very well.

The relative retentions of the neighbouring positional *cis*- and *trans*-isomers

TABLE I

STRUCTURAL INCREMENTS H_{130}^{Sq} OF C_{12}–C_{16} n-ALKENES

Alkene	H_{130}^{Sq}	
	trans-Isomer	cis-Isomer
2-Dodecene	− 2.4	3.7
2-Tridecene	− 2.5	3.7
2-Tetradecene	− 2.4	3.6
2-Pentadecene	− 2.5	3.6
2-Hexadecene	− 2.5	3.7
3-Dodecene	−14.2	−13.1
3-Tridecene	−14.5	−13.7
3-Tetradecene	−14.9	−13.8
3-Pentadecene	−14.7	−14.0
3-Hexadecene	−15.1	−14.5
4-Dodecene	−18.1	−18.1
4-Tridecene	−19.0	−19.0
4-Tetradecene	−19.7	−19.7
4-Pentadecene	−19.8	−20.3
4-Hexadecene	−20.3	−21.2
5-Dodecene	−18.1	−21.9
5-Tridecene	−19.0	−23.4
5-Tetradecene	−19.7	−25.1
5-Pentadecene	−20.3	−25.8
5-Hexadecene	−21.2	−27.0
6-Dodecene	−18.7	−22.4
6-Tridecene	−20.9	−25.9
6-Tetradecene	−22.2	−28.2
6-Pentadecene	−23.3	−30.0
6-Hexadecene	−24.7	−31.9
7-Tetradecene	−23.2	−29.9
7-Pentadecene	−24.7	−32.3
7-Hexadecene	−26.4	−35.0
8-Hexadecene	−28.3	−35.7

expressed as the differences in their retention indices, δI, characteristically decrease[1] according to the shift of the double bond towards the centre of the molecule, and increase with an increase in the number of carbon atoms. This trend and thereby also the possibility of identification is confirmed by the δI_{130}^{Sq} values calculated from the values of the retention indices, measured for C_{12}–C_{16} n-alkenes, as given in Table II.

When correlating the chromatographic behaviour of the positional and spatial isomers with the position of the double bond and the number of carbon atoms in the molecules, we also found certain regularities. These are illustrated in Fig. 2 by corresponding pairs of C_9–C_{13} cis- and trans-n-alkenes with the double bond in positions 2–6, and by the results for the isomers with the double bond in positions 7 and 8 as given in this paper. It can be seen that with the isomeric 2-alkenes, the trans-isomers are eluted first. The 3-isomers change the retention sequence gradually when the number of carbon atoms in the molecule is increased; with lower alkenes the trans-3-alkenes, and with higher alkenes the cis-3-alkenes, are eluted first. The change in the
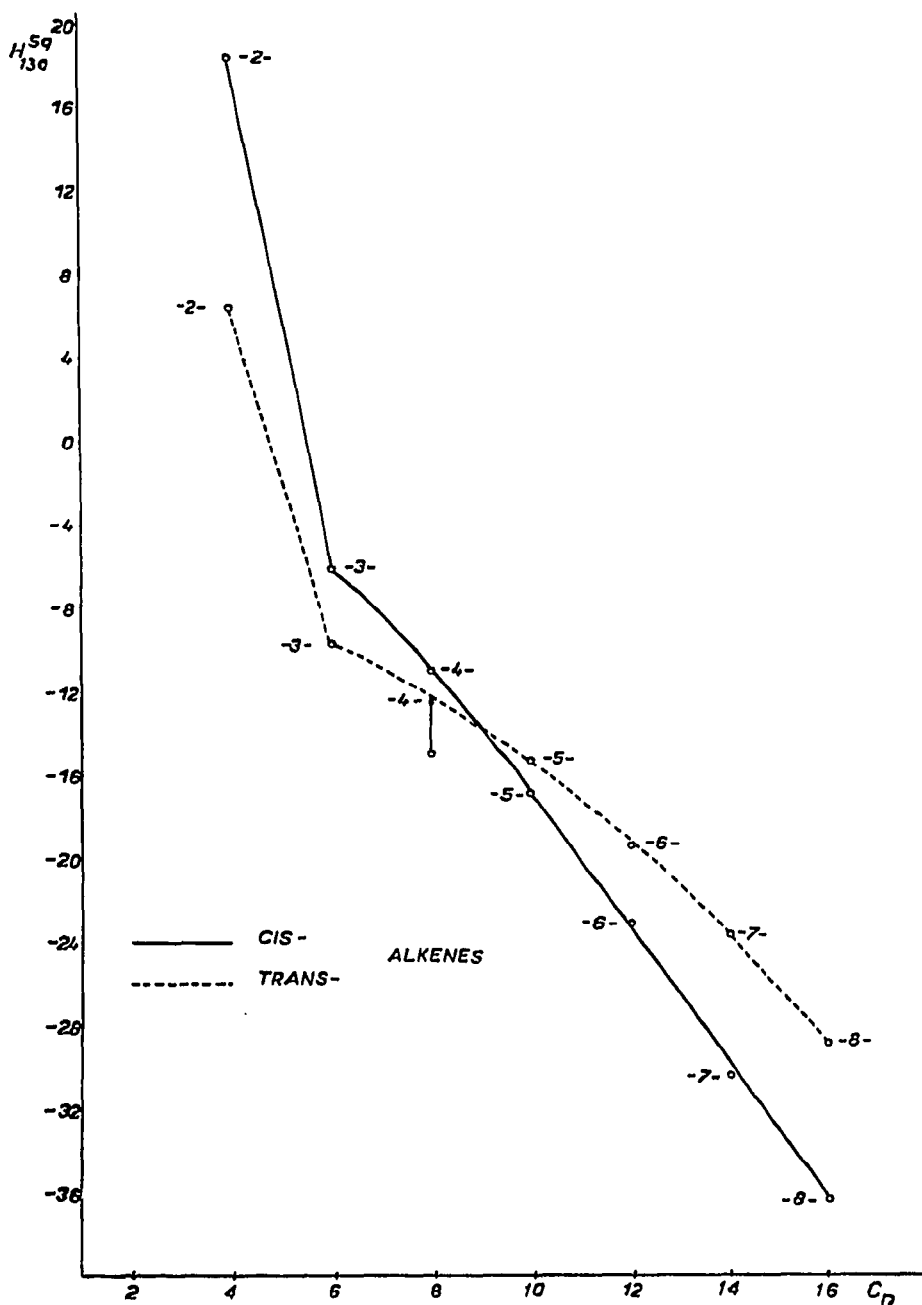
Fig. 1. Dependence of the structural increment H_{130}^{Sq} on the number of carbon atoms for the first members of the homologous series of *cis-* and *trans*-alkenes (with a new structural trait).

TABLE II

DIFFERENCES IN RETENTION INDICES, δI_{130}^{Sq}, OF THE NEIGHBOURING CONFIGURATIONAL PAIRS OF n-ALKENES

Number of C atoms	n-Alkene pairs compared											
	cis- 2–3	cis- 3–4	cis- 4–5	cis- 5–6	cis- 6–7	cis- 7–8	trans- 2–3	trans- 3–4	trans- 4–5	trans- 5–6	trans- 6–7	trans- 7–8
12	16.8	5.0	3.8	0.5	—	—	11.8	3.9	0.0	0.6	—	—
13	17.4	5.3	4.4	2.5	—	—	12.0	4.5	0.0	1.9	—	—
14	17.4	5.9	5.4	3.1	1.8	—	12.5	4.8	0.0	2.5	1.0	—
15	17.6	6.3	5.5	4.2	2.3	—	12.2	5.1	0.5	3.0	1.4	—
16	18.2	6.7	5.8	4.9	3.1	0.7	12.6	5.2	0.9	3.5	1.7	1.9

retention sequence of the 4-isomers gradually increases faster than that of the 3-isomers. With more internal isomers (double bond in positions 5, 6 and 7), the cis-isomer is eluted first. The $\delta I_{cis,trans}^{Sq}$ values[1] $(\delta I_{cis,trans}^{Sq} = I_{cis}^{Sq} - I_{trans}^{Sq})$ characteristically decrease with the shift of the double bond towards the centre of the molecule and also with the number of carbon atoms in the molecule so that they can be used for proof of identification (Table III).

TABLE III

DIFFERENCES IN THE RETENTION INDICES OF THE CORRESPONDING cis- AND trans-ISOMERS OF n-ALKENES, $\delta I_{cis,trans}^{Sq} = I_{cis}^{Sq} - I_{trans}^{Sq}$, AT 130°

Number of C atoms	Position of double bond						
	2-	3-	4-	5-	6-	7-	8-
12	6.1	1.1	0.0	−3.8	−3.7	—	—
13	6.2	1.2	0.0	−4.4	−5.0	—	—
14	6.0	1.1	0.0	−5.4	−6.0	−6.7	—
15	6.1	0.7	−0.5	−5.5	−6.7	−7.6	—
16	6.2	0.6	−0.9	−5.8	−7.2	−8.6	−7.4

The dependence of the H_{130}^{Sq} structural increment on the number of carbon atoms for all of the 113 possible isomers of n-alkenes up to C_{16} is shown in Fig. 3. The H_{130}^{Sq} values for n-pentadecenes and n-hexadecenes are corrected as mentioned above.

Separation

The results obtained show that, as the carbon chain of the n-alkenes becomes longer, the difficulties in the separation of the increasing number of positional and spatial isomers increase, especially for isomers with the most internal positions of the double bond. High-efficiency capillary chromatography therefore remains the most effective method in the analysis of the individual n-alkenes.

In the separation system used (200-m capillary column coated with squalane, temperature 130°), 26 of the 28 possible isomers of n-pentadecenes and n-hexadecenes were separated; only the pairs *trans*-5- –*cis*-4-pentadecene and *trans*-5- –*cis*-4-hexa-

Fig. 2. Separation of geometrical *cis-* and *trans-*isomers as a function of the position of the double bond and the number of carbon atoms in the molecules on squalane at 100°.
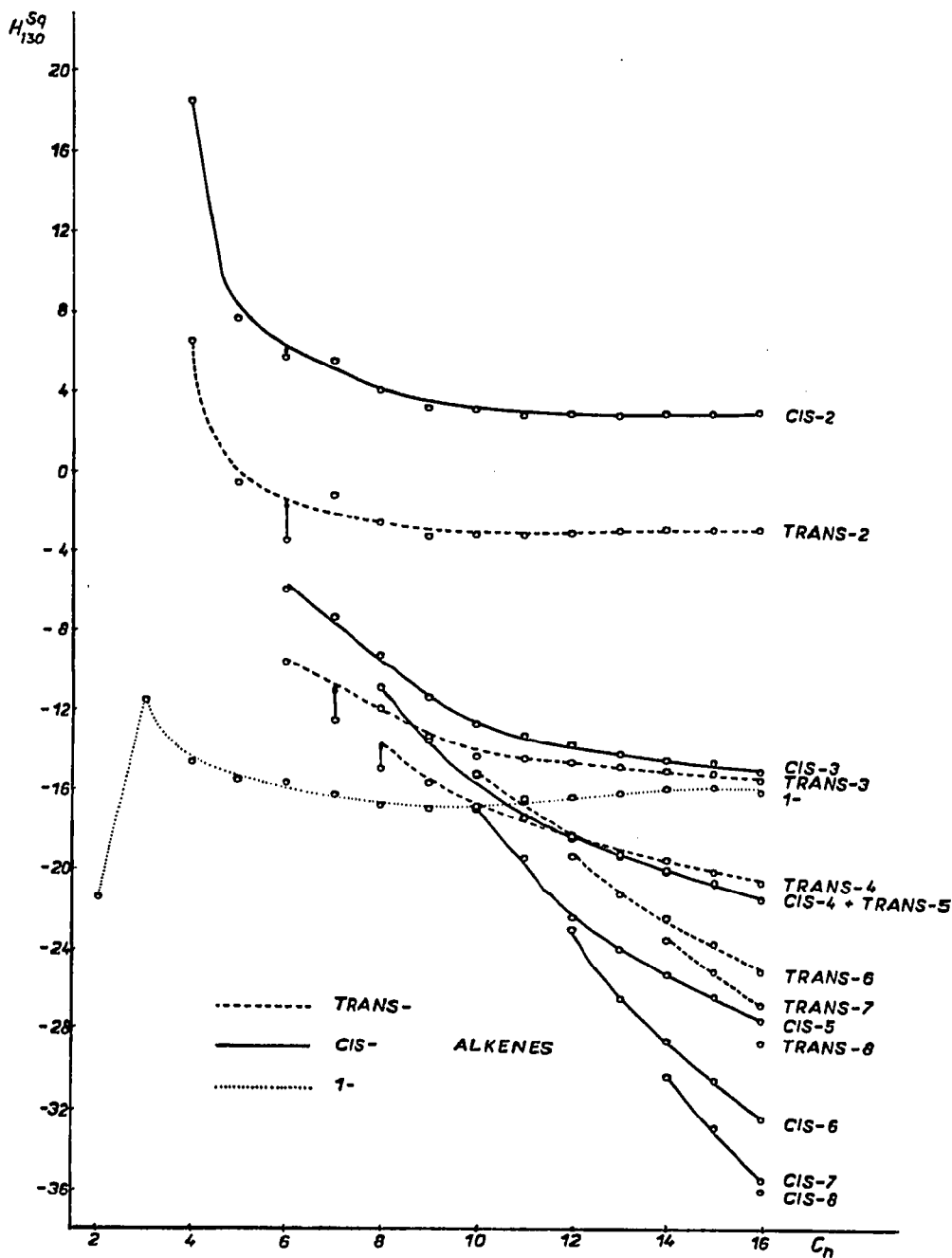
Fig. 3. Dependence of the structural increment H_{130}^{Sq} on the number of carbon atoms for the individual homologous series of n-alkenes.
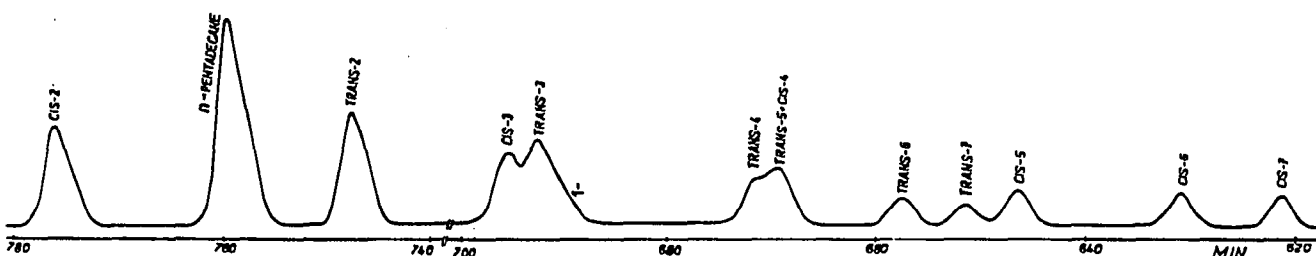
Fig. 4. Chromatogram of the separation of *n*-pentadecenes and *n*-pentadecane on squalane at 130°.

decene were not separated. The partial separation of 1-alkenes from the corresponding *trans*-3-isomers can be seen from the chromatogram of the separation of *n*-pentadecenes shown in Fig. 4. As the individual isomers of the above unseparated pairs have different temperature increments, they can be separated at lower column temperatures, and the *cis*-4-isomers will be eluted before the *trans*-5-isomers. The separation of 1-alkenes from the corresponding *trans*-3-alkenes can be improved in a similar manner. The complete separation of C_{15} and C_{16} alkanes from the corresponding *cis*-2- and *trans*-2-alkenes was also achieved at 130°.

Recently, separations of *n*-alkenes on polar phases have been described[2,3,7]. In Table IV are compared the retention indices for *n*-decenes (the most difficult to separate *n*-alkenes on squalane) at 50° on squalane[1], Apiezon L (*cf.*, ref. 2), bis-2-ethylhexyl tetrachlorophthalate[7], 7,8-benzoquinoline[3], di-*n*-butyl tetrachlorophthalate[7] and polyethylene glycol 4000 (*cf.*, ref. 2). It can be seen that the retention interval for *n*-decenes, δI, increases with an increase in the polarity of the stationary phase. Comparison of known data for straight-chain undecenes and dodecenes shows similar relationships. It is probable that the space, expressed in index units, in which the individual isomers with a certain length of the carbon chain will be eluted, will be extended on polar phases also with higher alkenes. This, however, does not mean that the separation of all pairs of positional or spatial isomers will similarly improve. It can further be expected that a number of regularities found on the squalane column will have analogous regularities on polar stationary phases, as seems to be the case when one compares the results obtained by other workers[2,7]. This is particularly important as the separation of alkenes higher than C_{15} and C_{16} is not possible on squalane as it requires a higher temperature than can be used with squalane.

TABLE IV

RANGE OF RETENTION INDICES OF *n*-DECENES ON DIFFERENT STATIONARY PHASES AT 50°

Stationary phase	Retention interval, I	δI
Squalane	979.2– 999.2	20.0
Apiezon L	983.0–1005.7	22.7
Bis-2-ethylhexyl tetrachlorophthalate	993.2–1023.3	30.1
7,8-Benzoquinoline	998 –1028	30
Di-*n*-butyl tetrachlorophthalate	998.0–1029.8	31.8
Polyethylene glycol 4000	1035.7–1068.9	33.2

Boiling points

Of the 13 possible isomers of *n*-pentadecenes, only the boiling point of 1-penta-decene (268.394°), and of the 15 possible isomers of *n*-hexadecenes, only the boiling point of 1-hexadecene (284.873°), are known[8]. The unknown boiling points of all other isomers were correlated from the retention indices measured for the individual *n*-pentadecenes and *n*-hexadecenes. The method is based on proportionality constants expressing the ratio of the boiling points and the retention indices ($k_p = \delta I/\delta T_b$), and also on the dependences of these constants on the number of carbon atoms, the structure of the isomers and the column temperature. Details have been given earlier[9]. The results for all of the isomers of *n*-pentadecene and *n*-hexadecene are summarized in Table V together with the found and corrected indices valid for squalane at 130°.

TABLE V

BOILING POINTS AND RETENTION INDICES, I_{130}^{Sq}, OF *n*-PENTADECENES AND *n*-HEXADECENES

Component	Boiling point (°C)	I_{130}^{Sq}	I_{130}^{Sq} (corr.)
cis-7-Pentadecene	266.1	1467.7	1467.0
cis-6-Pentadecene	266.4	1470.0	1469.3
cis-5-Pentadecene	267.0	1474.2	1473.5
trans-7-Pentadecene	267.4	1475.3	1474.8
trans-6-Pentadecene	267.6	1476.7	1476.2
cis-4-Pentadecene	267.8	1479.7	1479.3
trans-5-Pentadecene	268.0	1479.7	1479.3
trans-4-Pentadecene	268.1	1480.2	1479.8
1-Pentadecene	268.4	1484.7	1484.1
trans-3-Pentadecene	268.7	1485.3	1484.8
cis-3-Pentadecene	268.7	1486.0	1485.3
trans-2-Pentadecene	270.2	1497.5	1497.0
n-Pentadecane	270.6	1500.0	1500.0
cis-2-Pentadecene	271.0	1503.6	1502.8
cis-8-Hexadecene	282.2	1564.3	1563.7
cis-7-Hexadecene	282.3	1565.0	1564.3
cis-6-Hexadecene	282.7	1568.1	1567.4
trans-8-Hexadecene	283.3	1571.7	1571.2
cis-5-Hexadecene	283.4	1573.0	1572.3
trans-7-Hexadecene	283.5	1573.6	1573.1
trans-6-Hexadecene	283.7	1575.3	1574.8
cis-4-Hexadecene	284.2	1578.8	1578.4
trans-5-Hexadecene	284.3	1578.8	1578.4
trans-4-Hexadecene	284.4	1579.7	1579.3
1-Hexadecene	284.9	1584.4	1583.8
trans-3-Hexadecene	285.0	1584.9	1584.4
cis-3-Hexadecene	285.1	1585.5	1584.8
trans-2-Hexadecene	286.5	1597.0	1597.0
n-Hexadecane	286.8	1600.0	1600.0
cis-2-Hexadecene	287.4	1603.7	1602.9

CONCLUSIONS

Mixtures of straight-chain pentadecenes and hexadecenes on squalane can be separated by means of high-efficiency capillary gas chromatography at 130°. Using

a 200-m column (about $0.5 \cdot 10^6$ theoretical plates), 28 possible isomers were separated into 26 peaks. Pairs with similar structures (*trans*-5- –*cis*-4-isomers) were not separated.

It is possible to identify all individual isomers from the dependence of the gas chromatographic structural increments, H, of the individual homologous series of *n*-alkenes on the number of carbon atoms in the molecule and on the positional and spatial isomerism of *n*-alkenes. It seems also to be possible to find analogous correlations on polar stationary phases.

It is possible to correlate the boiling points of all *n*-pentadecenes and *n*-hexadecenes from the retention indices measured experimentally.

REFERENCES

1 L. Soják, J. Hrivňák, P. Majer and J. Janák, *Anal. Chem.*, 45 (1973) 293.
2 O. Eisen, A. Orav and S. Rang, *Chromatographia*, 5 (1972) 229.
3 W. Meltzow and B. Fell, *Erdöl, Kohle, Erdgas, Petrochem.*, 25 (1972) 311.
4 C. E. Döring, D. Estel, R. Fischer, W. Hegenbarth and G. Hey, *Chem. Tech. (Leipzig)*, 25 (1973) 299.
5 W. E. Falconer and L. G. Walker, *J. Chromatogr. Sci.*, 9 (1971) 184.
6 L. R. Chapman and D. E. Kuemmel, *Anal. Chem.*, 37 (1965) 1598.
7 M. Ryba, *Chromatographia*, 5 (1972) 23.
8 S. W. Ferris, *Handbook of Hydrocarbons*, Academic Press, New York, 1955.
9 L. Soják, J. Hrivňák, A. Šimkovicová and J. Janák, *J. Chromatogr.*, 71 (1972) 243.