

CHROM. 12,241

COMPARISON OF CAPILLARY COLUMNS COATED WITH C₈₇ HYDROCARBON AND SQUALANE IN THE ANALYSIS OF *n*-PENTADECENE ISOMERS

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SUMMARY

A 200-m long glass capillary column coated with C₈₇ hydrocarbon stationary phase was applied to the analysis of 13 possible positional and structural isomers of linear pentadecenes. It was found that an extremely efficient capillary column may be prepared by using this phase: $N = 670,000$ effective plates for *n*-pentadecane with $k = 11.8$ and temperature 110°, and separation number (n_{sep}) = 110 for C₁₄, C₁₅. It has been shown that n_{sep} is not constant and that it increases with the increasing number of carbon atoms in *n*-alkanes (with their mean capacity ratio) and decreases with the column temperature. Retention indices of *n*-pentadecenes measured on C₈₇ phase differ from those measured on squalane always by less than ± 2 index units. A slight difference has been found between the selectivity of C₈₇ hydrocarbon and that of squalane for the separation of *n*-pentadecene isomers. This selectivity being combined with an extremely efficient separation system, made it possible to separate these isomers more rapidly and more completely.

INTRODUCTION

The problems associated with the separation of all positional and structural isomers of linear pentadecenes in a high-efficient metal capillary column coated with squalane stationary phase were dealt with in our earlier paper¹. In a 200-m long column with 500,000 effective plates, the separation took 13 h at a temperature of 130° and at a carrier gas (hydrogen) inlet pressure of 0.3 MPa. Some of the isomeric pairs were not separated or were only separated partially. Although the temperature dependence of the retention of *cis-trans* isomers of *n*-alkenes on squalane differ, the use of these dependences for the separation of unresolved pairs was hindered by the additional growth of the time necessary for the analysis at lower temperatures and by an insufficient stability of squalane at higher temperatures.

With respect to the increasing interest associated with the analysis of isomers of higher linear alkenes, the design of a separation system permitting a more rapid and more complete separation, than do the existing procedures, has shown to be of importance. The present paper is aimed at the study of the separation properties of a synthetic hydrocarbon $C_{87}H_{176}$ (24,24-diethyl-19,29-dioctadecylheptatetracontane) suggested by Riedo *et al.*² as a standard non-polar stationary phase for the range of temperatures 30–300°. Difficulty with the separation and the problem of identification (lack of standards and published retention data), lead towards the preparation of a high-efficient glass capillary column and the study of the correlations between the structure and the retention behaviour of isomers of *n*-alkenes as means of identification.

EXPERIMENTAL

The mixture of linear pentadecene isomers, prepared by catalytic dehydrogenation of *n*-pentadecane and concentration of *n*-alkenes by means of column chromatography on silica gel using FIA indicator, was used as a model mixture for the present study. A Carlo Erba GI 452 gas chromatograph equipped with a flame ionisation detector and a glass capillary column 200 m × 0.25 mm I.D. coated with C_{87} hydrocarbon stationary phase was used for the separation. The column was prepared by combining a 115-m with an 85-m long column by means of a PTFE shrinkable tube. Capillary columns were prepared of soft soda-lime glass (Unihost type, Jablonec Glass Works, Jablonec, Czechoslovakia). The walls of the capillaries were etched with gaseous hydrogen chloride³ and deactivated with trimethylchlorosilane⁴. The coating with the stationary phase was carried out by the dynamic method^{5,6}. The characteristic data on the capillary columns prepared, measured for *n*-dodecane at 100° and using nitrogen carrier gas, are listed in Table I. The mixture of *n*-pentadecene isomers was

TABLE I

PARAMETERS OF THE PREPARED GLASS CAPILLARY COLUMNS COATED WITH C_{87} HYDROCARBON MEASURED FOR *n*-DODECANE AT 100° AND WITH NITROGEN CARRIER GAS

Parameters	Column length	
	115 m	85 m
Inner diameter (mm)	0.255	0.25
Inlet pressure of nitrogen (MPa)	0.19	0.25
Flow-rate of the carrier gas (cm/sec)	11.4	10.4
Capacity ratio (<i>k</i>)	2.50	2.10
Theoretical plate number (<i>n</i>)	431,000	491,000
Effective plate number (<i>N</i>)	220,000	230,000
Separation number (n_{sep}) ^a	69	66

^a The separation number was determined for *n*-undecane and *n*-dodecane according to the relationship

$$n_{sep} = \frac{t_{R,z+1} - t_{R,z}}{(y/2)_z + (y/2)_{z+1}} - 1,$$

where *z* denotes the number of carbon atoms in *n*-alkane, and *y*/2 the peak width at half height.

analysed at a temperature of 110, 130, 150 and 180°, with the use of hydrogen carrier gas at the pressure inlet of 0.3 MPa and at the corresponding linear velocity of the carrier gas 15.1–17.1 cm/sec. The repeatability of the measurements of the retention indices of linear pentadecenes was 0.2 index units (the standard deviation).

RESULTS AND DISCUSSION

Characterisation of the efficiency of the capillary column coated with C_{87} phase

The separation problem is given by the fact that the boiling points of 13 possible *n*-pentadecene isomers lie within the range of 4.9°, with 11 of these isomers within the range of 2.6°¹. Since this parameter determines the necessity of using an extremely efficient separation system, the recommended C_{87} hydrocarbon was tested. Fig. 1 shows the characteristics of the prepared column by coating with C_{87} stationary phase, expressed as a dependence of the number of theoretical plates, *n*, the number of effective plates, *N*, and the separation number^{7,8}, n_{sep} , on the capacity ratio for C_{10} – C_{15} alkanes separated at a temperature of 110°, the carrier gas (hydrogen) inlet pressure 0.3 MPa and the corresponding linear velocity of the carrier gas, $\bar{u} = 17.1$ cm/sec. For n_{sep} the value of \bar{k} , calculated as the mean of the capacity ratios of the two neighbouring *n*-alkanes, was taken into account.

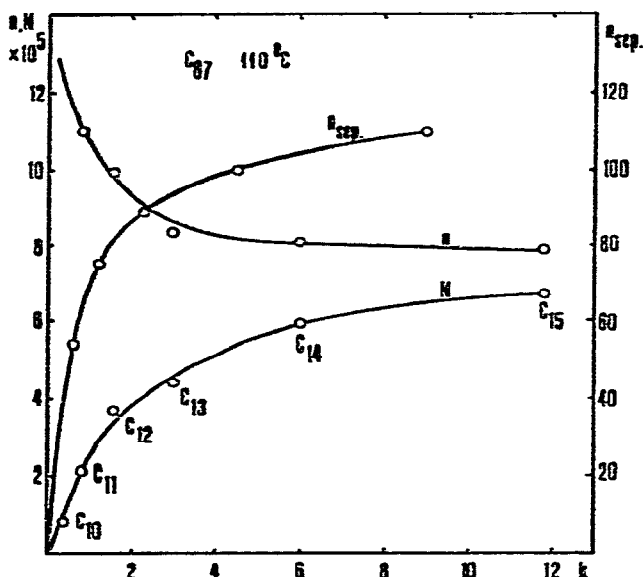


Fig. 1. Dependence of the number of theoretical plates, *n*, the number of effective plates, *N*, and the separation number, n_{sep} , on the capacity ratio of C_{10} – C_{15} *n*-alkanes, separated in a 200 m × 0.25 mm I.D. glass capillary column coated with C_{87} hydrocarbon; temperature 110°; inlet pressure of the carrier gas 0.3 MPa H_2 ; linear velocity, $\bar{u} = 17.1$ cm/sec.

It can be seen from Fig. 1 that the expected slopes of the dependences of both *n* and *N* on the capacity ratio of *n*-alkanes were really obtained. For the separation number, n_{sep} , a similar tendency of the dependence line to that of the effective plate number, *N*, was obtained, if the mean value of the capacity ratio, \bar{k} , was plotted.

In the range of *n*-pentadecene retention the value of the effective plate number is $N = 670,000$ plates and $n_{sep} = 110$ (even though the used linear velocity of the carrier gas (hydrogen) was, with regard to the equipment used, lower than $\bar{u}_{opt} = 30$ cm/sec)⁹. These values characterise the efficiency of the prepared column, *i.e.*, the possibility of a successful coating of the glass capillary column with C₈₇ hydrocarbon stationary phase.

It can be seen from Fig. 1 that the value of the separation number^{7,8}, n_{sep} , is not constant and that it is dependent on the number of carbon atoms in *n*-alkanes (their mean capacity ratio). The dependence of the separation number, n_{sep} , on the number of carbon atoms is shown for linear alkanes separated at various temperatures in Fig. 2; the lines are also drawn that connect the values of n_{sep} having the same capacity ratios ($\bar{k} = 1.2$; 2.2; and 4.5), at various temperatures of the column coated with C₈₇ phase. The value of n_{sep} obviously increases significantly with the increasing number of carbon atoms in alkanes and decreases with the increasing column temperature. It follows from these results that if the value of n_{sep} is advocated for characterisation of the column efficiency, the number of carbon atoms in *n*-alkanes (the mean value of their capacity ratio) and the column temperature must necessarily be taken into consideration. Clearly, this relationship would be still less lucid¹⁰ if the columns of different polarities were compared.

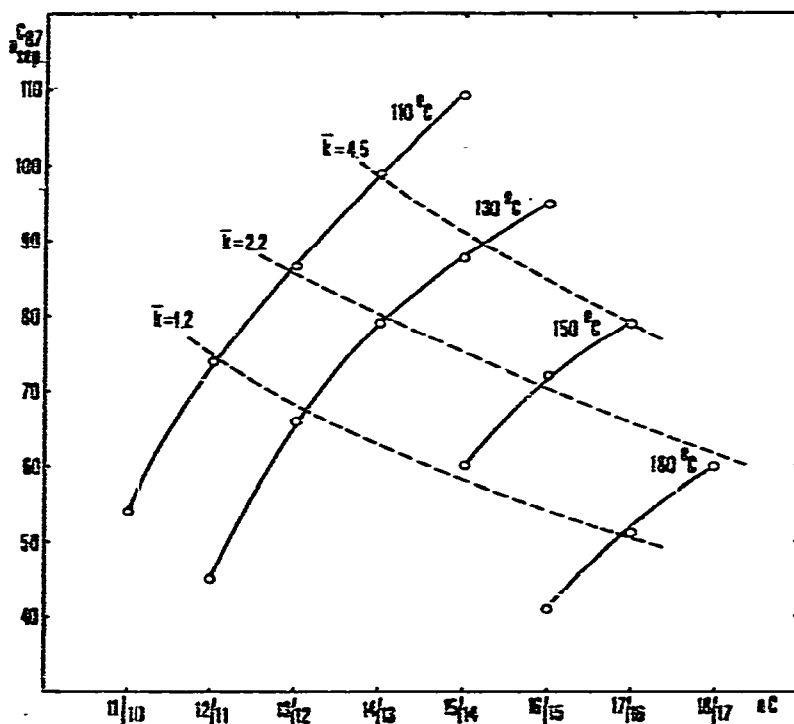


Fig. 2. Dependence of the separation number, n_{sep} , on the number of carbon atoms and on the column temperature for C₁₀–C₁₈ *n*-alkanes separated in a 200 m × 0.25 mm I.D. column coated with C₈₇ hydrocarbon; temperatures 110, 130, 150 and 180° with an inlet pressure of 0.3 MPa H₂.

Characterisation of the column coated with C₂₇ phase by analysing linear pentadecenes. The chromatogram obtained by separating the mixture of *n*-pentadecene isomers together with *n*-pentadecane is shown in Fig. 3. It can be seen that in spite of the extremely high column efficiency, the pairs of *cis*-3- plus 1- and *cis*-4 plus *trans*-4-pentadecene have not been separated at 130°. The separation of the above-mentioned pairs was, however, obtained at a temperature of 160° (Fig. 4).

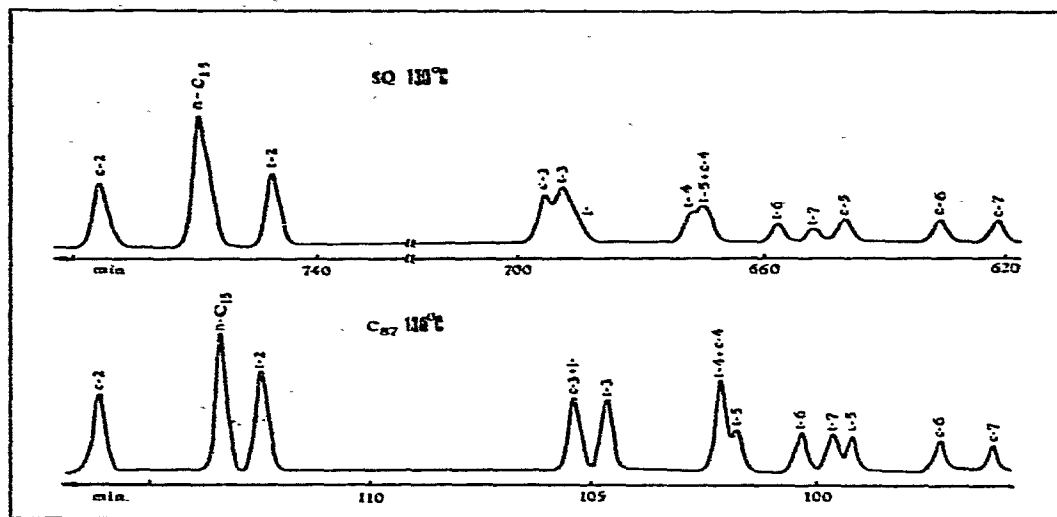


Fig. 3. Chromatograms of *n*-pentadecene isomers in 200 m × 0.25 mm I.D. columns at 130° with an inlet pressure of 0.3 MPa H₂ in a glass capillary column coated with C₂₇ hydrocarbon and in a metal column coated with squalane (*c* = *cis*- and *t* = *trans*-isomer).

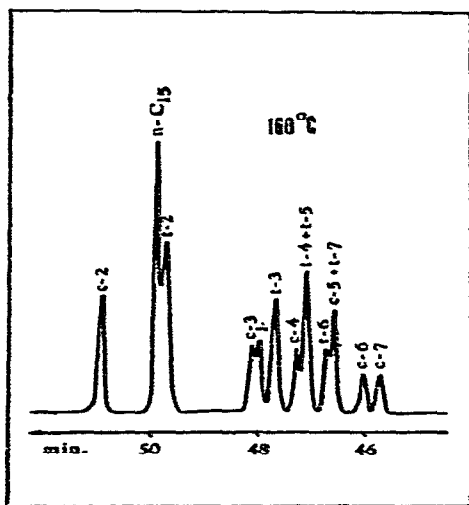


Fig. 4. Chromatogram of *n*-pentadecene isomers in a 200 m × 0.25 mm I.D. glass capillary column coated with C₂₇ hydrocarbon at 160° (*c* = *cis*- and *t* = *trans*-isomer).

In order to make the comparison, the upper part of Fig. 3 shows a chromatogram obtained by separating the same isomers in a 200-m long metal capillary column coated with squalane stationary phase¹. A significant difference in the time necessary for the analysis, on the one hand, and certain changes in the separation of isomers, on the other hand, are obvious from the comparison of the separation obtained in both columns of identical length and internal diameter, at the same temperature, with the same type and pressure of carrier gas. The time necessary for the analysis was reduced seven-fold as a result of a significantly thinner layer of C₃₇ hydrocarbon on the surface of the capillary column in comparison with the squalane layer.

In order to identify the isomers separated on C₃₇ hydrocarbon phase, structure-retention correlations were utilized, based on the regularities found for the squalane phase: on the dependence of the difference in the retention indices, δI , of the two neighbouring positional or corresponding structural isomers, on the position of the double bond as well as on the different temperature dependence of the retention of the corresponding structural *cis-trans* isomers of *n*-alkenes¹¹.

Table II presents the retention indices measured for linear pentadecenes at 130° and the values of the temperature increments of the retention indices, $dI^{C_{37}}/dT$. For the comparison, the values of the retention indices of these isomers measured under the identical conditions of squalane¹ are included. The values of dI^{S_0}/dT of *n*-pentadecenes have not been measured on squalane because of long analysis time. Since the values of dI^{S_0}/dT only vary slightly with the number of carbon atoms for the isomers corresponding in the position and geometry of the double bond, the values dI^{S_0}/dT measured previously for linear tetradecenes¹¹ were chosen for a comparison.

By comparing the values of the retention indices of linear pentadecenes measured on C₃₇ hydrocarbon and squalane (Table III), it can be seen that the dif-

TABLE II

RETENTION INDICES OF *n*-PENTADECENE ISOMERS AND THEIR TEMPERATURE INCREMENTS ON C₃₇ HYDROCARBON AND SQUALANE (0.3 MPa H₂ CARRIER GAS INLET PRESSURE)

Isomer	Hydrocarbon C ₃₇		Squalane	
	<i>I</i> ₁₃₀	<i>I</i> 0(<i>dI</i> / <i>dT</i>)	<i>I</i> ₁₃₀	<i>I</i> 0(<i>dI</i> / <i>dT</i>)
<i>cis</i> -7-Pentadecene	1466.5	1.10	1467.0	0.93
<i>cis</i> -6-Pentadecene	1469.1	1.00	1469.3	0.90
<i>cis</i> -5-Pentadecene	1473.2	0.90	1473.5	0.87
<i>trans</i> -7-Pentadecene	1474.1	0.70	1474.8	0.63
<i>trans</i> -6-Pentadecene	1475.5	0.60	1476.2	0.60
<i>cis</i> -4-Pentadecene	1479.2	0.80	1479.3	0.70
<i>trans</i> -5-Pentadecene	1478.4	0.50	1479.3	0.50
<i>trans</i> -4-Pentadecene	1479.2	0.40	1479.8	0.37
<i>trans</i> -3-Pentadecene	1484.1	0.20	1484.8	0.10
1-Pentadecene	1485.4	0.50	1484.1	0.27
<i>cis</i> -3-Pentadecene	1485.6	0.70	1485.3	0.43
<i>trans</i> -2-Pentadecene	1498.3	0.16	1497.0	0.03
<i>cis</i> -2-Pentadecene	1504.7	0.70	1502.8	0.43

TABLE III

THE DIFFERENCES IN THE RETENTION INDICES OF *n*-PENTADECENE ISOMERS ON C₃₇ HYDROCARBON AND SQUALANE AND ITS POSITION AND GEOMETRY OF THE DOUBLE BOND

$$\Delta I = I_{130}^{C_{37}} - I_{130}^{S}$$

<i>n</i> -Pentadecene isomer												
t-7	t-6	t-5	t-4	t-3	t-2	c-7	c-6	c-5	c-4	c-3	c-2	1-
-0.7	-0.7	-0.9	-0.6	-0.7	1.4	-0.5	-0.2	-0.3	-0.1	0.2	1.9	1.4

ferences tend to be 1 index unit (I.U.). They vary from a negative difference $\Delta I = I_{130}^{C_{37}} - I_{130}^{S} = -0.9$ I.U. to a positive value of 1.9 I.U. Even though the differences in the retention indices are relatively small, the accuracy obtained for the measurements enables the deviations to be analysed in detail. For *trans*-pentadecenes (except for *trans*-2-isomer) differences in ΔI are negative—the retention index is less on C₃₇ hydrocarbon than on squalane. Characteristically positive differences in ΔI —greater values of the retention indices on C₃₇ phase—were found for 1-, *trans*-2- and *cis*-2-pentadecenes. The values of the temperature increments of the retention indices of linear alkenes on C₃₇ and squalane are close, and they seem to be slightly greater on C₃₇ hydrocarbon. This tendency is again somewhat more distinct for 1- and 2-pentadecenes. Similar dependencies of the differences in the retention indices and their temperature increments on C₃₇ hydrocarbon and squalane on the structure of *n*-alkene isomers were also found for *n*-hexadecene isomers.

The preceding result agrees partially with the tendency shown by the values $\Delta I = I_{\text{polar}} - I_{\text{non-polar}}$ of *n*-alkene isomers in such a way that 1- and 2-positional isomers should show the greatest gas chromatographic polarity¹². In order to elucidate this relationship, the values of the retention indices were also measured in the same column for the isomers of C₈ aromatic hydrocarbons, for which this effect should appear more distinctly; at 50° 849.9 was obtained for ethylbenzene, 868.1 for *p*-xylene, 869.8 for *m*-xylene and 889.6 for *o*-xylene. These values were 16.3, 19.9, 19.4 and 20.9 I.U. greater than the values of the retention indices measured on squalane¹³, and hence the character of the dependence of ΔI , values on the fine structure of alkylbenzenes (*para* < *meta* < *n* < *ortho*-isomer) is different¹⁴.

Similarly, great differences between the retention indices of benzene measured on C₃₇ hydrocarbon and squalane are found by Haken and Ho¹⁵, who measured in a column packed with Chromosorb W AW DMCS support, a retention index for benzene greater by 21 I.U. on C₃₇ than that on squalane. On the other hand, however, the differences in the retention indices of linear alkenes, which are small, as well as the differences among *n*-alkene isomers, which are relatively great, do not correspond with a relatively great difference in the retention indices of aromatic hydrocarbons on C₃₇ and squalane. Since the retention indices of aromatic hydrocarbons measured in a column packed with a deactivated support¹⁵ are comparable with the data measured by the present authors in a capillary column, it may be suggested that the activity of the glass capillary surface affects the retention indices of *n*-alkenes to a small extent only. Hence the differences in the retention indices of *n*-pentadecenes obtained on C₃₇ and squalane are caused predominantly by the differences in disperse solute-solvent interactions in both separation systems.

In conclusion, high-efficient glass capillary columns may be prepared by using C_{27} hydrocarbon phase, permitting the operation can be performed under higher temperatures than those acceptable for squalane. Although the values of the retention indices are close, they are not identical, and the differences may be utilized for more complex separations (e.g. in the case of pentadecenes of critical triplets of *trans*-3-, *cis*-3- and 1-pentadecenes or *trans*-4-, *trans*-5- and *cis*-4-pentadecenes, see Fig. 1).

ACKNOWLEDGEMENTS

The authors are thankful to Prof. E. sz. Kováts from the Ecole Polytechnique Fédérale de Lausanne (Switzerland) for providing them with the samples of C_{27} hydrocarbon.

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