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GAS CHROMATOGRAPHIC BEHAVIOUR OF TRICYCLIC SATURATED HYDROCARBONS

THE RELATION BETWEEN THE RETENTION INDICES AND THE STEREOCHEMICAL STRUCTURE OF THE TRICYCLANES

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SUMMARY

The authors determined the Kováts retention indices of stereoisomers of 8 bicyclic and tricyclic saturated hydrocarbons containing five- and six-membered rings in a molecule. The retention data were obtained by means of capillary columns using polar (Carbowax 20M) and non-polar (SE-30) stationary phases. The relationships between the retention indices, the homomorphic factors, ΔI values and the chemical (or stereochemical) structures of the hydrocarbons (or stereoisomers) studied allow one to ascribe an unknown stereoisomer with its hydrocarbon structure (*i.e.* to differentiate between stereoisomeric mixtures of two or more hydrocarbons), to predict the retention values of the individual stereoisomers, and to contribute, on the basis of the retention data, to the determination of configurations of so far unknown stereoisomers.

INTRODUCTION

The comparison of gas chromatographic retention of diverse organic compounds on stationary phases of different polarity has recently become a general method used for identifying these compounds¹⁻³.

The most common method for the determination and interpretation of the relationships between the chemical structure of various compounds and their retention behaviour is a two-dimensional graphical presentation of the data obtained (most frequently on logarithmic scales). The chromatographic data measured on a non-polar stationary phase are plotted against the data of the same series of compounds, measured on a polar phase. The graph represents a number of dependences, the most important of them (for the given pair of stationary phases of different polarity) being the following:

(1) The points corresponding to compounds of a particular type occur in the graph in a particular characteristic zone.

(2) The points corresponding to members of homologous series lie on parallel straight lines, each straight line being characteristic for a particular homologous series.

(3) The points corresponding to isomers (*i.e.* the points lying on different straight lines of the homologous series) lie on separate segment lines parallel to one another, each of them being characterised by the molecular mass of the isomers lying on the particular segment line.

The above rules, which are valid generally, can be used to predict the chromatographic behaviour of known compounds as well as for attributing a particular chemical structure to unknown compounds on the basis of their chromatographic behaviour.

The stereoisomers of polycyclic naphthenic hydrocarbons containing five- and six-membered rings in a molecule are a specific case of isomerism based only on absolute configuration of the mutual attachment of the individual rings in a molecule. Our previous gas chromatographic analyses of stereoisomeric mixtures of tricyclic saturated hydrocarbons⁴, and the relationships found between the structure of adamantane compounds and their chromatographic behaviour^{5,6}, have given us the idea of trying to solve this complex problem of determining the configuration of the individual stereoisomers of the hydrocarbons mentioned by making use of gas chromatographic data and their interpretation.

Thus the purpose of the present work is, apart from the usual tabulating of gas chromatographic data of compounds so far undescribed on the usual stationary phases, to determine the relationship between the configurations of the individual stereoisomers and their gas chromatographic behaviour and to evaluate the possibility of utilising the dependences, so found, for the determination of the configurations of stereoisomers so far unknown.

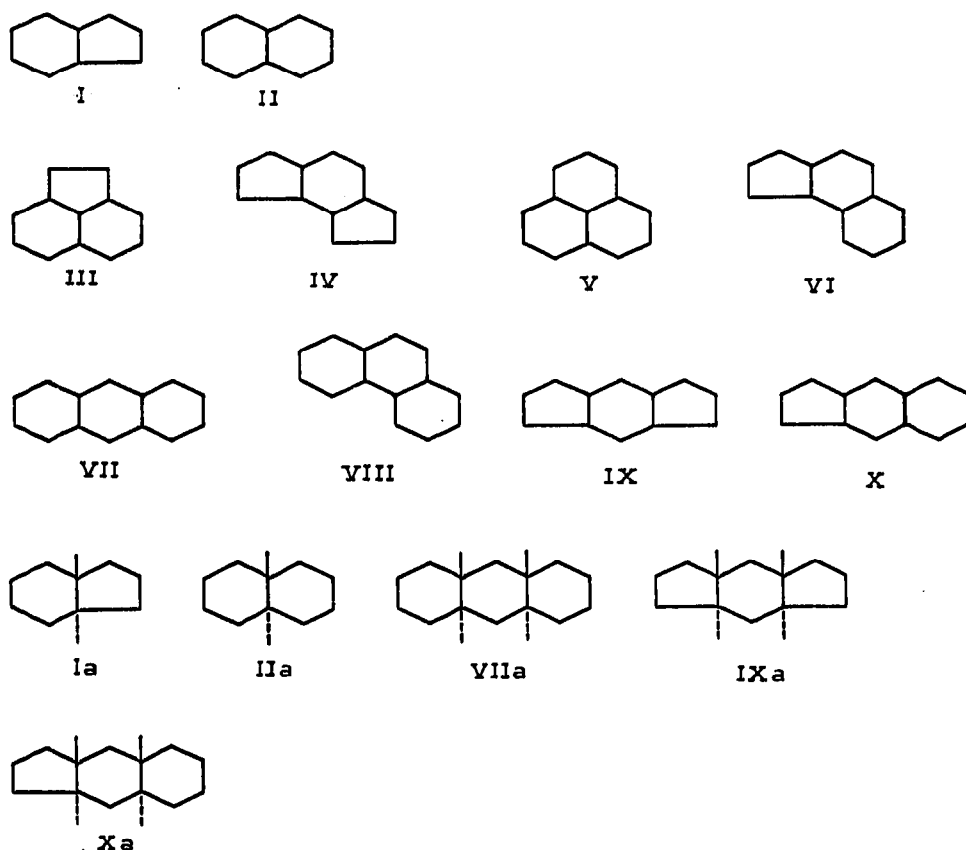
EXPERIMENTAL

The elution data were measured with a Chrom II instrument (Laboratorní přístroje, Prague, Czechoslovakia) fitted with a flame ionisation detector. Nitrogen was used as carrier gas. Stainless steel capillary columns, 0.25–0.30 mm in diameter, 50 m long, were used for the measurements. The elution data of the hydrocarbon series studied were measured on stationary phases of SE-30 and Carbowax 20M.

The following series of stereoisomeric mixtures of bicyclic and tricyclic saturated hydrocarbons, the preparation of which has been described previously⁴, were used for the measurements:

Bicyclo [4,3,0] nonane*	(I)
Bicyclo [4,4,0] decane*	(II)
Tricyclo [7,2,1,0 ^{5,12}] dodecane	(III)
Tricyclo [7,3,0,0 ^{2,6}] dodecane	(IV)
Tricyclo [7,3,1,0 ^{5,13}] tridecane	(V)
Tricyclo [8,3,0,0 ^{4,9}] tridecane	(VI)
Tricyclo [8,4,0,0 ^{3,8}] tetradecane	(VII)
Tricyclo [8,4,0,0 ^{2,7}] tetradecane	(VIII)

* Stereoisomeric mixtures of bicyclic hydrocarbons were obtained by the catalytic hydrogenation of the corresponding aromatic hydrocarbon.



The Kováts retention indices were measured by a standard method⁷ with the Carbowax 20M phase at 125, 150 and 175° and with the SE-30 at 150, 175 and 200°. In the actual calculations of the individual retention indices the retention distances reduced by those of methane injected simultaneously with the mixture analysed, were used. The values given in Table I are average values of 3–5 analyses. The difference of extreme values of the individual determinations did not exceed two units of the retention index. The average values were rounded-off to whole units.

RESULTS AND DISCUSSION

Influence of stereoisomer configuration on the magnitude of the homomorphic factor

Many studies (especially those of SCHOMBURG¹) dealing with the structural interpretation of gas chromatographic data of a great number of organic compounds have shown that the values of the retention index are subject to an incremental change. This incremental character will stand out clearly if the relative scale introduced by SCHOMBURG, called the homomorphic factor, is used for structural interpretation.

The *H* factor of the stereoisomers examined, and given in Tables I, II and IV, is the difference between the retention index of a stereoisomer and that of an *n*-paraffin with an equal number of C-atoms (both values being measured on the same phase and at the same column temperature).

TABLE I

THE KOVÁTS INDICES OF STEREOISOMERS OF TRICYCLANES ON SE-30 AND CARBOWAX 20 M

The stereoisomers of perhydroanthracene: number 1 = *trans-syn-trans*; number 3 = *cis-trans*; number 4 = *cis-syn-cis*.
 $H = I_{\text{stereoisomer } C_n} - I_{n\text{-alkane } C_n}$; $\Delta I = I_{\text{Carbowax 20M}} - I_{\text{SE-30}}$.

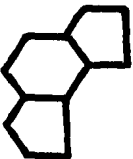



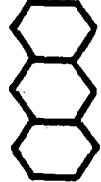

Compound	Stereo-isomer	SE-30			Carbowax 20 M			ΔI_{150}	
		I		H_{150}	I		H_{150}		
		150°	175°	200°	125°	150°	175°		
	1				1428	1458	1484	11.2	258
	2				1452	1480	1505	10.6	280
	3	1307	1326	1343		1508	1535	11.6	308
	4	1323	1343	1362	107	1537	1566	12.6	337
	5	1328	1348	1365	123	1547	1578	12.8	347
	6	1352	1373	1391	128	1585	1619	13.8	385
	1	1274	1291	1310	74	1462	1494	12.8	262
	2	1295	1314	1334	95	1499	1533	13.4	299
	3	1317	1338	1359	117	1539	1574	14.0	339
	4	1323	1344	1365	123	1539	1574	14.0	339
	5	1352	1374	1396	152	1591	1630	15.2	391
	1	1377	1400	1424	77	1590	1628	15.0	290
	2	1416	1442	1468	116	1652	1691	15.4	352
	3	1429	1456	1482	129	1681	1721	16.0	381
	1	1409	1433	1456	109	1628	1660	13.6	328
	2	1422	1446	1469	122	1652	1687	14.8	352
	3	1437	1461	1484	137	1674	1709	14.6	374
	4	1444	1468	1491	144	1685	1720	14.6	385
	5	1461	1486	1511	161	1718	1755	15.8	418
	1	1481	1506	1531	81	1696	1734	15.2	296
	2	1494	1519	1545	94	1718	1755	15.0	318
	3	1513	1537	1562	113	1744	1782	15.4	344
	4	1549	1576	1602	149	1804	1844	16.6	404
	5	1559	1587	1616	159	1819	1860	16.6	419
	1	1493	1515	1540	93	1712	1751	15.8	312
	2	1513	1538	1564	113	1747	1786	16.2	347
	3	1537	1563	1589	137	1786	1826	17.0	386
	4	1552	1575	1602	152	1810	1850	17.0	410
	5	1568	1596	1624	168	1845	1886	18.0	445

TABLE II
 THE KOVÁTS INDICES OF STEREOISOMERS OF BICYCLANES ON SE-30 AND CARBOWAX 20 M
 $H = I_{\text{stereoisomer } C_n} - I_{n\text{-alkane } C_n}$; $\Delta I = I_{\text{Carbowax 20 M}} - I_{\text{SE-30}}$.




Compound	Stereo-isomer	SE-30			Carbowax 20 M			ΔI_{150}
		I	$\delta I/10^\circ$	H_{150}	I	$\delta I/10^\circ$	H_{150}	
	1	100°	125°	150°	100°	125°	150°	
	2	963	975	987	1086	1102	1125	138
		996	1010	1023	1138	1158	1183	160
	1	1061	1075	1089	1195	1218	1244	155
	2	1101	1116	1132	1260	1285	1314	182

TABLE III


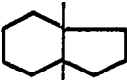
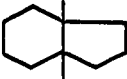
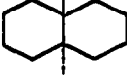
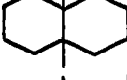


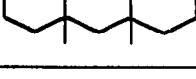
THE KOVÁTS INDICES OF CYCLOHEXANE ON SE-30 AND CARBOWAX 20 M

Compound	Stereo- isomer	SE-30			$\delta I/10^\circ$	Carbowax 20 M			$\delta I/10^\circ$
		I				I			
		50°	75°	100°		50°	75°	100°	
		662	667	675	2.6	740	746	751	2.2

In the case of saturated tricyclic hydrocarbons of the type examined, the absolute configurations of only a very limited number of stereoisomers are known; so far, only the absolute configurations of the stereoisomers of perhydroanthracene

TABLE IV

RELATIONSHIP BETWEEN H FACTOR AND CONFIGURATION OF STEREOISOMER

Stereoisomer	H_{180}		
	SE-30		
	Trans	Cis	
	88 ^a	163 ^a	
 87		225	
		123	283
 89			244
		132	314
 81			296
	113		344
		149	404

^a The values were obtained by the extrapolation of the measured values in Table III.

have been ascertained reliably, three of them being employed in the present work (*trans-syn-trans*, *cis-trans* and *cis-syn-cis*). For the purpose of structural interpretation of the H factors found, the series of tricyclic stereoisomers was extended by stereoisomers of bicyclo [4,3,0] nonane (hydrindane), bicyclo [4,4,0] decane and cyclohexane (Tables II and III).


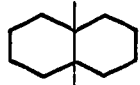
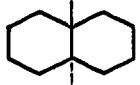
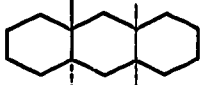

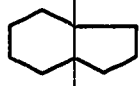
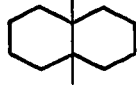
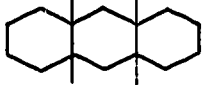

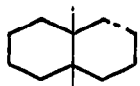
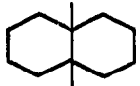
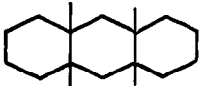

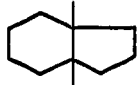
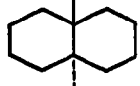
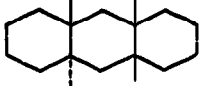
The survey given in Table IV shows that in the series of cyclic hydrocarbons chosen the magnitude of the H factors depends on configuration.

The influence of configuration is most pronounced in the values of the H factor measured on a non-polar phase (SE-30). With stereoisomers whose molecules contain only *trans* configurations, the value of the H factor is nearly constant (81-89), and is independent of the number of rings in the molecule as well as of whether they are six-membered or five-membered rings or a combination of the two. The above results may be compared with the data on monocyclic saturated hydrocarbons measured on a non-polar stationary phase (squalane) by SCHOMBURG⁸, who found that the enlargement of a five-membered saturated hydrocarbon ring to a six-membered one does not result in a change in the H factor of the compound, which is not true for the

TABLE V

THE INFLUENCE OF CONFIGURATION ON THE VALUE OF THE RETENTION INDEX INCREMENT IN THE CASE OF ENLARGEMENT OF MOLECULES BY OTHER SATURATED RINGS

n_{CA} , n_{CB} = C-number of the compounds C_A and C_B .

Hydrocarbon		δI_{SE-30}^{160}	$\delta I_{Ca3b-30M}^{160}$
C_A	C_B	$n_{CB} - n_{CA}$	$n_{CB} - n_{CA}$
		100	120
		98	113
		100	121
		95	107
		111	138
		104	122
		112	140
		106	125

enlargement of rings with a different number of carbon atoms. The *cis* configurations in the molecule (ranging in the given series from I23 to I49) give rise to an increase in the value of the *H* factor with the number and size of the rings. The *H* factor of *cis-trans* perhydroanthracene lies, in the middle, between the values of the *H* factors of stereoisomers with *trans* configurations only and those of stereoisomers with *cis* configurations only.

With the *H* factors measured on the polar Carbowax 20M the influence of the configurations was not so pronounced. The *H* factors corresponding to *trans* configurations are even lower here than those corresponding to *cis* configurations; the *H* factor, however, greatly increases with the number of rings.

The dependences found suggest that even in the other tricyclic hydrocarbons given in Table I the *H* factors for *trans* stereoisomers will be lower than those for *cis* stereoisomers.

Structural interpretation of the change in retention index caused by a change in polarity of the stationary phase

It can be assumed that the values of I^{SE-30} of the series of stereoisomers studied will, in general, be a function of the number of C-atoms in a molecule, the chemical structure of the hydrocarbon (common for all stereoisomers of one hydrocarbon) and the stereochemical structure (absolute configuration). The values of $I^{Carbowax\ 20M}$ will be further influenced by the dipole-dipole interaction of the molecules of the stereoisomers and the molecules of the stationary phase, the carbon rings being known to contribute to the ΔI values in general.

The graphical presentation of the values given in Tables I and II (Fig. 1) provides a system of line segments (corresponding to the respective stereoisomeric mixtures) designated by WALRAVEN^{2,9} as an imbricated series*. The stereoisomers of the individual hydrocarbons always lie on one line segment. The line segments of C₉, C₁₀, C₁₂, C₁₃, and C₁₄ hydrocarbons are separate and almost parallel. The stereoisomers of C₁₄ hydrocarbons all lie together on one line segment, the stereoisomers of C₁₃ hydrocarbons lie on two line segments, and those of C₁₂ hydrocarbons also lie on two line segments.

The nearly equal values of the *H* factors of the *trans* stereoisomers on a non-polar stationary phase (SE-30) given in Table IV mean that the points corresponding to stereoisomers with this configuration will be situated in the graph (Fig. 1) on a straight line. Stereoisomers Ia, IIa and VIIa may be considered to be members of a "homologous series", which offers the possibility of estimating the retention values of the missing members. It may be assumed that the points corresponding to stereoisomers IXa and Xa will be found on the straight line of the above mentioned "homologous series".

Fig. 1 also shows that all the stereoisomers of hydrocarbons VII and VIII lie on one segment line of the imbricated series. It may be assumed that the same will hold for tricyclanes with one or two five-membered rings in a molecule, and that stereoisomers of hydrocarbons VI and X will lie on a common segment line of the imbricated series. A common segment line may also be assumed for stereoisomers of hydrocarbons IV and IX.

* The area arrangement of the individual segment lines is similar for any kind of isomeric series and resembles the arrangement of roof tiles (hence called "roof-tile effect").

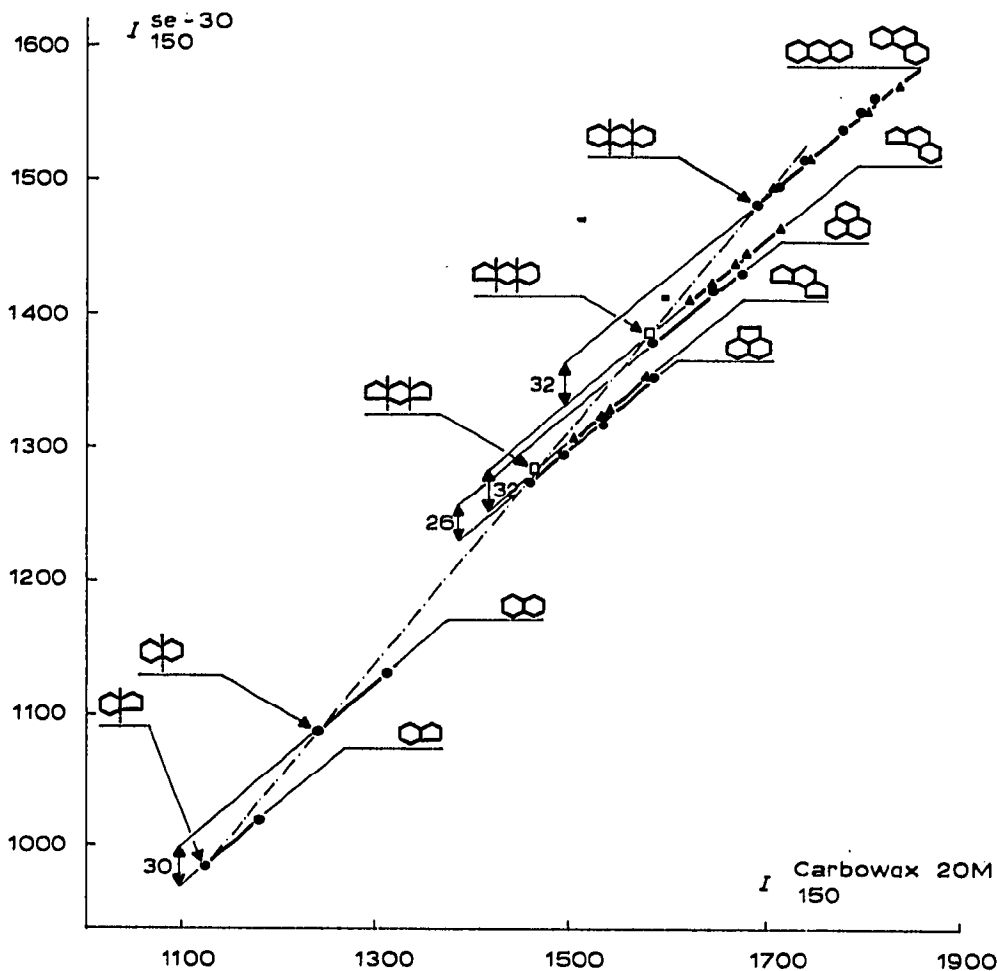
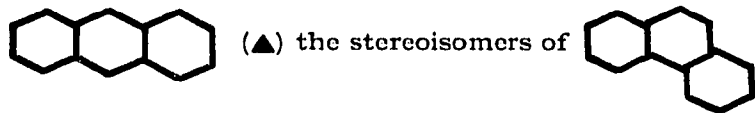


Fig. 1. The "rooftile effect" of the stereoisomers of bicyclic and tricyclic saturated hydrocarbons with five- and six-membered rings. (—) the segment lines of the imbricated series; (— · — · —) the "homologous series" line of *trans*-stereoisomers; (□) estimated retention values of the so far unknown stereoisomers. The segment line of C_{14} hydrocarbons: (●) the stereoisomers of



The point corresponding to stereoisomer IXa will occur on the graph at the point of intersection of the straight line (joining stereoisomers Ia, IIa and VIIa) with the segment line of the imbricated series common for stereoisomers of hydrocarbons IV and IX. For stereoisomer IXa, the following values were read off the graph:

$$I_{150^\circ}^{SE-30}: 1,280 \text{ and } I_{150^\circ}^{Carbowax 20M}: 1,463$$

The point corresponding to stereoisomer Xa will likewise be found at the point of intersection of the straight line of the "homologous series" of *trans* stereoisomers with the segment line of the imbricated series common for stereoisomers of hydrocarbons VI and X. The following values were read off the graph (for stereoisomer Xa):

$$I_{150^\circ}^{SE-30}: 1,378 \text{ and } I_{150^\circ}^{Carbowax 20M}: 1,577$$

It can also be seen from the graph that the segment lines of hydrocarbons IV, VI

and VIII are separated from each other by 32 units of the retention index, and those of hydrocarbons I and II by 30 units. Thus the enlargement of a five-membered saturated ring to a six-membered one in the hydrocarbons whose structure was being studied shifts the segment line of the imbricated series by 30–32 units (on the above mentioned pair of stationary phases). The stereoisomers of hydrocarbons containing one carbon atom common for all three rings (hydrocarbons III and V) lie on their own segment lines of the imbricated series and are separated from each other by 26 units only. They are also distinct from the segment lines of the hydrocarbons described above containing an equal number of carbon atoms in a molecule.

The location of a point corresponding to any stereoisomer of a polycyclic saturated hydrocarbon of the type studied (containing five-membered and six-membered rings in a molecule) will, in general, be determined on the graph by:

- (1) The number of carbon atoms in a molecule,
- (2) The molecular structure,
- (3) The absolute configuration of the stereoisomer.

Points 1 and 2 determine the segment line on which the point corresponding to the given stereoisomer should be situated; point 3 determines the position on this segment line.

Influence of configuration due to a substituent on the change in the retention index, caused by the extension of the molecule by a five- or six-membered saturated carbon ring

When enlarging the basic monocyclic skeleton to a bicyclic or tricyclic molecule, other rings can be attached either by two equatorial bonds or by one axial and one equatorial bond (which has a bearing on the possibility of *cis* and *trans* configurations of the ring attachment).

Table V shows that the change in the retention index caused by the attachment of other rings is affected by the following possibilities:

(1) The attachment of a second ring (to a monocyclic system) by two equatorial bonds results in a change in the retention index of 100 units (related to one $-\text{CH}_2-$ group) when measured on SE-30 and by 120 units on Carbowax 20 M. Attachment of a third ring (to a bicyclic system), results in a change, corresponding to one $-\text{CH}_2-$ group, which is somewhat lower.

(2) Enlargement of the basic skeleton by attaching another ring by means of one axial and one equatorial bond, causes a change in the retention index which is generally higher when compared with the previous method.

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