GAS CHROMATOGRAPHY AND MASS SPECTROMETRY OF ISOMERIC CYCLOHEXYLNONADECANES AND 1-CYCLOPENTYLICOSANE

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Dedicated to Dr Jan Fajkos on the occasion of his 75th birthday.

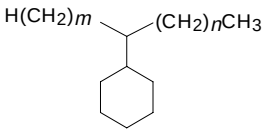
Gas-chromatographic behaviour of 1-, 2-, 3-, 4-, 5-, 6-, 7-, and 10-cyclohexylnonadecanes (**1**–**8**) and 1-cyclopentylicosane (**9**) was studied. Kováts retention indices (*I*) on capillary fused silica columns DB-1 and DB-WAX were calculated and complete mass spectra of all the nine isomeric hydrocarbons are described.

Key words: Capillary gas chromatography; Cyclohexylnonadecanes; Cyclopentylicosane; Branched alkanes; Kovats retention indices.

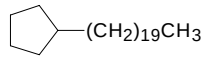
Branched hydrocarbons with methyl group in various positions are relatively abundant in nature[1]. On the other hand, branched hydrocarbons bearing a cyclohexyl or cyclopentyl group instead of a methyl are very rare. The literature on their occurrence in plants and animals until the year 1977 was summarized by Nelson[2]. Kuksis[3] reports on their presence in some crude and refined edible seed oil. Mold and coworkers[4] obtained the corresponding alkylcyclohexanes by the reduction of ω-cyclohexyl fatty acids. These relatively rare compounds were also found in fossil materials such as in geological sediments[5–10], crude oils[11], paraffin waxes[12,13], coal[14–17], graphite[18], or in meteorites[19,20] and in a mixture of environmental hydrocarbons[21,22]. The origin of cyclohexyl- and cyclopentylalkanes in nature has never been studied in detail. According to some theories[4,23], these compounds may arise in plants or animals *via* decarboxylation of the corresponding ω-cyclohexyl fatty acids. In geological samples, these substances might have been formed at higher temperatures under the catalytic influence of some sediment components.

In connection with our systematic studies of natural waxes, a series of isomeric 1-, 2-, 3-, 4-, 5-, 6-, 7-, and 10- cyclohexylnonadecanes (**1**–**8**) was synthesised earlier[24]. 1-Cyclopentylicosane (**9**), isomeric to the cyclohexylnonadecanes, was also prepared. None of these hydrocarbons is commercially available as a chromatographic standard. Calculations of Kovats retention indices, chromatographic behaviour on capillary fused

silica columns DB-1 (nonpolar) and DB-WAX (polar) as well as a survey of mass spectra are the subject of this paper.



	m	*n*
1	0	17
2	1	16
3	2	15
4	3	14
5	4	13
6	5	12
7	6	11
8	9	8



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EXPERIMENTAL

Synthesis of Hydrocarbons

Synthesis and purification of individual hydrocarbons using preparative thin layer chromatography and preparative gas chromatography was described earlier[24].

Gas Chromatography

Chromatography was performed with an HP 5890A gas chromatograph (Hewlett–Packard) equipped with a flame ionization detector and a split-splitless injector. The injector was used in split mode, manual injection was performed by the solvent flush method. Nitrogen was used as make-up gas at 30 ml/min. Column (oven), injector and detector temperatures were 200, 240 and 250 °C, respectively, for both DB-1 and DB-WAX columns (30 m × 0.25 mm × 0.25 μm, J&W Scientific). Average linear velocity of carrier gas (H_2) was 47 cm/s (DB-1) and 39 cm/s (DB-WAX), the split ratio was 49 : 1. Data were collected with an HP 3393A integrator (Hewlett–Packard).

Calculations of Kovats Retention Indices (*I*)

The calculations of *I* were carried out using the method for calculation of equivalent chain length values, described previously[25]. C_{18}–C_{28} n-alkanes were used as standards coinjected with the mixtures of all cyclohexylnonadecanes. For measurements on DB-WAX column, C_{25} and C_{26} n-alkanes were omitted to avoid coincidence with some cyclohexylnonadecanes. The standards were products of Applied Science Laboratory and Alltech Associates Applied Science Ltd.

Gas Chromatography-Mass Spectrometry

A Fisons instrument MD 800 in electron-impact ionization mode was used. Injector temperature was 240 °C, oven, interface and source temperature 200 °C, average linear velocity of carrier gas (He) 25 cm/s, the split ratio 30 : 1. A fused silica capillary column BPX-5 (30 m × 0.22 mm × 0.25 μm, SGE) was used.

Mass spectra, *m/z* (%)

All peaks with the relative intensity ≥1% are given.

1-Cyclohexylnonadecane (**1**): 351 (1), 350 (3), 266 (1), 167 (1), 153 (1), 139 (2), 126 (1), 125 (3), 124 (1), 112 (1), 111 (5), 110 (1), 99 (1), 98 (2), 97 (13), 96 (4), 95 (2), 85 (5), 84 (8), 83 (100), 82 (87), 81 (5), 79 (1), 71 (9), 70 (5), 69 (15), 68 (4), 67 (14), 58 (1), 57 (21), 56 (8), 55 (54), 54 (4), 53 (2), 43 (22), 42 (4), 41 (19), 39 (2), 29 (5) and 27 (2).

2-Cyclohexylnonadecane (**2**): 350 (1), 268 (1), 267 (4), 266 (7), 238 (1), 195 (1), 183 (1), 181 (1), 169 (1), 168 (1), 166 (1), 167 (1), 155 (1), 154 (1), 153 (2), 152 (1), 141 (1), 140 (1), 139 (2), 138 (1), 127 (2), 126 (2), 125 (5), 124 (2), 113 (3), 112 (5), 111 (39), 110 (13), 109 (2), 99 (4), 98 (3), 97 (16), 96 (3), 95 (2), 86 (1), 85 (13), 84 (9), 83 (87), 82 (100), 81 (7), 79 (2), 72 (1), 71 (19), 70 (8), 69 (38), 68 (5), 67 (23), 66 (1), 65 (1), 58 (2), 57 (35), 56 (15), 55 (76), 54 (5), 53 (3), 44 (1), 43 (31), 42 (6), 41 (28), 39 (3), 29 (8) and 27 (2).

3-Cyclohexylnonadecane (**3**): 350 (1), 322 (4), 321 (13), 320 (6), 268 (1), 267 (5), 266 (10), 251 (1), 238 (2), 237 (1), 225 (1), 223 (2), 211 (1), 209 (1), 197 (1), 196 (1), 195 (2), 183 (2), 182 (1), 181 (3), 180 (1), 169 (2), 168 (1), 167 (3), 166 (1), 155 (2), 154 (2), 153 (4), 152 (1), 141 (3), 140 (2), 139 (6), 138 (2), 137 (1), 127 (4), 126 (4), 125 (30), 124 (13), 123 (1), 113 (5), 112 (4), 111 (17), 110 (3), 109 (3), 100 (1), 99 (8), 98 (5), 97 (29), 96 (7), 95 (5), 93 (1), 86 (2), 85 (23), 84 (10), 83 (100), 82 (68), 81 (10), 80 (1), 79 (4), 77 (1),72 (2), 71 (30), 70 (12), 69 (48), 68 (6), 67 (26), 66 (1), 65 (1), 58 (3), 57 (55), 56 (19), 55 (95), 54 (7), 53 (4), 44 (2), 43 (45), 42 (8), 41 (38), 40 (1), 39 (4), 29 (11), 28 (1) and 27 (3).

4-Cyclohexylnonadecane (**4**): 350 (1), 308 (2), 307 (9), 306 (5), 268 (1), 267 (6), 266 (13), 238 (2), 237 (1), 223 (1), 211 (1), 209 (2), 197 (2), 196 (1), 195 (2),183 (2), 182 (1), 181 (2), 180 (1), 169 (2), 168 (1), 167 (3), 166 (1), 155 (3), 154 (1), 153 (4), 152 (2), 141 (3), 140 (3), 139 (19), 138 (13), 137 (1), 127 (4), 126 (2), 125 (10), 124 (2), 123 (1), 113 (6), 112 (3), 111 (15), 110 (3), 109 (4), 99 (9), 98 (5), 97 (38), 96 (9), 95 (5), 93 (1), 86 (2), 85 (25), 84 (11), 83 (100), 82 (57), 81 (11), 80 (1), 79 (3), 77 (1), 72 (2), 71 (33), 70 (12), 69 (33), 68 (5), 67 (25), 66 (1), 65 (2), 58 (3), 57 (56), 56 (17), 55 (93), 54 (7), 53 (3), 44 (2), 43 (46), 42 (8), 41 (37), 40 (1), 39 (4), 29 (11) and 27 (3).

5-Cyclohexylnonadecane (**5**): 350 (1), 294 (2), 293 (9), 292 (6), 268 (1), 267 (7), 266 (16), 238 (2), 237 (1), 223 (1), 211 (1), 209 (2), 197 (2), 196 (1), 195 (2), 183 (2), 182 (1), 181 (3), 180 (1), 169 (2), 168 (1), 167 (3), 166 (2), 155 (3), 154 (3), 153 (16), 152 (14), 141 (4), 140 (2), 139 (6), 138 (2), 127 (5), 126 (3), 125 (10), 124 (3), 123 (2), 113 (7), 112 (4), 111 (22), 110 (3), 109 (3), 100 (1), 99 (10), 98 (7), 97 (52), 96 (10), 95 (6), 93 (1), 91 (1), 86 (2), 85 (29), 84 (11), 83 (93), 82 (54), 81 (11), 80 (1), 79 (4), 77 (1), 72 (2), 71 (38), 70 (11), 69 (35), 68 (6), 67 (27), 66 (1), 65 (1), 58 (3), 57 (60), 56 (19), 55 (100), 54 (8), 53 (3), 44 (2), 43 (51), 42 (8), 41 (40), 40 (1), 39 (4), 29 (13) and 27 (3).

6-Cyclohexylnonadecane (**6**): 350 (1), 280 (2), 279 (8), 278 (6), 268 (1), 267 (8), 266 (17), 238 (2), 223 (1), 211 (1), 210 (1), 209 (1), 197 (2), 196 (1), 195 (2), 194 (1), 183 (3), 182 (1), 181 (3), 180 (1), 169 (3), 168 (3), 167 (14), 166 (13), 155 (3), 154 (2), 153 (4), 152 (2), 141 (4), 140 (2), 139 (6), 138 (2), 127 (5), 126 (3), 125 (12), 124 (3), 123 (1), 113 (7), 112 (5), 111 (28), 110 (3), 109 (4), 100 (1), 99 (11), 98 (7), 97 (48), 96 (11), 95 (6), 93 (1), 91 (1), 86 (2), 85 (32), 84 (11), 83 (89), 82 (53), 81 (12), 80 (1), 79 (4), 77 (1), 72 (2), 71 (39), 70 (13), 69 (36), 68 (6), 67 (26), 66 (1), 65 (1), 58 (3), 57 (61), 56 (19), 55 (100), 54 (8), 53 (3), 44 (2), 43 (52), 42 (7), 41 (42), 40 (1), 39 (4), 29 (13) and 27 (3).

7-Cyclohexylnonadecane (**7**): 350 (1), 268 (1), 267 (9), 266 (19), 265 (8), 264 (7), 251 (1), 238 (2), 236 (1), 211 (1), 209 (1), 197 (2), 196 (1), 195 (2), 194 (1), 183 (2), 182 (3), 181 (13), 180 (12), 169 (3), 168 (2), 167 (3), 166 (1), 155 (3), 154 (2), 153 (4), 152 (2), 151 (1), 141 (3), 140 (2), 139 (6), 138 (2), 137 (1), 127 (5), 126 (3), 125 (16), 124 (3), 123 (1), 113 (7), 112 (4), 111 (27), 110 (4), 109 (3), 100 (1), 99 (12), 98 (6), 97 (44), 96 (11), 95 (5), 93 (1), 86 (2), 85 (32), 84 (11), 83 (89), 82 (51), 81 (11), 80 (1), 79 (4), 77 (1), 72 (2), 71 (38), 70 (13), 69 (34), 68 (6), 67 (26), 66 (2), 65 (1), 58 (3), 57 (62), 56 (17), 55 (100), 54 (8), 53 (3), 44 (2), 43 (53), 42 (7), 41 (42), 40 (1), 39 (4), 29 (13) and 27 (4).

10-Cyclohexylnonadecane (**8**): 350 (1), 268 (2), 267 (10), 266 (18), 238 (2), 224 (4), 223 (17), 222 (16), 211 (1), 210 (1), 209 (2), 208 (2), 197 (2), 196 (1), 195 (1), 194 (2), 183 (2), 182 (1), 181 (1), 180 (1),

169 (2), 168 (2), 167 (4), 166 (1), 155 (3), 154 (2), 153 (6), 152 (2), 142 (1), 141 (4), 140 (2), 139 (9), 138 (3), 128 (1), 127 (6), 126 (4), 125 (15), 124 (2), 123 (1), 114 (1), 113 (7), 112 (5), 111 (24), 110 (3), 109 (3), 100 (2), 99 (12), 98 (7), 97 (44), 96 (10), 95 (5), 93 (1), 91 (1), 86 (2), 85 (33), 84 (12), 83 (91), 82 (50), 81 (11), 80 (1), 79 (4), 77 (2), 72 (2), 71 (40), 70 (12), 69 (32), 68 (6), 67 (25), 66 (1), 65 (1), 58 (3), 57 (61), 56 (16), 55 (100), 54 (8), 53 (3), 44 (2), 43 (50), 42 (7), 41 (43), 40 (1), 39 (4), 29 (14), 28 (1) and 27 (4).

1-Cyclopentylicosane (**9**): 351 (2), 350 (6), 322 (2), 280 (1), 279 (1), 266 (1), 264 (1), 252 (1), 250 (1), 238 (1), 237 (1), 236 (1), 224 (1), 223 (1), 222 (1), 210 (1), 209 (1), 208 (1), 196 (1), 195 (2), 194 (1), 183 (1), 182 (2), 181 (3), 180 (2), 169 (1), 168 (2), 167 (4), 166 (2), 155 (1), 154 (3), 153 (5), 152 (3), 141 (2), 140 (3), 139 (8), 138 (3), 137 (2), 127 (2), 126 (4), 125 (15), 124 (5),123 (2), 113 (3), 112 (6), 111 (24), 110 (5), 109 (2), 99 (5), 98 (9), 97 (44), 96 (11), 95 (6), 93 (1), 86 (1), 85 (18), 84 (12), 83 (61), 82 (32), 81 (8), 80 (1), 79 (3), 72 (2), 71 (28), 70 (20), 69 (100), 68 (72), 67 (23), 66 (2), 65 (2), 58 (3), 57 (58), 56 (21), 55 (69), 54 (8), 53 (4), 44 (2), 43 (55), 42 (13), 41 (47), 40 (1), 39 (5), 29 (12), 28 (1) and 27 (3).

RESULTS AND DISCUSSION

In the course of the column or thin-layer chromatography on silica gel of plants, insects, animal or geological sample extracts, elution with hexane or light petroleum gives a fraction where branched alkanes are present together with n-alkanes and alkenes. A follow-up chromatography on silica gel impregnated with $AgNO_3$ is needed for separation of saturated from the unsaturated alkanes. This step simplifies the chromatographic analysis and helps in the later interpretation of mass spectra. By treatment with urea[4,26–29] or thiourea[30,31], or after molecular sieving[13,26–28,32] which remove n-alkanes from the saturated fraction, we obtain a mixture where homologous series of several types of branched hydrocarbons are usually present. This mixture is already free of n-alkanes that usually strongly predominate in the starting material. The complexity of the obtained mixtures is given by the presence of different types of branched alkanes. Another method[33] described for the separation of different types of alkanes is chromatography on Sephadex LH-20.

Such complex mixtures of hydrocarbons could not be efficiently separated by gas chromatography on packed columns used earlier. Nowadays, standard fused silica capillary columns enable a significantly better separation of individual components. However, a coelution of some compounds with very similar structure and chemical properties cannot be excluded even when high resolution chromatographic columns are used. Thus, the recorded mass spectra for each chromatographic peak may not always belong to one chemical individual[34–38]. The interpretation of overlapping spectra of coeluting compounds is difficult. For a reliable identification of individual components, the interpretation of mass spectra must be combined with the knowledge of chromatographic properties of individual types of alkanes – and finally the knowledge of UV and IR spectra. Some of these data were already reported in the literature[24,39–41].

Gas chromatographic data and mass spectra of alkylcyclohexanes and alkylcyclopentanes, respectively, have been so far missing in the literature. Eglinton and coworkers[42]

described only relative retention times (packed column with Apiezon L) for compounds **1** and **9**. Kusmier *et al.*[41] published Kovats retention indices for cyclopentanes and cyclohexanes with alkyl substituents $C_{14,}$ C_{16}, and C_{18}.

Gas Chromatographic Properties

It can be seen from the chromatographic behaviour on both nonpolar (DB-1) and polar (DB-WAX) phases that the longest retention time belongs to the isomer with a cyclohexyl group in position 1 (Fig. 1). The shift of the substituent on the alkane chain toward the middle leads to shorter retention times. 10-Cyclohexyl isomer bearing the substituent exactly in the middle of the chain has the shortest retention time of all isomers. Similar rules are valid also for methyl-substituted alkanes. However, there is an anomaly in the case of alkanes with a methyl group in position 2 or 3: the 3-methyl isomer has a longer retention time than the corresponding 2-methyl isomer[24,43].

The calculated Kovats indices on DB-1 and DB-WAX phases are summarized in Table I. The chromatographic peak of compound **1** (I = 2 573.6) lies approximately in the middle between the peaks of n-alkanes C_{25} and C_{26}. Starting from the 4-cyclohexyl isomer, the elution times shorten so much that these isomers precede the peak of n-alkane C_{25} in the chromatogram. The shortest retention time belongs to compound **8** (I = 2 435.2)

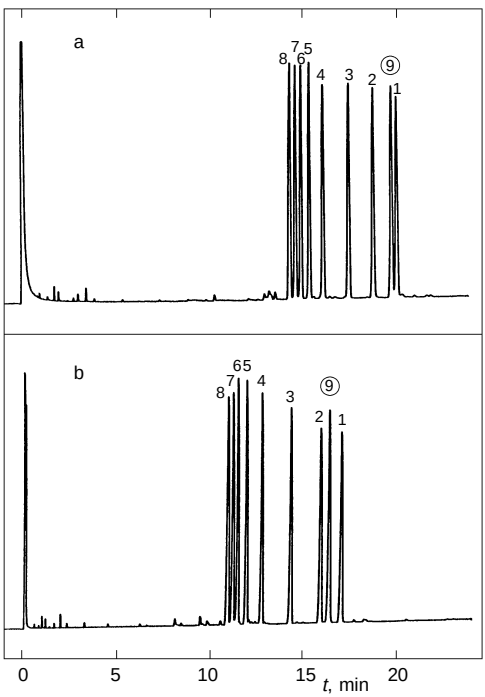

FIG. 1
Gas chromatogram of the mixture of 1-, 2-, 3-, 4-, 5-, 6-, 7-, and 10- cyclohexylnonadecane (**1**–**8**) and 1-cyclopentylicosane (**9**) on a DB-1 column (oven temperature 200 °C, rate 1 °C/min to 225 °C) and b DB-WAX column (oven temperature 180 °C, rate 1 °C/min to 205 °C)

which is found in the middle between the peaks of n-alkanes C_{24} and C_{25}. The difference in Kovats indices between 1-cyclohexylnonadecane (**1**) and 10-cyclohexylnonadecane (**8**) on the DB-1 column is 138.4 units. This difference is even more apparent on a DB-WAX column (172.1 units). While 1-isomer lies between n-alkanes C_{26} and C_{27}, the 10-isomer is eluted just before n-alkane C_{25}, *i.e.* almost two carbon atoms earlier. It is noteworthy that the largest difference in retention indices is found in the isomeric pair of 3- and 4-cyclohexylnonadecanes (**3** and **4**) on both chromatographic phases. Thus, peaks of alkanes differing in one or two carbon atoms can be found in chromatograms of mixtures of branched alkanes isolated from natural sources in close vicinity. These facts must be taken into account for a correct interpretation of mass spectra especially in the cases when the molecular ion, enabling the determination of molecular weight and thus the molecular formula, is present in the recorded spectrum in too low intensity. In cyclohexyl- or cyclopentylalkanes, the differences in retention indices are especially high compared with the methyl substituted alkanes where the shifts in retention indices are within one carbon atom only.

Mass Spectra

A general fragmentation scheme of both cyclohexyl- and cyclopentyl derivatives is shown in Fig. 2. In spectra of all the cyclohexylnonadecanes, the molecular peak (*m/z* 350) is present. The highest intensity of the molecular peak is found in spectra of 1-isomers

TABLE I
Kovats retention indices *I* of cyclohexylnonadecanes and 1-cyclopentylicosane (column temperature 200 °C)

Compound	DB-1			DB-WAX			$I^{DB-WAX} - I^{DB-1}$
	I	s.d.[a]	n^b	*I*	s.d.[a]	n^b	
1	2 573.56	0.09	9	2 665.56	0.07	11	92.00
2	2 544.89	0.06	8	2 638.73	0.07	11	93.84
3	2 513.70	0.07	9	2 596.76	0.08	11	83.06
4	2 480.65	0.07	9	2 551.31	0.10	11	70.66
5	2 462.32	0.10	9	2 525.67	0.06	11	63.35
6	2 450.80	0.08	9	2 510.65	0.06	10	59.85
7	2 443.00	0.11	9	2 502.12	0.07	11	58.93
8	2 435.19	0.10	9	2 493.46	0.06	11	58.27
9	2 568.68	0.09	9	2 647.71	0.09	11	79.03

[a] Standard deviation; [b] number of measurements.

(6% in 1-cyclopentylicosane). Cyclohexyl group gives a characteristic fragment **e** (*m/z* 83, C_6H_{11}) which is in all spectra very intensive if not the base peak[44,45]. The complementary fragment is **f** [*m/z* 266 (M – C_6H_{12})], especially significant in isomers with the cyclohexyl group in positions 2, 3, 4, 5, 6, 7, and 10. Similarly, fragment **e** (*m/z* 69, C_5H_9) is the base peak in mass spectrum of 1-cyclopentylicosane (**9**). On the basis of the fragment **b**, the position of branching can be determined unambiguously in isomers 3-, 4-, 5-, 6-, 7-, 8-, 9-, and 10-cyclohexylnonadecane. Fragment **c** is significant for branching in position 2 or higher. On the other hand, fragments **a** and **d** (complementary to **b** and **c**, respectively) are not significant and cannot be used for identification. Significant fragments in the mass spectra of all the isomeric hydrocarbons **1**–**9** are summarized in Table II.

TABLE II
Significant fragments for identification of isomeric cyclohexylnonadecanes and 1-cyclopentylicosane

Compound	$M^{+\bullet}$	Fragment[a], *m/z* (% BPI[b])			
		b	**c**	**e**	**f**
1	350 (3)	–	97 (13)	83 (100)	266 (1)
2	350 (1)	–	111 (39)	83 (87)	266 (7)
3	350 (1)	321 (13)	125 (30)	83 (100)	266 (10)
4	350 (1)	307 (9)	139 (19)	83 (100)	266 (13)
5	350 (1)	293 (9)	153 (16)	83 (93)	266 (16)
6	350 (1)	279 (8)	167 (14)	83 (89)	266 (17)
7	350 (1)	265 (8)	181 (13)	83 (89)	266 (19)
8	350 (1)	223 (17)	223 (17)	83 (91)	266 (18)
9	350 (6)	–	83 (61)	69 (100)	280 (1)

[a] See Fig. 2, [b] % of base peak intensity.

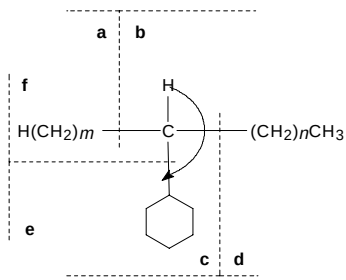

FIG. 2
Scheme of the mass spectral fragmentation of cyclohexylnonadecanes

On the basis of typical fragmentation and using chromatographic retention data, the studied compounds **1**–**9** can be unanbiguously identified in natural material.

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