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CHROMATOGRAPHIC CHARACTERISTICS AND IDENTIFICATION OF METHYLDICYCLOPENTADIENE AND DIMETHYLDICYCLOPENTADIENE ISOMERS

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Abstract

Dimers and codimers resulting from Diels-Alder reactions of 1-methyl-1,3-cyclopentadiene, 2-methyl-1,3-cyclopentadiene and cyclopentadiene were characterised in terms of their Kovats retention indices on a HP-PONA capillary column at 100°C. The proportion of individual isomers in dimerisation and codimerisation products under defined reaction conditions and their chromatographic characteristics were compared with published data. The chemical structure of isomer products was assigned based on agreement between experimental and literature data.

Key words: methyldicyclopentadiene, dimethyldicyclopentadiene, retention indices, gas chromatography, codimers, structure identification.

1. Introduction

So-called pyrolysis gasoline, one of the products of steam cracking of various hydrocarbon feedstocks, contains cyclopentadiene (CPD), dicyclopentadiene (DCPD), methylcyclopentadienes (MCPDs), methyldicyclopentadienes (MDCPDs) and dimethyldicyclopentadienes (DMDCPDs). Pyrolysis gasoline is one of the fractions obtained after C4 hydrocarbons are distilled off. It contains C5–C12 hydrocarbons. C9 and higher hydrocarbons are formed secondarily when the steam cracking reaction mixture is processing through a series of rectification columns. C9–C12 hydrocarbons are products of thermal dimerisation and codimerisation of lower unsaturated hydrocarbons. They mainly include DCPD, MDCPDs, DMDCPDs and small amounts of codimers of CPD with butadiene, isoprene or piperilenes. Dimers and mutual Diels-Alder 1:1 adducts of methyl-1,3-CPD isomers are called DMDCPD. Chemically these are positional and geometric isomers of dimethyl-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene. Codimers of 1,3-CPD with methyl-1,3-CPD isomers are called MDCPDs. According to the systematic nomenclature, they are geometric and positional isomers of methyl-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene. Diels-Alder reaction of methyl-CPD can theoretically provide numerous adducts with an *endo*- or *exo*-DCPD skeleton. However, it is generally accepted that *endo* forms are preferentially formed.[1]

To determine which components in multicomponent pyrolysis gasoline correspond to MDCPD and DMDCPD isomers, the Diels-Alder reaction products for systems with 1-MCPD + 2-MCPD and CPD + 1-MCPD + 2-MCPD were analysed using gas chromatography (GC) and the results were compared to literature data.

Technical mixtures of MDCPD isomers have similar use in the industry as DCPD [2]. They are used for synthesis of various types of resins (hydrocarbon, polyester or epoxy resins) or for production of auxiliary substances for rubber softening, modification of melt adhesives, alkyd resins, varnishes or construction materials (i.e. sulfur concrete). Owing to large-scale accessibility, low price and high synthetic potential of these MDCPD mixtures, the literature offers significant number of papers focused on their characterisation, separation and identification of the isomeric components present and their physicochemical characteristics, or papers focused on their formation.[3–16] Using studies by Diez et al.[3–5], Lauer et al.[7–9] and Thommen et al.[10] it is possible nowadays to assign chemical structures to products formed by Diels-Alder reactions of MCPD (or MCPD with CPD) even without NMR analysis,

based only on comparison of chromatographic characteristics between unknown components and known compounds.

2. Experimental

GC analyses were performed on a Shimadzu GC-17 A version 3 instrument equipped with a HP-PONA capillary column. The analysis conditions are summarised in Table 1. The HP-PONA column contains a non-polar stationary phase based on dimethylpolysiloxane and is typically used for analysis of petrochemical hydrocarbon mixtures. To determine the Kovats retention index RI, selected samples were analysed isothermally at a column temperature of 100°C and mixtures of reference alkanes were added to the samples.

A GC coupled to a quadrupole mass spectrometer (Shimadzu GCMS-QP 2010) was used to determine the molecular weight of the components analysed. The data were processed using GC-MS Solution Version 2.0 (Shimadzu).

Dimers and codimers were prepared by Diels-Alder reaction of the corresponding monomers in a pressure stainless steel vessel. Reactions were conducted in the liquid phase under isothermal conditions at several temperatures using cyclohexane as solvent. CPD was prepared by thermal decomposition of 99.5% DCPD in a reboiler under a distillation column with 18 theoretic plates. The distillate of pure CPD was cooled at the column head using a mixture of acetone and dry ice and was then kept at –20°C. MCPD was prepared similarly using a commercial DMDCPD mixture derived from pyrolysis gasoline.

Table 1. GC analysis conditions

Integration	Chromatography Station CSW32 software
Detector	FID
Column	Capillary HP-PONA
Column length	50 m
Inside column diameter	0.2 mm
Film thickness	0.5 μm
Column temperature program	40°C for 5 min, increased at 7°C min^{-1} to 250°C, held for 5 min
Detector temperature	200°C
Injector temperature	250°C
Carrier gas, inlet pressure	Helium, 370 kPa (initial linear velocity 40 cm s^{-1})
Split ratio	120
Injection volume	0.1 μl

3. Results and Discussion

3.1. Starting material for dimer and codimer preparation

A mixture of two MCPD isomers at a ratio of 44:56 and a small amount of CPD (3.8%) was obtained by thermal decomposition of a commercial DMDCPD mixture. According to the literature, 1-MCPD and 2-MCPD isomers are predominant. The 5-MCPD isomer content of pyrolysis products is very low.[1,3,17] Lauer et al. found that thermal decomposition of pure 2-MCPD or pure 1-MCPD dimer provides a mixture of both monomers.[7] Apparently, the isomers undergo isomerisation easily at the temperature used for DMDCPD thermal decomposition. According to Thommen et al., the equilibrium composition of the mixture was 5-MCPD/1-MCPD/2-MCPD=1:45:54.[10] Chromatographic analysis on a capillary column can separate 2-MCPD and 1-MCPD, especially on polar and moderately polar stationary phases, with 2-MCPD eluting first.[5,18,19] Since MCPD isomers in pure form were not available in this study (it is impossible to divide a mixture of 1-MCPD and 2-MCPD by distillation), dimers of MCPD and codimers of CPD and MCPD were prepared using a mixture of 1-MCPD and 2-MCPD isomers. However, heating a mixture of 1-MCPD and 2-MCPD creates both homodimers and mixed codimers of 1-MCPD and 2-MCPD. Both types are usually referred to as MCPD dimers, although they are actually dimethyldicyclopentadiene isomers.

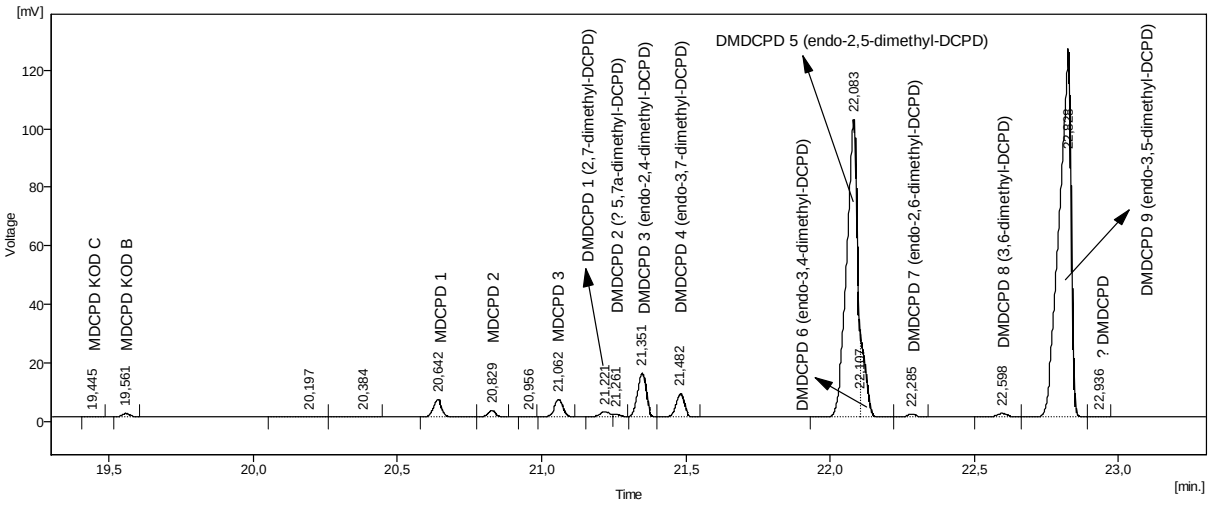
3.2. DMDCPD isomers

Diels-Alder reactions of 1-MCPD and 2-MCPD were examined at temperatures of 25, 60, 80, 100 and 120°C. The initial mixture contained 90% cyclohexane. Nine components in the reaction mixtures were identified as isomers of DMDCPD (MW=160) according to GC-MS on a 50-m HP-PONA capillary column. These are denoted DMDCPD 1–9. In the technical DMDCPD obtained from Aldrich, they occurred at a ratio of 1.3:0.5:5.3:3.3:32.0:3.7:1.0:1.3:36.2,

respectively. It cannot be said with certainty that two minor components with RT=22.36 and 22.94 min have a molecular weight matching that of DMDCPD.

The literature provides enough information and chromatographic characteristics for DMDCPD isomers for unambiguous structure identification of all nine components corresponding to *m*/*z*=160. First, based on comparison of the experimental data to those reported by Diez et al.[5], the structure of four main MCPD dimers was partly specified. Kovats retention index values experimentally measured on a HP-PONA column were congruent with values on an OV-101 column as reported by Diez et al. (Table 2). The OV-101 and HP-PONA columns are equivalent in polarity and type. By comparing the experimental data with the data reported by Lauer et al.[7,8] and Thommen et al.[10] it was possible to unambiguously identify the structures of the four main MCPD dimers, other MCPD dimers and the main codimers for CPD and MCPD (Tables 3 and 4). Lauer et al. determined structures of all analytically important MCPD dimers and codimers of CPD and MCPD using NMR analysis. Isomer ratios are reported for products of MCPD dimerisation and of codimerisation of CPD and MCPD, as well as RI values for the isomers on CP-SIL19CB, CP-WAX52CB and HP-1 GC columns. CP-SIL19CB columns are based on polysiloxane, but are much more polar than HP-PONA columns owing to the presence of cyanopropyl and phenyl side chains in the polymer. Therefore, the RI values for individual DMDCPD isomers are slightly higher for the CP-SIL19CB than for the HP-PONA column and direct comparison it is not possible. However, RI differences between individual isomers and RI differences versus *endo*-DCPD reference material are very similar for the HP-PONA and CPSIL19CB columns (Table 3). By comparing RI differences and the ratios of individual isomers in commercial DMDCPD mixtures, chemical structures were assigned to all nine DMDCPD isomers. The assignment accuracy was validated by comparison with another study conducted by Thommen et al.[10] The isomer ratios reported for a commercial DMDCPD product and for dimerisation products prepared at 20 or 110°C are in agreement with our experimental findings (Table 4).

Figure 1. Diels-Alder reaction products for 1-methyl- and 2-methylcyclopentadiene.

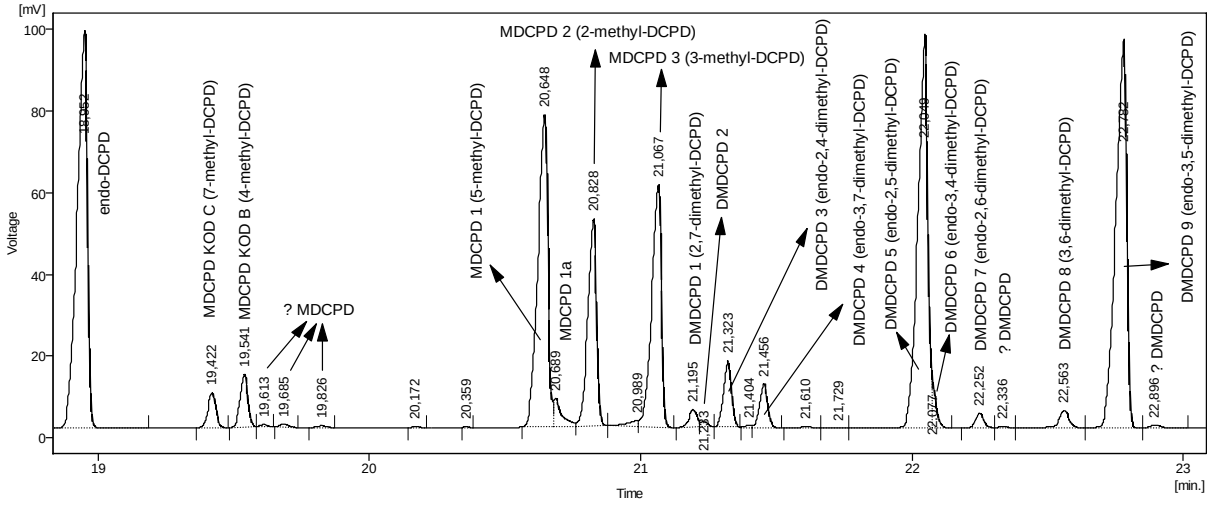


Large numbers of isomer adducts can be created by Diels-Alder reactions of MCPD isomers, but only nine components were detected in analytically significant amounts (Figure 1). Apparently all isomer products have a tricyclic skeleton in the *endo* configuration. Nevertheless, the *endo* configuration was confirmed only for DMDCPD 3–7 and 9 isomers.[5,10] MCPD dimerisation products are typically dominated by three components: *endo*-2,5-DMDCPD (DMDCPD 5), *endo*-3,4-DMDCPD (DMDCPD 6) and *endo*-3,5-DMDCPD (DMDCPD 9). However, during GC analysis on non-polar stationary phases, the first two isomers usually elute together. This was observed on the 50-m capillary HP-PONA column (DMDCPD 5–6). At higher temperature, *endo*-3,4-DMDCPD (DMDCPD 5) transforms by reversible [3,3]-sigmatropic rearrangement to the thermodynamically more stable *endo*-2,5-DMDCPD isomer (DMDCPD 6).[10] Isomerisation of DMDCPD 5 to DMDCPD 6 was also observed and confirms the accuracy of the structural assignment. Isomers 2,7-DMDCPD, 5,7*a*-DMDCPD, *endo*-2,4-DMDCPD and *endo*-3,7-DMDCPD eluted before the first dominant peak for DMDCPD 5–6, and *endo*-2,6-DMDCPD and 3,6-DMDCPD eluted between the two main peaks for DMDCPD 5–6 and DMDCPD 9.

3.3. MDCPD isomers

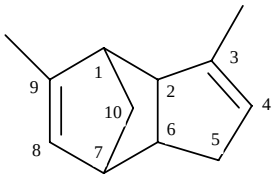
Diels-Alder reactions in the system CPD + 1-MCPD + 2-MCPD were observed at temperatures of 50, 70, 100 and 120°C. In the reaction mixtures six components were determined as codimers of CPD and MCPD (MW=146). Their distribution on the HP-PONA column is shown in Figure 2 and Table 3 lists their ratios in the reaction mixture at a temperature of 120°C. It is clear that apart from the codimers mentioned, the reaction mixture also contained DMDCPD isomers.

Figure 2. Diels-Alder reaction products for the CPD + 1-MCPD + 2-MCPD system.

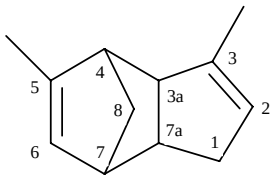


Two MDCPD isomers denoted KOD C and KOD B eluted closest to *endo*-DCPD. Three main MDCPD isomers eluted later (denoted MDCPD 1–3 or a MDCPD triple peak). At the end of the MDCPD 1 peak, a minor component (MDCPD 1a) eluted, which was identified by GC-MS as a codimer of CPD with MCPD. By comparing the experimental data to those reported by Lauer et al.[7,8], chemical structures could be assigned to components MDCPD KOD B, MDCPD KOD C and MDCPD 1–3 (Table 5). The comparison method was the same as for DMDCPD isomer identification. MDCPD KOD C was identified as 7-MDCPD and MDCPD KOD B as 4-MDCPD. The MDCPD triple peak can be attributed to 5-MDCPD, 2-MDCPD and 3-MDCPD. Position numbering for MDCPD and DMDCPD isomers here is in accordance with IUPAC nomenclature rule A-34 for so-called fused systems rather than the von Baeyer nomenclature principle (Figure 3).

Figure 3. Two alternative approaches to systematic naming of polycyclic hydrocarbons.



3,9-dimethyl
tricyclo[5.2.1.0^{2,6}]deca-3,8-diene
(von Baeyer principle)



3,5-dimethyl-
3a,4,7,7a-tetrahydro-1*H*-4,7-methanoindene
(rule A-34. IUPAC)

4. Conclusions

Table 6 lists MDCPD and DMDCPD isomers for which an unambiguous chemical structure was successfully assigned. These compounds were characterised in terms of their Kovats retention index on a HP-PONA capillary column at 100°C. Because isothermal GC analysis is not suitable for analysis of multi-component mixtures such as pyrolysis condensates, MDCPD and DMDCPD isomers were further characterised in terms of their retention time on a HP-PONA capillary column under a temperature programme.

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on Dicyclopentadiene" and by the project of the Ministry of Education, Youth and Sports, CEZ: MSM 6046137301.

Table 6. List of dimers and codimers with unambiguous assigned chemical structure

Diels-Alder product	Compound name	RT [min] HP-PONA temp. prog.	RI HP-PONA 100°C
MDCPD KOD C	7-MDCPD* (7-methyl-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene)	19.44	1042.4
MDCPD KOD B	4-MDCPD**	19.55	1046.5
MDCPD 1	5-MDCPD	20.62	1084.3
MDCPD 2	2-MDCPD	20.81	1090.7
MDCPD 3	3-MDCPD	21.04	1098.9
DMDCPD 1	2,7-DMDCPD**	21.22	1104.2
DMDCPD 3	*endo*-2,4-DMDCPD	21.26	1104.8
DMDCPD 4	*endo*-3,7-DMDCPD	21.35	1108.6
DMDCPD 5	*endo*-2,5-DMDCPD	21.48	1112.8
DMDCPD 6	*endo*-3,4-DMDCPD	22.08	1134.4
DMDCPD 7	*endo*-2,6-DMDCPD	22.11	1134.4
DMDCPD 8	3,6-DMDCPD	22.60	1154.1
DMDCPD 9	*endo*-3,5-DMDCPD	22.83	1160.8

**) Position numbering in accordance with IUPAC rule A-34 (3a,4,7,7a-tetrahydro-1H-4,7-methanoindene). **) The endo/exo stereoisomeric configuration was not confirmed for some isomers, however, based on the current knowledge it is possible to consider them compounds with endo-DCPD skeleton*

Symbols

CPD	1,3-cyclopentadiene
DCPD	dicyclopentadiene, 3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-methanoindene
DMDCPD	dimethyldicyclopentadiene
MCPD	methyl-1,3-cyclopentadiene isomer
MDCPD	methyldicyclopentadiene
MDCPD KOD C	methylcyclopentadiene isomer with the shortest retention time
MDCPD KOD B	methylcyclopentadiene isomer with the second shortest retention time
RI	Kovats retention index
ΔRI	retention index difference compared to the *endo*-dicyclopentadiene reference material
RT	retention time [min] under the analysis conditions shown in Table 1

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Table 2. Comparison of experimental data for methylcyclopentadiene dimerisation with data reported by Diez et al.[5]

Experimental data			Published data[5]		
Peak label	**RT** [min] HP-PONA temp. prog.	**RI** HP-PONA 100°C	Compound name	**RI** OV-101 100°C	**RI** OV-1701 80°C
DMDCPD 3	21.35	1108.6	*endo*-2,4-(or 2,7-)DMDCPD*	1107.6	1135.3
DMDCPD 5	22.08	1134.4	*endo*-2,5-(or 2,6-)DMDCPD	1133.9	1131.6
DMDCPD 6	22.11	1134.4	*endo*-3,4-(or 3,7-)DMDCPD	1133.9	1166.6
DMDCPD 9	22.83	1160.8	*endo*-3,5-(or 3,6-)DMDCPD	1159.9	1191.3
Reference material	*19.06*	*1026*	*endo-DCPD*	*1025.3*	*1065.5*

*) *Position numbering in accordance with IUPAC rule A-34 (3a,4,7,7a-tetrahydro-1H-4,7-methanoindene).*

Table 3. Comparison of experimental data for methylcyclopentadiene dimerisation with data reported by Lauer et al.[7]

Experimental data					Published data[7]			
Peak label	**RT** [min] HP-PONA temp. prog.	**RI** HP-PONA 100°C	**ΔRI** vs. *endo*DCPD	Isomer ratio in commercial product **	Compound name	**RI** CP-SIL19CB prog.	**ΔRI** vs. *endo*DCPD	Isomer ratio in commercial product ***
DMDCPD 1	21.22	1104.2	78	1.3	2,7-DMDCPD*	1130	73	2.0
DMDCPD 2	21.26	1104.8	79	0.5	5,7*a*-DMDCPD	1127	70	0.2
DMDCPD 3	21.35	1108.6	83	5.3	2,4-DMDCPD	1135	78	6.65
DMDCPD 4	21.48	1112.8	87	3.3	3,7-DMDCPD	1142	85	3.9
DMDCPD 5	22.08	1134.4	108	32.0	2,5-DMDCPD	1162	105	29.8
DMDCPD 6	22.11	1134.4	108	3.7	3,4-DMDCPD	1167	110	11.8
DMDCPD 7	22.28	1143.0	117	1.0	2,6-DMDCPD	1173	116	1.2
? DMDCPD	22.36	1145.7	120	0.10	?,?-DMDCPD	1177	120	0.05
DMDCPD 8	22.60	1154.1	128	1.3	3,6-DMDCPD	1187	130	1.25
DMDCPD 9	22.83	1160.8	135	36.2	3,5-DMDCPD	1193	136	39.7
? DMDCPD	22.94	1167.7	142	0.17	?,?-DMDCPD	1199	142	0.16
Reference material	*19.06*	*1026*	*0*		*endo-DCPD*	*1057*	*0*	

*) *Position numbering in accordance with IUPAC rule A-34 (3a,4,7,7a-tetrahydro-1H-4,7-methanoindene).*
) *DMDCPD Aldrich.* *) *DMDCPD Fluka.*

Table 4. Comparison of experimental data for methylcyclopentadiene dimerisation with data reported by Thommen et al.[10]

Experimental data					Published data[10]			
Peak label	**RT** [min] HP-PONA temp. prog.	Isomer ratio in dimerisation product (25°C)	Isomer ratio in dimerisation product (120°C, 2 h)	Isomer ratio in commercial product **	Compound name	Isomer ratio in dimerisation product (20°C)	Isomer ratio in dimerisation product (110°C, 3h)	Isomer ratio in commercial product ***
DMDCPD 3	21.35	3.0	6.6	5.3	*endo*-2,4-DMDCPD*	9	7	5
DMDCPD 4	21.48	1.6	4.3	3.3	*endo*-3,7-DMDCPD	4	5	3
DMDCPD 5	22.08	24.6	37.4	32.0	*endo*-2,5-DMDCPD	22	42	29
DMDCPD 6	22.11	3.7	1.1	3.7	*endo*-3,4-DMDCPD	24	4	10
DMDCPD 7	22.28	0.2	1.3	1.0	*endo*-2,6-DMDCPD	1	1	2
DMDCPD 9	22.83	36	36	36.2	*endo*-3,5-DMDCPD	36	36	36

*) *Position numbering in accordance with IUPAC rule A-34.* **) *DMDCPD Aldrich.* ***) *Technical DMDCPD Exxon.*

Table 5. Identification of cyclopentadiene–methylcyclopentadiene codimer structures

Experimental data					Data reported by Lauer et al.[7]			
Peak label	**RT** [min] HP-PONA temp. prog.	**RI** HP-PONA 100°C	**ΔRI** vs. *endo*DCPD	Isomer ratio in reaction mixture (120°C)**	Compound name	**RI** CP-SIL19CB prog.	**ΔRI** vs. *endo*DCPD	Isomer ratio in reaction mixture (70°C)**
MDCPD KOD C	19.44	1042.4	16	1.2	7-MDCPD*	1068	11	1.6
MDCPD KOD B	19.55	1046.5	21	3.4	4-MDCPD	1073	16	2.8
? MDCPD	19.61	1048.7	23	0.14				
? MDCPD	19.69	1051.2	25	0.2	?-MDCPD	1078	21	0.2
? MDCPD	19.83	1056.0	30	0.07	?-MDCPD	1084	27	0.1
MDCPD 1	20.62	1084.3	58	14.7	5-MDCPD	1113	56	17.0
MDCPD 1a	20.69	1085.6	60	1.0	?-MDCPD	1115	58	0.9
MDCPD 2	20.81	1090.7	65	8.2	2-MDCPD	1121	64	11.1
MDCPD 3	21.04	1098.9	73	13.9	3-MDCPD	1133	76	13.7
Reference material	*19.06*	*1026*	*0*	*32.7*	*endo-DCPD*	*1057*	*0*	*22.6*

*) *Position numbering in accordance with IUPAC rule A-34.* **) *Mixture of CPD, 1-MCPD and 2-MCPD brought to a certain temperature.*