CIS-CIS-TRANS-BICADINANE, A NOVEL MEMBER OF AN UNCOMMON TRITERPANE FAMILY ISOLATED FROM CRUDE OILS

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Abstract. *Cis-cis-trans*-bicadinane, an uncommon triterpane present in South East Asian crude oils has been isolated and its structure has been revealed with NMR-spectroscopic methods.

Several years ago the most abundant member of a new class of triterpenoids (1) present in crude oils from South East Asia was isolated and identified[1]. This compound ($2\beta,3a\alpha,4\alpha,6a\alpha,7a\alpha,8a\alpha,9\alpha,12\beta,12a\beta,13a\beta,13b\alpha,13c\beta$-2,6a,12-trimethyl-4,9-di(1-methylethyl)perhydrobenzo[de]naphthacene) was called bicadinane because it can be considered as a dimer of cadinane (2). Recently it was proposed that the precursor of this and similar compounds is polycadinene (3), a polymer present in dammar resins[2]. In this paper we report the isolation and structural elucidation of the second most abundant bicadinane ($2\alpha,3a\beta,4\beta,6a\alpha,7a\alpha,8a\alpha,9\alpha,12\beta,12a\beta,13a\beta,13b\alpha,13c\alpha$-2,6a,12-trimethyl-4,9-di(1-methylethyl)perhydrobenzo[de]naphthacene; 4) found in many crude oils and sediments[3]. We propose the names *trans-trans-trans*-bicadinane for 1 and *cis-cis-trans*-bicadinane for 4, based on the configuration of the perhydrophenalene substructure of the molecules.

1

2

4

3
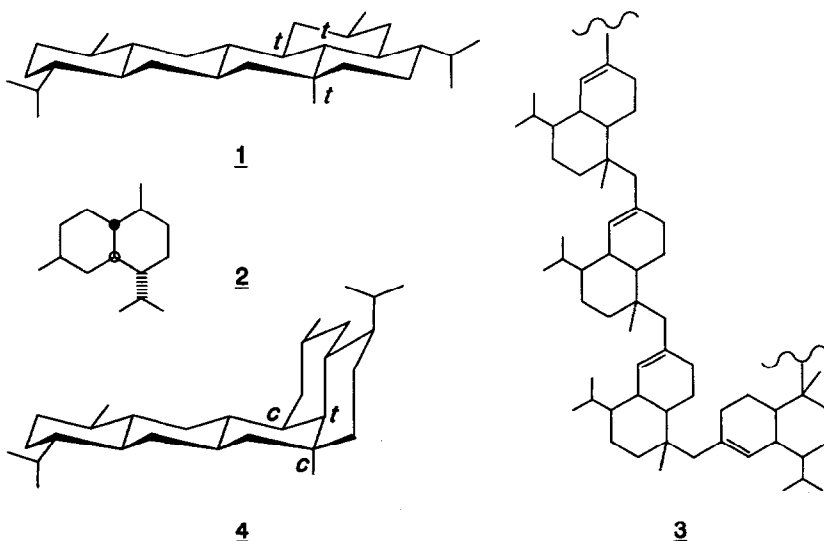
The crude oil was distilled at .05 mm Hg at 210 °C to remove relatively low boiling compounds. The alkanes were separated from the distillation residue with column chromatography using Al_2O_3/Si_2O_3 as the stationary phase and hexane as the eluent. The *n*-alkanes were subsequently removed by means of urea-adduction. The residual branched and cyclic hydrocarbons were further separated by reversed phase HPLC on a preparative Polygosil C_{18}-column (EtOAc/MeOH 60:40) and by reversed phase HPLC using an analytical Polygosil C_{18} column (THF/MeOH/H_2O 100:85:15). GC-analysis of the appropriate fraction indicated that compound **4** represented 65% of this fraction. The other 35% consisted of a complex mixture of hydrocarbons, none representing more than 5% of the total fraction; 84 mg of **4** was thus isolated in 65% purity from 180.5 g of crude oil.
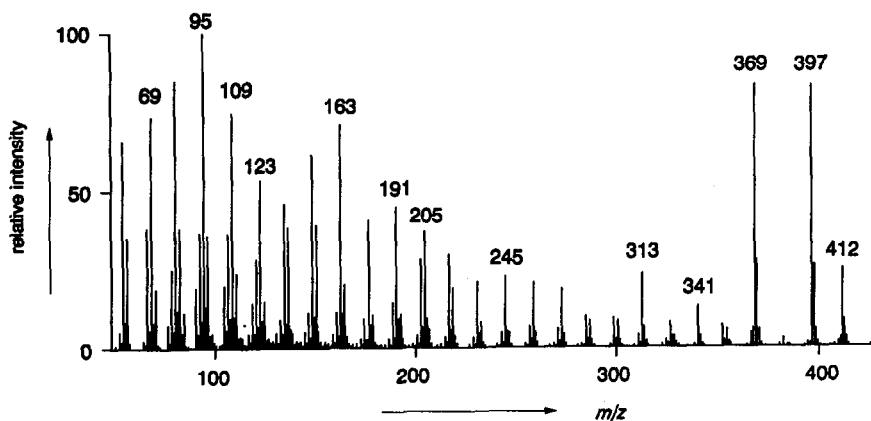

Figure 1. EIMS spectrum of *cis-cis-trans*-bicadinane (**4**).

The EIMS spectrum of obtained via GC-MS is very similar to that of *trans-trans-trans*-bicadinane, suggesting an isomeric structure for **4**. The major difference is the higher abundance of the peak at *m/z* 397 in the spectrum of **4**.
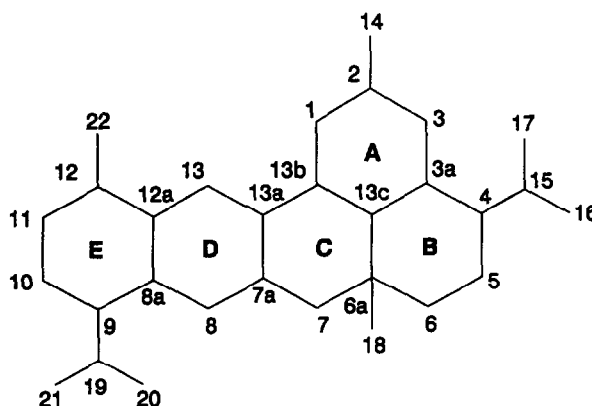
Table 1. ^{1}H and ^{13}C chemical shift data[a] of *cis-cis-trans-* (**4**) and all-*trans-* (**1**) bicadinane

proton	δ ^{1}H		carbon	δ ^{13}C	
	cct	*ttt*		*cct*	*ttt*
H-1eq	1.87	1.90	C-1	37.08	39.44
H-1ax	0.78	0.32			
H-2	1.47	1.19	C-2	26.27	31.32
H-3eq	1.85	1.84	C-3	39.81	39.41
H-3ax	0.33	0.31			
H-3a	1.45	1.10	C-3a	34.54	37.00
H-4	0.82	0.85	C-4	49.03	49.42
H-5eq	1.31	1.34	C-5	19.46	19.00
H-5ax	1.14	1.34			
H-6eq	1.38	1.36	C-6	41.81	42.13
H-6ax	1.19	1.04			
			C-6a	33.82	33.68
H-7eq	1.44	1.22	C-7	39.32	50.34
H-7ax	0.79	0.78			
H-7a	1.22	1.21	C-7a	38.99	37.27
H-8eq	1.71	1.67	C-8	37.88	37.87
H-8ax	0.55	0.44			
H-8a	0.89	0.86	C-8a	44.34	44.13
H-9	0.93	0.87	C-9	48.08	47.91
H-10eq	1.57	1.56	C-10	24.32	24.25
H-10ax	1.00	0.98			
H-10eq	1.70	1.68	C-11	36.20	36.12
H-11ax	0.98	0.97			
H-12	1.05	0.99	C-12	37.93	37.90
H-12a	0.64	0.56	C-12a	49.78	49.65
H-13eq	2.06	2.16	C-13	33.76	33.93
H-13ax	0.34	0.38			
H-13a	1.12	0.47	C-13a	39.18	49.47
H-13b	1.68	0.90	C-13b	37.87	40.33
H-13c	0.92	0.48	C-13c	51.73	54.10
14-CH₃	0.83	0.85	C-14	23.41	23.29
H-15	1.96	1.95[b]	C-15	26.14	26.35
16-CH₃	0.70	0.72[c]	C-16	15.24	15.18[e]
17-CH₃	0.85	0.84	C-17	21.64[d]	21.58[f]
18-CH₃	0.94	0.82	C-18	29.46	18.65
H-19	1.97	1.99[b]	C-19	26.42	26.35
20-CH₃	0.69	0.68[c]	C-20	15.24	15.16[e]
21-CH₃	0.85	0.84	C-21	21.60[d]	21.53[f]
22-CH₃	0.88	0.86	C-22	20.32	20.35

Table 2. NOE connectivities of **4**.

H-1eq	-	H-13eq
H-3ax	-	H-1ax
H-3ax	-	H-13c⁻
H-3eq	-	H-15
H-8eq	-	H-19
H-13a	-	H-2
H-13a	-	H-3a
H-13eq	-	22-CH₃

Table 3. ^{1}H-^{13}C long-range couplings of **4**.

H-13eq	-	C-7a
H-13eq	-	C-8a
14-CH₃	-	C-2
18-CH₃	-	C-6a
18-CH₃	-	C-7
22-CH₃	-	C-12

(a) Both measured in ^{12}C enriched CDCl₃. **1** on a 0.015 M solution and **4** on a 0.13 M solution. Values in the table bearing the same superscript may be interchanged.

Evidence for the structure of **4** was obtained from comparison of the NMR-data of **1**[4] with those obtained for **4**. All proton and carbon chemical shifts in the NMR spectra were unambiguously assigned and are shown in Table 1. Analysis of the ^{13}C NMR spectra, obtained by APT and DEPT pulse sequences in combination with a ^{1}H-^{13}C correlation experiment showed the presence of 7 CH₃, 9 CH₂, 13 CH-groups and 1 quarternary carbon atom in compound **4**, including two non-equivalent isopropyl groups. Bicadinane **1** possesses four CH₂-groups with a

large difference in proton chemical shifts between H_{eq} and H_{ax} at C-1, C-3, C-8 and C-13, combined with high-field absorptions of the axial protons. This phenomenon is characteristic of the protons of CH_2-groups in the 2-position of 1,3-diequatorially substituted cyclohexane rings[5]. The 62.8 MHz ^{1}H-^{13}C correlation experiment and a 600 MHz phase sensitive double quantum filtered ^{1}H-^{1}H COSY experiment indicated that bicadinane 4 has three such CH_2-groups with chemical shifts that correspond very well to those of the attached equatorial and axial protons at C-3, C-8 and C-13 of 1. Furthermore, a number of ^{1}H and ^{13}C chemical shifts in 4 are identical to chemical shifts observed in 1 for the carbon atoms and attached protons at positions 8, 8a, 9, 10, 11, 12, 12a, 13, 19, 20, 21 and 22. This leads to the conclusion that the "left hand" part of 4 has an identical structure as the "left hand" part of 1. The mere fact that the ^{13}C chemical shifts of C-8 and C-13 do not differ from those of 1 means that the *trans-syn-trans*-perhydroanthracene system[6], comprising of rings E, D and C, is present in both molecules. The upfield ^{13}C shifts of C-7 and C-13a in 4 of 10 and 10.5 ppm respectively, as compared to 1 are explained by assuming a double γ-gauche interaction for both carbon atoms. Compound 4 also displays a CH_3-absorption at δ=29.46, ascribed to C-18, which corresponds very well with the methyl-absorption observed in the NMR-spectrum of 9-methyl-*cis*-decalin[7] (δ=28.22). Both these phenomena indicate the *cis-cis-trans*-perhydrophenalene skeleton sub-structure for the second part of the molecule, *i.e.* rings C, B and A. The most convincing piece of evidence for the structure of 4 and in particular the positions of the methyl- and isopropyl-groups was obtained from a 600 MHz phase sensitive NOESY experiment and a ^{1}H-^{13}C correlation, optimized for long-range J_{CH} = 7 Hz. Relevant NOE connectivities and ^{1}H-^{13}C long-range couplings are indicated in Table 2 and Table 3 respectively. All ^{13}C-values for *cis-cis-trans*-bicadinane 4 could also be satisfactorily predicted using literature data on chemical shifts of all-*trans*-bicadinane[4], cadinane[4], *trans-syn-trans*-perhydroanthracene[6], *cis-trans*-perhydroanthracene[6] and *trans-anti-cis*-perhydrophenantrene[6].

The above mentioned relatively high abundance of m/z 397 in the mass spectrum of 4 as compared to that of 1 can be explained by steric relief due to loss of the C-18 methylgroup in 4. The similar structures of compounds 1 and 4 underline their common origin from polycadinene present in dammar resin[2]. Depolymerization and ring closure reactions induced by elevated temperatures in the subsurface appear to have led to the formation of both these bicadinanes.

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