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Studies on the Oxidation of cis- and trans-Pinane with Molecular Oxygen

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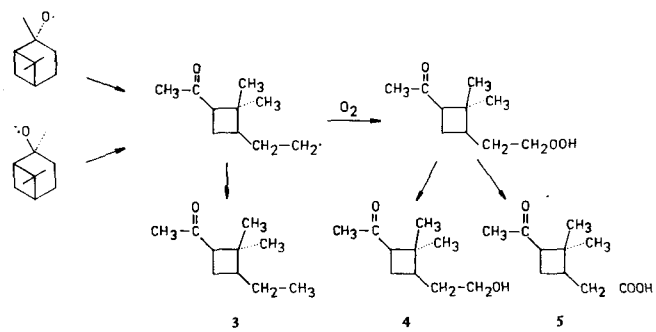
In memory of Dr. Wolfgang Schmidt-Renner (1948 – 1990)

Abstract. The pinanes are preferably attacked at the tertiary C-H bond in 2-position, but products of the oxidative attack at the secondary C-H bonds in 3- and 4-position are also found. At 100 °C cis-pinane is attacked more easily than trans-pinane ($k_{cis} : k_{trans} = 6.4$), the relative rates of attack at the secondary C-H bonds in positions 3 and 4 with respect to the tertiary C-H bond in 2-position were also determined (in cis-pinane $k_{sec} : k_{tert} = 0.027$; in trans-pinane $k_{sec} : k_{tert} = 0.20$). After the attack at the 2-C-H bond the radical formed can either react with oxygen to form the corresponding cis- and trans-peroxy radicals and further to give cis- and trans-2-hydroperoxy pinane or fragmentate to the monocyclic radical derived from α-terpinene, giving as final products α-terpinene hydroperoxide and the bicyclic 8-hydroperoxy 4,4,8-trimethyl 2,3-dioxabicyclo[3.3.1]nonane. The corresponding alcohols were found after reduction with sodium sulphite. The oxidation at position 2 of the pinanes delivers not only the cis- and trans-hydroperoxide but also, as short-lived intermediates, the corresponding 2-pinanyloxy radicals. These radicals fragmentate forming a carbon radical with cyclobutane structure whose oxidation products were identified. Besides fragmentation of the 2-pinanyloxy radical also an intramolecular H-transfer from the methyl group in 9-position to the oxygen of the trans-2-pinanyloxy radical takes place leading to 9-hydroperoxy trans-pinane-2-ol.

The autoxidation of cis-pinane **1a** was already studied intensively [1 – 7]. Main products are cis- (**2a**) and trans-pinane-2-ol (**2b**) (78 % cis- and 22 % trans-alcohol) and (as a product of the fragmentation of the 2-pinanyloxy radical) cis-1-acetyl 3-ethyl-2,2-dimethyl-cyclobutane.

Because the pyrolysis of cis/trans-pinane-2-ol delivers linalool [8, 9], the oxidation of the pinanes to cis/trans-2-hydroperoxy pinane and the subsequent reduction or hydrogenation of the hydroperoxide mixture to cis/trans-pinane-2-ol are of industrial interest.

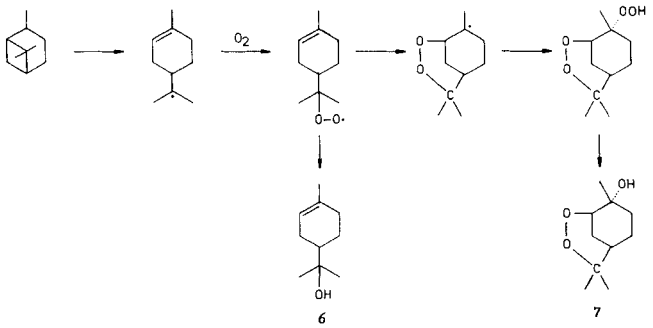
We studied the oxidation of cis-pinane with pure oxygen at temperatures between 70 and 130 °C and finished the reactions when 15 weight-% of pinane hydroperoxide were formed. The oxidates were reduced with aqueous sodium sulphite and then analyzed by gaschromatography. The results are shown in Table 1. Evidently the cis- and trans-2-hydroperoxy pinanes primarily formed as the main products are decomposed more and more rapidly at temperatures higher than 100 °C forming **3 – 5**, products of the fragmentation of the 2-pinanyloxy radicals (Formula Scheme 1). Moreover, with increasing temperature more and more products with p-menthane skeleton **6** and **7** are obtained. These compounds must be formed via fragmentation of the 2-pinanyl radical [10] (Formula Scheme 2). This fragmentation becomes more and more important with increasing temperature because of two reasons. Firstly, the activation energy of the fragmentation is higher than that of the competitive reaction of the 2-pinanyl radical with oxygen, secondly the steady state concentration of oxygen in the reaction mixture decreases with increasing temperature. A very



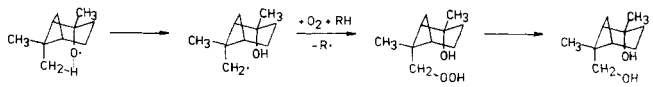
Formula Scheme 1 Fragmentation of the 2-pinanyloxy radicals: formation of the cyclobutane derivatives **3 – 5**

Table 1 Oxidation of cis-pinane with molecular oxygen at temperatures between 70 and 130 °C
Analysis of the reaction products after reduction with aqueous sodium sulphite

Temperature (°C)	70	80	90	100	110	120	130
reaction time (h)	34.0	16.5	7.0	3.5	1.8	1.0	0.7
hydroperoxide concentration (weight-%)	15.0	15.4	14.6	15.0	16.3	15.3	14.1
product after Na_2SO_3 reduction (mole-%)							
trans-pinane-2-ol (**2a**)	19.1	17.6	19.3	17.1	16.0	12.3	8.3
cis-pinane-2-ol (**2b**)	70.5	67.8	66.6	66.6	63.6	45.8	31.6
isopinocamphone (**9**)	0.6	0.8	0.8	0.9	0.8	1.3	1.6
isopinocampheol (**10**)	4.8	5.7	6.0	5.9	7.0	7.5	7.5
isoverbanone (**11**)	0.4	0.9	0.5	1.4	0.6	0.5	0.9
isoverbanol (**12**)	2.0	2.2	2.2	1.7	2.9	2.3	2.5
1-acetyl-2,2-dimethyl-3-ethyl-cyclobutane (**3**)	0.5	1.0	0.8	1.2	1.4	4.6	5.7
2-(1-acetyl-2,2-dimethyl-cyclobut-3-yl) ethanol (**4**)	0.5	1.1	0.8	1.1	1.9	3.7	4.3
α-pinonic acid (**5**)	0.4	0.5	0.5	0.8	1.2	2.2	8.0
α-terpineol (**6**)	0.5	1.0	1.2	2.1	1.3	3.3	5.7
4,4,8-trimethyl 2,3-dioxabicyclo-[3.3.1]nonane-8-ol (**7**)	0.2	0.5	0.6	0.9	2.0	14.5	19.9
trans-pinane-2,9-diol (**8**)	0.3	0.6	0.4	0.4	0.7	0.9	0.8
X	0.2	0.3	0.3	0.5	0.6	1.1	3.2



Formula Scheme 2 Fragmentation of the 2-pinanyl radical: formation of the p-menthane derivatives **6** and **7**



Formula Scheme 3 Intramolecular H-transfer in the trans-2-pinanyloxy radical: formation of the diol **8**

interesting reaction product is the trans-pinane-2,9-diol **8**. This diol must be formed via 9-hydroperoxy trans-pinane-2-ol according to the pathway shown in Formula Scheme 3. Such an intramolecular H-transfer was observed already in the oxidation of trans-pinane-2-ol with lead tetra-acetate [11 – 14], but products of this intramolecular H-transfer had not been found in autoxidation mixtures of cis-pinane until now.

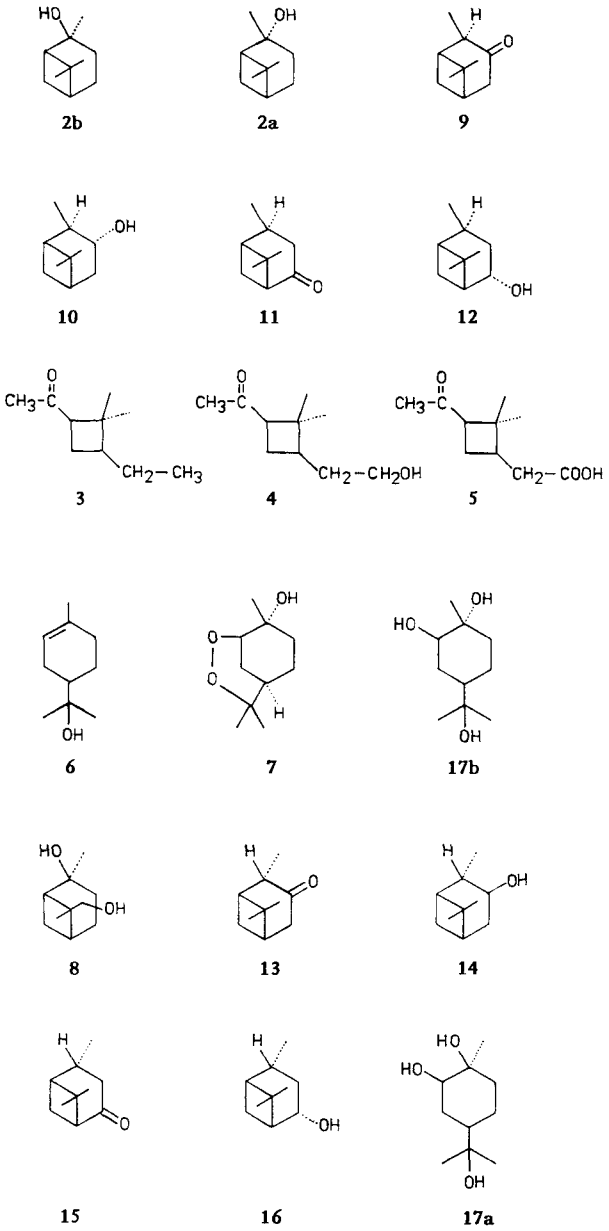
Table 1 shows that besides products of the attack of the tertiary C-H bond in 2-position also products of the attack of secondary C-H bonds in positions 3 (**9** and **10**) and 4 (**11** and **12**) are formed (isopinocampheol, isoverbanol and the corresponding ketones). Obviously, the secondary pinanyl radicals as also the tertiary 2-pinanyl radicals are attacked by molecular oxygen preferably from the less hindered direction trans to the dimethyl-methylene bridge. From the amounts of the reaction products formed at 100 °C one can evaluate the relative reactivities of one C-H bond in 3- and in 4-position with respect to the tertiary C-H bond in 2-position:

$k_{3\text{-sec}} : k_{tert} = 0.038$
$k_{4\text{-sec}} : k_{tert} = 0.017$

The relative reactivities of the secondary C-H bonds with respect to the tertiary C-H bond increase with increasing temperature due to the higher activation energy of an attack at secondary C-H bonds in comparison with an attack at tertiary C-H bonds.

We also studied the oxidation of trans-pinane **1b**. This compound contained 5 % cis-pinane which reacted far more rapidly than the trans-isomer. Therefore it was necessary to correct the amounts of reaction products in order to eliminate the products formed from cis-pinane. The corrected results of the oxidation of trans-pinane at 100 °C are shown in Table 2. Evidently the relative reactivities of the secondary C-H bonds with respect to the tertiary C-H bond are higher for trans- than for cis-pinane:

$k_{3\text{-sec}} : k_{tert} = 0.19$
$k_{4\text{-sec}} : k_{tert} = 0.20$



Formula Scheme 4 Formula of the products isolated after reduction of the oxidation mixtures of cis- and of trans-pinane (see Tables **1** and **2**)

This is due to the far lower reactivity of the cis-2-C-H bond in trans-pinane with respect to the trans-2-C-H bond in cis-pinane. The low reactivity of the cis-2-C-H bond is also responsible for the low relative reaction rate of trans-pinane with respect to cis-pinane. We determined $k_{cis} : k_{trans}$ by competitive oxidation of two different mixtures of the two isomers at 100 °C and found

$k_{cis} : k_{trans} = 6.2 \pm 0.4$ 1st experiment
$k_{cis} : k_{trans} = 6.6 \pm 0.4$ 2nd experiment.

Table 2 Oxidation of trans-pinane with molecular oxygen at 100 °C
Analysis of the reaction products after reduction with aqueous sodium sulphite.
Initial composition: 95 % trans-, 5 % cis-pinane
Final composition: 80,5 % trans-, 1,9 % cis-pinane
Yields corrected

product after Na_2SO_3 reduction	mole-%
trans-pinane-2-ol (**2a**)	5.1
cis-pinane-2-ol (**2b**)	16.9
pinocamphone (**13**)	11.4
pinocampheol (**14**)	10.4
verbanone (**15**)	9.1
verbanol (**16**)	12.9
1-acetyl-2,2-dimethyl-3-ethyl cyclobutane (**3**)	9.2
2-(1-acetyl-2,2-dimethyl-cyclobut-3-yl) ethanol (**4**)	6.3
α-pinoic acid (**5**)	11.7
α-terpineol (**6**)	1.0
4,4,8-trimethyl 2,3-dioxabicyclo[3.3.1]-nonane-8-ol (**7**)	1.9
trans-pinane-2,9-diol (**8**)	1.2
X	2.9

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Experimental

Preparation of cis- and trans-pinane

The cis-isomer was prepared from α-pinene by hydrogenation in a 2 l autoclave (80 °C/13 MPa; Raney-nickel as the catalyst). The trans-isomer was prepared by $LiAlH_4$-reduction of β-pinene [15, 16]. The cis-pinane had a purity of 94 % (the only impurity was trans-pinane), the trans-pinane had a purity of 95 % (impurity: 5 % cis-pinane).

Oxidation of cis-pinane

The oxidations were accomplished in a cylindrical glass vessel with a heating jacket. The oxidation vessel was equipped with a gas inlet tube (introduction of the oxygen through a glass frit), a thermometer and a reflux condenser. The gross volume of the oxidation vessel was 200 ml, it was filled with 100 ml (85 g) cis-pinane and thermostated to the temperature wanted.

Then a stream of 5 l h^{-1} oxygen was introduced into the oxidation apparatus. After definite times 0.5 ml samples were taken and exactly weighed; the hydroperoxide concentration was determined by iodometry [17]. The oxidations were finished when a pinane hydroperoxide concentration of about 15 weight % was reached.

Oxidation of trans-pinane

The oxidations were accomplished in a closed glass apparatus equipped with a heating jacket, a magnetic stirrer and a reflux condenser. The reflux condenser was connected with a 100 ml gas burette thermostated to 20 °C and filled with pure oxygen.

The gross volume of the closed oxidation vessel was 50 ml. The trans-pinane (10 ml, 8.5 g) was given into the oxidation apparatus and the heating jacket was connected with a thermostat heated to 100 °C. After an oxygen uptake of 290 ml (about 20 mmol per 100 mmol trans-pinane) the reaction was finished, and the hydroperoxide concentration was determined iodometrically.

Reduction of pinane oxidates with aqueous sodium sulphite

Into an 1 l flask, equipped with a stirrer, a dropping funnel and a reflux condenser, a solution of 80 g sodium sulphite in 500 ml water was given. The solution was heated to 60 °C, and then 80 ml of the pinane oxidate (exactly weighed) were added under stirring. The mixture was stirred for 4 h at 60 °C, then the organic phase was separated, and the aqueous phase was extracted twice with 50 ml ether each time. The organic phases were combined and dried over Na_2SO_4. The ether was distilled off, and the main part of the excess pinane was removed in vacuo. The residue was analyzed by gaschromatography.

The aqueous phase of the sulphite reduction was acidified with hydrochloric acid and extracted three times with 30 ml chloroform each time. The solvent was removed in vacuo, the remaining acids were esterified with diazomethane and analyzed gaschromatographically.

Hydrogenation of pinane oxidates over a palladium catalyst

The hydrogenation of the oxidates with about 15 weight-% hydroperoxy pinanes was accomplished at 50 °C/101.3 kPa in a continuously working reactor using a catalyst containing 2 % Pd on α-Al_2O_3. The liquid hourly space velocity was 0.1 h^{-1}, the reactor with a cooling jacket connected with a thermostat had a length of 60 cm and a diameter of 4.5 cm. The volume filled with the catalyst was 900 ml, the hydrogen flow was 100 l h^{-1}. The excess pinane was evaporated from the hydrogenated oxidates at 2 kPa (15 Torr). The mixture of the pinane-2-ols was isolated by distillation at 65 – 75 °C/0.13 kPa (1 Torr). The residue (about 5 % of the oxidation products) was analyzed gaschromatographically and contained p-menthane-1,2,8-triol (isomer B), trans-pinane-2,9-diol, 2-(1-acetyl-2,2-dimethylcyclobut-3-yl) ethanol and pinonic acid. 10 g of the residue were dissolved in 50 ml diethyl ether and extracted with 50 ml water. From the aqueous extract 2.3 g of a high-boiling mixture containing 90 % p-menthane-1,2,8-triol were obtained by evaporation of the water in vacuo. The organic layer was extracted with 50 ml of a 1 n aqueous NaOH solution. The aqueous extract was acidified and then extracted with chloroform. After evaporation of the chloroform 1.3 g of a residue containing 80 % pinonic acid was obtained. The ether solution after extraction with water and with aqueous NaOH was worked up by distillation. The fraction boiling at 100 – 140 °C/0.13 kPa (2.6 g) contained 30 % trans-pinane-2,9-diol and 40 % 2-(1-acetyl-2,2-dimethyl-cyclobut-3-yl) ethanol.

Gaschromatographic analyses

The pinenes and pinanes were analyzed using a 6 m column with 15 % SE 30 on chromatone N-super (100 °C; 2.51 h^{-1} H_2; heat conductivity detector). The retention times are collated in Table 3. The monofunctional oxidation products of the pinanes were analyzed using a 6 m column with 15 % polyester from phthalic acid and diethylene glycol, crosslinked with 1 % trimethylol propane (170 °C; 31 h^{-1} H_2; heat conductivity detector). For the retention times see Table 4.

Table 3 Retention times of the pinenes and pinanes (6 m column with 15 % SE 30 on Chromatone N-super; 100 °C; 2.51 h^{-1} H_2; heat conductivity detector)

compound	retention time (min)
α-pinene	14
trans-pinane	23
β-pinene	25
cis-pinane	26
p-cymene	29

The identification of the products was accomplished by comparison of their retention times with those of authentic samples. Moreover, all oxidation mixtures were also analyzed using the GC/MS System HP 5992B (Hewlett-Packard). The results could not be used for an exact quantitative determination of the products, but their unambiguous identification was possible by comparison of both the retention times and the mass spectra with those of authentic samples. In the case of the GC/MS analyses a 30 m × 0.3 mm capillary column with DB1 (SE 30) was used (100 °C; 2 ml min^{-1} He). The di- and trifunctional oxidation products were analyzed using a 6 m column with 15 % SE 30 on Chromatone N-super (200 °C; 31 h^{-1}; H_2; heat conductivity detector). The retention times are shown in Table 5. Also in this case the assignment of the peaks was accomplished by comparison with authentic samples. The unambiguous identification of the di- and trifunctional products took place by GC/MS analyses (capillary column 30 m × 0.3 mm with DB1 (SE 30); 100 – 200 °C/16 K min^{-1}; 2 ml min^{-1} He).

The methyl esters of the acidic reaction products were analyzed using the same conditions as for the di- and trifunctional products. The retention times are shown in Table 5.

Table 4 Retention times of the monofunctional oxidation products of the pinanes (after reduction with aqueous sodium sulphite)
(6 m column with 15 % polyester from phthalic acid and diethylene glycol, crosslinked with trimethylol propane, on Inertone N-super; 170 °C; 31 h^{-1} H_2; heat conductivity detector)

compound	retention time (min)
1-acetyl-2,2-dimethyl-3-ethyl-cyclobutane	3.7
trans-pinane-2-ol	5.7
cis-pinane-2-ol	7.3
pinocamphone	7.6
isopinocamphone	8.9
α-terpineol	9.3
pinocampheol	9.5
isopinocampheol	10.1
verbanol	10.1
isoverbanol	11.6
verbanone	11.9
isoverbanone	13.0

Table 5 Retention times of the di- and trifunctional oxidation products of the pinanes (after reduction with aqueous sodium sulphite; acid esterified with diazomethane) (6 m column with 15 % SE 30 on Chromatone N-super; 200 °C; 31 h $^{1}H_2$; heat conductivity detector)

compound	retention time (min)
1-acetyl-2,2-dimethyl-3-ethyl cyclobutane	3.5
cis-pinane-2-ol	4.0
2-(1-acetyl-2,2-dimethyl-cyclobut-3-yl) ethanol	8.4
α-pinonic acid methyl ester	8.8
trans-pinane-2,9-diol	10.3
p-menthane-1,2,8-triol (isomer A)	14.9
p-menthane-1,2,8-triol (isomer B)	16.5

The analysis of the 4,4,8-trimethyl-2,3-dioxabicyclo [3.3.1]nonane-8-ol in the oxidates reduced with sodium sulphite was difficult because of its decomposition under the conditions of the gaschromatography. The analysis was possible with the GC/MS system using the capillary column (30 m × 0.3 mm with DB1 (SE 30)) at 100 – 200 °C/16 K min with 2 ml min $^{-1}$ He. The temperature of the evaporator was fixed to 230 °C. The retention times are collated in Table 6. The quantitative determination of 4,4,8-trimethyl-2,3-dioxabicyclo[3.3.1]nonane-8-ol was possible by comparison of the total ion flow with that of 2-(1-acetyl-2,2-dimethyl-cyclobut-3-yl) ethanol after a calibration with test mixtures of the two compounds.

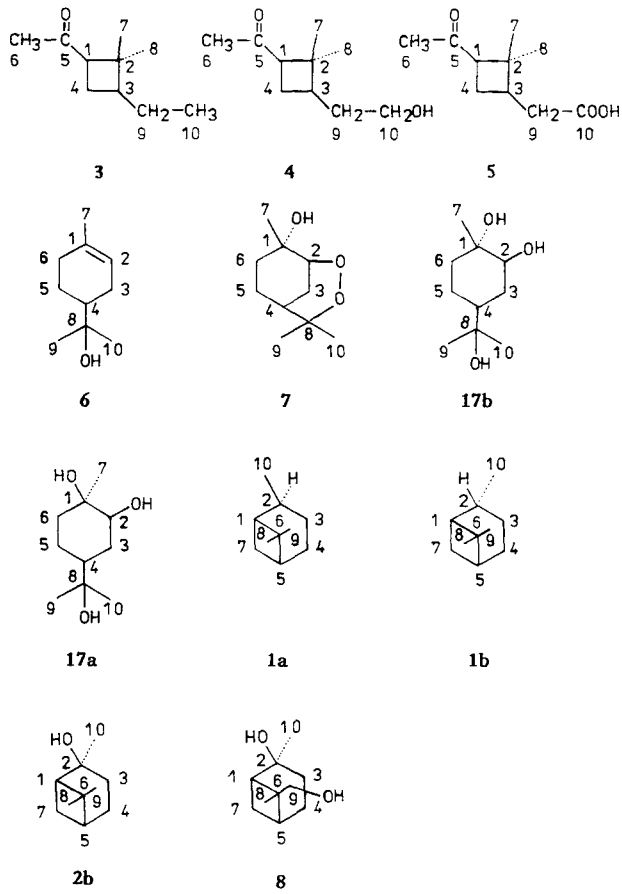
Isolation and identification of 4,4,8-trimethyl-2,3-dioxabicyclo[3.3.1]nonane-8-ol

This compound was enriched by vacuum distillation of an oxidation mixture obtained at 130 °C from cis-pinane and reduced with sodium sulphite. Thus 3.6 g of a colourless liquid boiling between 100 and 130 °C at 0.13 kPa was isolated.

This fraction was a mixture of 82 % 4,4,8-trimethyl-2,3-dioxabicyclo[3.3.1]nonane-8-α and 18 % 2-(1-acetyl-2,2-dimethylcyclobut-3-yl) ethanol. The structure of the isolated compound was elucidated by ^{13}C-NMR spectroscopy (Table 7).

Table 6 Retention times of some of the oxidation products of the pinanes (after reduction with aqueous sodium sulphite) using the GC/MS system HP 5992B (capillary column 30 m · 0.3 mm with DB 1 (SE 30); 100 – 200 °C/16 K min $^{-1}$; 2 ml min $^{-1}$ He; temperature of the evaporator 230 °C)

compound	retention time (min)
cis-pinane-2-ol	2.7
isopinocampheol	3.4
isoverbanol	3.8
4.4.8-trimethyl-2,3-dioxabicyclo[3.3.1]nonane-8-ol	7.0
2-(1-acetyl-2,2-dimethyl-cyclobut-3-yl) ethanol	7.4
trans-pinane-2,9-diol	8.3



Formula Scheme 5 Numbering of the C-atoms of those products whose ^{13}C-NMR spectra were taken (see Table 7)

The compound oxidized potassium iodide in acetic acid. The hydrogenation of 1 g of the isolated fraction over a palladium catalyst (methanol as the solvent) delivered isomer B of p-menthane-1,2,8-triol (^{13}C-NMR spectrum see Table 7). The same triol could also be isolated from a cis-pinane oxidate hydrogenated over a palladium catalyst at 50 °C/101.3 kPa by distillation in vacuo and extraction of the residue with water. The water extract was once washed with ether, then the water was evaporated in vacuo. The residue contained 90 % isomer B of p-menthane-1,2,8-triol; isomer A of the triol is formed by $KMnO_4$ oxidation of α-terpineol [18] (NMR-spectra of both isomers see Table 7).

Isolation and identification of trans-pinane-2,9-diol

This diol was isolated from a cis-pinane oxidate, hydrogenated over a Pd-catalyst at 50 °C/101.3 kPa, by distillation in vacuo, removal of the pinane and all products distilling at 65 – 75 °C/0.13 kPa), and extraction of the residue with water and with a sodium hydroxide solution. The remaining portion of the residue, insoluble both in water and in aqueous sodium hydroxide, was distilled in vacuo. The fraction boiling at 100 – 140 °C/00.13 kPa contained 30 % trans-pinane-2,9-diol and 40 % 2-(1-acetyl-2,2-dimethyl-cyclobut-3-yl) ethanol. The ^{13}C-NMR spectrum (Table 7) proved the structure of the pinane-2,9-diol. The trans-confi-

Table 7 ^{13}C-NMR spectra of some of the oxidation products of the pinanes (after reduction with aqueous sodium sulphite or hydrogenation over a palladium catalyst). Numbering see Formula Scheme 5

compound	^{13}C-signal (δ in ppm) for carbon atom										reference
	1	2	3	4	5	6	7	8	9	10	
1-acetyl-2,2-dimethyl-3-ethyl cyclobutane (**3**)	54.0 53.6	43.2 42.8	44.1 43.6	23.0 22.6	207.5 207.2	30.8 30.4	17.0 16.5	30.0 29.7	23.0 22.6	11.9 11.5	[7]
2-(1-acetyl-2,2-dimethyl-cyclobut-3-yl) ethanol (**4**)	54.0 54.3	43.2 43.2	37.9 38.8	23.0 23.1	207.5 208.1	30.8 30.5	17.0 17.1	30.0 30.0	33.1 33.2	60.9 60.8	calculated
α-pinonic acid (**5**)	53.6 54.0	42.9 43.1	36.7 37.6	22.7 22.9	207.5 207.8	30.8 29.9	16.6 17.0	29.6 29.9	34.0 34.7	177.9 177.5	calculated
α-terpineol (**6**)	133.3 132.9	120.9 120.0	27.0 26.8	45.0 44.7	24.0 23.8	31.1 31.0	23.3 23.1	72.2 72.4	27.3 27.2	26.0 26.0	[22]
p-menthane-1,2,8-triol (isomer B) (**17b**)	74.0 74.6 s	75.8 77.3 d	30.0 32.8 t	47.8 47.6 d	25.6 24.7 t	37.5 38.8 t	20.5 18.7 q	72.3 73.0 s	27.1 27.1 q	26.7 26.6 q	calculated
p-menthane-1,2,8-triol (isomer A) (**17a**)	73.9	76.2	31.5	48.1	27.1	37.9	24.8	72.3	27.1	26.7	
4,4,8-trimethyl-2,3-dioxabicyclo[3.3.1]-nonane-8-ol (**7**)	71.4 s	81.5 d	24.5 t	32.6 d	23.6 t	35.4 t	27.9 q	81.4 s	24.5 q	24.4 q	
cis-pinane (**1a**)	48.1 48.2	36.0 36.0	23.8 23.9	26.5 26.6	41.3 41.5	38.7 38.8	33.9 34.0	28.2 28.3	23.1 23.2	22.8 22.9	[23]
trans-pinane (**1b**)	47.8 47.8	29.5 29.4	24.0 24.0	23.2 23.1	41.0 41.0	39.5 39.5	24.7 24.7	26.9 26.8	20.1 20.1	21.6 21.6	[24]
trans-pinane-2-ol (**2b**)	53.8 d	76.2 s	32.1 t	24.4 t	40.9 d	38.4 s	28.5 t	27.6 q	23.6 q	31.7 q	[24]
trans-pinane-2,9-diol (**8**)	51.6 d	75.3 s	32.1 t	23.9 t	39.2 d	41.6 s	27.6 t	22.9 q	66.4 t	30.8 q	

guration is not exactly proven by the ^{13}C-NMR-spectrum but it follows from the mechanism of the formation of the diol by an intramolecular H transfer.

^{13}C-NMR spectroscopy

The ^{13}C-NMR spectra were taken using an apparatus Bruker HX 90R. The preferred solvent was $CDCl_3$, only for the p-menthane-1,2,8-triols D_2O was used. The standard was hexamethyl disiloxane (δ = 1.91 ppm). In some cases it was necessary to find out the multiplicity of the signals. In these cases the APT spectra were taken using an apparatus Bruker Ac 250.

In order to calculate the ^{13}C-NMR spectra of 2-(1-acetyl-2,2-dimethylcyclobut-3-yl) ethanol and α-pinoic acid on the basis of the known spectrum of 1-acetyl-2,2-dimethyl-3-ethyl cyclobutane [7] we used the increment system collated in Table 8 [19, 20].

Another increment system (Table 9) [19, 21] was used for the calculation of the chemical shifts in the p-menthane-1,2,8-triols from the spectrum of one of the diasteromers taken by us. The estimated chemical shift of the methyl group in position 7 is lower for **17b** than for **17a** (difference 4.3 ppm). In the case of these compounds we supposed that the 2-hydroxyisopropyl group is always present in the equatorial position.

Table 8 Increments for the estimation of ^{13}C-NMR shifts in aliphatic compounds [19, 20]

substituent	increments for the shift (ppm) in position				shift (ppm) for the substituent
	1	2	3	4	
CH_3	9.1	9.4	−2.5	0.4	
OH	49.0	10.1	−6.2	0.0	
COOH	20.1	2.0	−2.8	0.0	177.9

Table 9 Increments for the estimation of the ^{13}C-NMR shifts in derivatives of cyclohexane [19, 21]

sub-stituent	position	increments for the ^{13}C-NMR shift (ppm) in position			
		1	2	3	4
CH_3	equatorial	6.0	9.0	0.1	−0.2
	axial	1.4	5.4	−6.4	−0.1
OH	equatorial	42.6	8.5	−1.7	−1.0
	axial	37.9	5.3	−6.7	−0.6

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