

## Copaborneol, Constitution and Synthesis\*

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Copaborneol has been found to possess the structure (1) by chemical and spectroscopic investigations. This has been confirmed by a synthesis from santalol.

Copaborneol (1) is the major sesquiterpene alcohol occurring in the wood of *Pinus silvestris* L.<sup>1</sup> and in Swedish sulphate turpentine.<sup>2</sup> Preliminary reports described the elucidation of its structure based on its chemical and spectroscopic properties<sup>3</sup> and on a stereospecific synthesis from santalol.<sup>4</sup> In this paper, the details of this work will be presented.

Copaborneol was shown to be a saturated, secondary alcohol by a tetranitromethane test and by treatment with ozone at  $-80^{\circ}$ , which gave copacamphor (2). This ketone was more conveniently obtained by Jones'<sup>5</sup> oxidation of copaborneol. Reduction of copacamphor with sodium in ethanol gave the original alcohol, but on lithium aluminium hydride reduction, the main product formed was an isomeric alcohol, copaisoborneol (3).

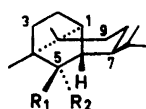
On treatment with bromobenzenesulphonyl (brosyl) chloride in pyridine at room temperature, copaborneol gave a crystalline brosylate. When a pyridine solution of this ester was heated, a mixture of hydrocarbons was obtained. The major component was isolated by chromatography on silver nitrate-silica gel. The IR and NMR (see Table 1) data were very similar to those reported for sativene (4).<sup>6</sup> However, the hydrocarbons were not identical, as different diols were obtained on osmium tetroxide oxidation. Apparently, the hydrocarbons differ only by being epimeric at C-7. The configuration of sativene at C-7 shown in formula (4), "ylangocamphene", is obvious from its partial<sup>6</sup> and total<sup>7</sup> syntheses. On this basis the new hydrocarbon should have the copacamphene structure (5) and hence copaborneol structure (1). The course of the elimination reaction of copabornyl brosylate is analogous to similar transformations of bornyl and isobornyl derivatives (*cf. e.g.* Ref. 8).

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Table 1. NMR data for copaborneol and related compounds.

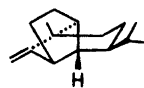
Structural unit	$\delta$ ppm	$J$ Hz	Signal pattern	Number of protons
<i>Copaborneol (1)</i>				
Isopropyl	0.84	6	doublet	
	0.90	6	doublet	6
Quaternary methyl	0.82		singlet	6
Carbinol methine	3.41		singlet, broad	1
<i>Copaisoborneol (3)</i>				
Isopropyl	0.90	5.5	doublet	6
Quaternary methyl	0.78		singlet	3
	0.86		singlet	3
Carbinol methine	3.59	8	doublet	1
<i>Copacamphene (5)</i>				
Isopropyl	0.90	5.5	doublet	6
Quaternary methyl	1.01		singlet	3
Allylic proton	2.47		multiplet, unres.	1
Olefinic proton	4.50		singlet	1
	4.78		singlet	1
<i>Sativene (4) <sup>a</sup></i>				
Isopropyl	0.87	5	doublet	3
	0.90	5	doublet	3
Quaternary methyl	1.05		singlet	3
Olefinic proton	4.40		singlet	1
	4.72		singlet	1



- 1  $R_1 = \text{OH}; R_2 = \text{H}$   
 2  $R_1 R_2 = \text{O}$   
 3  $R_1 = \text{H}; R_2 = \text{OH}$



4

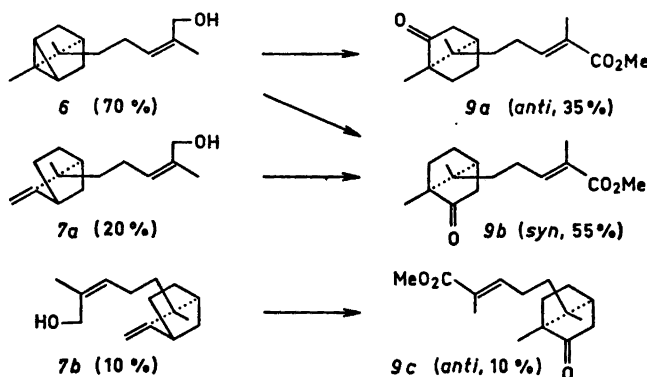


5

The NMR data (60 and 100 MHz) of copaborneol and its derivatives support the assigned structures (Table 1). The signal pattern of the isopropyl protons of copaborneol was obvious only at 100 MHz. The broadening of the carbinol methine singlet was probably due to coupling to the vicinal proton at C-6 and long-range coupling to the *exo*-proton at C-3 (for similar "W-coupling" in borneol, *cf.* Ref. 9). In accord with this interpretation, the corresponding signal in the spectrum of copaisoborneol is a relatively sharp doublet.

The chemical and spectroscopic investigations of copaborneol described above do not definitely establish that it has structure (I), but this has been proved by synthesis.

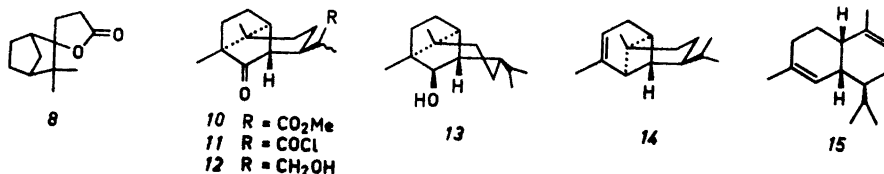
The starting material employed was a commercial mixture of (+)- $\alpha$ -santalol (6) and (-)- $\beta$ -santalol (7) (ratio *ca.* 70:30). Selenium dioxide oxidation gave a mixture of santalals. According to the NMR spectrum of this product (for NMR spectra of similar unsaturated aldehydes, *cf.* Ref. 10) the configuration at the double bond had been inverted during the oxidation. When manganese dioxide was used instead of selenium dioxide, the configuration was found to be partially retained. As this stereochemical point was unimportant for the outcome of the synthesis, the more convenient (see Experimental) selenium dioxide procedure was used. The santalal mixture was oxidised with silver oxide and the product formolysed (*cf.* Ref. 11). The silver oxide oxidation resulted in partial degradation of the side chain, presumably *via* a retroaldol condensation. During the formolysis the product of this side-reaction was converted into a mixture of lactones mainly consisting of (8)<sup>12</sup> which was removed from the desired C<sub>15</sub>-products simply by partitioning between ether and aqueous sodium bicarbonate. Hydrolysis followed by Jones' oxidation and esterification gave after chromatography a mixture of stereoisomeric oxo esters. These could not be separated by thin layer chromatography.



Scheme 1

Natural  $\beta$ -santalol appears<sup>13</sup> to be a mixture of the stereoisomers (7a) and (7b) (ratio *ca.* 70:30). On this basis the expected composition of the oxo ester mixture would be as shown in Scheme I. The NMR spectrum confirmed that the oxo ester mixture consisted of roughly equal quantities of *syn*- and *anti*-isomers. The methoxycarbonyl protons gave two signals ( $\delta$  3.64 and 3.67, *ca.* 1.5 H each). A singlet at  $\delta$  0.98 (*ca.* 1.5 H) was assigned to the protons of the C-10 methyl group in the *syn*-isomer (9b), while the C-4 methyl protons of this isomer as well as the C-4 and C-10 methyl protons of the antipodal *anti*-isomers (9a) and (9c) gave overlapping signals appearing as a somewhat broad singlet at  $\delta$  0.86 (*ca.* 4.5 H) (for chemical shifts of the methyl protons of camphor, *cf.* Ref. 14).

When the mixture of the unsaturated *syn* and *anti* oxo esters (9) was treated with potassium *tert.*-butoxide in dioxan at room temperature, the *syn* isomer was rapidly cyclised, while the *anti* isomers remained virtually unchanged. The saturated oxo ester (10) formed was separated from the unsaturated *anti* oxo esters by silica gel chromatography, (overall yield from the mixture of  $\alpha$ - and  $\beta$ -santalol *ca.* 5 %). The NMR spectrum showed that this product was a mixture of stereoisomers (ratio *ca.* 1:1). The methoxycarbonyl protons gave two singlets ( $\delta$  3.60 and 3.62) and the signals from the C-11 methyl protons appeared as two doublets ( $\delta$  1.11 and 1.13, each with  $J$  6.5 Hz).



Attempts to protect the keto group of the oxo ester (10) by ketalisation were unsuccessful. However, because of the low reactivity of this keto group, it was found to be unnecessary to protect it during the ensuing transformation of the methoxycarbonyl group into a methyl group. Alkaline hydrolysis followed by treatment with thionyl chloride in benzene yielded the oxo acid chloride (11), which was reduced with sodium borohydride in dioxan at room temperature. The hydroxy ketone (12) obtained was treated with methanesulphonyl chloride in pyridine. Lithium aluminium hydride reduction of the crude oxo methanesulphonate took place in the expected manner to yield an alcohol [overall yield from oxo ester (10), *ca.* 30 %], identical with copaisorneol (3).

The synthetic copaisorneol, on chromic acid oxidation, gave copacampbor (2), which was reduced with sodium in alcohol to yield copaborneol, identical in all respects with the natural product.

A single copaborneol isomer was obtained in spite of the fact that the saturated oxo ester (10) was a mixture of stereoisomers. Thus, the cyclisation of the unsaturated oxo ester (9b) must have been stereospecific with respect to the configuration at C-7 in the product (10), and the latter must have consisted of C-11 epimers.

Although stereospecific, the synthesis is not informative of whether the configuration at C-7 is as shown in formula (1) or reversed (13). Fortunately, this point was settled by the chemistry of copaborneol. As mentioned above, dehydration gave a hydrocarbon not identical with sativene (4), which would have been obtained if the alcohol had possessed structure (13).

As (+)- $\alpha$ -santalol (6) has been synthesised from (+)-camphor, the present synthesis formally is a total synthesis of copaborneol, which proves its structure and absolute configuration shown in formula (1). This configuration is in accord with its plausible biogenetic relationship to copaene (14) and the muurolenes, *e.g.*  $\alpha$ -muurolene (15), the major sesquiterpenes of *Pinus silvestris*, which possess the absolute configurations <sup>15,16</sup> indicated.

## EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer No. 237 grating instrument (sample as liquid film unless otherwise stated) and NMR spectra on Varian A60 and HA100 instruments (solvent carbon tetrachloride, internal standard tetramethyl silane). For gas-liquid chromatography (GLC) a PYE argon chromatograph (column length 1.2 m, inner diameter 4 mm, 1 % Reoplex 470 on Chromosorb W, 80–100 mesh) was used.

Rotations were taken in chloroform. Light petroleum refers to the fraction b.p. 40–60°.

Copaborneol, m.p. 47.5–48°, was isolated from Swedish sulphate turpentine as previously described.<sup>2</sup>

*Oxidation of copaborneol.* a. Jones' reagent<sup>5</sup> (1.55 ml of a solution made up from chromium trioxide, 17.5 g, water, 50 ml, and conc. sulphuric acid, 4.8 ml) was added with stirring during 0.5 h to a solution of copaborneol (1.30 g) in acetone (2 ml). After 1 h the reaction mixture was diluted with water and extracted with ether. The ether extract was washed with aqueous sodium bicarbonate, dried over sodium sulphate and the solvents evaporated. The residue (1.20 g) was chromatographed on silica gel (40 g, eluent 10 % ether in light petroleum). After 100 ml had been collected, the next portion (150 ml) eluted *copacamphor* (2) (0.93 g, pure according to TLC and GLC),  $[\alpha]_D +98.7^\circ$  (c 1.7),  $\nu_{\max}$  1738  $\text{cm}^{-1}$ . (Found: C 81.5; H 10.9.  $\text{C}_{15}\text{H}_{24}\text{O}$  requires C 81.8; H 11.0).

b. Copaborneol (28 mg) in ethyl acetate (1 ml) was treated with ozone at  $-78^\circ$  during 0.5 h. Excess ozone was removed by a stream of nitrogen. Evaporation and chromatography as above gave *copacamphor* (13 mg).

*Sodium/alcohol reduction of copacamphor.* Copacamphor (75 mg) was dissolved in ethanol (absolute, 0.5 ml) and sodium (10 mg) was added under cooling. The mixture was refluxed for a few minutes, cooled, diluted with water and extracted with light petroleum. After washing with water, the light petroleum solution was dried (sodium sulphate) and the solvent evaporated. The crude product (95 mg) was chromatographed on silica gel (5 g, eluent 5 % ether in light petroleum). After 70 ml had been collected, the next portion (50 ml) eluted copaborneol (24 mg), m.p. and mixed m.p. 49–50°.

*Lithium aluminium hydride reduction of copacamphor.* A mixture of copacamphor (0.25 g), lithium aluminium hydride (45 mg) and dry ether (10 ml) was refluxed for 1 h under nitrogen. Excess hydride was decomposed by dropwise addition of water. Dilute hydrochloric acid was added, and the aqueous layer was extracted with ether. The ether extract was washed with aqueous sodium bicarbonate, dried (sodium sulphate) and the ether evaporated. The residue (0.24 g) was chromatographed on silica gel (8 g, eluent 5 % ether in light petroleum). After 60 ml had been collected, the next portion (40 ml) eluted pure (TLC, GLC) *copaisoborneol* (3) (0.20 g),  $[\alpha]_D +15.3$  (c, 2.0),  $\nu_{\max}$  3470, 1103 and 1069  $\text{cm}^{-1}$ . (Found: C 81.0; H 11.7.  $\text{C}_{15}\text{H}_{26}\text{O}$  requires C 81.0; H 11.8). Elution with ether (10 %) in light petroleum gave copaborneol (16 mg), m.p. and mixed m.p. 42–45°.

*Copacamphene* (5). Copaborneol (0.50 g) in pyridine (10 ml) was treated with brosyl chloride (0.56 g) at room temperature for 15 h. Water was added, and the mixture was extracted with ether. The extract was washed with dilute hydrochloric acid, dried and the solvent removed. The crystalline residue melted at 66–68° after recrystallisation from light petroleum. The crude residue in pyridine (10 ml) was heated at 90° for 2 h and the mixture worked up as above. The crude product (0.39 g) was chromatographed on silica gel-silver nitrate<sup>17</sup> (12 g, eluent light petroleum). In the first fraction (25 ml) a mixture of hydrocarbons (40 mg), probably (IR, NMR) with cyclopropane ring and tetrasubstituted double bond, was obtained. After a further 25 ml fraction had been collected, the next portion (75 ml) eluted pure (TLC, GLC) *copacamphene* (5) (0.14 g),  $[\alpha]_D +28.9^\circ$  (c, 1.2),  $\nu_{\max}$  3075, 1657 and 877  $\text{cm}^{-1}$ . (Found: C 88.2; H 11.8.  $\text{C}_{16}\text{H}_{24}$  requires C 88.2; H 11.8).

*Osmium tetroxide oxidation of copacamphene.* Copacamphene (80 mg) in pyridine-dioxan (7:1, 3.5 ml) was treated with osmium tetroxide (120 mg) at room temperature for 30 days. Ethanol (95 %, 5 ml) was added and the solution was purged with hydrogen sulphide. After 10 h at room temperature the solution was filtered and the filtrate evaporated to give crude diol (72 mg). Chromatography on alumina (basic, activity III, 5 g, eluent ether) gave copacamphene (4 mg) and pure *diol* (63 mg), m.p. 46–47° (vacuum sublimed),  $[\alpha]_D -30^\circ$  (c, 0.5). (Found: C 75.4; H 10.8.  $\text{C}_{16}\text{H}_{26}\text{O}_2$  requires C 75.6; H 11.0).

*Selenium dioxide oxidation of santalol.* A mixture of (+)- $\alpha$ -santalol and  $\beta$ -santalol (Fluka, ratio ca. 70:30 according to GLC, 20.0 g) was added to a solution of selenium dioxide (7.0 g) in ethanol (95 %, 400 ml), and the mixture was refluxed for 2.5 h. Most of the ethanol was evaporated, water (200 ml) was added and the mixture extracted with ether. The extract was washed with aqueous sodium bicarbonate, dried (sodium sulphate) and evaporated to give a yellow oil (20.5 g). A sharp singlet in the NMR spectrum at  $\delta$  9.36 (ca. 1 H) indicated<sup>10</sup> that only unsaturated aldehydes with *trans* double bonds were present in the mixture.

*Manganese dioxide oxidation of santalol.* The above santalol mixture (0.50 g) in light petroleum (10 ml) was stirred with activated<sup>18</sup> manganese dioxide (2.0 g) for 4 h. Starting material was still present, but this was not consumed on continued stirring. The aldehydic products were isolated by rapid chromatography on deactivated (10 % water) silica gel. The NMR spectrum of the mixture obtained showed a sharp singlet at  $\delta$  9.36 (ca. 0.3 H) and at 9.97 (ca. 0.7 H) indicating<sup>10</sup> that both *cis* and *trans* unsaturated aldehydes were present.

*Silver oxide oxidation of santalol.* The crude product from the above selenium dioxide oxidation (20.3 g) in methanol (900 ml) was added to a solution of silver nitrate (60 g) in water (340 ml). To this was added with stirring during 45 min a solution of sodium hydroxide (19.2 g) in water (300 ml). After 4 h the solution was filtered and the precipitate thoroughly washed with hot water. The combined filtrate and washings were diluted with water to ca. 2 l, the solution extracted with ether, the ether extract washed with water and dried. Evaporation gave a neutral fraction (3.2 g), which was not investigated. The alkaline water solution was acidified with dilute sulphuric acid and extracted with ether. After drying (sodium sulphate) the extract was evaporated to give an acid fraction (13.3 g). The IR bands at 1719 and 1737  $\text{cm}^{-1}$  ( $\text{CCl}_4$ ) of a small sample esterified with ethereal diazomethane indicated that it was a mixture of santalic acids and saturated (presumably  $\text{C}_{11}$ ) acids.

*Preparation of the unsaturated oxo esters (9) (mixture of stereoisomers).* A solution of the crude acid fraction from the above silver oxide oxidation (13.2 g) in formic acid (98 %, 20 ml) was kept at room temperature for 36 h and then at 45° for 8 h. Ether was added, and the solution was washed with several small portions of saturated aqueous sodium chloride. The ethereal solution was then extracted with saturated aqueous sodium bicarbonate, dried over sodium sulphate and evaporated. The crystalline product (4.83 g) gave after recrystallisation from light petroleum the lactone (8),<sup>12</sup> m.p. 103°,  $\nu_{\text{max}}(\text{CCl}_4)$  1777  $\text{cm}^{-1}$ . The alkaline extract was acidified with dilute sulphuric acid, saturated with sodium chloride and extracted with ether. The ether extract was dried and evaporated and the residue (7.34 g) hydrolysed by refluxing for 1 h in a mixture of ethanol (95 %, 20 ml) and aqueous sodium hydroxide (2 M, 50 ml). After cooling ice was added, the mixture acidified with dilute sulphuric acid, saturated with sodium chloride and extracted with ether. The extract was dried (sodium sulphate) and the ether evaporated. The crude product (6.82 g) in acetone (30 ml) was oxidised by adding Jones' reagent<sup>5</sup> (see above) (8.0 ml) during 40 min at -5° with stirring. After 0.5 h at 0° water was added and the mixture extracted with ether. After washing with water, the ether extract was dried and evaporated. Fischer esterification of the crude product gave a mixture of methyl esters (6.11 g). This was chromatographed on silica gel (180 g, eluent 30 % ether in light petroleum) to give the *unsaturated oxo ester (9)* (3.05 g, TLC: one spot) as a mixture of stereoisomers,  $\nu_{\text{max}}$  1744, 1718 and 1650  $\text{cm}^{-1}$ , NMR signals at  $\delta$  0.86 (ca. 4.5 H, singlet) 0.98 (ca. 1.5 H, singlet), 3.64 (ca. 1.5 H, singlet), 3.67 (ca. 1.5 H, singlet) and 6.65 (1 H, triplet of doublets,  $J$  6.5 and 1.5 Hz). (Found: C 72.5; H 9.2.  $\text{C}_{16}\text{H}_{24}\text{O}_3$  requires C 72.7; H 9.2).

*Cyclisation of the unsaturated oxo ester (9).* The mixture of stereoisomeric oxo esters (9) (2.95 g) was dissolved in dioxan (dry, 100 ml) and potassium *tert.* butoxide (freshly sublimed, 0.50 g) was added to the stirred solution in an atmosphere of dry nitrogen. After further stirring at room temperature for 45 min water was added, the solution was acidified with dilute sulphuric acid and then extracted with ether. The extract was washed with water, dried and evaporated. The residue (2.90 g) was chromatographed on silica gel (200 g, deactivated with 8 ml water, eluent 10 % ether in light petroleum). After 1600 ml had been collected, the next portion of the same solvent (1400 ml) eluted a mixture of unchanged unsaturated oxo esters [ $\nu_{\text{max}}(\text{CCl}_4)$  1742, 1718, 1648 and 1283  $\text{cm}^{-1}$ ] (1.12 g). Further elution with 20 % ether in light petroleum gave the *saturated*

oxo ester (10) (1.24 g),  $\nu_{\max}(\text{CCl}_4)$  1744, 1735 (shoulder) and  $1165\text{ cm}^{-1}$ , NMR signals at  $\delta$  0.88 (3H, singlet), 0.91 (3H, singlet), 1.11 (ca. 1.5 H, doublet,  $J$  6.5 Hz), 1.13 (ca. 1.5 H, doublet,  $J$  6.5 Hz), 3.60 (ca. 1.5 H, singlet) and 3.62 (ca. 1.5 H, singlet). (Found: C 72.7; H 9.3.  $\text{C}_{16}\text{H}_{24}\text{O}_3$  requires C 72.7; H 9.2).

*Preparation of the hydroxyketone (12).* A solution of the oxo ester (10) (1.00 g) in ethanol (95 %, 100 ml) and aqueous sodium hydroxide (2 M, 100 ml) was refluxed for 1.5 h. The solution was cooled, acidified with dilute sulphuric acid, saturated with sodium chloride and extracted with ether. The ethereal solution was washed with saturated aqueous sodium chloride, dried and evaporated. The crude product (0.85 g) and thionyl chloride (10 ml) in benzene (dry, 100 ml) were refluxed for 2 h. Solvent and excess thionyl chloride were evaporated under reduced pressure. The residue was dissolved in dioxan (dry, 60 ml), sodium borohydride (1.45 g) was added and the mixture was stirred for 15 h. Aqueous sodium hydroxide (2 M, 30 ml) and ethanol (95 %, 30 ml) were added and the mixture was heated at  $100^\circ$  for 1 min. After cooling, water was added, the solution saturated with sodium chloride and extracted with ether. The extract gave after drying and evaporation crude hydroxyketone (0.75 g). This was chromatographed on silica gel (25 g, eluent ether-light petroleum 1:1) to give the hydroxyketone (12) (0.43 g),  $\nu_{\max}(\text{CCl}_4)$  3640, 3460 and  $1744\text{ cm}^{-1}$ , NMR signals at  $\delta$  0.90 (6 H, singlet), 0.93 (3 H, doublet,  $J$  6.5 Hz) and 3.47 (2 H, broad singlet). (Found: C 76.1; H 10.4.  $\text{C}_{15}\text{H}_{24}\text{O}_2$  requires C 76.2; H 10.2).

*Copaisoborneol (3) from the hydroxyketone (12).* The hydroxyketone (73 mg) was dissolved in pyridine (1 ml) and methane sulphonyl chloride (75 mg) was added. The solution was heated at  $45^\circ$  for 1 h. Ether followed by a small amount of aqueous sodium hydroxide (0.5 M) was added and the mixture was shaken for 1 min. After acidification (2 M hydrochloric acid) the layers were separated and the aqueous phase was extracted with ether. The combined ether solutions were dried (sodium sulphate) and evaporated. The crude product (81 mg) was dissolved in tetrahydrofuran (dry, 2.5 ml) and lithium aluminium hydride (100 mg) was added. The mixture was stirred under nitrogen at  $45^\circ$  for 1 h and then cooled in ice. Water was added dropwise, followed by aqueous sulphuric acid (2 M). The product was extracted with ether, the extract washed with aqueous sodium bicarbonate (saturated), dried and evaporated. Filtration on silica gel (2 g, eluent benzene) and distillation gave copaisoborneol (36 mg, pure according to GLC and TLC),  $[\alpha]_{\text{D}} +16.9^\circ$  (c 1.5). The IR and NMR spectra were identical with those of copaisoborneol derived from natural copaborneol.

*Conversion of synthetic copaisoborneol into copaborneol.* Synthetic copaisoborneol (20 mg) was oxidised with Jones' reagent as described above for copaborneol. The crude product was reduced with sodium in ethanol as for copacamphor (see above). From the reduction product copaborneol (6 mg) was isolated by preparative TLC (eluent 2 % ether in benzene) followed by distillation. It crystallised on seeding with natural copaborneol, m.p. and mixed m.p.  $46-48^\circ$ , IR spectra identical.

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