

The Configuration of *endo*-Dehydro-norborneol and α -Norborneol

PEKKA HIRSJÄRVI

Institute of Chemistry, University of Helsinki, Finland

The 5-hydroxy-*cyclopentane*-1,3-*cis*-dicarboxylic acid (5-hydroxy-norcamphoric acid), m.p. 169–170°, prepared by permanganate oxydation and hydrolysis of the so called "*endo*"-dehydro-norbornyl acetate, is a *cis*-hydroxy acid according to the intramolecular hydrogen bonding verified by the author on the infrared absorption spectra of its dimethylester in carbon tetrachloride. From this configuration it follows that "*endo*"-dehydro-norborneol and α -norborneol, its hydrogenation product, have both an *endo*-configuration, as has been generally supposed, but never established. The "*endo*"-dehydro-norbornyl acetate prepared through diene syntheses of vinyl acetate and *cyclopentadiene*, used as starting material in this work, was catalytically hydrogenated. The hydrolysis product of the hydrogenation product was composed of 75.3 % α -norborneol and 24.7 % β -norborneol on the basis of the infrared spectral analysis. The effect of an addition of boric acid on the electrical conductivity of the solutions of the 5-hydroxy-norcamphoric acid (m.p. 169–170°) in water was investigated. The results are discussed.

In a previous paper¹ a method to investigate the *cis-trans*-configurations of β -hydroxy-*cyclopentane*-carboxylic acid esters was presented. With this method based on the verification of the intramolecular hydrogen bond formation by means of the infrared absorption spectra, I have now investigated the dimethylester of the 5-hydroxy-norcamphoric acid, prepared by permanganate oxydation of the so called "*endo*"-dehydro-norbornyl acetate*.

The "*endo*"-dehydro-norbornyl acetate is prepared from vinyl acetate and *cyclopentadiene* through diene syntheses³. Owing to the general spectroscopic course (cf. Ref. ⁴) of the diene syntheses proved by them on other classes of adducts only⁵, Alder and Rickert³ supposed that this compound analogically has *endo*-configuration. The hydrogenation of "*endo*"-dehydro-norborneol yields α -norborneol⁶. Applying their *exo*-addition theory to the catalytic hydrogenation of norcamphor, Alder and Stein⁷ drew the conclusion that

* A reaction carried out previously by others in this laboratory².

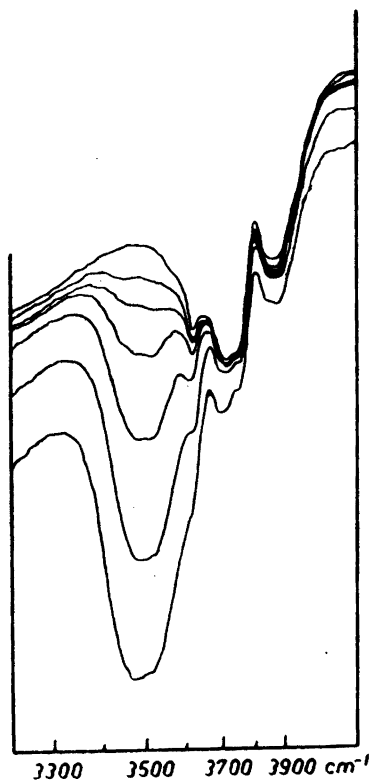


Fig. 1. Infrared absorption spectra of 0.0224–0.0007 M solutions of the 5-hydroxy-norcamphoric acid dimethylester (prepared from the endo-dehydro-norbornyl acetate) in CCl_4 and that of the solvent in the region of 3 200–3 900 cm^{-1} .

α -norborneol must have *endo*-configuration, whereas the "endo"-dehydro-norborneol and its acetate must have *endo*-configuration. Direct evidence for the configurations of norborneols and dehydro-norborneols has not been presented; Alder and Stein⁷, however, have communicated that they are (1936) studying the configuration of α -norborneol in order to prove it. Their method seems possible in theory, but so far no results have been published.

In the Bertram-Walbaum-reaction of a mixture of norbornylene and nortricyclene β -norbornyl acetate is obtained⁸. On the basis of this fact the conclusion may be drawn that the latter has *exo*-configuration (*cf.* Ref. ⁹).

According to H. Toivonen¹⁰ the oxydation of α -norborneol with concentrated nitric acid yields norcamphor, whereas β -norborneol in the same circumstances yields nitric acid ester. Further, according to H. Toivonen¹¹ the *endo*-form of the terpene alcohols for which the *endo-exo*-configurations are chemically explained, *viz.* for borneol, *isoborneol*¹², α -fenchol and β -fenchol¹³, is oxidised with nitric acid to the corresponding ketone, while the *exo*-form is esterified. In this reaction thus α -norborneol behaves like the aforementioned *endo*-alcohols and β -norborneol like their *exo*-forms.

To check the steric purity of the starting material in this work a part of the dehydro-norbornyl acetate used was hydrogenated and hydrolysed. Ac-

Table 1. Transmission of the solution of 5-hydroxy-norcamphoric acid dimethylester in OCl_4 on hydrogen bonded O-H-absorption band ($3\ 468\ \text{cm}^{-1}$) (Fig. 1).

| Concentration mole \cdot l $^{-1}$ | $\log_{10} \frac{P}{P_0}$ | k l \cdot mole $^{-1}$ |
|---|---------------------------|-------------------------------|
| 0.0224 | 0.150-1 | 38.0 |
| 0.0112 | 0.574-1 | 38.0 |
| 0.0056 | 0.789-1 | 37.7 |
| 0.00280 | 0.8965-1 | 37.0 |
| 0.00140 | 0.9474-1 | 37.6 |
| 0.00070 | 0.9731-1 | 38.5 |

According to the infrared spectral analysis¹⁴ the product was composed of 75.3% α -norborneol and 24.7% β -norborneol (cf. Ref. 4). 33.9% of the crystalline, in ether very slightly soluble 5-hydroxy-norcamphoric acid isomer (m.p. 169–170°) was isolated from the permanganate oxydation product of the dehydro-norbornyl acetate. On the basis of the amount of the yield this isomer can arise only from the dehydro-norbornyl acetate of the α -norborneol series.

The infrared absorption spectra of 5-hydroxy-norcamphoric acid dimethylester (0.0224–0.0007 M solutions in carbon tetrachloride) in the region 3 900–3 200 cm^{-1} investigated in this work are given in Fig. 1. The absorption band of the (hydrogen-)bonded hydroxyl group is here broader (double (?) 3 468, 3 515 cm^{-1}) than in the case of the 5-*cis*-hydroxy-*isofenchoic* acid dimethylester and 5-*cis*-hydroxy-camphoric acid dimethylester¹. Even in such a small concentration as 0.00070 M one cannot with certainty verify the absorption band of the free hydroxyl group (in the region of 3 600–3 640 cm^{-1}).

The values of $\frac{P}{P_0}$ were obtained from the center of the 3 468 cm^{-1} absorption band in the spectra given and the values of the coefficient k in the Beer's law formula $\log_{10} \frac{P}{P_0} = -k \cdot c, (k = a \cdot b)$ were calculated and are given in Table 1. (The same $b = 1.003\ \text{cm}$ quartz cell was used as in the previous work¹). The value of k is constant in the limits of experimental error. The hydrogen bond absorption band must thus in this case belong to the intramolecular one¹.

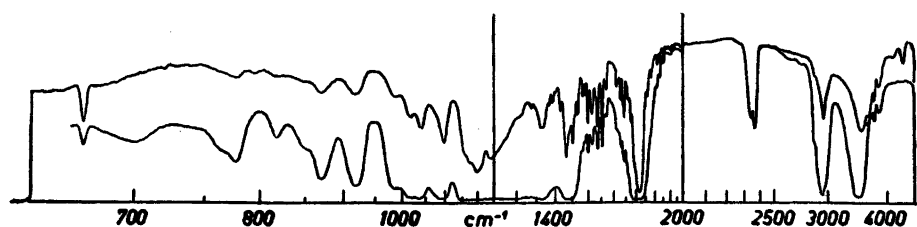
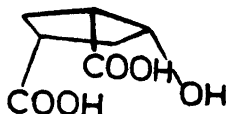
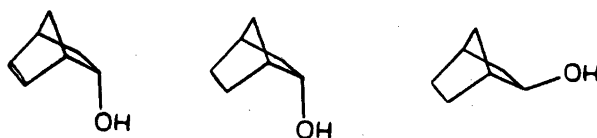


Fig. 2. Infrared absorption spectrum of *cis*-5-hydroxy-norcamphoric acid dimethylester (with atmospheric background, upper a capillary film and lower a 0.05 mm thick sample).

This intramolecular hydrogen bonding on the 5-hydroxy-norcamphoric acid dimethylester is possible only when the (1-)carboxyl group and the (5-)hydroxyl group are in *cis*-position with regard to the five ring; since, further, this is a *cis*-dicarboxylic acid (anhydride formation² and preparation by the permanganate oxydation from dehydro-norborneol), the hydroxyl and both carboxyl groups must be on the same side of the five ring plane. This 5-hydroxy-norcamphoric acid isomer is thus 5-*cis*-hydroxy-cyclopentane-1,3-*cis*-dicarboxylic acid (*cf.* Fig. 3).



From this configuration it follows that α -norborneol and "endo"-dehydro-norborneol have both *endo*-configuration and that β -norborneol must have *exo*-configuration:



endo-Dehydro-norborneol α -Norborneol β -Norborneol

The absorption band of the bonded O-H-stretching frequency is here broader, as mentioned above, and the value of k is smaller (38.0) than it was in the case of the β -hydroxy-cyclopentane carboxylic acid esters studied in the mentioned previous work¹ (69.0). The 5-*cis*-hydroxy-cyclopentane carboxylic acid dimethylester can form at least four different intramolecular hydrogen bonds (the hydrogen atom of the hydroxyl group is directed either below the molecule or outwards and the bonding occurs either with the carbonyl- or the ether-oxygen atom); *cf.* Fig. 3. The free rotation of the (5-)hydroxyl group and of the (1-)carboxyl group is hindered only by one another. (If the carboxyl group rotated unhindered, the shortest distance between the centers of the oxygen atom of hydroxyl group and of the nearest oxygen atom of (1-)carboxyl group would be *ca.* 2.0 Å. The oxygen-oxygen distance varies in unstrained hydrogen bonds from 2.5 to 2.9 Å). The occurrence of different intramolecular hydrogen bonding possibilities seems to cause a broadening in the absorption band related to the bonded O-H-stretching vibration.

The effect of boric acid on the electrical conductivity of the solution in water of the 5-hydroxy-norcamphoric acid isomer, studied in this work, was also investigated. The method is described elsewhere¹. The results are given in Table 2. There is no change in the specific conductance when $\frac{1}{4}$ M boric acid is used as solvent instead of water. Of all β -hydroxy-cyclopentanecarboxylic acids previous studied^{1,15,16} boric acid causes an increase in specific conductance of *cis*-hydroxy acid isomers and a slight decrease in that of *trans*-hydroxy acid isomers. In these latter compounds the boric acid complex formation is not possible for steric reasons. On the basis of these facts the results reported in Table 2 can mean boric acid complex formation, though to so very slight an extent that no certain conclusions can be drawn.

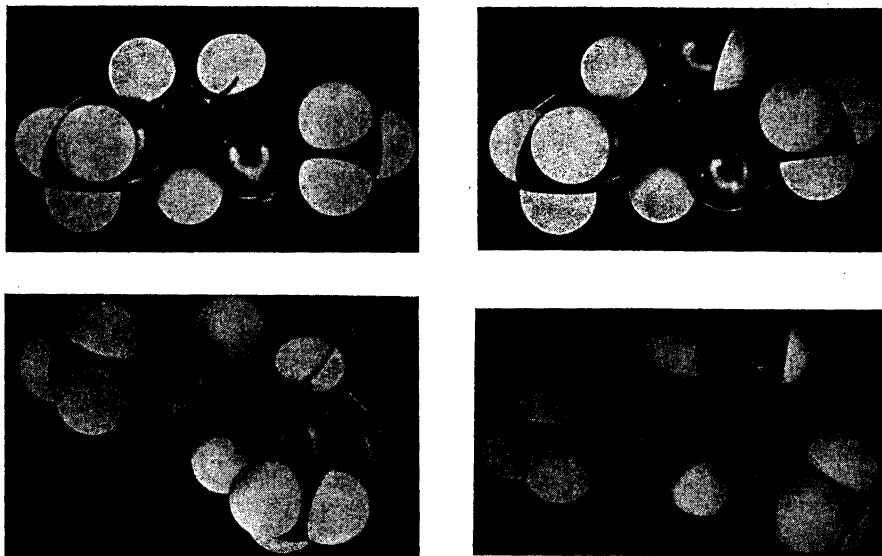


Fig. 3. Stuart-Briegleb models of four different possible intramolecular hydrogen bond types on 5-cis-hydroxy-cyclopentane-1,3-cis-dicarboxylic acid dimethylester

The hydrogen ion activities of the conductivity measurement solutions were compared in pairs. In all concentrations studied, the solution of 5-hydroxy-norcamphoric acid in $\frac{1}{4}$ M boric acid was more acidic than that of the same concentration in pure water and the difference in pH was greater than that calculated when no boric acid complex formation was taken into consideration. There can thus be weak boric acid complex formation.

Table 2. The electrical conductivity of the solutions of 5-hydroxy-norcamphoric acid (m.p. 169–170°) in water and in $\frac{1}{4}$ M boric acid–water solution at 25°. The cell constant: 0.283 cm⁻¹. Water κ^{25} $1.42 \cdot 10^{-6} \text{ohm}^{-1} \cdot \text{cm}^{-1}$; $\frac{1}{4}$ M boric acid–water solution κ^{25} $9.25 \cdot 10^{-6} \text{ohm}^{-1} \cdot \text{cm}^{-1}$.

| Concentration mole · l ⁻¹ | Solvent | | | |
|---|---------------------------------------|--|---------------------------------------|--|
| | Water | | $\frac{1}{4}$ M boric acid | |
| | Resistance of the solution ohms | Specific con- ductance of the solution $10^4 \kappa \text{ohm}^{-1} \cdot \text{cm}^{-1}$ | Resistance of the solution ohms | Specific con- ductance of the solution $10^4 \kappa \text{ohm}^{-1} \cdot \text{cm}^{-1}$ |
| 1/8 | 295 | 9.60 | — | — |
| 1/16 | 407 | 6.95 | 405 | 6.98 |
| 1/32 | 587 | 4.82 | 585 | 4.84 |
| 1/64 | 835 | 3.39 | 835 | 3.39 |
| 1/128 | 1 190 | 2.38 | 1 190 | 2.38 |
| 1/256 | 1 720 | 1.65 | 1 720 | 1.65 |

As mentioned before, in all previously studied cases the boric acid has caused, in general, a considerable increase in the electrical conductivity of β -*cis*-hydroxy-cyclopentane carboxylic acids and a slight decrease in the conductivity of β -*trans*-hydroxy-cyclopentane carboxylic acids. In this case the possible weak boric acid complex formation can be explained as follows: The intramolecular hydrogen bonding is here very strong and sterically favored, and it competes with success with boric acid complex formation for the not hydrogen bonded hydroxy acid molecules. The magnitude of the equilibrium constants of both reactions and their relation determine the concentration of boric acid complex molecules and the extent of the increase in specific conductance.

EXPERIMENTAL

"endo"-*Dehydro-norbornyl acetate* was prepared from vinyl acetate and dicyclopentadiene by a method similar to that of Alder and Rickert³. The product was distilled four times under reduced pressure with an efficient column, and fraction b.p. 87.5° (11.5 mm) was employed. n_D^{20} 1.4693, d_4^{20} 1.0502. A part of this sample of dehydro-norbornyl acetate (4.50 g) was hydrogenated in the presence of a Raney-nickel catalyst at 65° and 100 atm. initial pressure. The product was hydrolysed with sodium hydroxide in water-ethanol. The reaction mixture was extracted with ether-light petroleum mixture (50 + 50) and dried over potassium carbonate. After removal of the ether and light petroleum, 3.68 g of white crystalline powder, m.p. 142.5–145°, was obtained. According to the infrared spectral analysis¹⁴ this is a mixture of 75.3 % α -norborneol and 24.7 % β -norborneol.

5-Hydroxy-norcamphoric acid. To a mixture of 26.6 g of "endo"-dehydro-norbornyl acetate, 100.0 g of $MgSO_4 \cdot 7 H_2O$ and 500 ml of water 73.2 g of potassium permanganate was gradually added during two hours. When the color of the permanganate had disappeared, 450 ml of 2 N sodium hydroxide was added. After 12 hours staying the mixture was filtered, and the filtrate extracted with ether for removal of the neutral materials. The water layer was acidified with sulphuric acid and extracted with ether in a continuous extraction apparatus for 50 hours. A part of the ether extract precipitated during the extraction as a white crystalline powder and was filtered off; 9.87 g, m.p. 165–168°. The ether solution was dried over sodium sulphate, and the ether was removed. Of the oily residue the acetic acid was evaporated in a vacuum and additional 0.45 g of crystals m.p. 165.5–170° was isolated by means of rubbing with ether. The yield of oily product was 10.68 g. In all, 10.32 g (33.9 % of theory) of crystals was obtained. After recrystallisation of water the m.p. was 169–170°. (Found: C 48.15; H 5.84. Calc. for $C_7H_{10}O_5$: C 48.27; H 5.79. The acid was titrated with 0.1 N NaOH: equiv.wt. 87.0. Calc. for twobasic acid $C_7H_{10}O_5$: equiv.wt. 87.1). This 5-hydroxy-norcamphoric acid is very soluble in water and very slightly soluble in ether.

5-Hydroxy-norcamphoric acid dimethylester was prepared in ether of the silver salt and methyl iodide. The product, a colorless, viscous liquid, very soluble in water, was distilled in a high vacuum, n_D^{20} 1.4694. (Found: C 53.60; H 6.88. Calc. for $C_9H_{14}O_5$: C 53.46; H 6.98. Total hydrolysis: equiv.wt. 101.0. Calc. 101.1.) Infrared spectrum in Fig. 2.

REFERENCES

1. Hirsjärvi, P. *Acta Chem. Scand.* **8** (1954) 12.
2. Toivonen, N. J. *Private communication*.
3. Alder, K. and Rickert, H. F. *Ann.* **543** (1940) 1.
4. Roberts, J. D., Trumbull, E. R. Jr., Bennett, W. and Armstrong, R. *J. Am. Chem. Soc.* **72** (1950) 3116.
5. Alder, K. and Stein, G. *Angew. Chem.* **50** (1937) 510.
6. Komppa, G. and Beckmann, S. *Ann.* **512** (1934) 172.

7. Alder, K. and Stein, G. *Ann.* **525** (1936) 183.
8. Pulkkinen, E. *Suomen Kemistilehti A* **27** (1954) 26.
9. Toivonen, N. J. *Suomen Kemistilehti B* **24** (1951) 62.
10. Toivonen, H. *Suomen Kemistilehti B* **26** (1953) 75.
11. Toivonen, H. *Suomen Kemistilehti B* **25** (1952) 69.
12. Toivonen, N. J., Hirsjärvi, P., Melaja, A., Kainulainen, A., Halonen, A. and Pulkkinen, E. *Acta Chem. Scand.* **3** (1949) 991; Asahina, Y., Ishidate, M. and Sano, T. *Ber.* **69** (1936) 343.
13. Toivonen, N. J. *Sjätte Nordiska Kemistmötet, Lund, 1947*, p. 276; Hirsjärvi, P. *Ann. Acad. Sci. Fennicae Ser. A. II.* **45** (1952) 1.
14. Hirsjärvi, P. *To be published in another connection.*
15. Böseken, J., Slooff, G. and Lutgerhorst, A. G. *Proc. Acad. Sci. Amsterdam* **34** (1931) 932.
16. Böseken, J., Slooff, G., Hoeffelman, J. M. and Hirsch, H. E. *Rec. trav. chim.* **52** (1933) 881.

Received October 31, 1955.