*NMR Spectra of α-Glycols**

By Shin-ichiro Fujise, Genjiro Hazato,
Tsuneo Ikenoue, Shin-ichi Sasaki
and Yasuhisa Senda

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We wish to report that the NMR spectra of α-glycols show a deviation caused by the differences in the steric configurations of the hydroxyl groups.

In the spectra of α-glycols, a characteristic difference between two isomers appeared in the chemical shift of the hydroxyl protons. The experimental results are shown in Table I. These findings are very interesting in comparison with those reported by Kuhn1).

1) In α-glycol, which is in a liquid state at ordinary temperatures, the signal of the hydroxyl proton of the erythro-isomer was generally observed at a lower magnetic field than that of the threo-isomer, and in the trans rather than in the cis state.

2) When α-glycols are dissolved in a basic solvent, these hydroxyl protons are exchanged with the base; therefore, their signals show a single peak and the chemical shifts show a curve with a shape like that of Fig. 1, without exception between two isomers.

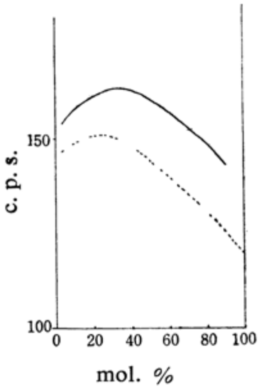

Fig. 1
Cyclopentane-1, 2-diol
Solvent : Pyridine
cis ---- trans ——

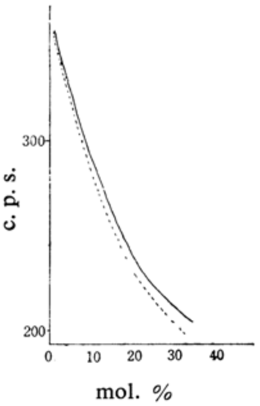

Fig. 2
Cyclohexane-1, 2-diol
Solvent : CH_3COOH
cis ---- trans ——

3) In organic acid, the protons of the carboxyl group and the hydroxyl group are exchanged, and their signals appear as a concentration shift. The shape of the curve in the two-phase system is different from that in a basic solvent (Fig. 2), but its behavior between two isomers is the same as in those cases without a solvent or in a base.

The following are the exceptions to our experimental rule which were observed.

4) In the spectrum of five-membered ring compounds such as cyclopentane-1, 2-diol or α, β-dihydroxyvalerolactone, which take the planar conformation, the signal of the hydroxyl proton of the cis-isomer in acidic solvents was less shielded than that of the corresponding

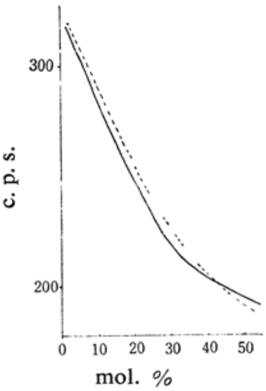

Fig. 3
Cyclopentane-1, 2-diol
Solvent : CF_3COOH
cis ---- trans ——

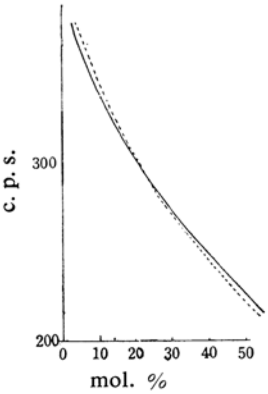

Fig. 4
Cyclopentane-1, 2-diol
Solvent : CH_3COOH
cis ---- trans ——

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* Read at the 11th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1958.

1) L. P. Kuhn, *J. Am. Chem. Soc.*, **76**, 4223 (1954).

TABLE I

1) Solvent : Pyridine

Sample	Isomer	Concn. mol. %	Shifts c. p. s.	Diff. c. p. s.
α,β-Dihydroxybutyric acid	erythro	14.1	315.3	11.0
	threo		304.3	
Methyl α,β-dihydroxybutyrate	erythro	32.5	221.3	26.0
	threo		195.3	
Tartaric acid	meso	33.4	322.6	51.4
	DL		271.2	
Dimethyl tartrate	meso	31.3	151.3	6.6
	DL		144.7	
Cyclopentane-1, 2-diol	cis	43.9	150.0	17.7
	trans		167.7	
Cyclohexane-1, 2-diol	cis	32.3	163.2	22.5
	trans		185.7	
α,β-Dihydroxyvalerolactone	cis	34.0	240.5	17.3
	trans		257.8	
9, 10-Dihydroxystearic acid	erythro	11.1	293.4	2.6
	thero		290.8	
Octadecane-1, 9, 10-triol	erythro	5.9	192.1	13.0
	threo		179.1	

2) Solvent: Acetic acid

Sample	Isomer	Concn. mol. %	Shifts c. p. s.	Diff. c. p. s.
Methyl α,β-dihydroxybutyrate	erythro	31.3	276.1	21.5
	threo		254.6	
Dimethyl tartrate	meso	25.0	360.5	45.1
	DL		315.4	
Cyclopentane-1, 2-diol	cis	35.3	256.8	2.9
	trans		259.7	
Cyclohexane-1, 2-diol	cis	31.7	252.4	7.5
	trans		259.9	
α,β-Dihydroxyvalerolactone Solvent : CF_3COOH	cis	18.0	319.1	−6.7
	trans		312.4	

trans-isomer in areas of a higher acid content (Figs. 3 and 4). This fact was recognized when trifluoroacetic acid instead of acetic acid was used as a solvent, a smaller amount of trifluoroacetic acid being sufficient to show this experimental fact, it is also well known that triflouroacetic acid is weaker than acetic acid in acidity.

The NMR spectra were obtained with a Varian V-4300 high resolution spectrometer at a fixed frequency of 40 Mc./sec., and the chemical shifts of the hydroxyl proton were relative to the signal of the proton of the group which was seen at the highest field in the spectra.

Chemical Research Institute of
Non-Aqueous Solution
Tohoku University
Katahira-cho, Sendai
(G. H. & T. I.)

Department of Chemistry
Faculty of Science
Tohoku University
Katahira-cho, Sendai
(S. F., S. S. & Y. S.)