Intramolecular Hydrogen Bonds. II.[1] On the Configuration of Isomeric Methyl 9, 10-Dihydroxyoctadecanoates

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A high-melting isomer (I: m. p. 131°C) of two 9, 10-dihydroxyoctadecanoic acids was obtained by the oxidation of oleic acid with permanganate and another isomer (II: m. p. 95°C) was obtained similarly from elaidic acid. On the basis of the cis addition of the two hydroxyl groups, the former was assigned to the erythro form and the latter to the threo form.[2]

Further evidence for the configuration was the difference in the rates of the oxidation between the acids with lead tetraacetate[3] and with periodic acid[4], although the relative rates (II/I) were not so high as those of isomeric cycloalkane-1, 2-diols. Also, Swern and his co-workers[5] deduced the above configuration from the strikingly high ability of compound II to form a complex with urea and boric acid.

The present paper provides other support for the assignments through the infrared measurements of their methyl esters III and IV in the O-H stretching region of 3400—3700 cm^{-1}, together with those of ethyl ω-hydroxy-pelargonate V and -caprinate VI for the purpose of comparison. The measurements were carried out with a solution in 0.004 mol./l. in carbon tetrachloride at 25°C with a Perkin-Elmer 21 spectrophotometer equipped with a lithium fluoride prism and with a cell 3 cm. long; the observed frequencies

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[1] Part I: N. Mori, S. Ōmura, O, Yamamoto, T. Suzuki and Y. Tsuzuki, This Bulletin, **36**, 1401 (1963).

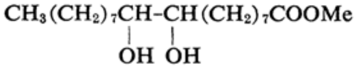
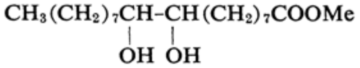
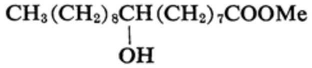
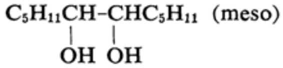
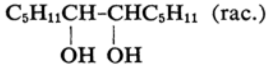
[2] D. Swern, *J. Am. Chem. Soc.*, **70**, 1235 (1948), and previous papers, as well as references therein cited.

[3] T. P. Hilditch and H. Jasperson, *Nature*, **147**, 327 (1941).

[4] H. W. Wittcoff, O. A. Moe and M. H. Iwen, *J. Am. Chem. Soc.*, **70**, 742 (1948).

[5] D. Swern, L. P. Witnauer and H. B. Knight, ibid., **74**, 1655 (1952).

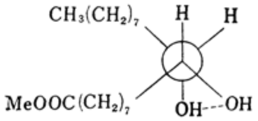
TABLE I. DATA OF HYDROXYL BANDS

	Compound	M. p., °C (B. p., °C/mmHg)	ν_{OH}, cm^{-1}		Lit.
			Free (ε)*	Bonded (ε)*	
III	 $CH_3(CH_2)_7\underset{OH}{CH}-\underset{OH}{CH}(CH_2)_7COOMe$	105[8]	3636 (50)	3593 (48)	
IV	 $CH_3(CH_2)_7\underset{OH}{CH}-\underset{OH}{CH}(CH_2)_7COOMe$	69[8]	3634 (54)	3584 (61)	
V	$HO(CH_2)_8COOEt$	(131—132/2)[9]	3638 (29)		
VI	$HO(CH_2)_9COOEt$	(146/3)[10]	3641 (30)		
VII	 $CH_3(CH_2)_8\underset{OH}{CH}(CH_2)_7COOMe$		3629		11
VIII	 $C_5H_{11}\underset{OH}{CH}-\underset{OH}{CH}C_5H_{11}$ (meso)		3636	3593	6
IX	 $C_5H_{11}\underset{OH}{CH}-\underset{OH}{CH}C_5H_{11}$ (rac.)		3636	3583	6

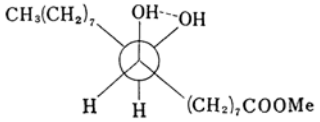
* $\varepsilon = 1/cl \cdot \log I_0/I$ for the apparent OH band.

were calibrated against that of atmospheric vapor. At that concentration, all of the esters were free from intermolecular hydrogen bonding, and only a very weak broad band was observed at 3462 or 3466 cm^{-1}; this may be the first overtone of a carbonyl group.

The hydroxyl band of the methyl esters III and IV was a doublet with almost the same intensity, but compounds V and VI had only one sharp band in the region of the free primary alcoholic hydroxyl group. Thus, the esters III and IV had no intramolecular hydrogen bond between the hydroxyl and the methoxycarbonyl group; substantially all of their molecules exist in the conformation containing an intramolecular hydrogen bond between the two hydroxyl groups:



(III)



(IV)

In general, threo 1, 2-diols (racemic form) form a stronger hydrogen bond between the hydroxyl groups than do the corresponding erythro diols (meso form)[6,7] because of the conformational preference of the former for intramolecular hydrogen bonding,[6] as is seen in the case of the dodecane-6, 7-diols, VIII and IX, in Table I. As the table shows, the separation ($\Delta\nu$) between the two peaks is 43 cm^{-1} for compound III and 50 cm^{-1} for compound IV; this supports the above assignment of the configuration for compounds I and II.

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[7] G. Chiurdoglu, R. de Groote, W. Masschelein and M. H. van Risseghem, *Bull. soc. chim. Belges*, **70**, 342 (1961).

[8] D. Swern and E. F. Jordan, *J. Am. Chem. Soc.*, **67**, 902 (1945). M. p. 105 and 71°C, obtained from compounds I and II, respectively.

[9] P. Chuit and J. Hausser, *Helv. Chim. Acta*, **12**, 466 (1929). Me ester: b. p. 147—150°C/13 mmHg.

[10] A. Grün and T. Wirth, *Ber.*, **55**, 2206 (1922). Me ester: b. p. 154°C/7 mmHg.

[11] J. Grundy and L. J. Morris, *Spectrochim. Acta*, **20**, 695 (1964).