six parts of absolute alcohol and four parts of pyridine (c, 0.58). After one day the rotation became constant at −34.5°. On the basis of these data the substance was identified as pure glucosazone.

Summary

The present structures of turanose and melezitose are based on the supposed 1,3,4-trimethylfructose, a sirupy product obtained by Zemplén and by Leitch from the fully methylated melezitose. The existence of the true, crystalline 1,3,4-trimethylfructose and the number and properties of the octaacetates and other derivatives of turanose indicate that neither carbon atom 5 nor carbon atom 6 of the fructose part of turanose can carry the glucosidic linkage. Carbon atom 4 is also eliminated because turanosazone is not identical with maltosazone. If carbon atom 1 were the position of the linkage, 1-β-glucosidofructose would be the β-glycosidic isomer of turanose. This new disaccharide has been synthesized by condensation of acetylbromoglucose with β-diacetonefructose and subsequent hydrolysis of the acetyl and isopropylidene groups. The synthetic sugar is entirely different from turanose and unlike the latter it does not give an osazone except for a small quantity of glucosazone. Turanose, therefore, must be 3-α-glucosidofructose and melezitose the corresponding sucrose derivative. Based on the true formula of turanose the correct structures of the more important turanose derivatives are given.

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Infrared Absorption Studies of Some Glycols and Ethoxyalcohols

BY F. T. WALL AND W. F. CLAUSSEN

It has been recognized for some time that hydroxy compounds such as the alcohols and acids can undergo association through the formation of hydrogen bonds.[1,2] This association can lead to the formation of well-defined dimers in certain cases, or to the formation of polymers of indefinite size. Thus the monocarboxylic acids form definite dimers,[3] whereas water and the alcohols can associate to form aggregates of varying sizes.[4]

It has been observed further that certain hydroxy compounds such as water not only can associate with themselves,[5] but also can bond to other molecules such as the ethers.[6] Ethyl ether has no active hydrogens, and so cannot form hydrogen bonds by itself, but its oxygen readily can take part in the formation of a hydrogen bond by serving as an acceptor for an active hydrogen atom from another molecule.

In addition to molecules bonding to others of the same kind or to suitable molecules of a different kind, it also has been found that internal bonding, giving rise to ring formation, can occur in certain cases. This type of bonding known as "intramolecular" bonding (to be distinguished from "intermolecular" bonding) occurs, for example, in o-nitrophenol,[7] and salicyl aldehyde,[8] in which cases a stable six-membered ring containing a hydrogen bond is formed.

Evidence for the above-described effects has been provided in numerous ways, but one of the most convenient methods is through the study of infrared absorption. Infrared studies show that, whereas a certain absorption frequency to be associated with an OH group is generally present in hydroxy compounds, that frequency is shifted by an appreciable amount when hydrogen bonding occurs.[1,8] The shifted or hydrogen bond frequency occurs at wave lengths higher than is found for the fundamental OH, and the magnitude of the shift is usually sufficiently large so as to leave no doubt that a change in the nature of the hydroxyl group has taken place.

The effects discussed above were first observed for the simple hydroxy compounds, by themselves or in combination with simple ethers. It was accordingly felt desirable to investigate by means of infrared absorption studies the association of the glycols and ethoxyalcohols. It is clear from their structures that these molecules offer the possibility of not only associating with one another,

(1) Errera, Helv. Chim. Acta, 20, 1373 (1937).
(2) Buswell, Rodebush and Roy, THIS JOURNAL, 60, 2239 (1938).
(3) Pauling and Brockway, Proc. Natl. Acad. Sci., 20, 336 (1934).
(4) Zachariasen, J. Chem. Phys., 3, 158 (1935).
(5) Morgan and Warren, J. Chem. Phys., 6, 666 (1938).
(6) Unpublished work of Mr. I. T. Krohn of this Laboratory.
(7) Buswell, Dietz and Rodebush, J. Chem. Phys., 5, 501 (1937).
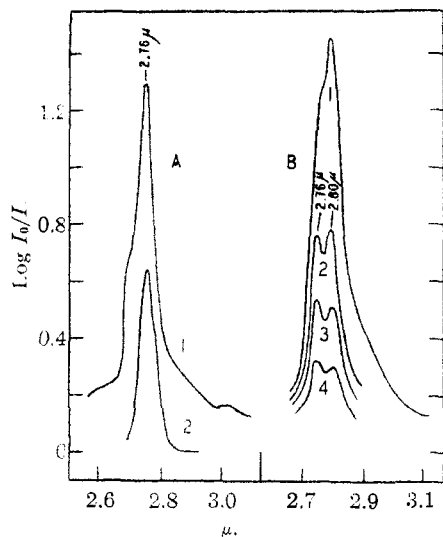(8) Hilbert, Wulf, Hendricks and Liddell, Nature, 135, 147 (1935).

Fig. 1.—A, Ethylene glycol (1) saturated solution, (2) $1/4$ saturated solution; B, propylene glycol (1) saturated solution, (2) $1/2$ saturated solution, (3) $1/4$ saturated solution, (4) $1/8$ saturated solution. Cell length, 10.18 cm.

but that they might also undergo intramolecular bonding when the chain length is suitable. It was the purpose of these studies to find out which effect or to what extent both effects take place when these compounds are introduced into an inert solvent like carbon tetrachloride.

Substances Used.—The glycols studied were ethylene, propylene, butylene, pentamethylene, hexamethylene, decamethylene and octadecamethylene glycols. Of these, ethylene and propylene glycols have been investigated previously,[9] but under different conditions, so that it was felt desirable to repeat them here. Most of these compounds were obtained from the preparation stock rooms of our organic chemistry division. However, the pentamethylene glycol was specially prepared by the hydrolysis of pentamethylene dibromide in an alkaline water–alcohol solution. Octadecamethylene glycol was prepared under the direction of Professor C. S. Marvel by the reduction of the corresponding ester of the dibasic acid

TABLE I

		°C., Mm.
Ethylene glycol	B. p.	88/10
Propylene glycol	B. p.	105/10
Butylene glycol	B. p.	124/ 8
Pentamethylene glycol	B. p.	104/ 4
Hexamethylene glycol	M. p.	42
Decamethylene glycol	M. p.	70
Octadecamethylene glycol	M. p.	91

(9) Barnes, Bonner and Condon, J. Chem. Phys., 4, 772 (1936).

with sodium and alcohol. All of these compounds were carefully distilled or recrystallized, the physical constants being recorded in Table I.
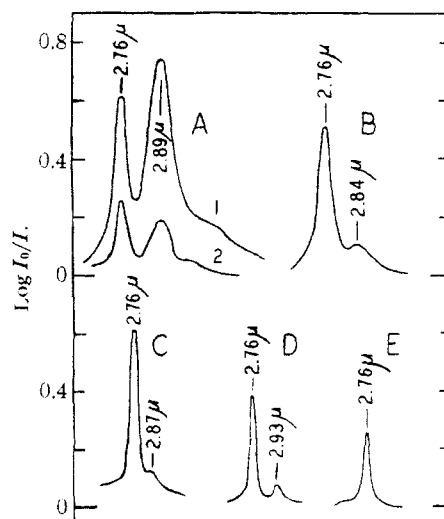

Fig. 2.—A, Butylene glycol (1) satd. solution, (2) $1/4$ saturated solution; B, pentamethylene glycol, satd. soln.; C, hexamethylene glycol, satd. soln.; D, decamethylene glycol, satd. soln.; E, octadecamethylene glycol, satd. soln. Cell length, 10.18 cm.

With the exception of 2-ethoxyethanol-1 ("cellosolve"), which is commercially available, all of the ethoxyalcohols used in these studies were prepared in this Laboratory. 3-Ethoxypropanol-1 was synthesized from propylene chlorohydrin and sodium ethylate. 4-Ethoxybutanol-1 was prepared from the monosodium derivative of tetramethylene glycol and ethyl bromide. 5-Ethoxypentanol-1 was made by hydrolyzing the product from the reaction of equimolar quantities of pentamethylene dibromide and sodium ethylate. These ethoxy alcohols were carefully fractionally distilled, and the resulting boiling points are recorded in Table II.

TABLE II

Compound	B. p., °C.
Ethyl cellosolve	132
3-Ethoxypropanol-1	158–159
4-Ethoxybutanol-1	181
5-Ethoxypentanol-1	75–80 (4 mm.)

Experimental

The technique employed for the absorption studies has been described previously.[2] The spectroscope used was of the prism type, the rock salt prism being on a Littrow–Wadsworth mounting. The source of radiation was a Nernst glower, and the intensity of the beam was measured

by means of a thermocouple–galvanometer arrangement. In some cases a Moll amplifier[10] was used to increase the deflections.

The glycols were not very soluble in carbon tetrachloride, so approximately saturated solutions which were about 0.002 molar were used for the most part. In some cases more dilute solutions were investigated in order to study the effect of concentration. The solutions were placed in absorption cells of length 10.18 cm.

The ethoxyalcohols were more soluble than the glycols so they were studied for a concentration range from 0.004 to 0.256 molar. In the case of the ethoxyalcohols, the length of the cell times the concentration of the solute was kept constant for the different runs, so that the radiation passed the same amount of material in each case.
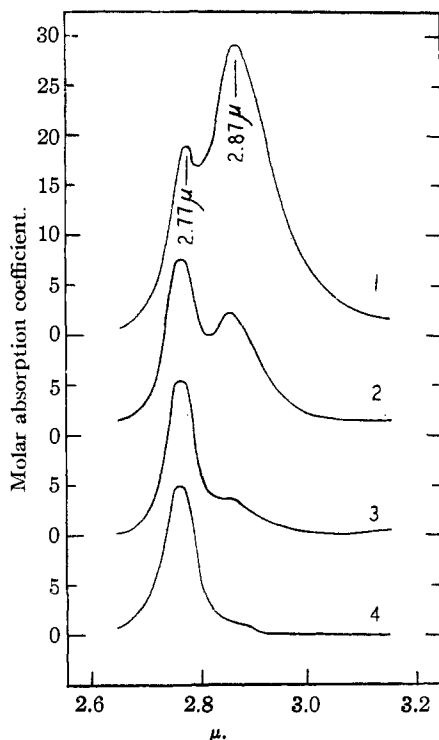

Fig. 3.—2-Ethoxyethanol-1 (1) 0.256 M in 0.162-cm. cell, (2) 0.064 M in 0.640-cm. cell, (3) 0.016 M in 2.53-cm. cell, (4) 0.004 M in 10.18-cm. cell.

The results of the experimental investigation are shown in Figs. 1 to 6. For the glycols the values of log I_0/I are plotted against wave length where I_0/I is the ratio of the intensities of light transmitted by pure solvent to that transmitted by the same length of solution. For the ethoxyalcohols, there are plotted the molar extinction coefficients defined as

$$K = \frac{1}{cd} \log \frac{I_0}{I}$$

where c is the concentration in moles per liter and

(10) Moll and Burger, *Phil. Mag.*, **50**, 724 (1925).

d is the length of the cell in centimeters. The published curves show the absorption only in the 2.8 μ region. It should be added that all the molecules show absorption in the neighborhood of 3.35 μ and beyond, which is due to carbon–hydrogen absorption. Since we are concerned here only with hydrogen bonding possibilities, the carbon–hydrogen absorption is not included in the curves.
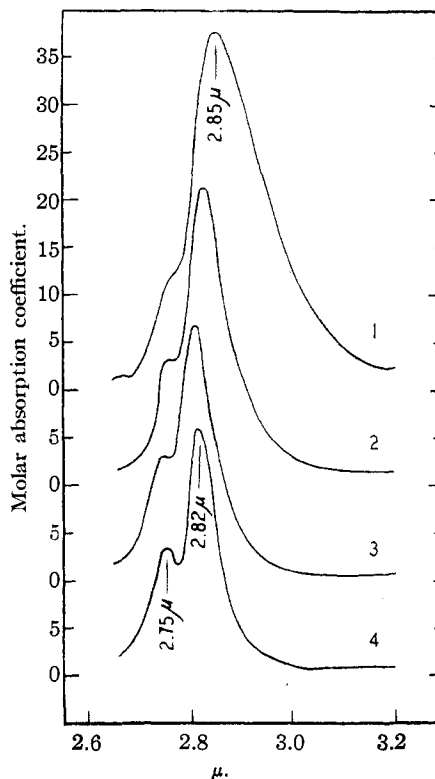

Fig. 4.—3-Ethoxypropanol-1 (1) 0.256 M in 0.162-cm. cell, (2) 0.064 M in 0.640-cm. cell, (3) 0.016 M in 2.53-cm. cell, (4) 0.004 M in 10.18-cm. cell.

Discussion of Results

The results for the glycols are somewhat difficult to interpret because their limited solubility in carbon tetrachloride prevented their study over a wide concentration range. Ethylene glycol gives no evidence for a bonded peak, but does show the fundamental OH at 2.76 μ. The failure to bond might well be due to the low concentration.

A saturated solution of propylene glycol shows a peak at 2.80 μ with a shoulder on the short wave length side. Upon dilution, using the same length cell, however, this shoulder can be resolved into an absorption maximum at 2.76 μ. Upon further dilution the 2.80 μ peak becomes relatively less im-
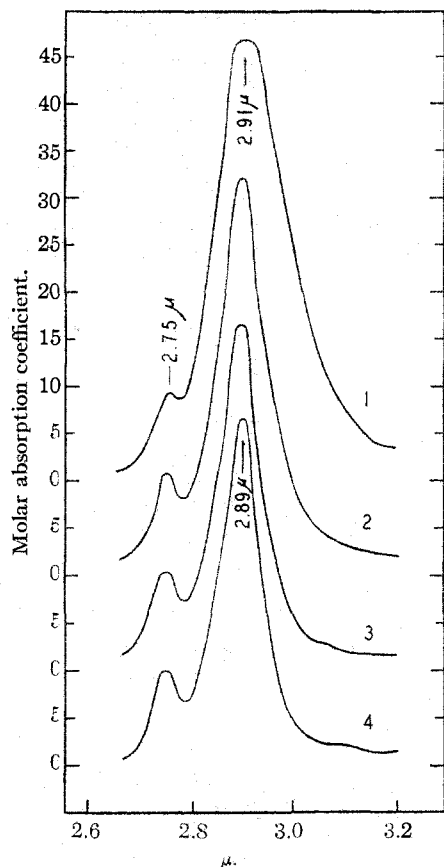
Fig. 5.—4-Ethoxybutanol-1 (1) 0.256 *M* in 0.162-cm. cell, (2) 0.064 *M* in 0.640-cm. cell, (3) 0.016 *M* in 2.53-cm. cell, (4) 0.004 *M* in 10.18-cm. cell.
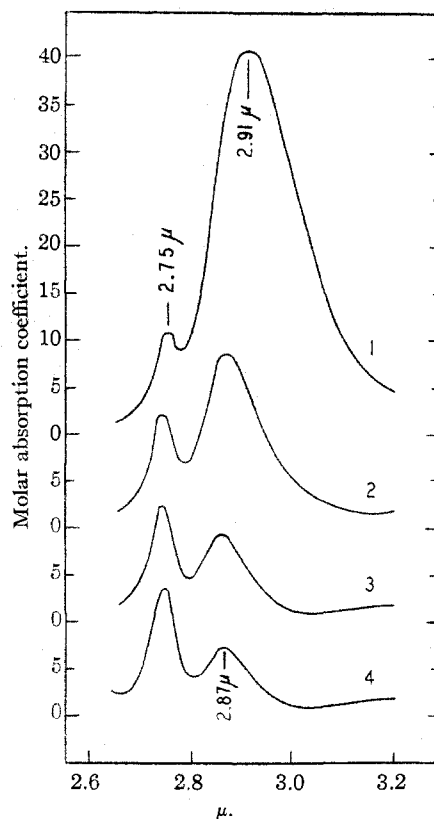

Fig. 6.—5-Ethoxypentanol-1 (1) 0.256 *M* in 0.162-cm. cell, (2) 0.064 *M* in 0.640-cm. cell, (3) 0.016 *M* in 2.53-cm. cell, (4) 0.004 *M* in 10.18-cm. cell.

portant suggesting that it is due partly to association. In the light of the results obtained for the ethoxyalcohols, the association peak for propylene glycol very likely is due to intramolecular bonding. It is possible that two non-linear hydrogen bonds are formed when the ends of propylene glycol are joined together. Such non-linear bonds would show a much smaller shift in frequency from the fundamental OH than would a regular hydrogen bond, which is in agreement with the observation.

Butylene glycol shows two well-defined peaks at 2.89 μ and 2.76 μ. Upon dilution the 2.89 μ absorption maximum goes down considerably suggesting that it is largely due to association. However, some ring formation is to be expected. The 2.76 μ absorption is due of course to the fundamental OH vibration.

The penta-, hexa-, and decamethylene glycols all show two maxima, a strong fundamental OH and a weaker bonded peak. In the case of these

molecules ring formation is not probable. Octadecamethylene glycol gave evidence only for the fundamental OH frequency.

The ethoxyalcohols provide a much more interesting set of data because of their greater solubility. Each of these compounds shows two peaks, one due to the fundamental OH and the other due to the hydrogen bonded OH. Since the absorption results for these molecules were obtained by keeping $c \times d$ constant, the relative heights of the peaks have a quantitative significance capable of immediate interpretation. For each compound, the bonded or higher wave length peak decreased in height as the concentration was lowered. However, the decrease was not the same in each instance. By plotting the height of the bonded peak against concentration (Fig. 7), an idea as to what is taking place can be obtained. By extrapolating those curves to zero concentration, one can determine the molar hydrogen bond absorption at infinite dilution.

At infinite dilution, any hydrogen bonding must be of the intramolecular (ring form) type. This

follows from equilibrium considerations. The extrapolation in Fig. 7 shows that there is no bonding whatsoever for the ethoxyethanol at infinite dilution. This means that any bonding which the molecule undergoes in actual solutions must be of the intermolecular type. On the other hand, the substituted propanol and butanol show considerable bonding even at infinite dilution. This is to be attributed to ring formation. Moreover, ethoxypentanol shows only small hydrogen bonding at zero concentration. This can be associated with the fact that the pentanol would form a ring too long for stability.

It appears from these results that the most stable rings involving hydrogen bonds contain 6 or 7 atoms, including the hydrogen. These numbers are greater by one than those usually given for rings involving only the ordinary electron pair type of bond. No explanation seems immediately forthcoming as to why a five-membered hydrogen bond ring should be unstable, yet there seems to be no doubt as to the absence of ring formation in 2-ethoxyethanol-1.

Conclusion

The infrared absorption spectra of carbon tetrachloride solutions of various glycols and ethoxyalcohols have been studied in the neighborhood of
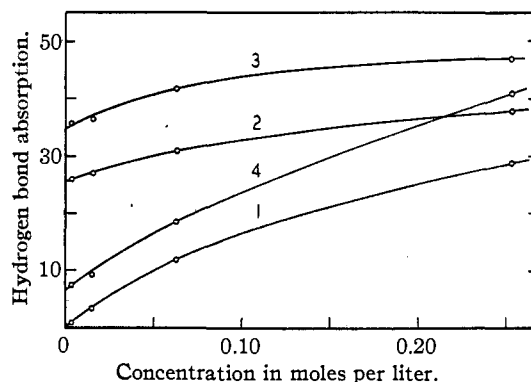

Fig. 7.—Heights of hydrogen bond peaks (1) 2-ethoxyethanol-1, (2) 3-ethoxypropanol-1, (3) 4-ethoxy-butanol-1, (4) 5-ethoxypentanol-1.

2.8 μ. The results show that the ethoxyalcohols can associate through the formation of intermolecular hydrogen bonds. Also the substituted propanol and butanol can form stable rings, whereas ethoxyethanol shows no evidence of ring formation. The glycols likewise demonstrate hydrogen bonding, but the evidence for their precise behavior is not conclusive because of their limited solubility. The authors are indebted to Professors W. H. Rodebush and A. M. Buswell for many helpful suggestions and for their kind interest in the work.

On the Degassing of Hydrogen-Charged Palladium

BY F. D. BENNETT[1]

For a long time experimenters have recognized that palladium sorbs very great quantities of hydrogen gas. Metals such as iron and nickel are known to sorb hydrogen and other gases in varying quantities, portions of which are held tenaciously even when the metals are heated to the melting point in vacuum. While there is considerable indirect evidence suggesting that palladium releases its sorbed gas quickly at comparatively low temperatures, apparently no direct measurements have been made of the degassing of palladium in vacuum.

In a recent investigation of the palladium–hydrogen equilibrium by Gillespie and Gal-

staun,[2] a series of pressure–composition isotherms over the range 80–313° is presented and several palladium hydrides postulated to explain the existence of certain discontinuities in the isotherms.

In the preparation of the palladium black with which these experiments were carried out, Gillespie and Galstaun reduced palladosammine chloride in hydrogen. The black was degassed of hydrogen at 500° in a stream of carbon dioxide and then cooled. It was further degassed in an evacuated Pyrex bulb by heating with a hand torch until the glass began to soften. The black was then transferred to the reaction bulb and hydrogen admitted in order to clean up adsorbed oxygen.