of single independent molecules of hydrocarbon in the dilute aqueous medium, because this is still essentially water and large amounts of other ordinary solvents are required to modify it. Hence, it must involve some kind of association with the dissolved detergent itself. It may well involve the different kinds as well as sizes of colloidal micelles which various authorities agree to preëxist in the soap solutions themselves. Kiessig and Philippoff in Hess's laboratory[3] have proven by X-ray measurements of clear solutions of benzene in soap solution that some, at least, of the benzene is sandwiched between the lamellar micelles whose spacing is correspondingly increased in the direction normal to the lamellar faces to which the soap molecules themselves are normal.

Colloidal particles are visible in the ultramicroscope in all cases so far tested where a sufficiently dilute detergent solution has taken up nearly the saturation amount of water-insoluble material. There are no microscopically visible particles or droplets. The unsaturated solutions of hydrocarbon appear clear until they near saturation. Hartley's suggestion that it is mere solution in the water-insoluble portion of the detergent micelle is in disagreement with his own data with Miss Parsons showing that the amount taken up was fivefold greater. It is likewise out of accord with the fact, shown in Fig. 4, that the addition of a small amount of silicate increases the solubility of a hydrocarbon in the soap solution, where by itself it has no solvent action whatsoever.

It has been known since 1874 that *concentrated* soap solutions dissolve cresols and tar oil, and the important paper of Engler and Dieckhoff,[4] in which a clear distinction is made between solution and emulsification, has been generally overlooked or forgotten. They made numerous measurements of the dissolving power of soap solutions for hydrocarbons, fatty acid, phenols and mixtures. These effects are of great importance in pharmacy, cosmetics and industry. The action of solubilizers is of vital importance in biological processes.

(3) H. Kiessig and W. Philippoff, *Naturwiss.*, **27**, 593 (1939).

Summary

Hydrocarbons, such as methylcyclopentane, normally insoluble in water dissolve to the extent, in this case, of 0.19 mole/liter in 0.18 mole/liter potassium oleate solution, and to an even greater extent in soap solutions containing small additions of silicate or hydroxide. The colloidal solutions formed are thermodynamically stable because the vapor pressure is significantly less than that of the free hydrocarbon until the solution is approximately saturated.

(4) C. Engler and E. Dieckhoff, *Arch. Pharm.*, **230**, 561 (1892).

STANFORD UNIV., CALIF. RECEIVED MAY 27, 1940

[CONTRIBUTION FROM THE PHYSICAL-BIOLOGICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

Hydrogen Bridging in Cellulose as Shown by Infrared Absorption Spectra

BY JOSEPH W. ELLIS AND JEAN BATH

As early as 1926 it was predicted by Sponsler and Dore[1] that the orientation of the cellulose chains in the cell walls of naturally occurring Ramie fibers is stabilized laterally by secondary valence forces associated with the hydroxyl groups of the glucose residues. Similar suggestions have been made by Huggins in a review of hydrogen bridging in organic compounds[2] and by Mark in a recent review of the X-ray investigations on carbohydrates.[3] It is the purpose of this paper to cite evidence for these suggestions on the basis of infrared absorption studies.

By means of a correlation of X-ray investigations with the model proposed by the organic chemists it was initially shown by Sponsler and Dore[1] and later by Meyer and Mark[4] that cellulose may be thought of as consisting of long, chain-like molecules, which in the case of Ramie fibers lie approximately parallel to the fiber axis. The fundamental repetition unit of 10.3 Å. along the axis of the long molecule was shown to correspond to the calculated length of one anhydrocellobiose unit consisting of two β-*d*-glucose residues united by a glucosidic linkage between carbons 1 and 4 of the two pyranose rings as seen

(1) O. L. Sponsler and W. H. Dore, *Colloid Symposium Monograph*, **IV**, 174 (1926).

(2) M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1938).

(3) H. Mark, *Chem. Rev.*, **26**, 169 (1940).

(4) K. H. Meyer and H. Mark, *Ber.*, **61**, 593 (1928); *Z. physik. Chem.*, **B2**, 115 (1929).

in Fig. 1. The question of the orientation of these long, chain molecules with respect to one another within the naturally formed material is still in a state of controversy as may be seen readily from an examination of the literature.[3,5,6,7,8,9] It is hoped that the following evidence may cast some light on this problem.

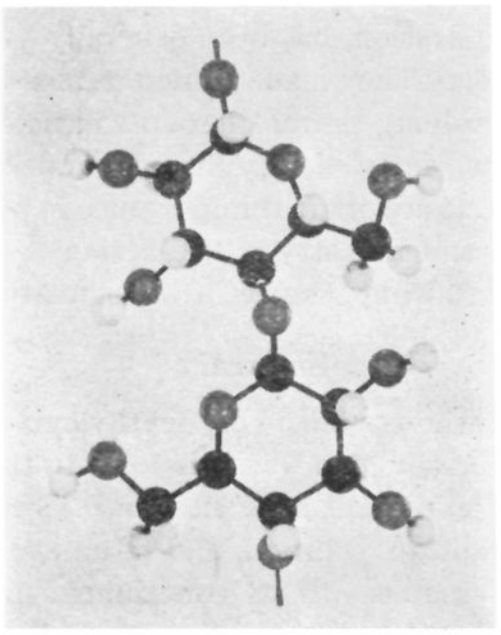

Fig. 1.—Model photograph of cellobiose unit. The black balls indicate carbon atoms; the gray, oxygen atoms; and the small white ones, hydrogen atoms.

The method of preparing the cellulose fibers for infrared study was as follows. A packet of either oriented or unoriented Ramie fibers (that is, the bast fibers of Boehmeria) of about 1 mm. thickness was dried at 110–115°. To make a semi-transparent specimen it was then placed in a mixture of carbon disulfide and carbon tetrachloride having a refractive index of approximately 1.57. Infrared absorption spectra in the region 1–2.5 μ were then obtained, using a recording quartz spectrograph.[10] Records were taken both with unpolarized light and with light plane polarized with a Glan–Thompson prism.

Although the cellulose molecule is complex, its infrared absorption spectrum may be interpreted as arising essentially from C–H and O–H oscillators. The discussion in the following paragraphs deals entirely with the hydroxyl bands; namely, the first overtone valence vibration, 2 ν, near 1.5 μ and the combination valence-deformation band, $\nu + \delta$, near 2 μ. The concept of perturbed and unperturbed hydroxyl groups is involved. By an unperturbed OH group we mean one not involved in hydrogen bridging. By "perturbed group" we mean here that the OH unit is involved in hydrogen bridging, either as the donor or as the acceptor of the proton of the bridge. The interpretations, given here, are based mainly on previous infrared studies of hydroxyl groups, particularly in crystalline sucrose.[11]

In the 1.5 μ region the spectrum of crystalline sucrose shows three absorption bands. One relatively sharp band at 1.44 μ we associate with valence oscillations of unperturbed OH groups. Broader bands with centers at 1.51 and 1.58 μ we associate with perturbed groups, the absorbing OH oscillators giving rise to these bands being the acceptors and the donors, respectively, of the hydrogen of the bridge.[11] Similarly a sharp band at 2.02 μ and a very broad one at 2.11 μ are associated, respectively, with unperturbed and perturbed OH oscillators; in the latter band the contributions of groups acting as proton donors and acceptors merge together in an unresolved manner.

With the analysis of sucrose as a basis it is possible to consider the structure of this region in the spectrum obtained from the dried, unoriented Ramie fibers. The 1.44 μ band is exceedingly weak, showing the presence of relatively few unperturbed OH groups. The major portion of the absorption is in the longer wave length region, indicating the existence of hydrogen bridging; however, in this instance the types of perturbation are not so well defined as in sucrose. Instead, three broad diffuse bands with centers at 1.49, 1.54 and 1.58 μ occur. It appears that in cellulose the perturbations are more variable and that the effects of strain as well as of distance must eventually be considered. It is believed that a comparison of the infrared absorption of the α and β forms of resorcinol, in conjunction with their X-ray models,[12] may give some information about the effects of strain involved in hydrogen bridging.

With a packet of oriented Ramie fibers absorption records were taken with plane polarized infrared rays. Lack of perfect alignment of the fibers was responsible for some depolarization in the beam, but the transmitted light was sufficiently polarized to show an appreciable difference between records taken with the electric vector E of the beam parallel to and perpendicular to the fiber

(5) O. L. Sponsler, *Quart. Rev. Biol.*, **VIII**, I (1933).
(6) E. G. Cox, *Ann. Rept. Chem. Soc.*, **XXXIV**, 176 (1938).
(7) E. Sauter, *Z. physik. Chem.*, **35B**, 113 (1937); **43B**, 294 (1939).
(8) H. Kiessig, *ibid.*, **43B**, 103 (1939).
(9) S. T. Gross and G. L. Clark, *Z. Krist.*, **99**, 357 (1938).
(10) J. W. Ellis, *Rev. Sci. Instruments*, **4**, 123 (1933).
(11) J. W. Ellis and J. D. Bath, *J. Chem. Phys.*, **6**, 221 (1938).
(12) J. M. Robertson and A. R. Ubbelohde, *Proc. Roy. Soc.*, **A167**, 136 (1938).

axes. In the latter instance the central 1.54 μ component of the band was practically absent.

It is interesting to observe that this 1.54 μ component was also absent when a specimen of unoriented, *mercerized* fibers was studied with unpolarized light. Mercerization of cellulose was accomplished by treating the material for about thirty minutes with 20% sodium hydroxide, washing thoroughly with distilled water, washing with very dilute acetic acid and then repeating the washing process with distilled water. This material was then dried and immersed in a mixture of carbon disulfide and carbon tetrachloride of the proper refractive index. It has been demonstrated by means of the X-ray analysis of this mercerized material[13,7] that a shift in the natural arrangement of the cellulose chains occurs. This movement produces no alteration in the *b* axial dimension but changes both *a* and *c*. This may be interpreted as a shifting of the cellulose chains with respect to one another parallel to the fiber axis with a probable rearrangement in the hydrogen bridging. The observations that the 1.54 μ band is present when *E* is parallel to the axis but not when it is perpendicular to it and that it disappears upon mercerization indicate that certain OH groups having orientations in the direction of the axis are released from hydrogen bridging upon mercerization. In general, it may be stated that mercerization results in an increase in the absorption representing the least amount of perturbation.

(13) O. L. Sponsler and W. H. Dore, THIS JOURNAL, **50**, 1940 (1928).

In the 2 μ region of the spectrum of unmercerized Ramie the absence of a sharp band at 2.02 μ and the presence of a broad one at 2.11 μ confirm the conclusion that all, or practically all, of the OH groups in the natural condition are involved in hydrogen bridges. The diminution in the magnitude of the average perturbation upon mercerization is shown again by a shift of the 2.11 μ band to 2.09 μ.

As an example of naturally occurring cellulose obtained from another source a packet of dried wall material from the large alga, *Valonia*, was studied with unpolarized light. The spectrum obtained in this instance was very similar to that for unoriented ramie fibers.

Summary

Observations of absorption bands characteristic of hydroxyl groups in the region 1.5 and 2.0 μ have been made for cellulose. The extreme weakness of the band at 1.44 μ and the failure to detect a band at 2.02 μ indicate that in natural cellulose fibers relatively few "unperturbed" hydroxyl groups are present. The shifts toward longer wave lengths in the absorption bands in these two regions indicate the presence of OH vibrators which are perturbed through hydrogen bridging. However, in the natural arrangement of these extremely large molecules it appears that intermediate conditions of perturbation occur, corresponding to hydrogen bridges of variable distances and variable bond angles between the hydroxyl groups of the adjacent cellulose chains.

LOS ANGELES, CALIF. RECEIVED JUNE 21, 1940

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, HARVARD UNIVERSITY, AND THE RESEARCH LABORATORIES, MERCK AND CO., INC.]

Extensions of the Vitamin K_1 Synthesis

BY LOUIS F. FIESER, MAX TISHLER AND NORMAN L. WENDLER

A preliminary account has been given[1] of the synthetic experiments presented in this paper and of some of the assays for antihemorrhagic activity conducted by W. L. Sampson of the Merck Institute for Therapeutic Research. A full report of the biological experiments will be published elsewhere.

Variations in the synthetic method developed for the preparation of vitamin K_1[2] hitherto have been concerned chiefly with the use of a series of β-unsaturated alcohols and dienes for condensation with a given type of phenolic component,[2,3] and with the employment of various condensing agents (oxalic,[2] trichloroacetic,[2] phosphoric[4] and acetic[5] acids, heat[3]). Phytol, geraniol, and cinnamyl alcohol react much more readily than allyl or benzyl alcohol and at least as well as 2,3-

(1) Fieser, Tishler and Sampson, THIS JOURNAL, **62**, 996 (1940).
(2) Fieser, *ibid.*, **61**, 3467 (1939).
(3) Fieser, Campbell, Fry and Gates, *ibid.*, **61**, 3216 (1939).
(4) Fieser, *J. Biol. Chem.*, **133**, 391 (1940).
(5) Tishler, Fieser and Wendler, THIS JOURNAL, **62**, 1982 (1940).