

[Van Ekenstein and Blanksma, *Chem. Weekblad*, **6**, 374 (1909); also Levene, "Nucleic Acids," A. C. S. Monograph No. 56, p. 131, 1931], it seemed desirable to apply the methods [*Bur. Standards J. Res.*, **8**, 615 (1932); **10**, 337 (1933)] which had been developed for the study of other sugars to the investigation of *d*- and *l*-ribose.

Measurements taken at 20 and at 1° show that both *d*-ribose and *l*-ribose exhibit a very remarkable mutarotation. The mutarotation takes place rapidly and direction of the change reverses after a few minutes, so that the initial and final rotations are not greatly different. On account of the rapidity with which the reaction takes place the mutarotation can be best observed at low temperatures.

A 2.0236-g. sample of *d*-ribose (m. p. 87°) dissolved in 45.223 g. of water at 1° gave  $[\alpha]_D^{20}$  -23.1°, 1.5 minutes after solution; -21.3°, five minutes; -19.5°, ten minutes; -18.8° (minimum), twenty minutes; -19.1°, thirty minutes; -21.2°, sixty minutes; -23.1°, one hundred and twenty minutes; -23.7°, three hundred minutes. A 1.9941-g. sample of *l*-ribose (m. p. 87°) dissolved in 45.223 g. of water at 1° gave  $[\alpha]_D^{20}$  +23.2°, two minutes; +21.5°, five minutes; +19.9°, ten minutes; +18.7° (minimum), twenty minutes; +19.4°, thirty minutes; +21.5°, sixty minutes; +23.2°, one hundred and twenty minutes; +24.3°, three hundred minutes; +24.0°, twenty-eight hours.

The complex character of the mutarotation curves shows that crystalline *d*-ribose and also *l*-ribose in water solution establish equilibrium with at least three isomers. One of the isomers is less levorotatory than the crystalline *d*-sugar and the other is more levorotatory. The mutarotation resembles that of the labile calcium chloride compound of mannose reported by Dale [*THIS JOURNAL*, **51**, 2225 (1929)] which Isbell has shown [*ibid.*, **55**, 2166 (1933)] gives  $\gamma$ -mannonic lactone when oxidized with bromine water in the presence of barium carbonate, and which probably has a 1,4 ring structure.

Oxidation of *d*- and *l*-ribose by the barium carbonate-bromine method shows that they are oxidized rapidly at first and then more slowly. The decrease in reaction rate is presumably caused by a less readily oxidized substance formed by the mutarotation reaction.

Since the rotation of *d*-ribose changes initially from a negative to a less negative value, in ac-

cordance with the usual nomenclature, the crystalline sugar will be tentatively designated as  $\beta$ -*d*-ribose and its mirror image as  $\beta$ -*l*-ribose. The similarity of  $\beta$ -*d*- and  $\beta$ -*l*-ribose to the labile calcium chloride compound of mannose suggests that these substances may have furanose structures which on solution in water change spontaneously into the corresponding pyranose forms. However, no definite classification of structures is possible until further experiments are completed.

BUREAU OF STANDARDS  
WASHINGTON, D. C.

FRANCIS P. PHELPS  
HORACE S. ISBELL  
WARD PIGMAN

RECEIVED FEBRUARY 13, 1934

#### THE ASSUMED NON-IDENTITY OF COTTON AND WOOD CELLULOSE

Sir:

On the basis of methylation experiments carried out on cotton and  $\alpha$ -celluloses prepared from five different woods, D. J. Bell [*Biochem. J.*, **26**, 590-597 (1932); **26**, 598-608 (1932); **26**, 609-614 (1932)] has questioned the identity of the chemical structure of cotton and wood cellulose. He found that a maximum methoxyl content of 36.3-39.0% was attained with the wood  $\alpha$ -celluloses as contrasted with a theoretical value of 45.6%. Bell ascribes this resistance to methylation shown by the wood  $\alpha$ -celluloses to the presence of a so-called "resistant portion." These results have been regarded by Irvine as having a marked bearing on the conclusions drawn by other authors with respect to chain length.

In an attempt to duplicate these results with rayon pulps from spruce, beech and maple wood it was not found possible to confirm the work of Bell with respect to the presence in the cellulose of a portion resistant to methylation. The following results were obtained.

Source of $\alpha$ -cellulose	No. of methylations	OMe, %
Spruce	9	44.24
Beech	5	43.08
Maple	5	43.72

The methoxyl values given above are not maximum figures since the reaction has given as yet no indication of an end-point and the methylations are therefore being continued in order to arrive, as closely as possible, at the theoretical value of 45.6% OMe.

DIVISION OF INDUSTRIAL AND  
CELLULOSE CHEMISTRY  
MCGILL UNIVERSITY  
MONTREAL, CANADA

J. BARSHA  
HAROLD HIBBERT

RECEIVED FEBRUARY 21, 1934