tartaric acids and that under normal atmospheric conditions there is little likelihood of trouble from absorption of water from the air by malic acid in storage.

Much of the experimental work reported in this paper was carried out by Messrs. R. M. Burns, H. P. Corson, A. E. Craver, C. W. Fisher and H. E. Williams, and we wish to express our appreciation of their interested coöperation.

Summary

As the work presented is merely a digest of data on physical properties there are no conclusions to be drawn. There are many gaps in the available data and we hope other investigators will supply much of the missing information. The stereo-isomerism of these acids makes any data on them of great theoretical interest and it is to be hoped that further and more complete studies will furnish the means by which modern ideas of intramolecular structure of compounds of this type may be clarified and amplified.

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MANNOSE FROM WHITE SPRUCE CELLULOSE

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In a recent paper[3] attention was called to the fact that mannose is present in cellulose prepared by either the Cross and Bevan method or by the sulfite process. Further investigation has shown that it is also present in the cellulose isolated from white spruce by the soda or sulfate method and that it is distributed throughout the α-, β- and γ-celluloses of the Cross and Bevan product. The quantities of mannose obtained from these different celluloses are shown in Table I. The question naturally arose as to whether the mannose is chemically combined or is present as a mannan or in the adsorbed state. Although the problem is difficult of solution, this paper contains some experimental evidence which indicates that it is probably present in the combined state, and substantiates Bertrand's[4] theory of the existence of a mannocellulose.

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[3] Sherrard and Blanco; a paper presented at the Meeting of the American Chemical Society at Birmingham, Alabama, April, 1922.

[4] Bertrand, *Compt. rend.*, **129**, 1027 (1899).

TABLE I

HYDROLYSIS OF DIFFERENT CELLULOSES WITH 5% HYDROCHLORIC ACID

		Mannose		
Sample	Sugar %	Dry sample %	Total sugar %	Remarks
Absorbent cotton	7.49	None	...	Autoclaved
Raw cotton; Cross and Bevan treated	8.55	None	...	More soluble material in this sample
α-Cellulose from raw cotton; Cross and Bevan treated	33.77	None	...	
White spruce sulfite pulp, unbleached	10.06	1.86	18.48	
White spruce sulfite pulp, bleached	8.45	1.56	18.46	
White spruce cellulose, Cross and Bevan	29.20	7.64	26.16	
White spruce soda pulp	12.53	2.12	16.92	
White spruce sulfate pulp	12.45	2.68	21.52	
Douglas fir, Cross and Bevan cellulose	23.20	3.93	17.0	
Yellow birch, Cross and Bevan cellulose	24.96	None	...	

It has already been shown[5] that celluloses isolated from cotton, white spruce, Douglas fir and yellow birch by the Cross and Bevan method exhibit similar curves when dissolved in conc. hydrochloric acid and the rate of change of their optical rotations has been studied. Since the white spruce cellulose was known to contain mannose, and yellow birch no mannose but instead a large quantity of pentoses, the similarity of their optical behaviors indicated that the method was of itself of little value as a means of differentiating celluloses.

Until recently the mannose obtained from most coniferous woods by mild acid hydrolysis was generally considered as being present as a mannan. However, efforts to isolate a mannan from white spruce wood by methods known to be successful in the isolation of this material from other plant substances have failed completely.

The method used for the determination of mannan was that described by Brown[6] for the isolation of mannan from plant materials.

Fifteen g. of spruce wood flour (80–100 mesh) was refluxed with 200 cc. of 2.8% sodium hydroxide solution for 2 hours. The wood residue was removed by filtering through cloth with suction and the filtrate made up to 500 cc. Two hundred and fifty cc. of this solution was treated with 60 cc. of Fehling solution and warmed on a water-bath. A small quantity of copper oxide was deposited but no insoluble copper-mannan compound was precipitated. The remaining 250 cc. of original alkaline solution was refluxed with 3% hydrochloric acid for 3 hours after the alkali had been neutralized. The total reducing sugars formed corresponded to 1.86% of the original wood, but they gave no test for mannose.

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[5] Sherrard and Froehlke; a paper presented at the Meeting of the American Chemical Society at Birmingham, Alabama, April, 1922.

[6] Brown, "Sugar Analysis," Wiley and Sons, **1912,** p. 594.

The 73.3% of the original wood remaining after extraction was washed, dried and hydrolyzed with 5% hydrochloric acid for 4 hours, giving a conversion of 8.75% of the wood into total reducing sugar.

The mannose yield was equivalent to 1.12% of the extracted wood, or 12.65% of the total sugar produced. Since the alkali-extracted wood is supposedly mannan-free but still hydrolyzes to give a quantity of mannose, it is safe to conclude that the mannose is not present as a mannan but combined with the cellulose or possibly some other groups to form an alkali-resistant complex.

The belief that mannose resulted from the hydrolysis of a mannan was largely based on the fact that most of the mannose can be removed from the wood by boiling for a few hours at atmospheric pressure with dil. hydrochloric or sulfuric acid. It has been found that such a treatment forms an equal or even greater quantity of glucose. This would indicate that these sugars might come from a mannan or a glucosan or possibly a mannoglucosan, were it not for the fact that the cellulose removed by such a reaction corresponds quantitatively with the sugars produced. Since the glucose is usually considered as resulting from the hydrolysis of the cellulose, it is not illogical to conclude that the mannose comes from the same source and is combined in a similar manner. If these sugars do not result from the cleavage of the cellulose complex some explanation must be advanced for the disappearance of the cellulose without a consequent formation of sugar. The close relationship between sugars formed and celluloses removed is shown in Table II.

TABLE II

HYDROLYSIS OF WHITE SPRUCE WOOD

Percentage of dry original wood

Treatment	Cellulose Before hydrol.	Cellulose After hydrol.	Loss in cellulose	Sugars	Mannose	Theoretical sugar yield
Autoclave cook No. 36; wood containing some bark	58.33	39.47				
	58.32	39.87				
Av...	58.33	39.67	18.66	19.35	6.60	20.71
Refluxed with 5% HCl, wood containing no bark	56.09	38.33	17.93	19.81	9.09	...
	56.42	37.72	18.54	19.89	9.20	20.24
Av...	56.26	38.02	18.24	19.85	9.14	

That the mannose is not combined in the same way as all of the glucose residues is shown by the fact that all of the mannose can be removed by successive hydrolyses with dil. acid. Table III shows that 7.64% of mannose is obtainable from a single hydrolysis with dil. hydrochloric acid, while in the second hydrolysis only a trace is obtained. The third hydrolysis showed that all the mannose had been removed, as was the case with a complete solution in 72% sulfuric acid of the same residue from the second experiment. It is of interest to note, however, that in all cases an even greater quantity of glucose was obtained than of mannose. This indicates one of two things, (1) if the mannose is not in true combination with the cellulose neither is a portion of the glucose, (2) both mannose and glucose are loosely attached to the cellulose nucleus and hydrolyze with equal readiness.

TABLE III

HYDROLYSIS OF WHITE SPRUCE WOOD AND WHITE SPRUCE CELLULOSE

	Material	Number of hydrolysis	Sugar Sample %	Sugar Wood %	Mannose Sample %	Mannose Wood %	Mannose Sugars %
1.	White spruce wood	1 5% HCl	...	19.45	....	7.81	40.15
2.	White spruce cellulose	1 5% HCl	29.20	17.52	7.64	4.6	26.16
3.		2	10.13	3.61	Qualitative test only	..	...
4.		3	13.60	5.04	None	..	...
5.		2 Cellulose residue from No. 2 with 72% H_2SO_4	95.56	40.60	None	..	...
6.		Autoclave	29.92	17.95	5.75	..	19.18

Since the mannose is present in cellulose which is isolated from wood by very vigorous reagents it must either be combined with the cellulose or present with glucose in a grouping as resistant as cellulose itself. If it is combined it should be fairly uniformly distributed and should be found in the α-, β- and γ-portions. Table IV contains data showing that it is found in all 3 fractions obtained from Cross and Bevan cellulose. It will be noticed that considerable loss occurs in this determination. A discrepancy in total sugar is also experienced which is not entirely accounted for by the loss in mannose. This discrepancy in total sugar as well as in mannose may be due to a loss of cellulose itself in separating the fractions, since the loss would be considered and calculated as γ-cellulose. The

TABLE IV

MANNOSE CONTENT OF α-, β- AND γ-CELLULOSES, CROSS AND BEVAN WHITE SPRUCE CELLULOSE

	Sugars		Mannose				
Cellulose sample	In sample %	Total sugars in original cellulose %	In sample %	Mannose in original cellulose %	Total mannose in original cellulose %	Total sugars in sample %	Sugar hydrolyzed based on total cellulose %
α............	22.10	12.10	1.56	0.85	11.1	7.0	16.4
β............	40.12	9.93	7.54	1.86	24.3	18.7	13.60
γ............	9.73	2.00	2.12	0.43	5.6	21.8	+
Total.......		24.03		3.14	41.0		30.2+
Total cellulose.		29.20		7.64	100.0		29.2

loss might also be attributed to the error involved in the preparation and isolation of the mannose-phenylhydrazone, since the solutions used contained very small amounts of mannose. It is of interest, however, to find mannose present in all 3 fractions after 30 minutes' treatment with alkali. It has been found that mannose is still present in α-cellulose after a 3-hours' treatment with 17.5% sodium hydroxide solution at room temperature. This condition would be rather surprising if the mannose were adsorbed by the cellulose fibers, since it should in that case be in condition to react with alkali. Pure cotton which had previously received the same treatment contained no mannose, a fact which indicates that the mannose found in the white spruce cellulose was not produced by the reagents used.

The observation has also been made that Cross and Bevan cellulose that has been dissolved in zinc chloride-hydrochloric acid solution or in copper ammonium solution and reprecipitated still contains a quantity of mannose. Apparently, some of the mannose is removed when the cellulose is dissolved, since the ratio of mannose to cellulose is different than in the original sample. The ratio of mannose to cellulose also differs in the celluloses prepared by the use of zinc chloride-hydrochloric acid and Schweitzer's reagent. The latter solution removes the least mannose.

Since mannose and glucose are so closely related it is difficult to consider them as present in cellulose in dissimilar combinations or configurations. We know that alkali will partly convert mannose into glucose, but when cellulose is treated with a 17.5% sodium hydroxide solution no change in mannose content occurs even after the mixture has stood for 24 hours. If it were held in the adsorbed state one would expect such a reaction to take place. On the other hand, little or no change would be expected if it were in the combined state.

It cannot be denied that each successive treatment in the purification process alters the product, so that the more treatments that are given the greater the product differs from the original cellulose. Some of the so-called impurities withstand the action of the most vigorous reagents but are still considered impurities. It would appear much simpler to assume that the pentoses as well as hexoses other than glucose are chemically combined. It is not more unreasonable or illogical to expect different celluloses from different plants than not to expect the presence of di-, tri-, and poly-saccharides in the tissues of different plants. In most of the tri- and tetrasaccharides one sugar is more susceptible to hydrolysis than the others and may easily be removed, leaving a more resistant residue in the form of a di- or trisaccharide depending upon the sugar used. This is true of raffinose, melezitose, gentianose, and stachyose. The analogy between the action of these sugars and cellulose containing mannose is quite striking and strengthens the view that mannose and pentoses may be chemically combined with the cellulose nucleus.

The hypothesis that mannose is present in some celluloses in a chemically combined state does not affect Hibbert's formula for cellulose, since it may be used to indicate a combination of mannose or even pentoses with glucose as readily as a combination of glucose residues alone. As a matter of fact, it strongly supports his hypothesis, but it is not in accord with Heuser's fundamental premise that cellulose consists only of glucose residues and is the same, regardless of source.

Throughout this paper and the preceding ones the terms Cross and Bevan cellulose and normal cellulose have been used quite indiscriminately and this use has excited criticism. We are aware of the fact that the former contains oxycellulose, some lignin, and other impurities. Our chief concern has been with the mannose and pentose content which differs but little in these two products. It is extremely difficult to decide upon a standard cellulose for comparison, since all celluloses contain groupings that are regarded by some as impurities. Dr. L. F. Hawley has pointed out that the tendency is to compare a hypothetical cellulose from one source with another hypothetical cellulose from another, since in all cases impurities remain even after the most vigorous treatment and must be accounted for by calculation.

Summary

In view of the fact that mannose cannot be isolated from white spruce wood or cellulose as a mannan, that it persists in cellulose prepared by use of most vigorous reagents, and that when it is removed from the cellulose by hydrolytic means an equal or greater quantity of glucose is removed simultaneously, we are forced, at least for the present, to conclude that it is attached to the cellulose residue in much the same way as is a portion of the glucose. It is not attached as firmly as all of the glucose residues in the cellulose, however, a fact that rather supports the view that cellobiose constitutes the nucleus of white spruce cellulose as well as of cotton.

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