CCIX. WOOD CELLULOSE.

IV. FURTHER INVESTIGATION OF THE "RESISTANT PORTION" OF THIRIENA PULP.

By DAVID JAMES BELL.

*From the Chemistry Research Laboratories of the United College of
St Salvator and St Leonard, The University of St Andrews.*

(Received September 7th, 1932.)

THE discovery by the author of the existence within wood celluloses of fractions resistant both to complete etherification and to hydrolysis has already been described in this *Journal* [1932, 1, 2, 3]. The causes underlying this peculiar inactivity of certain of the free hydroxyl groups attached to the glucose residues composing the resistant material could not be explained on grounds either of physical condition or of the positions occupied by these groups. Acetylation of the methylated resistant portions, which had compositions approximating to that of a dimethylcellulose, was easily effected by Barnett's process [1921], when it was found that extensive depolymerisation had accompanied the acylation of the free hydroxyl group. Cleavage of these products, by the action of methyl alcohol containing hydrogen chloride, could now be readily carried out, and it was found that the cleavage products consisted of a mixture of at least five partially methylated glucoses (as the methylglucosides). Individually these substances were 2:3:6-trimethylglucose; 2:3-dimethylglucose; 2:6-dimethylglucose; 3:6-dimethylglucose; 6-monomethylglucose. Other isomerides of trimethyl- and dimethylglucose were absent. No monomethylglucose other than the 6-derivative could be detected, although the absence of isomerides was not proved.

The extremely scanty information at present available regarding the structure of polysaccharides narrowed down to a small range the methods of investigation applicable to the present problem. It was decided to effect a comparison of the dimethyl-sugars produced on hydrolysis of the resistant portions with those derived from the partially methylated non-resistant fractions. To this end a specimen of Thiriena pulp was methylated to a methoxyl content of 27.9 %. Cleavage of the methylate yielded 29.2 % of resistant material, showing a methoxyl content of 19.1 %. Hence, calculation shows that the remaining 70.8 % of non-resistant material had, in the methylate, a methoxyl content of 31.3 %, a value closely similar to the methoxyl content of the fully methylated resistant portion of Thiriena pulp, namely 30.3 %.

The resistant material, after methylation and acetylation, displayed properties identical with those of previous preparations. The mixed glucosides derived from the non-resistant portion contained about 50 % of the dimethyl compounds: after removal of trimethyl derivatives by extraction of an aqueous solution with chloroform, the dimethyl-methylglucosides were purified by the process of extraction from strong potassium carbonate solution [Bell, 1932, 1] and finally distilled in a high vacuum. The resulting colourless syrup was employed in the comparative experiment, the material from the resistant portion having been previously investigated and briefly reported on [Bell, 1932, 3].

The methods employed were those devised by Rutherford [1932], and Oldham and Rutherford [1932], which have been applied to the hydrolysis products of methylated starch by Irvine and Rutherford [1932]. Since complete condensation of the free sugars with methyl alcoholic hydrogen chloride took place in the cold, neither batch of material contained derivatives of glucose with the 4th position substituted. The method of investigation of the mixed glucosides is summarised diagrammatically, as follows.

A. *Estimation of the amount of substitution of the fourth group in the glucose chains. Estimation of the amount of 3:6 dimethylglucose.*

Methoxyl estimation of the mixture indicates the proportion of 3:6 dimethylglucose.

B. *Estimation of the amount of 2:3-dimethylglucose by determination of the amount of free hydroxyl in group 6.*

(The above mixture was heated with sodium iodide in acetone whereby the *p*-toluenesulphonyl group in position 6 (*D*) was substituted by iodine with the formation of (*G*). Iodine estimation of the product therefore indicates the amount of 2:3-dimethylglucose.)

2:3-dimethyl-4-*p*-toluenesulphonyl-6-iodo-methylglucoside

The result of the comparison was striking, for, although the same three individual dimethylglucoses were obtained in both cases, their relative proportions were very different. The three partially methylated glucoses, 2:3-dimethylglucose, 2:6-dimethylglucose, 3:6-dimethylglucose, were in the following relative proportions:

Dimethylglucose	Portion of the wood cellulose	
	Resistant %	Non-resistant %
2:3	4.4	20.7
2:6	58.6	61.3
3:6	37.0	18.0

EXPERIMENTAL.

Tabulated details of the condensation with 1% acid acetone of the mixtures of the γ -glucosides.

Source of material	Resistant	Non-resistant
Amount of glucosides g.	1.721	1.000
Yield of acetone condensation product g.	1.589	0.862
Yield %	80.0	73.8
Mean OMe (2 determinations) %	31.6	33.6
3 : 6-Dimethylglucose found %	37	18
Theoretical OMe for 3 : 6-dimethyl-1 : 2-monoacetoneglucose		25.0 %
Theoretical OMe for monoacetonedimethyl-methylglucoside		35.5 %

Details of the treatment of the normal glucosides with *p*-toluenesulphonyl chloride are appended. The yields of the products were not good; opportunity did not permit of retreatment of the unreacted materials.

Acylation of the mixtures of dimethyl-methylglucosides.

Source	Resistant	Non-resistant
Amount of starting material g.	2.50	5.47
Yield of di- <i>p</i> -toluenesulphonates g.	4.06	8.22
Yield %	68.0	63.2
OMe content %	17.2	17.7
Theoretical OMe for dimethyldi- <i>p</i> -toluenesulphonyl-methylglucoside 17.5 %		

The estimation of the 2 : 3-dimethylglucose.

Amount of material used g.	3.50	4.46
Yield, after NaI treatment g.	3.09	4.32
2 : 3-Dimethylglucose (by iodine estimation)	4.4	20.7
present %		
Yield of residue, after AgNO ₃ treatment g.	3.06 (Theoretical)	3.56 (Theoretical)

DISCUSSION.

As Irvine and Rutherford [1932] found in the case of partially methylated starch, derivatives having the 6th position etherified preponderate in the mixture of dimethylglucoses. In neither case now under consideration were the relative proportions of the different sugar derivatives of the same magnitude as found in starch. Further, although the proportion of 2 : 6-dimethylglucose is the same, whether derived from the resistant or the hydrolysable portions of the wood cellulose, quite marked differences exist between the relative amounts of the 2 : 3- and the 3 : 6-derivatives, indicating that etherification first attacks the 6th group in both cases; in the two fractions of the wood cellulose methylation of groups 2 and 3, together, must pursue different courses when 6 is unsubstituted.

Since 2 : 3 : 6-trimethylglucose is obtained as a cleavage product of the resistant portion, a part of that material must be composed of the ubiquitous polysaccharide unit, the 1 : 5- (or 1 : 4-) anhydroglucose chain. There is at present no evidence that the units giving rise to the dimethylated sugars are not similarly constituted. There must, however, be some peculiar steric effect

produced by the arrangement of the units, since these unetherifiable hydroxyl groups can be easily acetylated. This steric effect would seem, also, to be a property of the fundamental groupings, as the resistant properties persist after depolymerisation of the intact cellulose.

SUMMARY.

A fundamental distinction has been demonstrated between the glucose units composing the resistant and the non-resistant portions of a wood cellulose. Comparison of the three dimethylglucoses (2:3-, 3:6-, 2:6-) derived from the fully methylated resistant portion, and from the non-resistant residue methylated to the same extent as the resistant material, showed that they were formed in different relative proportions, indicating that etherification did not pursue the same course in the two portions of the wood cellulose.

The author is greatly indebted to Sir J. C. Irvine for the interest which he has displayed in this work, and to Mr Walter Caldwell for much practical assistance.

REFERENCES.

- Barnett (1921). *J. Soc. Chem. Ind.* **40**, 8 T.
Bell (1932, 1). *Biochem. J.* **26**, 590.
—— (1932, 2). *Biochem. J.* **26**, 598.
—— (1932, 3). *Biochem. J.* **26**, 609.
Irvine and Rutherford (1932). In the Press.
Oldham and Rutherford (1932). *J. Amer. Chem. Soc.* **54**, 366.
Rutherford (1932). Private communication.