XCI. WOOD CELLULOSE

V. "TRIMETHYLATED" CELLULOSE FROM THIRIENA PULP

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SOME years ago we carried out the first systematic investigation by the methylation process of the constitution of α -celluloses from several different woods [Bell, 1932, 1, 2, 3]. Employing the principles of manipulation current then, we found it impossible to methylate the celluloses above 37–39 % methoxyl, a value considerably short of the theoretically attainable maximum of 45 %. After cleavage by the procedure of Irvine & Rose [1906] under carefully controlled conditions, we were able to obtain two distinct products from the methylated celluloses (a) almost pure 2:3:6-trimethyl methylglucoside and (b) a so-called "resistant portion", thus termed because it resisted further cleavage and could not be methylated above a maximum of 32 % OMe.

As this behaviour persisted throughout the whole series of wood celluloses examined, we were forced to conclude that the presence of resistant portions in wood celluloses was a manifestation of some intramolecular condition distinguishing them from cotton. Moreover, resistance to methylation and to cleavage persisted after complete dissolution of the cellulose fibres in an acetylating medium.

Recently however Barsha & Hibbert [1936] reported a method for completing the etherification of wood cellulose by disintegrating the partially methylated fibres by dissolving in CHCl_3 , thus presumably exposing fresh surfaces for reaction. In this way a product having over 44 % OMe was obtained. After cleavage by HCl in CH_3OH at 100–125° only a very slight residue remained, but no characterization of the cleavage products was made beyond recording boiling points. Furthermore, no description was afforded of the procedure adopted to induce solution of the fibres in CHCl_3 , nor were the CHCl_3 solubility of the partly methylated material and the properties of the trimethylated product described.

We have therefore applied Barsha & Hibbert's technique to a wood cellulose previously examined, namely the so-called Thirienna pulp (a mild sulphite-bleach pulp from soft woods), and we have been able substantially to confirm the findings of the above authors with respect to our material.

As before, methylation ceased at 40 % OMe and the fibrous material was only partially soluble in chloroform at -10 to 80° . However, it was found possible by a simple process of hand-grinding with Na_2SO_4 , CHCl_3 and glacial acetic acid to effect gradual solution of over 90 % of the material. Methylation of the solubilized material raised the OMe content above 43 % and cleavage of over 90 % resulted under conditions optimum for the isolation of the resistant portions. The residual solid (8 %) thus obtained, after precipitation from CHCl_3 solution by light petroleum, left a negligible residue on cleavage with fresh reagents.

In agreement with Barsha & Hibbert, we can therefore state that wood celluloses do not contain any appreciable amount of material defying complete etherification or cleavage. We desire to make the point, however, that complete identity between cotton and wood celluloses remains still an open question.

EXPERIMENTAL

Methylation. 3 g. Thirienna pulp were treated 8 times by Barsha & Hibbert's technique [1936]. Thoroughly washed and dried material showed OMe 39.7 %. Four further treatments were given, making a total of 12. The final yield was 2.7 g. OMe, 40.0 %.

A specimen of this fibrous material was shaken at 20° for 48 hr. with 20 parts dry CHCl_3 , when less than 25 % of the cellulose dissolved. The residue resisted further attempts at dissolution, confirming previous findings [Bell, 1932, 1].

Almost complete solution was obtained in the following way: 2.712 g. material (OMe 40 %) were shaken for 48 hr. with a mixture of 400 ml. CHCl_3 and 135 ml. glacial acetic acid, when much dissolved. The gelatinous residue was separated by filtration through a 1 cm.-deep layer of anhydrous Na_2SO_4 packed on a G 3 Jena glass filter. After washing with CHCl_3 , the insoluble residue was isolated by dissolving out the salt with hot water. The white glassy residue was ground with several g. Na_2SO_4 moistened with CHCl_3 and glacial acetic acid, and when well dispersed, the whole was shaken with CHCl_3 for 24 hr. Insoluble material was recovered as before and reground and shaken with CHCl_3 . The same filter was used throughout to minimize mechanical loss. By this treatment the insoluble material was diminished to 0.169 g. (6.2 % of the starting material).

The united soluble fractions were isolated by distilling off the CHCl_3 in the presence of excess water, filtering, washing and drying. 2.458 g. were obtained (90.6 % of starting material). This was then methylated 4 times according to Barsha & Hibbert; the product was completely soluble in CHCl_3 and after removing a trace of precipitate by centrifuging at 14,000 r.p.m. showed $[\alpha]_D^{20} 0.0^\circ$ ($c=1.3$; $l=2.0$) and OMe, 43.1 %.

Cleavage. 2.21 g. material (OMe 43.1 %) were heated in a sealed tube at 80° for 400 hr. with 23 ml. CH_3OH containing 1 % dry HCl gas. The contents of the tube were then washed into centrifuge tubes, spun and the supernatant fluid collected. The residue was washed 3 times with CH_3OH , dried and weighed. It amounted to 0.18 g. (8.1 % of starting material). Unlike the original "resistant portions" it was completely soluble in CHCl_3 , giving a brown solution which was decolorized by shaking with charcoal and filtering through BaCO_3 . After removing the chloroform in the presence of water, the colourless dried residue (0.16 g.) was treated for 400 hr. as before with CH_3OH —HCl in a sealed tube, when only a minute trace of solid remained. The hydrolyzed material was added to the main fraction of the cleavage products.

The cleavage products. These amounted to 2.016 g. Since Haworth *et al.* [1937] have shown that treatment with acid CH_3OH seems to induce some condensation between molecules of 2:3:6-trimethyl glucose, and since the small amount of material available rendered separation by fractional distillation impracticable, the cleavage products were heated with 25 ml. 0.6 *N* HCl until a constant rotation was observed (4 hr.) and the hydrolysate worked up in the usual manner after neutralization by Ag_2CO_3 . Yield, 1.75 g. colourless syrup.

1.65 g. of this material were extracted 6 times with 50 ml. amounts of dry ether. The residue weighed 0.07 g. (4.2 %) and showed OMe 37 %. The ether

extract on evaporation yielded 1.555 g. colourless syrup, n_D^{20} 1.4770, which rapidly crystallized in the manner characteristic of 2:3:6-trimethyl glucose and was identified as such by the usual methods. No evidence of isomeric trimethyl glucoses could be obtained.

SUMMARY

1. Methylation of wood cellulose to a methoxyl content of over 43 % has been effected, confirming the findings of Barsha & Hibbert. The product shows $[\alpha]_D 0^\circ$ in CHCl_3 , whereas trimethyl cotton shows $[\alpha]_D -10^\circ$.

2. Over 90 % of the trimethyl cellulose is transformed into simple glucosides by the action of CH_3OH containing 1 % HCl at 80° . The only cleavage product identifiable was 2:3:6-trimethyl glucose.

3. Previous findings by the author of a portion of wood celluloses resisting methylation and cleavage would seem to have their basis in mechanical rather than purely chemical circumstances.

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