[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY[1]]

Studies on Reactions Relating to Carbohydrates and Polysaccharides. L. The Chemical Identity of Cotton and Wood Cellulose

BY J. BARSHA AND HAROLD HIBBERT

In a recent series of papers, D. J. Bell[2] has drawn attention to the question of the identity of celluloses from different natural sources and to the lack of thorough investigations upon which to base conclusions regarding the constitutional similarity between cotton and wood celluloses. In order to establish the identity, or otherwise, of different wood celluloses with one another and with cotton cellulose, he carried out a number of methylation experiments on cotton and on the alpha-celluloses prepared by the action of chlorine and sodium hydroxide on wood meal from four different woods (*Quercus pedunculata*, *Q. sessiliflora*, *Fagus sylvatica* and Sitka spruce) as well as an alpha-cellulose from "Thiriena pulp."[3]

By successive treatments with dimethyl sulfate and sodium hydroxide solution in the presence of acetone, Bell obtained products from these wood celluloses with maximum methoxyl contents of 36.3 to 39.1%, while under similar conditions a methylated cotton was obtained having a methoxyl value of 44.3% (calculated for trimethyl cellulose, CH_3O, 45.56%). Upon hydrolysis of the methylated wood celluloses with methyl alcohol containing anhydrous hydrogen chloride, he obtained from each a "resistant portion" having a methoxyl content of about 28%. The latter on further repeated methylation gave a maximum methoxyl value of 32%.

These results have a marked bearing on the constitution of wood cellulose and, in view of the industrial importance of refined wood pulps, a repetition of the work was undertaken.

Highly refined sulfite pulps prepared from spruce and maple wood were methylated, using a much larger excess of reagents than employed by Bell, and methylated products obtained having methoxyl contents close to the theoretical value for trimethyl cellulose. Cleavage of these with methyl alcohol and anhydrous hydrogen chloride[4] yielded no insoluble "resistant portion" but gave 2,3,6-trimethylmethylglucoside in good yield.

The only difference between the authors' experimental methylation technique and that of Bell was (1) the use of a larger proportion of the methylating reagents and (2) solution of the methylated celluloses in chloroform after having reached an apparent maximum methoxyl value and reprecipitation by petroleum ether. Apparently in this way fresh surfaces are exposed and the free hydroxyl groups thus rendered more available to the methylating reagents.

The results show that the wood celluloses examined do not contain a portion "resistant to methylation" and that the methylated products can be readily hydrolyzed to 2,3,6-trimethylmethylglucoside. They thus behave in a manner similar to cotton cellulose.

Experimental

Methylation of Spruce (A) and Maple (B) Wood Sulfite Pulps.[5]—The pulps were both methylated by the same method. About 5 g. (dry weight) of the pulp was disintegrated in 300 cc. of acetone contained in a three-necked flask fitted with a mechanical stirrer, two dropping funnels and a reflux condenser. Methylation was effected with 96 cc. of dimethyl sulfate and 256 cc. of sodium hydroxide solution (30% by weight). The reagents were added in eight portions, one every thirty minutes at 56°. At the end of the reaction, the acetone was distilled off, the mixture heated to 95°, filtered immediately through a steam-jacketed Büchner funnel and washed thoroughly with boiling distilled water.

The methoxyl contents of (A) and (B) after the first methylation were 39.45 and 41.16%, respectively. After three similar additional methylations these values had increased to 43.32 and 43.54%. The values were not increased on a fifth methylation.

Each of the methylated celluloses (A') and (B') was now dissolved in 500 cc. of chloroform and reprecipitated in finely divided form by dropping the solution into 2500 cc. of petroleum ether (b. p. 30–50°) with rapid stirring. Each was centrifuged, washed with more petroleum ether, finally with acetone and then methylated further using the same procedure as before. After three such methylations constant methoxyl values of 44.39 and 44.63% were obtained. The total number of methylations carried out with (A') and (B') was eight and seven, respectively. The yields of the final products were 82.0 and 78.6%.

---

[1] With financial assistance from Mr. Harry Bronfman, to whom the authors wish to express their appreciation for his kindness.

[2] Bell, *Biochem. J.*, **26**, 590, 598, 609 (1932).

[3] "Thiriena pulp" was a technical preparation of alpha-cellulose isolated by a particularly mild treatment of soft woods, obtained from Messrs. Tullis, Russell, of Markinch, Fife.

[4] Irvine and Hirst, *J. Chem. Soc.*, **123**, 518 (1923).

[5] These highly purified pulps were supplied by the Fraser Companies, Limited, Edmundston, New Brunswick, and the authors wish to express their thanks to them for this kindness.

Hydrolysis of the Methylated Celluloses (A′) and (B′).—The fully methylated celluloses (A′) and (B′) (weights 3.45 and 3.49 g.) were dried thoroughly in the vacuum oven and hydrolyzed by heating under pressure with 50 cc. of methanol containing anhydrous hydrogen chloride (1%), first for sixty hours at 100° and then for fifty hours at 125°. Only a very slight residue remained. Each solution was neutralized with silver carbonate, filtered, evaporated under reduced pressure to 25 cc., diluted with 25 cc. of anhydrous ether, boiled with activated charcoal, filtered and the solution evaporated under reduced pressure to constant weight. Weights of crude products from (A′) and (B′), 3.55 g. (89.0%) and 3.62 g. (89.7%), respectively. The identity of these products was shown by their boiling point, 106–108° (0.015 mm.). Yields of the pure distilled products were 3.25 g. and 3.30 g., respectively.

Summary

1. The difficulties encountered in effecting complete methylation of refined sulfite wood pulps from spruce and maple, by means of dimethyl sulfate and sodium hydroxide, can be overcome readily by dissolving the partially methylated products in chloroform, reprecipitating into petroleum ether and subsequent remethylation with the same reagents.

2. Using this technique no chemical differences can be noted in the behavior of cotton and refined wood pulps, respectively, nor in their hydrolysis products.

3. The previous assumption of the presence of a "resistant" type of cellulose in wood pulps responsible for incomplete methylation and differing therefore from cotton cellulose does not appear to be warranted.

MONTREAL, CANADA RECEIVED APRIL 24, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

The Olefin–Benzene Condensation with the Sulfuric Acid Catalyst

BY H. L. WUNDERLY, F. J. SOWA AND J. A. NIEUWLAND

A number of investigators[1] have employed sulfuric acid alone and with other combinations as a catalyst in the olefin–benzene condensation.

The purpose of this investigation was to show the influence of: boron fluoride as a promoter, the amount of sulfuric acid, time and temperature on the olefin–benzene condensation and to study the mechanism of the reaction.

Ipatieff, Corson and Pines[1e] claimed that the propylene–benzene condensation proceeded in exactly the same manner when sulfuric acid was used alone as it had in the presence of boron fluoride and sulfuric acid. It seemed doubtful that the conditions of the experiments of Ipatieff, Corson and Pines[1e] and of Slanina, Sowa and Nieuwland,[1d] were sufficiently comparable to draw this conclusion. Two series of experiments were performed, similar in every detail, except in the first case 80 g. of sulfuric acid alone, while in the second case 80 g. of sulfuric acid with 10 g. of boron fluoride, was used; two moles of benzene was employed. The rate of addition of propylene was controlled carefully and the temperature was maintained at 4 ± 1° for all experiments. The results are given in Table I.

TABLE I

THE EFFECT OF BORON FLUORIDE AND TIME ON OLEFIN–BENZENE REACTION

Time, hrs.	BF_3 g. used	Isopropylbenzene Mono	Di	Tri
2	0.0	62.9	22.8	7.7
2	10.0	91.1	32.7	5.2
4	0.0	97.1	56.2	20.3
4	10.0	97.1	82.4	22.9

It should be noted that boron fluoride exerted a remarkable influence on the propylene–benzene condensation. The effect of time upon this reaction is also shown in Table I. Again, the effect of boron fluoride was pronounced in the ethylene–benzene reaction. Although ethylene did not condense with benzene in the presence of sulfuric acid alone under the conditions employed in this investigation, it was interesting that condensation took place when the mixed catalyst composed of sulfuric acid and boron fluoride was used.

A series of propylene–benzene condensations using sulfuric acid as the catalyst are shown in Fig. 1.

The reactions were all performed under identical conditions except that the quantity of sulfuric acid

---

(1) (a) Kraemer and Spilker, *Ber.*, **23**, 3269 (1890); (b) Brochet, *Compt. rend.*, **117**, 115 (1893); (c) Ipatieff, U. S. Patent 2,006,695; *C. A.*, **29**, 5456 (1935); (d) Slanina, Sowa and Nieuwland, THIS JOURNAL, **57**, 1547 (1935); (e) Ipatieff, Corson and Pines, *ibid.*, **58**, 919 (1936).