

## Dimethylsulphoxide, a Solvent for Hemicelluloses

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Part of the holocellulose of birch or spruce can be extracted with dimethylsulphoxide and further quantities are extracted from the swollen material by a subsequent treatment with water. The extraction is quite mild, and the fractions still contain a high percentage of the acyl groups (acetyl and formyl) originally present in the wood. Partial fractionation of the hemicellulose components is achieved by the extractions. Dimethylsulphoxide can also be used as a rather selective precipitating agent for hemicelluloses.

In a recent investigation at this Institute<sup>1</sup>, it was found that dimethylsulphoxide (D.M.S.) was an excellent solvent for cellulosexanthates of a low D.S., in which the xanthate groups had previously been reacted with chloro-di-N-ethyl-acetamide. It was superior to other solvents, *e. g.* dimethylformamide. We therefore considered it worth while to investigate the possibilities of D.M.S. as a solvent for hemicelluloses, and in the present paper a preliminary study on this subject is reported.

A birch holocellulose, a spruce holocellulose and a spruce sulphite pulp have been investigated. They were all extracted with D.M.S. at room temperature, with cold and with hot water and finally with 18 % sodium hydroxide solution. The fractions were collected and analysed, the results being summarized in Tables 1, 2 and 3. The recovery of extracted material is not quantitative, partly because further fractionations were performed before the fractions were dried and weighed, which involved losses, and partly because the polysaccharides in some extracts were not completely precipitated. In separate experiments, however, it was shown that a good recovery could be obtained.

From the Tables 1, 2 and 3 it is evident that a considerable part of the hemicellulose is extracted with D.M.S. The cellulosic material exhibits considerable inter-micellar swelling during the extraction and this is probably the reason why so much material is extracted during the subsequent treatment with water. In the D.M.S. extract from the birch holocellulose, a high percentage of acyl groups was found, recorded as acetyl, although it is known that

Table 1. Birch holocellulose (*Betula verrucosa* + *B. pubescens*).

Fraction	Extraction residue, % of original holocell.	Yield, g	Acetyl, %	Uronic acids % a)	Methoxyl %	Galactose : Glucose : Mannose : Arabinose : Xylose
Holocellulose	100	14.6	5.80	9.5	1.82	b) 1.5 : 58.5 : 0.5 : 0.5 : 39.0
D. M. S. extract	—	4.4	11.2	11.1	2.76	4.7 : 8.1 : (30.4) : 56.8
Water extract	87	4.8	11.4	29.4	4.70	(+) : 2.7 : (3.0) : 94.3
18 % NaOH extract	48	45.8	—	13.0	—	(7.4) : 5.6 : 0 87.0
Residue	—	70.8	—	1.2	—	(+) : 94.7 : 3.0 : (+) : 2.3

a) Given as free uronic acids. b) Values taken from Gustafsson *et al.*<sup>2</sup> for *B. verrucosa*.

Table 2. Spruce holocellulose (*Picea excelsa*).

Fraction	Extraction residue, % of original holocell	Yield, g	Acetyl, %	Uronic acids, %	(Galactose + Glucose):Mannose: Arabinose : Xylose
Holocellulose	100	77	—	—	74.6 : 15.4 : 0.9 : 9.1
D. M. S. extract	94	—	5.0	18.0	9.7 : 23.4 : 8.3 : 58.6
Water extract	88	—	10.1	12.6	17.7 : 66.4 : 1.5 : 14.4
18 %, NaOH extract	76	—	—	10.9	13.5 : 48.0 : 2.3 : 36.7
Residue	—	58	—	—	85.8 : 13.5 : 0 : 0.7

Table 3. Spruce sulphite pulp (*Picea excelsa*)

Fraction	Extraction residue, % of original pulp	Uronic acids, %	Methoxyl, %	Glucose : Mannose : Xylose
Pulp	100	—	—	84.5 : 9.5 : 6.6
D. M. S. extract	98.3	12.8	3.85	3.4 : (+) : 96.6
18 %, NaOH extract	89.8	—	—	— : — : —
Residue	—	—	—	94.8 : 4.4 : 0.8

formyl group are also present. One of the chief advantages of the extraction method is that hemicellulose fractions, with the original acyl groups still present, have been made available for investigation. The xylose still dominates in the D.M.S. fraction but the non-xylan polysaccharides have been considerably enriched, and the fraction is a good starting material for an investigation of these completely unknown polysaccharides. The water extract is essentially a pure xylan with high percentages of acetyl and of uronic acids. As it is possible that the acetic and formic acids in the wood are chiefly combined

with the xylans, this is an especially interesting starting material for further investigations.

The polysaccharides in conifers constitute a complicated mixture, and it is obvious that a considerable partial fractionation has been obtained by the extraction of the spruce holocellulose. There are great differences in composition between the D.M.S. extract and the water extract, xylose dominating in the first and mannose in the second. Also here the acyl groups have survived the extractions. Mannose seems to occur in two different types of polysaccharides, one easily extracted and one very insoluble, which, of course, is known also from previous investigations. It is unknown whether there are structural differences between the two types or if the different solubilities are due to morphological reasons. The two types are enriched in the D.M.S. fraction and in the extraction residue, respectively. The high percentage of arabinose in the D.M.S. fraction probably comes from an arabogalactan, which seems to be present in most conifers, and in this case most of the combined glucose-galactose of this fraction, recorded in Table 2, should be galactose.

From the spruce sulphite pulp, an almost pure xylan, with a high percentage of uronic acids, was obtained from the D.M.S. extract.

It is evident from the experiments described above that some types of polysaccharides are quite soluble in D.M.S. and others are not. One would deduce that the more highly branched or substituted polysaccharides should show the greatest solubility. It was therefore natural to investigate whether D.M.S. could be used, too, as a selective precipitating agent. The 18 % sodium hydroxide fraction from spruce holocellulose in aqueous, neutral solution was added to six times its volume of D.M.S. and after 16 hours, the precipitate was collected. The residual solution was then added to ethanol four times the volume of the original aqueous solution, when further amounts of material precipitated. The analyses of the fractions (Table 4) show that a considerable fractionation has been achieved and that chiefly the mannose-containing polysaccharides were precipitated by D.M.S.

When some of the material precipitated by D.M.S. was treated with 7 % sodium hydroxide solution at room temperature, only part of it went into solution. The insoluble material contained glucose and mannose as the only sugars, with the latter dominating. The recent work of Anthis<sup>3</sup> strongly indicates that at least part of the mannose in conifers is present as a glucomannan, and this fraction thus might be a homogeneous polysaccharide. The material

Table 4. Fractionation with D.M.S. as precipitating agent.

Fraction	Uronic acids, %	(Galactose + Glucose) : Mannose : Arabinose : Xylose
18 % NaOH extract, precipitated with ethanol	11.0	13.5 : 48.0 : 2.3 : 36.2
18 % NaOH extract, precipitated with D.M.S.	8.56	13.7 : 66.5 : 0.7 : 19.1
Residual solution, precipitated with ethanol	16.1	5.3 : 16.0 : 4.2 : 74.5

obtained by precipitation of the residual solution with ethanol was rich in xylose and uronic acids, contained only traces of mannose but other sugars were not detected in the hydrolysate.

When extracted but undelignified wood powder under the same conditions was treated with D.M.S. no significant amounts of carbohydrate material went into solution.

In this preliminary work, no attempts have been made to study the optimum conditions of extraction and precipitation with regard to the concentration and pH of the D.M.S. and of the temperature and duration of the treatment. The D.M.S. is a very slightly alkaline solvent obtained as a white crystalline material (M. p. 18.5° C) and shows partly an "aldehydic" and partly an unsaturated character. It is easily recoverable by distillation under reduced pressure and is miscible with many organic solvents, except the aliphatic hydrocarbons, and with water. As with dimethylformamide it is strongly hygroscopic and at 20° C has an equilibrium moisture content of 10 %. Because of these properties it should have great potentialities in the isolation of undenatured polysaccharides. Whether it effects any marked degradation in the cellulose and hemicellulose components and its exact mode of operation is not yet known. It does appear that the swelling of the pulps and holocelluloses is mainly inter-micellar from experiments on the moisture regain of the samples.

#### EXPERIMENTAL

The D.M.S. used in this investigation was as obtained from the manufacturer and was not further purified.

All concentrations were carried out at reduced pressure and at about 40° C. All precipitates were investigated by qualitative chromatography after total hydrolysis, using the solvent systems; ethyl acetate-acetic acid-water (3:1:1), butanol-pyridine-water (6:2:3) and butanol-formic acid-water (100:23:77). Most fractions were also investigated by quantitative paper chromatography, using the method of Saeman *et al.*<sup>4</sup>. As aldobiuronic acids are essentially not hydrolysed under the conditions used, the values for xylose are consistently too low.

*Birch holocellulose.* The birch wood used was a technical mixture of *Betula verrucosa* and *B. pubescens*. The chips were handsorted, ground in a Wiley mill and the fraction of particle size less than 0.5 mm removed by sieving. The remaining wood powder was extracted with acetone in a continuous extractor for 24 h, air-dried and delignified, using the sodium chlorite method as modified by Saarnio, Wathén and Gustafsson<sup>5</sup>. The yield of air-dried holocellulose, based on the extracted wood, was 82.7 %, a rather high value, indicating that the delignification was not complete.

The holocellulose (146 g, calc. as oven-dried weight) was extracted with D.M.S. (1 000 ml) at room temperature for 20 h. The extraction was performed in a desiccator and by applying and releasing a vacuum a number of times a good penetration of the solvent was effected. The mixture was filtered and the residue given a further treatment with D.M.S. (760 ml) for 2 h. After this extraction the holocellulose was washed with water (1 000 ml) for five min and filtered. The residue was extracted with water (1 000 ml) at room temperature for 20 h and then with hot water (1 000 ml, 90–95°) for 4 h. To each of the extracts was added four times its volume of ethanol and a few drops of conc. hydrochloric acid and the mixtures were allowed to stand for 24 h. The cold water extract yielded no precipitate but from all the others precipitates were recovered by decantation and centrifugation. The precipitates were washed with ethanol and with benzene and dried under a vacuum, and were thus obtained as white or almost white powders.

Concentration of the residual solutions from the aqueous extracts to small volumes (~ 150 ml) and addition of large excesses of ethanol yielded further precipitates, rather

similar in composition to the first precipitate from the hot water extract. Further concentration of the mother liquors from the aqueous extracts produced no additional amounts of polysaccharide material but deep orange or brown syrups which probably contained modified lignin products. The residues from the D.M.S. extracts were not further investigated but probably contained more soluble polysaccharides.

Part of the holocellulose residue (60 g) after the extractions with D.M.S. and water was given an extraction with 18.1 % sodium hydroxide solution (1 000 ml) for 25 min at room temperature, the mixture was then diluted with water (3 000 ml), stirred for 5 min and filtered. The residue was washed with water, 10 % acetic acid and water again and air-dried in order to determine the yield. The extract was adjusted to pH 6, then to pH 2, and kept at this pH-values for several days at 4°, according to the procedure of McPherson and Rånby<sup>6</sup>, but no substantial amounts of material were precipitated. The polysaccharides were then precipitated by addition of ethanol (9 000 ml) and the precipitate washed and dried as described above.

The analyses given in Table 1 for the D.M.S. and the water extracts refer to the first D.M.S. extract and the first precipitate from the hot water extract, but qualitative analyses indicate that they are typical for all the precipitates from the D.M.S. and water extracts, respectively.

*Spruce holocellulose.* Spruce wood chips were handsorted, extracted with benzene-ethanol and the air-dried extracted wood was converted to holocellulose using sodium chlorite according to the method of Wise *et al.*<sup>7</sup> Yield, 66.1 %. The holocellulose was then extracted and worked up analogously to the birch holocellulose. The various precipitates were divided into a number of subfractions by fractionated precipitation with ethanol. No significant fractionation into different types of polysaccharides was, however, obtained. Quite different and more efficient separations were achieved by using D.M.S. as a precipitating agent for the hemicelluloses extracted by 18 % sodium hydroxide solution, as described in the general part, where also the separation of a subfraction from this fractionation into a "glucomannan" and a xylan by partial dissolution with 7 % sodium hydroxide solution is described.

The second and third analysis given in Table 2 refer to the precipitates from the combined D.M.S. extracts and from the hot water extract, but, as mentioned above, are typical for all the precipitates from the D.M.S. and water fractions, respectively.

*Spruce sulphite pulp.* The preparation of the chemical grade sulphite pulp is described by McPherson and Rånby<sup>6</sup>. It was extracted and worked up analogously to the birch holocellulose.

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