be achieved, although these two sugars appear to move at the same rate in the systems ordinarily used.

Generally, the preparation of parallel chromatograms on borate- and phosphate-impregnated paper affords a simple micro-method for the detection of borate reactive groupings. Apart from the analytical use in separating isomers, the method may be of value for the determination of the relative positions of hydroxyl groups in complex natural products. Thus it will sometimes be possible to localize the position of methoxyl- or acyl-groups.

1. Levi, A. A., in *Partition chromatography (Biochemical Society Symposia No. 3)* Cambridge (1949).
2. Wachtmeister, C. A. *Acta Chem. Scand.* In print.
3. Koch, J. E., and Krieg, W. *Chem. Ztg.* **62** (1938) 140.
4. Böeseken, J. *Advances in Carbohydrate Chem.* **4** (1949) 189.

Received July 20, 1951.

Hemicellulose Extracted from Wood Holocellulose Swollen in Liquid Ammonia

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The chemistry of the so-called hemicellulose portion of the woods is still far from being clarified [1,2]. This is partly due to the difficulties encountered in the extraction of the hemicellulose portion without changing it chemically. The preparation and the use of holocellulose as a starting material in the isolation of hemicelluloses was a large step forwards, but still rather strong alkaline solution had to be applied in the isolation of the various fractions.

It is well known [3] that liquid ammonia will swell cellulosic fibers, and after evaporation of the ammonia, change the native cellulose structure (Cellulose I) into the hydrate structure (Cellulose II). The swelling of wood in liquid ammonia to render the lignin portion more accessible was first applied by Yan [4]. Later Purves and Neubauer [5] used this swelling on maple wood. They investigated the carbohydrates in the water soluble portion. A deesterification was noted at the conditions applied, pressure and room temperature. Bishop and Adams [6] recently described the isolation of hemicellulose fractions from wheat straw holocellulose swollen in liquid ammonia at the boiling temperature of ammonia (— 33° C). Noteworthy, was the pronounced increase in the water soluble portion (an increase from 3 to 20.2 %) from the unswollen to the swollen material. It is believed that the

Table 1. Yield of hemicelluloses extracted from ammonia-swollen wood.

Fraction	Birch *Betula verrucosa*	Spruce *Picea excelsa*
Hot water	14.4 %	7.1 %
1 % sodium carbonate	2.3 »	2.8 »
2 » » hydroxide	19.1 »	7.3 »
5 » » »	7.9 »	9.9 »
Residue	52.3 »	69.0 »
Total recovery	96.0 %	96.1 %

Table 2. The pentosan and uronic acid content of birch and spruce holocellulose and extracted hemicellulose fractions (expressed in %).

Fraction	Pentosan birch	Pentosan spruce	Uronic acids birch	Uronic acids spruce
Holocellulose	28.0	7.8	6.0	5.1
Hot water	62.7	25.3	12.8	16.6
1 % sodium carbonate	50.4	47.3	17.9	20.3
2 » sodium hydroxide	40.5	40.8	4.9	8.0
5 » sodium hydroxide	52.3	13.8	7.1	7.5
Residue	6.4	1.4	0.14	0.01

Table 3. Constituent sugars in birch and spruce holocellulose and extracted hemicellulose fractions (relative amounts expressed in %).

Fraction	Galactose		Glucose		Mannose		Arabinose		Xylose	
	b.	spr.	b.	spr.	b.	spr.	b.	spr.	b.	spr.
Holocellulose	0	3.0	65.5	70.5	2.7	17.9	2.3	1.0	29.5	8.0
Hot water	0	5	5	12	tr.	45	tr.	17	95	21
1 % sodium carbonate	0	5	5	15	tr.	24	tr.	22	95	34
2 » » hydroxide	0	tr.	5	20	tr.	30	tr.	20	95	30
5 » » »	0	tr.	10	27	5	50	tr.	5	85	18
Residue	0	0	83	90	4	10	0	0	13	tr.

deesterification may be avoided at this low temperature during the swelling.

We have applied a similar technique to holocellulose from birch and spruce wood. The holocelluloses were prepared from ethanol-benzene extracted wood (12—20 mesh) according to Wise [7]. The sample to be extracted was dried under high vacuum (0.1 mm) for 36 hours over phosphoric anhydride at 20° C. The evacuated flask with the sample was then cooled to — 70° C in dry ice-acetone mixture and filled with liquid ammonia from a cylinder. The flask was then allowed to stand at room temperature for 30—40 hours. The ammonia evaporated slowly and the last traces thereof were removed at high vacuum at 35° C. The swollen holocellulose was then successively extracted with water (70—75° C), 1 % sodium carbonate, 2 % sodium hydroxide and 5 % sodium hydroxide. The solid-solvent ratio was approximately 1 : 10 and three extractions of three hours each were required for exhaustive extraction. The fractions were precipitated with acetone and separated by centrifuging. The yields are given in Table 1. Table 2 gives the pentosan and uronic acid content of the fractions. All calculations are based on absolute dry holocellulose.

No marked drop in DP of the cellulose could be observed during the swelling and extraction of the holocellulose as measured by the viscosities of corresponding cellulose nitrates in acetone. The constituent sugars were determined after hydrolysis by a paper partition chromatographic technique similar to that of Jermyn and Isherwood [8]. The results are recorded in Table 3, analytical data should only be regarded as approximative.

These results differ very highly from results we obtained by direct alkaline extraction of unswollen wood hemicellulose. Water will dissolve only traces thereof and the total recovery is 85 %, apparently because the hemicelluloses are degraded and changed by strong alkali. It should be mentioned that all the hemicellulose fractions obtained from liquid ammonia treated holocelluloses are, in contrast to those from unswollen extracted holocelluloses, completely soluble in warm water. This will facilitate further investigations of them.

1. Norman, A. G. *in* Wise: *Wood chemistry*, New York (1944) p. 252; *in* Ott: *Cellulose and cellulose derivatives*, New York (1943) p. 427.
2. Wise, L. E. *Tech. Sec. Proceedings, Canada* (1949) 159.
3. Hess, K., and Gundermann, J. *Ber.* **70** (1937) 1788.
4. Yan, M. M. Thesis. McGill University, Montreal (1947).
5. Neubauer, L. G. Thesis. McGill University, Montreal (1949).
6. Bishop, C. T., and Adams, G. A. *Can. J. Research*, **B 28** (1950) 754.
7. Wise, L. E., Murphy, M., and D'Addieco, A. A. *Tech. Assoc. Papers* **29** (1946) 210.
8. Jermyn, M. A., and Isherwood, F. A. *Biochem. J.* **44** (1949) 402.

Received September 20, 1951.