hexane. *Analysis time:* About 7 minutes to octadecane.

1. Hallgren, B. and Larsson, S. O. *Acta Chem. Scand.* **13** (1959) 2147.
2. Hallgren, B. and Larsson, S. *J. Lipid Res.* **3** (1962) 31.
3. Tsujimoto, M. *J. Ind. Eng. Chem.* **9** (1917) 1098.
4. Toyama, Y. *Chemische Umschau* **30** (1923) 181.
5. Sörensen, N. A. and Mehlum, J. *Acta Chem. Scand.* **2** (1948) 140.
6. Sörensen, J. S. and Sörensen, N. A. *Acta Chem. Scand.* **2** (1948) 166.
7. Sörensen, J. S. and Sörensen, N. A. *Acta Chem. Scand.* **3** (1949) 939.
8. Swain, L. A. *Progress in the Chemistry of Fats and Other Lipids* **5** (1958) 118.
9. Hirsch, J. and Ahrens, E. H., Jr. *J. Biol. Chem.* **233** (1958) 311.
10. Lipsky, S. R., Landowne, R. A. and Godet, M. R. *Biochim. Biophys. Acta* **31** (1959) 336.

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Alkali Stability of 2-*O*-(4-*O*-Methyl-α-D-Glucopyranosyluronic Acid)-D-Xylopyranose

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The alkaline degradation of 1,4-linked polysaccharides proceeds by a peeling process starting from the reducing end group. A substituent at the C-2 hydroxyl group will prevent the peeling process "because saccharides substituted in the C-2 hydroxyl group are unable to form the necessary carbonyl group in the position *beta* to the substituted hydroxyl group" [1]. If the substituent is split off the peeling can proceed and it will continue until a stable metasaccharinate ion, terminating the chain, is formed [2]. The average number of units peeled off in a cellulose chain has recently been estimated to be of the order of 70—90 [3].

The behaviour of a substituent at the C-2 hydroxyl is of special importance to the xylans in kraft pulping of hardwoods. Hardwood xylan consists of straight 1,4 β-linked xylose chains, substituted in every tenth to fifteenth unit by a 4-*O*-methyl-D-glucuronic acid residue in the C-2 hydroxyl group [4]. The substituent will prevent the peeling to proceed, when the reaction reaches it. On the basis of this fact, it has been postulated that as long as the xylan chain contains glucuronic acid groups, these groups will protect the xylan against peeling, disregarding the initial peeling reaction [5,6]. During the kraft cook most of the glucuronic acid residues are split off, but xylan isolated from birch kraft pulps still contains 3—5 % glucuronic acid [6]. If the glucuronic acid residues were randomly distributed and if they had the postulated preventing effect on the peeling, this type of stopping of the peeling reaction would be of considerable importance. The major part of the xylan chains would then be terminated by reducing xylose units substituted at the C-2 hydroxyl by glucuronic acid residues and the minor part would be terminated by xylometasaccharinic acid units.

The above reasoning presumes, however, that the rate of hydrolysis of a glucuronic acid residue attached to a reducing xylose end-group is the same as that of a glucuronic acid residue attached to a nonreducing xylose unit. Experimental evidence indicates that this is not the case. If xylan is exposed to alkali at 100°C for some hours, its percentage of glucuronic acid is not influenced, but the degree of polymerization is lowered and only 65—70 % of

Table 1. The alkali stability of 2-*O*-(4-*O*-methyl-α-D-glucurono)-D-xylose

Treatment, 4 % NaOH		Presence of aldobiouronic acid
Temperature °C	Time, h	
20	0.5	+++
40	64	++
70	8	+
100	1	0

the xylan can afterwards be isolated from the solution. This result indicates that the glucuronic acid groups do not stop the peeling at this temperature. When peeling is prevented by reduction of the xylan end-groups with sodium tetrahydridoborate, the degree of polymerization is practically uneffected and the yield close to 100 % after a corresponding treatment [7].

Further evidence of the low alkali stability of a reducing xylose unit substituted at the C-2 hydroxyl with 4-*O*-methyl-D-glucuronic acid was obtained by alkaline treatment of a simple model substance, 2-*O*-(4-*O*-methyl-α-D- glucopyranosyluronic acid)-D-xylopyranose. The conditions used and the results obtained are given in Table 1. The aldobiouronic acid was obtained by acid hydrolysis of native birch xylan essentially according to Croon and Enström [6]. The degradation of the aldobiouronic acid was followed by paper chromatography. At 40°C the aldobiouronic acid was comparatively stable, but at 100°C it disappeared completely in one hour. No efforts were made to identify the degradation products. The result is well in line with that obtained by Whistler and Corbett on the alkali stability of 2-*O*-D-xylopyranosyl-α-arabinose [8].

In a complementary experiment 2-*O*-methyl-D-glucose was treated with 4 % sodium hydroxide at 100°C for 2 h. After the treatment no 2-*O*-methyl-D-glucose was detected.

The results obtained indicate that a reducing sugar, substituted in the C-2 hydroxyl, is rather sensitive to alkaline degradation at higher temperatures. As a consequence, the 4-*O*-methyl-D-glucuronic acid groups in hardwood xylans will not prevent peeling in the kraft cooking process.

Experimental. Isolation of 2-O-(4-O-methyl-α-D-glucopyranosyluronic acid)-D-xylopyranose. Birch xylan (20 g) was treated with 72 % H_2SO_4 (200 ml) at 30°C for one hour and then refluxed in 4 % H_2SO_4 for 4 h. The solution was cooled and neutralized with $Ba(OH)_2$, centrifuged and filtered through Celite. The uronic acids were adsorbed on an anion exchange column (Dowex 2, acetate form). The column was irregated with water-2 M acetic acid of increasing concentration. (The concentration of acetic acid was 0, 0.1 M, 0.2 M etc.) The fractions containing chromatographically pure aldobiouronic acid were combined and concentrated under reduced pressure.

Treatment of aldobiouronic acid. 1/10 of the solution obtained containing the aldobiouronic acid was diluted to 250 ml. 50 ml was used as a reference and the rest was divided into 4 parts. In these 4 samples NaOH was added to a concentration of 4 %. The conditions of the treatment are given in Table 1. The treatment was made under nitrogen and the samples were then treated with cation exchange resin (Dowex 50) in the hydrogen form and evaporated to 10 ml. In the chromatographic examination, 60 μl samples of these solutions and three samples of reference solution, concentrated to 10 ml (60, 30 and 10 μl) were spotted on sheets of Whatman No. 1 filter paper. The solvent was ethyl acetate-acetic acid-water (3:1:1) and anisidine hydrochloride in ethanol was used as spraying reagent.

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1. Whistler, R. L. and BeMiller, J. N. *Advan. Carbohydrate Chem.* **13** (1958) 289.
2. Machell, G. and Richards, G. N. *J. Chem. Soc.* **1957** 4500.
3. Albertsson, U. and Samuelson, O. *Svensk Papperstid.* **65** (1962) 1001.
4. Timell, T. E., Glaudemans, C. P. J. and Gillham, J. K. *Pulp Paper Mag. Can.* **59** (1958) Oct. 242.
5. Hamilton, J. K. and Thompson, N. S. *Pulp Paper Mag. Can.* **61** (1960) T 263.
6. Croon, I. and Enström, B. F. *Tappi* **44** (1961) 870.
7. Hartler, N. and Lund, A. *To be published.*
8. Whistler, R. L. and Corbett, W. M. *J. Am. Chem. Soc.* **77** (1955) 3822.

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