Reducing End Groups in Birch Xylan and Their Alkaline Degradation

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Summary. The structure of the reducing end group in xylan can be written:

\[ \beta-D-Xylp-(1 \rightarrow 4)\beta-D-Xylp-(1 \rightarrow 3)\alpha-L-Rhap-(1 \rightarrow 2)\alpha-D-GalpA-(1 \rightarrow 4)-D-Xyl \]

In alkaline media the reducing xylose group is easily isomerized and removed by a \( \beta \)-elimination which leads to a reducing galacturonic acid end group. The 1,2-linkage between rhamnose and the galacturonic acid explains the retarding effect on the alkaline peeling. Even under fairly mild conditions the galacturonic acid group is converted to other groups which are very stable in alkaline media. Model experiments permit the conclusion that OH-3 in the reducing group is subjected to \( \beta \)-hydroxyelimination. The 3-deoxy-2-O-\( \alpha \)-L-rhamnopyranosyl-D-threo-hex-2-enuronic acid group formed is unstable in acid medium and escapes observation by the techniques employed for determination of the end groups.

Upon prolonged alkaline treatment an increased proportion of these groups is lost and a rapid peeling proceeds until a xylose group with a 4-O-methylglucuronic acid substituent is liberated. The consecutive reactions of this group are similar to those of the galacturonic acid groups.

The formation of 3-deoxyaldonic acid end groups, an important stopping reaction in cellulose, is of minor importance in xylan.

Introduction

The high yield of pulp after alkaline pulping of hardwood is due to the high xylan content of the wood. As observed by Lindström and Samuelson [1975] xylan present in the wood contains reducing xylose end groups. This suggests that the xylan must be subjected to a rapid endwise degradation (peeling) in alkaline medium. The comparatively high yield of xylan must therefore be ascribed to competing retarding (stopping) reactions. Model experiments indicate that the 4-O-methylglucuronic acid substituents, glycosidically linked along the xylan molecule by 1 \( \rightarrow \) 2-linkages, retard the peeling considerably [Aurell, Hartler, Persson 1963; Hartler, Svensson 1965].

Recent investigations show that galacturonic acid groups present in the xylan may also have a retarding effect [Ericsson, Samuelson 1977]. The purpose of this paper

* The financial support from the 1959 Års Fond för Teknisk och Skoglig Forskning samt Utbildning is gratefully acknowledged.
is to elucidate this and other questions related to the retardation of the alkaline peeling of xylan.

**Experimental**

**Isolation of xylan**

Birch meal (0.125–0.375 mm; *Betula verrucosa*) was extracted with acetone for one day and then with water for 2 days under stirring. The air-dried meal was treated with 10% KOH for 3 hours at room temperature. After filtration the solution was poured into ethanol containing excess acetic acid. The precipitated xylan was recovered and washed with ethanol and ethyl ether and dried. The crude xylan (20 g) was dissolved in 2 litres of 5% KOH. After filtration, 1.5 litres of ethanol was added slowly and the solution acidified with acetic acid to pH 4.5. The purified xylan was isolated as above.

**Alkali treatment and borohydride reduction**

The alkali treatments were made in 0.25 M NaOH under nitrogen. The ratio liquor : xylan was 25 : 1. At 95 ºC the xylan dissolved in the liquor, while a large proportion was undissolved at 40 ºC. The reaction was interrupted by cooling and acidification with acetic acid. The xylan was recovered as above.

To determine the reducing moieties in the xylan, NaOH was added to pH 8.2. After 4 hours the slurry was neutralized, and potassium borohydride added to obtain a 0.2 M solution. After 3 days the solution was acidified with acetic acid. The xylan was isolated as above.

**Hydrolysis and determination of acids and sugars**

The xylan was hydrolyzed for 12 hours in a boiling water bath in 0.25 M hydrochloric acid. The ratio liquor : xylan was 20 : 1. Small amounts of insolubles were filtered off. To remove chloride and organic acids, the solution was stirred overnight with an excess of an anion exchanger (Dowex 1-X8, 20–50 mesh) in its bicarbonate form. Neutral sugars and alditols were washed out with water until orcinol-sulfuric acid gave a negative test for sugars. The neutral fraction was concentrated to a small volume. Alditols and rhamnose were determined by partition chromatography in 85 per cent aqueous ethanol according to Päärt and Samuelson [1970].

The monocarboxylic acid fraction eluted with 5 M acetic acid was resolved on a preparative scale first in 0.08 M sodium acetate buffered to pH 5.9. The fractions were rechromatographed in 0.5 M acetic acid. The acids were identified by their Dₜ values and colour responses [Kolmodin, Samuelson 1973] and by gas chromatography-mass spectrometry of their trimethylsilyl derivatives [Petersson 1970].