A Gas Chromatographic Method for the Identification of 4-*O*-Methyl-D-glucuronic Acid Groups in Wood Xylan

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There are no satisfactory methods for the determination of 4-*O*-methyl-D-glucuronic acid groups attached to the wood xylan backbone. One great difficulty is the fact that the linkages between uronic acid and xylose are much more resistant toward acid hydrolysis than the linkages between neutral sugar units (see, *e.g.*, Ref. 1). Therefore, if conditions resulting in a complete cleavage of these linkages are used, a considerable decomposition of the uronic acid cannot be avoided.

The idea of the present work was to reduce the carboxyl groups after which the resulting 4-*O*-methyl-D-glucose units can be easily hydrolysed from the xylan backbone. Sodium borohydride was used; this is a very convenient reducing agent even if not effective on free carboxyl groups. Therefore, prior to reduction, the carboxyl groups were first esterified. This was carried out with propylene oxide, which has shown to be very useful for esterification of solid samples in aqueous suspension.[2] After reduction, the sample was hydrolysed in sulphuric acid solution in a usual way. The presence of 4-*O*-methyl-D-glucose was established by gas chromatography after converting it to the corresponding alditol acetate derivative, *i.e.* 4-*O*-methyl-D-glucitol pentaacetate (3-*O*-methyl-L-gulitol pentaacetate).

Most experiments were carried out with a xylan sample isolated from birchwood (*Betula verrucosa*). The unknown peak had the same retention time as the peak of the reference substance, *i.e.* 4-*O*-methyl-D-glucitol pentaacetate.

The retention time of the 4-*O*-methyl-D-glucitol pentaacetate differs from that of the common sugars (alditol acetates) present in wood carbohydrates (Table 1). The method may be, therefore, directly applicable for the analysis of uronic acid in various wood and pulp samples. However, further experiments are necessary

Table 1. Relative retention times of alditol acetates.

Column (1/8″ × 2 m): 1.5 % ethylene glycol succinate and 1.5 % silicone oil (XF-1150) on 100–120 mesh silanised Gas-Chrom P. Column temperature: 170°. Carrier gas: Nitrogen, 25 ml/min.

Sample	Relative retention time
L-Arabinitol pentaacetate	0.29
D-Xylitol pentaacetate	0.39
D-Mannitol hexaacetate	0.75
4-*O*-Me-D-glucitol pentaacetate	0.79
D-Galactitol hexaacetate	0.90
D-Glucitol hexaacetate	1.00

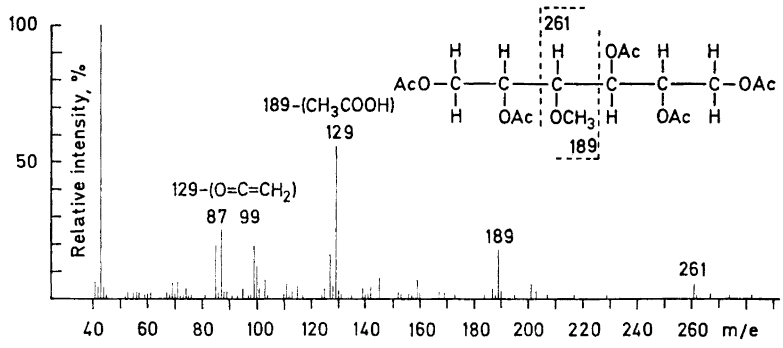

Fig. 1. Mass spectrum of 4-*O*-methyl-D-glucitol pentaacetate.

in order to make the method quantitative. The uronic acid content of the present xylan sample was 10.3 %, but only about 5 % was found after gas chromatography. The mass spectra of the sample peak and that of the reference substance were identical and thus definitely verified the presence of 4-*O*-methyl-D-glucitol penta-acetate (Fig. 1).

Experimental. Materials. The xylan sample and the methyl 4-*O*-methyl-β-D-glucopyranoside, used as reference substance, were obtained from Doc. O. Theander, Swedish Forest Products Research Laboratory, Stockholm, Sweden. The alditol acetates were prepared as described earlier.[3]

Procedure. The cations present in the xylan sample were first removed by acid-treatment in order to liberate all the carboxyl groups.[4] The esterification was then carried out by adding 10 ml 37 % (w/w) propylene oxide solution to *ca.* 100 mg of xylan sample and the mixture was allowed to stand at room temperature for 7 days. The ester was reduced overnight in the presence of 100 mg sodium borohydride. The treated sample as well as the reference substance were then hydrolysed in 4.0 % (w/w) sulphuric acid solution at 120°C for 1 h. The monosaccharides formed were finally reduced, acetylated, and subjected to gas chromatography according to the procedure described elsewhere.[3]

Apparatus. A Perkin-Elmer gas chromatograph, Model 900, equipped with a differential flame detector was used. The peak areas were measured by an Infotronics electronic integrator, Model CRS-1, connected to the gas chromatograph. The mass spectra were recorded by a Perkin-Elmer mass spectrometer, Model 270 B.

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The Sulphur-Sulphur Bonds in 2-Methyl-4-phenyl-thiothiophthene

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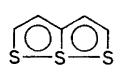
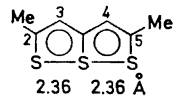
Gleiter and Hoffmann [1] have calculated potentional energy curves for the three-centre four-electron bond in thiothiophthene (I) with and without the utilization of sulphur 3*d* orbitals. The molecular dimensions found for the thiothiophthene system in (II) [2] is used as a model structure, and the potential energy is calculated as a function of a displacement of the central sulphur atom towards one of the terminal sulphur atoms.

From the energy curves a symmetric structure is preferred when 3*d* orbitals are utilized and an asymmetric structure is preferred when 3*d* orbitals are not utilized. The energy minimum in the former case is flat and broad, about 0.3 Å.



(I)



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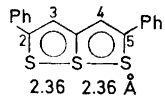

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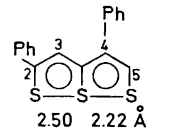

(IV)

X-Ray studies of thiothiophthene derivatives show that the S—S bonds in the sulphur sequence may be of equal or of different lengths, *e.g.* compounds II, III, and IV.[2–4] From additional structure data available on thiothiophthene derivatives [5–9] the differences in S—S bond lengths vary within a range of 0.3 Å. This indicates that the three-centre bond in thiothiophthene has a rather flat and broad energy minimum about the symmetric structure in agreement with the results from Gleiter and Hoffmann's calculations.