

## Oxidation of 4-*O*-Methylglucuronic Acid and 2-*O*-(4-*O*-Methyl- $\alpha$ -D-glucopyranosyluronic acid)-D-xylose with Chlorine in Aqueous Solution

THOMAS ERICSSON and OLOF SAMUELSON

Department of Engineering Chemistry, Chalmers University of Technology, Fack, S-402 20 Göteborg, Sweden

Treatment of 4-*O*-methylglucuronic acid with chlorine leads to 4-*O*-methylglucaric acid which is subjected to endwise oxidation resulting in the formation of methylpentaric and methyl-tetraric acids plus carbon dioxide. Demethylated aldaric acids are produced in minor amounts.

For 2-*O*-(4-*O*-methyl- $\alpha$ -D-glucopyranosyluronic acid)-D-xylose an oxidation of the xylose moiety to a xylonic acid moiety is a rapid reaction. Hydrolytic cleavage of the glycosidic bond results in the expected products.

A complex mixture of oligomeric acids and monomeric carboxylic acids, formed by fragmentation, is produced during the treatment of 4-*O*-methylglucuronoxylan with chlorine in aqueous solution.<sup>1</sup> These acids are also present in the effluent from the chlorination of wood pulp. To elucidate the reactions which occur during these treatments model experiments were made with 4-*O*-methylglucuronic acid and 2-*O*-(4-*O*-methyl- $\alpha$ -D-glucopyranosyluronic acid)-D-xylose.

### EXPERIMENTAL

4-*O*-Methylglucuronic acid (100 mg) and 2-*O*-(4-*O*-Me- $\alpha$ -D-GAp)-D-xylose (100 mg) were in separate experiments treated in darkness for 7 days at 28°C with 200 cm<sup>3</sup> of an aqueous solution containing 5.1 g of Cl<sub>2</sub> per litre. The excess chlorine was destroyed with sulfurous acid. After neutralization the reaction mixtures were kept at pH 8.5–9.0 for 5 h at room temperature to split lactones. The solutions were then applied to anion exchange columns (Dowex 1- $\bar{X}$ 8, acetate).

No appreciable amounts of non-electrolytes were present in the effluents collected after washing with water, and no traces of sugar were detected. Monocarboxylic acids were eluted with 15 column volumes of 0.08 M sodium acetate and dicarboxylic acids with 15 column volumes of 0.3 M sodium acetate in 2 M acetic acid. Finally, oxalic acid was eluted with 4 column volumes of 0.5 M magnesium acetate.

After removal of the metal cations by cation exchange, the acid fractions were evaporated to dryness and weighed. The monocarboxylic acids were identified by GC of the trimethylsilyl (Me<sub>3</sub>Si) derivatives on two stationary phases (OV-1 and QF-1) and by GC-MS.<sup>2</sup> In addition to this technique anion exchange chromatography in 0.3 M sodium acetate in 2 M acetic acid on preparative and analytical columns was employed for identification of the acids present in the dicarboxylic acid fraction.<sup>3</sup> An analytical column was used to determine the volume distribution coefficients,  $D_v$ .

The quantitative determinations of the organic acids by GC were based on the assumption that the peak areas were proportional to the weight of the derivatives.

Carbon dioxide was determined gravimetrically as barium carbonate.

Most of the methylated aldaric acids obtained in this work were identified in a study of the alkaline degradation of 4-*O*-methylglucuronic acid.<sup>4</sup> The structure determinations were based on analogies with the previously studied mass-spectrometric fragmentation of the derivatives of unsubstituted aldaric acids.<sup>5</sup> The same approach was used for the identification of 2-*O*-methylxylaric acid in this study. A peak at the  $m/e$ -value 467 ( $M-15$ ) in the spectrum of the Me<sub>3</sub>Si derivative indicated  $m/e$  482 as the mass ( $M$ ) of the molecular ion and suggested an *O*-methylpentaric acid. Moreover, an ion ( $m/e$  349) of mass ( $M-15-118$ ) was recorded

as anticipated for a pentaric acid. Peaks which could be explained by the predictable chain cleavages of a 2-*O*-methylpentaric acid were observed at *m/e* 321 and *m/e* 263. Prominent peaks at *m/e* 277 and *m/e* 219 were accounted for by secondary loss of carbon dioxide. Among the peaks in the upper part of the spectrum those at *m/e* 292 and *m/e* 234 were very prominent. They are characteristic of a structure-specific McLafferty-type rearrangement of a Me<sub>2</sub>Si group and confirmed that the acid was a 2-*O*-methylpentaric acid. Since the acid was produced from 4-*O*-methylglucuronic acid, the 2-*O*-methylpentaric acid must be 2-*O*-methylxylaric acid.

## RESULTS AND DISCUSSION

Table 1 shows that 82 % of the added 4-*O*-methylglucuronic acid was consumed after treatment with chlorine in aqueous solution for 7 days at 28 °C. Carbonic acid and dicarboxylic acids were the major reaction products. A carbon balance showed that the recovery was 97 %. Except for a slight amount of

glucuronic acid formed by demethylation, no monocarboxylic acids were detected.

4-*O*-Methylglucaric acid formed by oxidation of the aldehyde group was the most abundant dicarboxylic acid. It has previously been shown<sup>6</sup> that aldonic acids are subjected to an endwise oxidation which results in a loss of C-1 as carbon dioxide and the formation of a new carboxyl group. A similar fragmentation of 4-*O*-methylglucaric acid explains the formation of 3-*O*-methylarabinaric (loss of C-1) and 2-*O*-methylxylaric (loss of C-6) acids. The presence of appreciable amounts of methylated tetraric acids indicates an endwise oxidation of the pentaric acids. The amount of *O*-methylerythraric acid derived from 3-*O*-methylarabinaric acid was somewhat less than that of *O*-methylthrearic acid which can be formed from both *O*-methylpentaric acids. Oxidation of the *O*-methyltetraric acids will give rise to *O*-methyltartronic acid. Gas chromatography indicated that only a trace amount was present.

Table 1. Organic acids formed on treatment of 4-*O*-methylglucuronic acid (MeGA; 100 mg) and 2-*O*-(4-*O*-methyl- $\alpha$ -D-glucopyranosyluronic acid)-D-xylose (MeGAp-Xyl; 100 mg) with chlorine for 7 days at 28 °C.

Product	Amount of acid produced from		Distribution coefficient <sup>b</sup>		
	MeGA mg	mol <sup>a</sup>	MeGAp-Xyl mg	mol <sup>a</sup>	<i>D<sub>v</sub></i>
Xylonic			3.9	8.0	
Threonic			0.6	1.5	
Glyceric			1.2	3.8	
Glycolic			4.3	19.2	
4- <i>O</i> -Methylglucuronic	18.3	18.3	12.0	19.6	
Glucuronic	0.6	0.6	0.2	0.4	
2- <i>O</i> -(4- <i>O</i> -Me- $\alpha$ -D-GAp)-D-xylose			0.3	0.3	
2- <i>O</i> -(4- <i>O</i> -Me- $\alpha$ -D-GAp)-D-xylonic			65.6	62.7	4.1
4- <i>O</i> -Methylglucaric (3- <i>O</i> -Methylgularic)	23.5	21.8	1.7	2.6	8.5
Glucaric	3.8	3.8	0.2	0.3	
3- <i>O</i> -Methylarabinaric	12.2	13.1	0.8	1.4	11.3
2- <i>O</i> -Methylxylaric	13.0	13.9	1.2	2.1	10.1
Arabinaric	1.2	1.4	0.1	0.2	
Xylaric	1.1	1.3	0.1	0.2	
<i>O</i> -Methylerythraric	6.1	7.7	0.6	1.2	9.3
<i>O</i> -Methylthrearic	7.8	9.9	0.7	1.5	14.7
Erythraric	0.8	1.1	<0.1	—	
Threaric	3.0	4.2	0.3	0.7	
Tartronic	0.2	0.3	0.3	0.9	
Oxalic	2.8	6.5	0.8	3.0	
Carbon dioxide	15.0	70.9	12.1	93.5	

<sup>a</sup> Mol per 100 mol starting material. <sup>b</sup>  $D_v = \bar{V}/X - \epsilon$ , where  $\bar{V}$  is peak elution volume,  $X$  is the column volume and  $\epsilon$  the interstitial fraction ( $\epsilon = 0.39$ ). Marker: galactaric acid ( $D_v = 12.5$  in 0.3 M sodium acetate—2 M acetic acid, 30 °C).

A demethylation of the *O*-methylaldaric acids occurred to an appreciable extent, and, as expected, all demethylated species were present. Only a small amount of glucuronic acid was formed, indicating that the oxidation of 4-*O*-methylglucuronic acid was strongly favoured compared to demethylation.

Under the same reaction conditions the biouronic acid was consumed almost completely. The yield of products (Table 1) was 96 % calculated on a carbon basis. Fig. 1 shows that a primary reaction is an oxidation of the xylose moiety to a xylonic acid moiety,<sup>6</sup> and that this reaction is more rapid than the consecutive

reactions which lead to fragmentation. Except for 2-*O*-(4-*O*-methyl- $\alpha$ -D-glucopyranosyluronic acid)-D-xylonic acid, no other compounds containing two glycosidically linked moieties were formed. Evidently the 4-*O*-methylglucuronic acid substituent at C-2 in the xylonic acid moiety and the pyranosyl structure of the uronic acid moiety prevent an endwise oxidation of this compound.

A hydrolytic cleavage of the glycosidic bond resulted in appreciable amounts of 4-*O*-methylglucuronic and xylonic acids already during an early period of the treatment. During the whole reaction period the concentration of 4-*O*-methylglucuronic acid was higher than that of xylonic acid. In consecutive reactions the liberated 4-*O*-methylglucuronic acid gave rise to the same reaction products as observed in the experiments with this acid (Table 1). The amount of carbon dioxide shows that the main part must be derived from the xylose moiety (~70 %). Xylonic acid was further degraded to threonic, glyceric, and glycolic acids.<sup>6</sup> The higher stability towards endwise oxidation of the uronic acid compared to xylonic acid is explained by the fact that in aqueous solution hexuronic acids are predominantly present in the pyranose form.

The experiments with 2-*O*-(4-*O*-methyl- $\alpha$ -D-glucopyranosyluronic acid)-D-xylonic acid included in Fig. 1 confirm that this acid is decomposed to 4-*O*-methylglucuronic and xylonic acids. The higher concentration of the uronic acid confirms that its oxidative degradation is slower than that of the aldonic acid.

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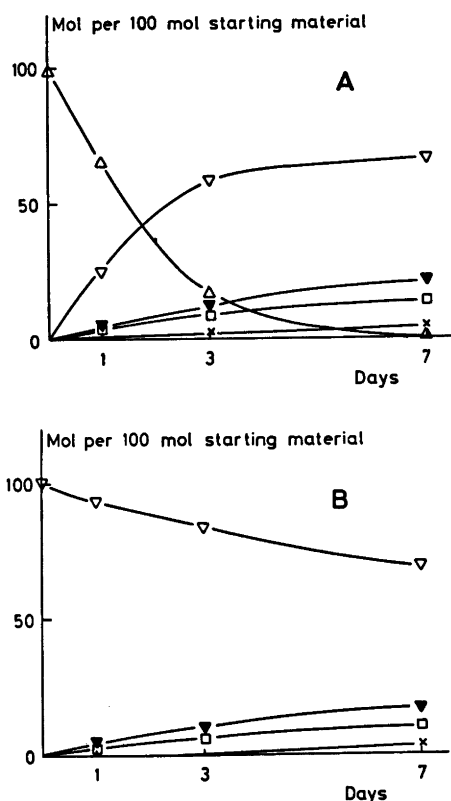


Fig. 1. Treatment of 2-*O*-(4-*O*-methyl- $\alpha$ -D-glucopyranosyluronic acid)-D-xylose (A) and 2-*O*-(4-*O*-methyl- $\alpha$ -D-glucopyranosyluronic acid)-D-xylonic acid (B) with chlorine (4.8 g/l) in aqueous solution at 27.3 °C.  $\Delta$ , 2-*O*-(4-*O*-Methyl- $\alpha$ -D-glucopyranosyluronic acid)-D-xylose;  $\nabla$ , 2-*O*-(4-*O*-Methyl- $\alpha$ -D-glucopyranosyluronic acid)-D-xylonic acid;  $\blacktriangledown$ , 4-*O*-Methylglucuronic acid;  $\square$ , Xylonic acid;  $\times$ , 4-*O*-Methylglucuronic and methylpentaric acids.