

## Dicarboxylic Acids Produced by Oxygen-Alkali Treatment of Birch Xylan

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In recent years great interest has been focussed on processes in which wood pulp and wood are delignified by oxygen in alkaline media. Unfortunately, the carbohydrates are attacked and give rise to soluble carboxylic acids. 4-*O*-Methylglucuronoxylan is a major constituent in birch

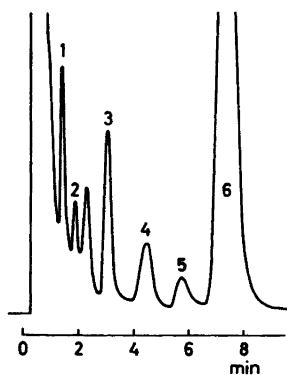


Fig. 1. Gas chromatographic separation on QF-1 at 120 °C of the dicarboxylic acids as Me<sub>3</sub>Si derivatives. Identified acids: 1. Oxalic. 2. *C*-Methyltartronic. 3. Tartronic. 4. Deoxytetra- and *C*-(hydroxymethyl)tartronic. 5. *O*-Methylerythric. 6. *C*-(2-Hydroxyethyl)tartronic.

and the formation of monocarboxylic acids from this material was recently studied.<sup>1</sup> The present paper deals with the formation of dicarboxylic acids. Under the severe conditions applied, the yield of the dicarboxylic acid fraction was 21 % compared to 35 % for the non-volatile monocarboxylic acids and 18 % for the non-electrolytes.

The use of trimethylsilyl (Me<sub>3</sub>Si) derivatives permitted analyses of the dicarboxylic acids by gas chromatography (Fig. 1). Similarly, excellent separations of the acids were obtained by anion exchange chromatography. The amount of individual acids and their retention data are given in Table 1.

*C*-(2-Hydroxyethyl)tartronic acid is predominant among the dicarboxylic acids and its formation in 12 % yield makes it a major product from xylan. The structure indicates that it is formed from terminal, oxidized xylose units by  $\beta$ -elimination at C-4 and subsequent benzilic acid rearrangement (Fig. 2). It is noteworthy that the corresponding acid with six carbon atoms, *C*-(2,3-dihydroxypropyl)tartronic acid, is the major dicarboxylic acid formed from

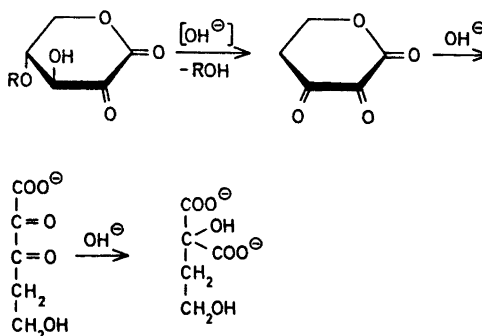


Fig. 2. Schematic representation of the formation of *C*-(2-hydroxyethyl)tartronic acid.

Table 1. Chromatographic data and amounts of dicarboxylic acids formed during oxygen-alkali treatment of xylan.

Acids	Yield g <sup>a</sup>	<i>r</i> <sup>b</sup>			<i>D<sub>v</sub></i> <sup>c</sup>
		OV-1 160 °C	OV-17 160 °C	QF-1 120 °C	
<i>C</i> -(2-Hydroxyethyl)tartronic	11.9	0.252	0.444	0.479	15.7
<i>C</i> -(Hydroxymethyl)tartronic	0.3	0.154	0.261	0.275	22.6
<i>O</i> -Methylerythric	0.6	0.130	0.303	0.374	11.0
Deoxytetra- ric	0.7	0.106	0.211	0.281	8.7
<i>C</i> -Methyltartronic	0.3	0.056	0.104	0.110	24.7
Tartronic	1.5	0.065	0.148	0.188	33.4
Oxalic	0.7	0.017	0.044	0.075	—

<sup>a</sup> Obtained from 100 g xylan. <sup>b</sup> Retention of Me<sub>3</sub>Si derivatives in GLC relative to the glucitol derivative.

<sup>c</sup> Values in ion exchange chromatography, 0.3 M NaOAc + 2 M HOAc.

cellulose<sup>2</sup> and cellobiose.<sup>3</sup> Evidently, the two acids are formed in analogous reactions. These observations suggest that 2-ulosonic acid end-groups or ulosono-1,5-lactone end-groups, related in structure to the ascorbic acids are formed as precursors. The formation of the lactones can be envisaged as oxidation of an enediol grouping at C-1 to C-2 of aldulosose end-groups in the pyranose form. Since aldulosose end-groups are formed as intermediates,<sup>1</sup> the reaction path *via* ulosono-1,5-lactone end-groups appears to be most likely. Oxidative cleavage may explain the formation of oxalic acid and contribute to the large production of 3-hydroxypropanoic acid.<sup>1</sup>

On the average, every tenth xylopyranose unit in birch xylan is substituted at carbon atom 2 by a 4-*O*-methylglucuronic acid unit. Appreciable amounts of 4-*O*-methylglucuronic acid were detected in the solution after oxygen-alkali treatment of birch xylan carried out under such conditions that the alkali was consumed.<sup>1</sup> Under conditions comparable to those applied in the present work, the liberated 4-*O*-methylglucuronic acid is decomposed rapidly<sup>3</sup> and as expected only a very small amount (less than 0.1 % of the xylan) could be traced in the monocarboxylic acid fraction obtained in the present work. *O*-Methylerythric and deoxytetraric acids are the most abundant dicarboxylic acids formed during oxygen-alkali treatment of 4-*O*-methylglucuronic acid. Obviously *O*-methylerythric acid (Table 1) originates from liberated 4-*O*-methylglucuronic acid and most likely deoxytetraric acid is at least in part derived from the same source.

**Experimental.** Water (160 ml) was heated to 98 °C in a bubbling column made of Teflon. Xylan isolated from birch meal<sup>4</sup> was added, oxygen was bubbled through the column, and a sodium hydroxide solution injected. The concentration of xylan was 1.3 % and of sodium hydroxide 1.1 %. After a 4 h treatment at a gauge pressure of 0.6 MPa and an oxygen flow rate of  $1.3 \times 10^{-2}$  mol cm<sup>-2</sup> min<sup>-1</sup>, the solution was analysed. The dicarboxylic acids were separated by anion exchange chromatography<sup>2</sup> from non-volatile monocarboxylic acids and non-electrolytes. They were analysed by gas chromatography as acyclic Me<sub>3</sub>Si derivatives<sup>5</sup> and by anion exchange chromatography (30 °C) with 0.3 M sodium acetate in 2 M acetic acid as eluent.<sup>6</sup>

*C*-(2-Hydroxyethyl)tartronic acid was identified by mass spectrometry of its Me<sub>3</sub>Si derivative.<sup>3</sup> To confirm the structure, a sample of the mixture of dicarboxylic acids was evaporated with 3 M hydrochloric acid and reduced with potassium borohydride. The major product was shown by gas chromatography-mass spectrometry to be the anticipated 3-deoxy-2-*C*-(hydroxymethyl)tetraric acid. *O*-Methylerythric and *C*-(hydroxymethyl)tartronic acids were identified by comparison of the

retention data (Table 1) and the mass spectra with those of acids identified in previous work from this laboratory. The identification of the other acids by gas chromatography and ion exchange chromatography was confirmed by a comparison of their mass spectra with those of commercial samples.

The quantitative determination of *C*-(2-hydroxyethyl)tartronic acid was made from the peak area recorded on automatic analysis by chromic acid oxidation of the eluate from ion exchange chromatography.<sup>7</sup> The other acids were determined by gas chromatography assuming that the peak areas were proportional to the weight of the derivatives. The quantities determined for oxalic and tartronic acids may be somewhat low because their Me<sub>3</sub>Si derivatives decompose easily.

**Acknowledgements.** The authors are greatly indebted to 1959 Års Fond för Teknisk och Skoglig Forskning samt Utbildning for financial support.

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Received March 17, 1975.

## Berichtigung zu »Reaktionen von Trichlormethansulfenylchlorid mit Stickstoffverbindungen. IV. Substituenteneffekte in 5-Aryl-1,3,4-oxathiazol-2-onen«\*

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Auf Seite 2170, Zeile 18 muss es statt «0,056» richtig »5,6 × 10<sup>-5</sup>» heissen.

Eingegangen am 4. April 1975.

\* *Acta Chem. Scand.* 27 (1973) 2161.