

Conversion of Glucoisosaccharinic Acid by Heating under Pressure

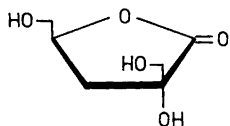
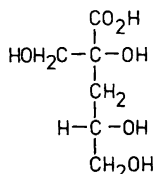
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Alén, R. and Oasmaa, A., 1988. Conversion of Glucoisosaccharinic Acid by Heating under Pressure. – *Acta Chem. Scand.*, Ser. B 42: 563–566.

An alkaline aqueous solution of glucoisosaccharinic acid has been pressure-heated for 15 min at both 300 and 350 °C and in both the presence and absence of a reducing atmosphere. Variable amounts of water-soluble (40–70 % of total organic starting material), volatile (10–55 %), and oil-like (5–15 %) products were formed. Detailed GLC analysis indicated that most of the aqueous-phase products were monocarboxylic and dicarboxylic acids formed from the starting material by various degradation reactions. The influence of temperature and gas atmosphere (carbon monoxide, hydrogen or nitrogen) on the formation of the main product groups is discussed.

The organic material in kraft black liquors is composed mainly of degraded lignin and aliphatic carboxylic acids, most of the latter being degradation products of wood polysaccharides.¹ One of the main alkaline degradation products of cellulose and glucomannans is 3-deoxy-2-*C*-hydroxymethyl-*D*-pentonic acid (glucoisosaccharinic acid). In conjunction with our studies on the thermochemical conversion of black liquor constituents, it was of interest to determine the simple reaction products formed by heating α -glucoisosaccharinic acid (**1**) in aqueous alkaline solution under pressure and in the presence and absence of a reducing atmosphere. The treatment conditions used were the same as those previously used by McKeough *et al.*² for the corresponding conversion of the organic material of pine kraft black liquor. The water-soluble products were separated by GLC after having been trimethylsilylated.



Results and discussion

Heat treatments of a neutralized concentrate of **1** (Table 1) under the chosen conditions produced, among other products, a mixture of acid derivatives (Table 2), most of which are present in ordinary black liquor.^{3,4} Primarily due to their low concentrations, the diastereoisomers of 3,6-dideoxyhexonic (*arabino*- and *ribo*-forms), galactometasaccharinic (α - and β -forms), and glucoisosaccharinic (α - and β -forms) acids as well as the isomers of anhydroglucoisosaccharinic acid (originating from both α - and β -forms of **1**) were not resolved completely, and these forms are not reported separately.

The formation of most of the acid products can be explained by assuming various alkaline oxidative cleavages of **1** with the simultaneous formation of volatile degradation products and hydrophobic compounds representing the reduced reaction products. Because of the multitude of products, the reaction pathways cannot be precisely determined. Nonetheless, an examination of the relative compositions of the aliphatic acids reveals definitive trends in the effects of the reaction parameters upon the thermal degradation of **1** (Table 2). It is also obvious that the hydroxy acid impurities present in the starting material have no significant influence on the acid composi-

Table 1. Relative composition of the glucoisosccharinic acid concentrate used in the conversion treatments.

| Acid | Content (% of hydroxy acids) |
|-------------------------------|---------------------------------|
| Monocarboxylic acids | 98.5 |
| Glycolic | 0.1 |
| Lactic | 0.5 |
| 2-Hydroxybutanoic | 0.1 |
| 2-Deoxytetronic | 0.1 |
| 3-Deoxytetronic | 0.2 |
| 3-Deoxypentonic | 0.4 |
| Xyloisosaccharinic | 0.6 |
| Anhydroglucoisosaccharinic | 0.3 |
| Galactometasaccharinic | 2.7 |
| α -Glucoisosaccharinic | 89.7 |
| β -Glucoisosaccharinic | 3.8 |
| Dicarboxylic acids | 0.4 |
| Unidentified | 1.1 |

tion after treatments. The degradation apparently proceeds via 3-deoxypentonic acid (equal amounts of *erythro*- and *threo*-forms being detected) to the lower-molecular-weight components. This intermediate was the most abundant component detected at 300 °C and was probably formed by the cleavage of the C-2 hydroxymethyl group from **1**. Furthermore, it is clear that an increase in temperature from 300 to 350 °C considerably increases the extent of the disappearance of **1** with a corresponding increase in the extent of formation of lower acids, especially methanoic, ethanoic, lactic, and 2-hydroxypentonic acids. It should be also noted that, in the experiment performed under a carbon monoxide atmosphere, the gas reacted to a significant extent with alkali yielding sodium formate.

Unlike the hydroxy monocarboxylic acids, the dicarboxylic acids represented only a minor product fraction. However, the heat treatments led to significant increases in the relative amounts of dicarboxylic acids. The results also indicate that, regardless of the gas atmosphere used, the formation of dicarboxylic acids was much more extensive in the treatments at 350 °C than in those at 300 °C. Most of the dicarboxylic acid structures can be considered as oxidation products of the monoacids detected.

The yields of the three major product groups (carboxylic acids, oil-phase, and volatile com-

Table 2. Relative composition of aliphatic acids detected in the aqueous phase after the conversion treatments.^a

| Compound | 300 °C | | 350 °C | |
|----------------------------|----------------|-------------------|----------------|----------------|
| | N ₂ | CO | N ₂ | H ₂ |
| Monocarboxylic acids | 89.9 | 88.7 | 81.0 | 86.7 |
| Methanoic | 8.5 | 46.1 ^b | 23.9 | 32.1 |
| Ethanoic | 1.6 | 1.7 | 9.3 | 7.8 |
| Propanoic | + | + | 3.5 | 2.3 |
| Butanoic | 0.1 | 0.1 | 0.3 | 0.3 |
| Pentanoic | 1.3 | 0.8 | 4.7 | 4.5 |
| Glycolic | + | + | 0.9 | 0.1 |
| Lactic | 2.0 | 4.1 | 9.6 | 6.7 |
| 3-Hydroxypropanoic | 4.8 | 0.4 | 1.3 | 4.6 |
| 2-C-Methylglyceric | 0.3 | 0.1 | 1.3 | 0.8 |
| 2-Hydroxybutanoic | 4.3 | 0.3 | 4.0 | 8.5 |
| 2-Hydroxybutanoic | 0.2 | 2.4 | 1.1 | 0.8 |
| 2-Deoxytetronic | 0.1 | 0.2 | 0.1 | 0.1 |
| 3-Deoxytetronic | 0.6 | 2.7 | 0.8 | 0.7 |
| 3-Deoxy-2-C-methyltetronic | 1.0 | 2.8 | 0.9 | 0.8 |
| 2-Hydroxypentonic | 0.8 | 0.3 | 9.1 | 5.3 |
| 3,4-Dideoxypentonic | 5.4 | 6.2 | 5.5 | 6.5 |
| 3-Deoxypentonic | 49.1 | 13.2 | 0.4 | 0.4 |
| Xyloisosaccharinic | 5.1 | 1.3 | 3.3 | 3.2 |
| Anhydroglucoisosaccharinic | 2.4 | 4.9 | 1.0 | 1.2 |
| Galactometasaccharinic | 0.9 | 0.5 | + | – |
| 3,6-Dideoxyhexonic | 0.5 | 0.2 | + | – |
| Glucoisosaccharinic | 0.9 | 0.4 | + | – |
| Dicarboxylic acids | 1.6 | 1.4 | 9.7 | 7.5 |
| Oxalic | + | 0.6 | 0.7 | 0.9 |
| Tartronic | 0.4 | 0.1 | 0.4 | 0.3 |
| C-Methyltartronic | 0.3 | 0.2 | 2.3 | 0.8 |
| Succinic | 0.5 | 0.4 | 0.1 | 0.2 |
| 2,3-Dideoxypentonic | 0.4 | 0.1 | 6.2 | 5.3 |
| Unidentified | 8.5 | 9.9 | 9.3 | 5.8 |

^aThe figures are given as a percentage of the total aliphatic acids; heating time 15 min. + indicates figures below 0.1%; – indicates that the compounds were not detected. ^bIncluding the portion derived from carbon monoxide.

pounds including other organics) are presented in Table 3. Although monomeric organic acids represent the largest organic fraction, another significant fraction is composed of predominantly volatile compounds. The yield of this fraction was estimated by subtracting the amounts of carboxylic acids and oil-product from the amount of the

Table 3. Conversion of the glucoisosaccharinic acid concentrate on heating.^a

| Product group | 300°C | | 350°C | |
|--|----------------|-------------------|----------------|----------------|
| | N ₂ | CO | N ₂ | H ₂ |
| Carboxylic acids | 65.1 | 84.5 ^c | 35.4 | 50.4 |
| Oil-phase | 14.3 | 15.5 | 5.0 | 3.6 |
| Volatile compounds and other organics ^b | 20.6 | — ^d | 59.6 | 46.0 |

^aThe figures are given as weight % of the starting material. ^bIncluding gases (mainly carbon dioxide), reaction water, alcohols and hydrophilic polymeric compounds. Obtained by difference. ^cIncluding the portion formed from carbon monoxide. ^dNot reported as the precise extent of the CO-alkali reaction unknown.

organic starting material. In agreement with recent results on the thermochemical conversion of black liquor organics,⁵ the latter fraction contained, in addition to gaseous compounds (mainly carbon dioxide) and reaction water, small amounts of volatile alcohols, some of which were detected by the GLC method applied in this study. This fraction presumably also contained minor amounts of polymeric acid components, which were not detected by GLC. The amount of methanoic acid formed from carbon monoxide and alkali was estimated on the basis of the results of the experiment carried out under an inert atmosphere. This amount was about 40 % of total acids. The results indicate that the extent of acid degradation was, to some degree, greater in the experiment performed under carbon monoxide than in the corresponding experiment carried out under nitrogen. In contrast, the degradation of acids seemed to be retarded under a hydrogen atmosphere. The yield of the third product group, the hydrophobic oil-phase, was significantly smaller than the combined yield of acids and volatiles. The formation of this phase was favoured by the lower treatment temperature.

Experimental

Materials. The concentrate of 3-deoxy-2-C-hydroxymethyl-D-erythro-pentono-1,4-lactone (**2**; α -glucoisosaccharinic acid 1,4-lactone) was separated from an alkaline pulping liquor of pine

wood by ion-exchange partition chromatography.⁶ The crystalline product obtained contained about 90 % of **2**, the impurities being other hydroxy acids (Table 1). For the heating experiments a 12 g sample of the acid fraction was dissolved in 80 ml of water and neutralized with NaOH (4 g). Finally, an excess of sodium ions was added in the form of Na₂CO₃ (1.6 g).

Heat treatments. A portion of the aqueous acid solution (about 17 g) was placed in an agitated batch reactor (30 ml), which was rapidly heated in a fluidized sand bath to a temperature of 300 or 350°C. The apparatus included a gas charging system and was of similar construction to that described in detail by Maa *et al.*⁷ After a reaction time of 15 min, the reactor was quench-cooled, and the gaseous, the oil-like (a portion that was adhering to the reactor wall was removed with ethanol), and the aqueous phases were recovered separately. The total yield of the oil-phase was determined gravimetrically. The conversion experiments were carried out under three different atmospheres: a reducing atmosphere of carbon monoxide (initial pressure of 8 MPa), a reducing atmosphere of hydrogen (initial pressure of 4.5 MPa) and an inert atmosphere of nitrogen (initial pressures of 7 MPa at 300°C and 3 MPa at 350°C). These initial pressures were selected so that final pressures of 20–22 MPa were obtained. The conditions employed in each experiment are given in Table 2. After the treatments the pH values were 8.1 (N₂/300°C), 4.8 (CO/300°C), 7.4 (N₂/350°C), and 7.3 (H₂/350°C).

Analytical determinations. The hydroxy monocarboxylic and dicarboxylic acids (non-volatile acids) were analysed as their trimethylsilyl derivatives by GLC as described elsewhere.^{8,9} The low-molecular-weight monocarboxylic acids (volatile acids) were determined as their benzyl esters by GLC.¹⁰

Acknowledgements. Financial support from the Finnish Ministry of Trade and Industry, Energy Department is gratefully acknowledged. Special thanks are expressed to Dr. Paterson McKeough for many valuable suggestions during the preparation of the manuscript. Thanks are also due to Miss Katja Heiskanen, Mrs. Sirkka Huru and Mr. Reijo Häkkinen for their assistance with the experimental work.

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Received March 14, 1988.