

# Condensation of Glycolic, Lactic and 2-Hydroxybutanoic Acids during Heating and Identification of the Condensation Products by GLC-MS

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Glycolic, lactic and 2-hydroxybutanoic acids are partly converted to various condensation products during heating. This conversion was studied at 100 °C and 125 °C by identifying the trimethylsilylated products using GLC-MS. Most of the products consisted of both linear (dimers and trimers) and cyclic (dimers) structures. The influence of the condensation on the recovery and purification of the hydroxy acids by distillation is discussed.

As a result of alkaline degradation a variety of hydroxy acids is formed from wood polysaccharides during kraft pulping.<sup>1</sup> These acids can be isolated from the black liquor by distillation.<sup>2</sup> Because some of the acids are partly condensed when subjected to distillation temperatures, it was of interest to separate and identify the simple condensation products of glycolic, lactic, and 2-hydroxybutanoic acids, which are the most important components in this connection. The experiments were performed simply by heating samples of these acids at 100 or 125 °C for certain times and following the conversion by GLC-MS after trimethylsilylation.

## RESULTS AND DISCUSSION

### Conversion during heating

Glycolic acid 1 (Table 1) was the most unstable of the acids studied, as shown by the rapid decrease in its concentration in the reaction mixture. Besides linear dimer 3 and glycolide 5, higher

polymerization products were probably also formed, as indicated by the viscous state of the samples after prolonged heating. Surprisingly, no linear trimer 20 was detected, although at least traces of the corresponding compounds were formed from lactic and 2-hydroxybutanoic acids.

Table 2 shows the conversion of lactic acid 6 into lactyl lactic acid 8, lactide 10 and lactyl lactyl

$\begin{array}{c} \text{OR}' \\   \\ \text{R} \cdot \text{CH} \cdot \text{CO}_2\text{R}' \end{array}$		$\begin{array}{c} \text{OR}' \quad \text{R} \\   \quad   \\ \text{R} \cdot \text{CH} \cdot \text{CO}_2 \cdot \text{CH} \cdot \text{CO}_2\text{R}' \end{array}$	
	$\begin{array}{c} \text{R} \quad \text{R}' \\   \quad   \\ \text{H} \quad \text{H} \end{array}$		$\begin{array}{c} \text{R} \quad \text{R}' \\   \quad   \\ \text{H} \quad \text{H} \end{array}$
1	H	3	H
2	H	4	H
6	CH <sub>3</sub>	8	CH <sub>3</sub>
7	CH <sub>3</sub>	9	CH <sub>3</sub>
13	C <sub>2</sub> H <sub>5</sub>	15	C <sub>2</sub> H <sub>5</sub>
14	C <sub>2</sub> H <sub>5</sub>	16	C <sub>2</sub> H <sub>5</sub>
$\begin{array}{c} \text{O} \\    \\ \text{R} \cdot \text{CH} \cdot \text{O} - \text{C} - \text{CH} \cdot \text{R} \\   \quad   \\ \text{C} - \text{O} \\    \\ \text{O} \end{array}$		$\begin{array}{c} \text{OR}' \quad \text{R} \quad \text{R} \\   \quad   \quad   \\ \text{R} \cdot \text{CH} \cdot \text{CO}_2 \cdot \text{CH} \cdot \text{CO}_2 \cdot \text{CH} \cdot \text{CO}_2\text{R}' \end{array}$	
	$\begin{array}{c} \text{R} \\   \\ \text{H} \end{array}$		$\begin{array}{c} \text{R} \quad \text{R}' \\   \quad   \\ \text{CH}_3 \quad \text{H} \end{array}$
5	H	11	CH <sub>3</sub>
10	CH <sub>3</sub>	12	CH <sub>3</sub>
17	C <sub>2</sub> H <sub>5</sub>	18	C <sub>2</sub> H <sub>5</sub>
		19	C <sub>2</sub> H <sub>5</sub>
		20	H

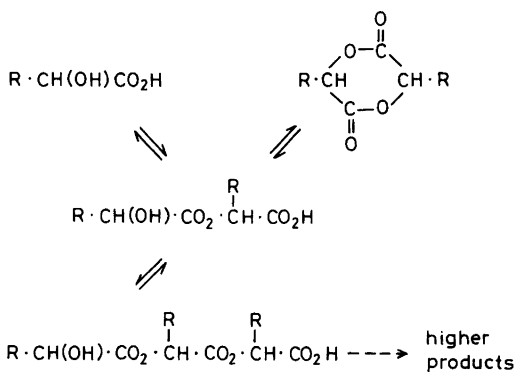


Fig. 1. Formation scheme for the simple condensation products of glycolic ( $R=H$ ), lactic ( $R=CH_3$ ), and 2-hydroxybutanoic ( $R=C_2H_5$ ) acids on heating.

Table 1. Conversion of glycolic acid (GA) on heating.<sup>a</sup> Peak symbols: GA, 2; GA/1, 4; GA/2, 5.

Time/h	2	4	5
100 °C			
1	82.4	17.6	—
2	78.8	21.2	—
4	65.4	34.6	+
6	64.2	35.0	0.8
125 °C			
1	75.0	25.0	—
2	67.4	32.6	+
4	67.6	24.5	7.9
6	56.0	26.5	17.5
Distillate <sup>b</sup>	97.3	2.5	—

<sup>a</sup>Figures are given as % of the total observed.  
<sup>b</sup>Distillation yield of 50–60%.

lactic acid 11. Although reported as one peak, the gas chromatographic peak LA/4 was in some cases resolved into two separate peaks. Analogous condensation products were also obtained from 2-hydroxybutanoic acid 13, but the corresponding cyclic dimer 17 was formed more easily than the open-chain trimer 18 (Table 3). Fig. 1 illustrates the principal reaction scheme for the reversible formation of the condensation products. When glycolic, lactic and 2-hydroxybutanoic acids were separately distilled batchwise at pressures of 0.02–0.20 kPa (90–120 °C) only small amounts of condensation products were present in the distillates, but the

Table 2. Conversion of lactic acid (LA) on heating.<sup>a</sup> Peak symbols: LA, 7; LA/1, 9; LA/2 and LA/3, 10; LA/4, 12.

Time/h	7	9	10 <sup>c</sup>	10 <sup>d</sup>	12
100 °C					
1	85.5	14.5	—	—	—
2	78.4	20.9	—	—	—
4	72.3	27.2	—	—	+
6	66.5	30.2	+	+	2.4
125 °C					
1	74.6	24.4	—	—	—
2	67.4	31.1	+	+	0.7
4	55.1	36.1	0.7	1.5	6.2
6	49.8	36.7	1.3	2.6	8.9
Distillate <sup>b</sup>	98.4	1.6	—	—	—

<sup>a</sup>Figures are given as % of the total observed.  
<sup>b</sup>Distillation yield of 90–95%. <sup>c</sup>HBA/2. <sup>d</sup>HBA/3.

Table 3. Conversion of 2-hydroxybutanoic acid (HBA) on heating.<sup>a</sup> Peak symbols: HBA, 14; HBA/1, 16; HBA/2 and HBA/3, 17; HBA/4, 19.

Time/h	14	16	17 <sup>c</sup>	17 <sup>d</sup>	19
100 °C					
1	98.3	1.3	—	—	—
2	85.7	14.1	+	+	—
4	65.3	32.2	0.8	0.7	—
6	62.7	34.1	1.4	1.6	—
125 °C					
1	97.3	2.7	—	—	—
2	85.7	14.3	+	+	—
4	67.6	29.3	0.9	0.9	—
6	46.0	44.7	3.0	3.5	+
Distillate <sup>b</sup>	99.7	0.2	—	—	—

<sup>a</sup>Figures are given as % of the total observed.  
<sup>b</sup>Distillation yield of 85–90%. <sup>c</sup>LA/2. <sup>d</sup>LA/3.

distillation residues contained dimeric and trimeric compounds as well as higher polymerization products (Tables 1, 2 and 3).

#### Identification of compounds

All the intense peaks in the mass spectra of the monomeric acid derivatives 2, 7 and 14 are in accordance with the data reported by Petersson,<sup>3</sup>

which are also useful in the identification of the linear condensation products.

The gas chromatographic peaks GA/1, LA/1 and HBA/1 appeared in the same region, representing the silylated condensation products which are formed most easily. The mass spectra are indicative of linear dimeric structures corresponding to the compounds 4, 9 and 16. Peaks at  $m/e$  263, 291 and 319 are derived from the typical ion peaks  $[M-15]^+$  resulting from the well-known cleavage of a methyl group linked to silicon.

The mass spectra corresponding to the gas chromatographic peaks GA/2, LA/2, LA/3, HBA/2 and HBA/3 showed no ion peaks typical of silylated compounds, and are indicative of structures belonging to homologous cyclic dimers. The relative intensities of their main ion peaks are nearly identical with the data reported by Goulden and Millard<sup>4</sup> for the expected cyclic structures. Therefore, it is assumed that GA/2 corresponds to compound 5, LA/2 and LA/3 to compound 10, and HBA/2 and HBA/3 to compound 17. With the exception of 5, these compounds can exist both as a *trans* form and a pair of *cis* enantiomers. Although it seems possible to resolve these *cis* and *trans* isomers by gas chromatography, their mass spectra were almost identical, as would be expected: a ring fission mechanism leads to the same fragment ion in both isomers.<sup>4</sup>

By comparing the mass spectra of the remaining gas chromatographic peaks (LA/4 and HBA/4) with those of the above-mentioned linear compounds, it seems obvious that they represent the linear trimers 12 and 19. The typical ion peaks  $[M-15]^+$  exist at  $m/e$  363 and 405, respectively. These spectra, as well as those of compounds 9 and 16, also represent the various stereoisomers in question.

## EXPERIMENTAL

### Materials

Glycolic acid was obtained from Fluka AG and was gas chromatographically pure. Lactic acid was a product from J. T. Baker Chemicals V. N. and contained the dimer 8 (12%) in addition to the monomeric acid (88%). 2-Hydroxybutanoic acid was prepared from the corresponding sodium salt (Fluka AG) by removing sodium with cation exchange resin (Dowex 50 W X8, H<sup>+</sup> form) and was gas chromatographically pure.

The following compounds were separated by

GLC after silylation in the samples from the heat treatments:

*Hydroxyethanoic acid* (1). MS of 2:  $m/e$  (% rel. int.) 220 (1, M<sup>+</sup>), 205 (14), 177 (10), 161 (6), 147 (99), 133 (9), 131 (4), 117 (3), 103 (5), 95 (2), 88 (4), 81 (4), 75 (13), 73 (100), 66 (22), 59 (7), 58 (6), 45 (16), 43 (8).

*Hydroxyacetoxyethanoic acid* (3). MS of 4:  $m/e$  (% rel. int.) 263 (16), 205 (21), 177 (12), 147 (59), 133 (6), 131 (5), 117 (2), 103 (28), 95 (4), 88 (5), 81 (7), 75 (36), 73 (100), 66 (14), 59 (7), 58 (8), 45 (13), 43 (7).

*1,4-Dioxan-2,5-dione* (5). MS:  $m/e$  (% rel. int.) 116 (32, M<sup>+</sup>), 42 (100), 31 (26), 30 (18), 29 (26), 14 (7).

*2-Hydroxypropanoic acid* (6). MS of 7:  $m/e$  (% rel. int.) 219 (6), 191 (12), 190 (11), 147 (74), 133 (5), 117 (76), 102 (3), 88 (6), 75 (13), 73 (100), 66 (11), 59 (7), 45 (14), 43 (6).

*2-(2-Hydroxypropanoyloxy)propanoic acid* (8). MS of 9:  $m/e$  (% rel. int.) 291 (4), 219 (9), 218 (7), 191 (7), 190 (1), 147 (26), 129 (9), 117 (82), 102 (3), 88 (10), 75 (25), 73 (100), 66 (5), 59 (6), 55 (11), 45 (12), 43 (8).

*3,6-Dimethyl-1,4-dioxan-2,5-dione* (10). MS:  $m/e$  (% rel. int.) 144 (<1, M<sup>+</sup>), 56 (100), 45 (35), 44 (7), 43 (26), 29 (12), 28 (67), 27 (12).

*2[2-(2-Hydroxypropanoyloxy)propanoyloxy]-propanoic acid* (11). MS of 12:  $m/e$  (% rel. int.) 363 (3), 291 (8), 290 (6), 219 (9), 218 (5), 217 (9), 191 (7), 190 (2), 147 (22), 129 (11), 117 (100), 102 (4), 88 (8), 75 (28), 73 (96), 66 (3), 59 (5), 56 (19), 55 (16), 45 (12), 43 (8).

*2-Hydroxybutanoic acid* (13). MS of 14:  $m/e$  (% rel. int.) 233 (5), 205 (8), 190 (6), 147 (83), 131 (100), 100 (13), 95 (3), 93 (4), 81 (7), 79 (4), 75 (29), 73 (99), 66 (13), 59 (8), 45 (16), 43 (6).

*2(2-Hydroxybutanoyloxy)butanoic acid* (15). MS of 16:  $m/e$  (% rel. int.) 319 (5), 233 (10), 232 (8), 217 (3), 205 (9), 190 (2), 147 (58), 131 (99), 95 (9), 93 (17), 81 (5), 79 (16), 75 (48), 73 (100), 69 (12), 66 (5), 59 (9), 55 (6), 52 (12), 51 (6), 45 (14), 44 (8), 43 (6).

*3,6-Diethyl-1,4-dioxan-2,5-dione* (17). MS:  $m/e$  (% rel. int.) 144 (24), 70 (87), 59 (40), 58 (9), 57 (18), 55 (100), 42 (25), 41 (20), 29 (19), 27 (21).

*2-[2-(2-Hydroxybutanoyloxy)butanoyloxy]butanoic acid* (18). MS of 19:  $m/e$  (% rel. int.) 405 (3), 319 (6), 318 (5), 249 (3), 245 (4), 233 (8), 232 (3), 217 (2), 205 (5), 190 (1), 177 (4), 161 (9), 159 (6), 155 (6), 147 (21), 143 (13), 131 (100), 75 (33), 73 (78), 69 (27), 59 (12), 55 (13), 45 (9).

### Heat treatments

Model substances (1–2 g) were placed in open, pear-shaped flasks, which were heated in an oil bath at 100 or 125°C. At the end of the heating period (1–6 h) samples were taken and silylated immediately for GLC. The reported data represent the mean values of several experiments. Batch distillations were made as described before.<sup>2</sup>

### Analytical methods

For GLC-MS the compounds (about 20–50 mg) were silylated with a stock mixture (1–2 ml) of pyridine, hexamethyldisilazane, and trimethylchlorosilane (10:2:1).<sup>5</sup>

GLC was performed on a Perkin-Elmer 900 instrument equipped with a differential FID using a stainless steel column (3.175 mm × 2 m) packed with 3% silicone oil (OV-210) on 100–120 mesh Gas Chrom Q. The temperature program was 40–200 °C, 2.5 °C/min, and the flow rate of carrier gas (N<sub>2</sub>) was 30 ml/min. The temperature of the injection port and manifold was 230 °C. The peak areas were measured with a Hewlett-Packard 3380 A electronic integrator. The relative retention times for the gas chromatographic peaks GA, GA/1, GA/2, LA, LA/1, LA/2, LA/3, LA/4, HBA, HBA/1, HBA/2, HBA/3 and HBA/4 compared with D-mannono-1,4-lactone (1.00) were, respectively, 0.19, 0.55, 0.58, 0.15, 0.51, 0.58, 0.60, 0.79, 0.20, 0.60, 0.67, 0.70 and 0.89.

For GLC-MS the compounds were injected into a Perkin-Elmer 270 B (70 eV) fitted with the same column as mentioned above. The carrier gas was helium. The injection port was maintained at 230 °C and the manifold at 280 °C.

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