

Identification of Some Minor Aliphatic Carboxylic Acids in Birch Kraft Black Liquor

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In a recent study¹, twenty-six hydroxy monocarboxylic acids and sixteen dicarboxylic acids were identified in birch kraft and kraft/anthraquinone black liquors. More recently, some additional hydroxy monocarboxylic acids have been reported.^{2,3} We have now identified several novel carboxylic acids in black liquor using capillary gas-liquid chromatography and mass spectrometry.

Low molecular weight compounds of black liquor (similar to that used in a previous investigation¹) were converted into their trimethylsilyl derivatives as described elsewhere.⁴ The mass spectra were recorded with a JEOL JMS-DX303 mass spectrometer (70 eV) coupled with a Hewlett-Packard 5790 A gas chromatograph and an

OV-101 fused silica capillary column (0.32 mm i.d. × 25 cm). Details of this technique are given elsewhere.⁵

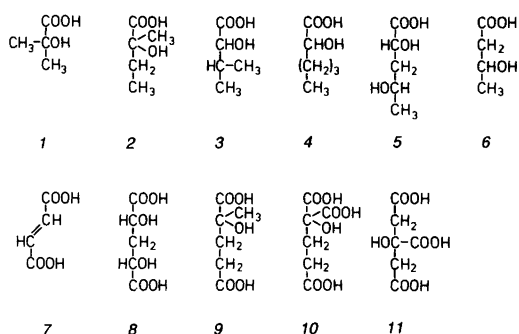
Compounds 1–4, 6–8, 10, and 11 were identified as their TMS derivatives using reference spectra (see Table 1). Two new mass spectra (TMS derivatives of 5 and 9) are shown in Fig. 1. The identification of 9 was confirmed by means of a reference sample, obtained from levulinic acid by cyanohydrin formation and subsequent sulfuric acid hydrolysis. The *threo* configuration of 5 was indicated by its retention time.⁶

Monocarboxylic acids. Very little is known at present about the origins or formation routes of

Table 1. Novel aliphatic carboxylic acids identified in birch kraft black liquor.

Carboxylic acid	Origin	MS Data (Ref.)
1 2-Hydroxy-2-methylpropanoic	Lignin ⁷	8
2 2-Hydroxy-2-methylbutanoic	Unknown	8
3 2-Hydroxy-3-methylbutanoic	Unknown	8,9
4 2-Hydroxyhexanoic	Unknown	8,9
5 3,5-Dideoxy- <i>threo</i> -pentonic	Rhamnose(?)	Fig. 1
6 3-Hydroxybutanoic	Rhamnose(?)	8,9
7 Fumaric	Lignin ^{10–12}	8,9,13
8 3-Deoxy- <i>erythro</i> -pentaric	Pectic substances ¹⁴	15
9 2,3-Dideoxy-4- <i>C</i> -methylpentaric	Pectic substances	Fig. 1
10 2- <i>C</i> -Carboxy-3,4-dideoxypentaric	Pectic substances ¹⁴	14
11 Citric	Original compound	7,9,16

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compounds 1–6 during alkaline pulping. 2-Hydroxy-2-methylpropanoic acid 1 is probably a degradation product of lignin,⁷ but its branched structure leaves open the possibility of its formation from some carbohydrates by benzilic acid rearrangement of 2,3-butanedione formed as an intermediate. Analogously, 2 might be formed from carbohydrates via 2,3-pentandione, but there are no data which support this explanation. The origins of 3 and 4 are as yet not explained. Homologues of 4, 2-hydroxypentanoic^{1,17} and 2-hydroxyheptanoic² acids have also been identified in alkaline pulping liquors, but no origins or formation routes have been proposed.

The presence of the ω "deoxy group" may be

due to the formation of 5 from rhamnose moieties of both xylan and pectic substances. Even though 3,5-dideoxypentonic acids are known degradation products of unsubstituted rhamnose,¹⁸ their formation from birch wood rhamnose is, however, rather unexpected because the 1,3 links to the xylan molecules favor the generation of 3,6-dideoxyhexonic acids.^{19,20} 3-Hydroxybutanoic acid 6 is also a minor alkaline degradation product of rhamnose,¹⁸ but its formation from cellulose under oxidative conditions has also been reported.²¹ Small amounts of 6 are formed during hypochlorite bleaching of birch xylan,²² most probably by oxidative degradation of rhamnose. Another ω deoxyaldonic acid, 4-deoxythreonic acid, has been identified from pine kraft black liquor by Löwendahl *et al.*,²³ but no formation route has been ascertained.

Dicarboxylic acids. Fumaric acid 7 has previously been detected in appreciable proportions in spent liquors of oxygen/alkali cooking of hardwood,^{24–27} and its origin has been attributed to lignin.^{10–12} Traces of this acid in black liquor indicate that some oxidative breakdown of lignin also occurs during kraft pulping. The presence of small amounts of 3-deoxy-*threo*-pentaric acid in black liquors^{1,17,23,28} has been previously reported, and the present data show the formation of the

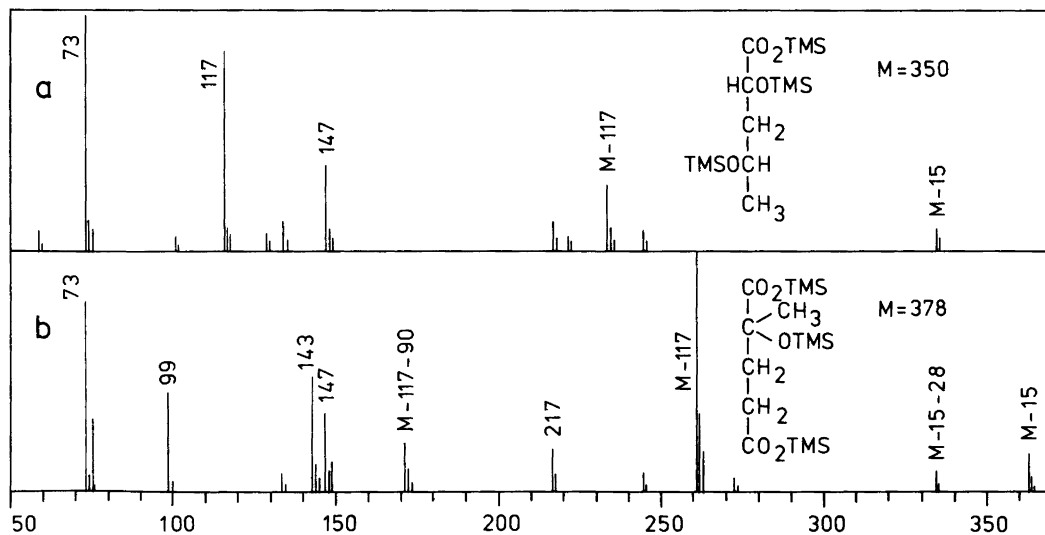


Fig. 1. The mass spectra at 70 eV of the TMS derivatives of 3,5-dideoxypentonic (a) and 2,3-dideoxy-4-C-methylpentaric (b) acids.

erythro form 8 in addition, as expected from the model experiments with pectic acid.¹⁴ 2,3-Dideoxy-4-C-methylpentaric acid 9 has not been identified up to now as an alkaline degradation product of pectic acid,¹⁴ but a reinvestigation of the reaction mixture with the methods used in this work revealed small amounts of 9, thus indicating its origin during alkaline pulping of wood. The corresponding straight chain compound, 2,3,4-trideoxyhexaric acid, has been previously identified from black liquors,^{1,17,23,28} and is known to be derived from cellulose²⁹ and glucomannan.³ It should be noted that acids 8 and 9 may also be formed from 4-O-methylglucuronic acid groups of xylan (cf. Ref. 30).

Tricarboxylic acids. Of the first tricarboxylic acids now identified from black liquors, 2-C-carboxy-3,4-pentaric acid 10 is known to be formed from pectic substances,¹⁴ whereas citric acid 11 is most probably an indigenous constituent of birch wood.

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