

Short Communications

Identification of Two Novel Hydroxy Monocarboxylic Acids from Alkaline Pulping Liquors

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At least 34 aliphatic hydroxy monocarboxylic acids have so far been identified from the alkaline spent liquors (black liquors) of softwood^{1–3} and hardwood,^{4–6} and they are known to be derived almost exclusively from carbohydrates. Of the unidentified peaks in the gas chromatograms of TMS derivatives⁷ we have now been able to identify two new compounds.

Compound 1 was firmly identified as 2-hydroxyheptanoic acid by comparing the mass spectrum of its TMS derivative (Fig. 1) with those of 2-hydroxypropanoic,⁸ 2-hydroxybutanoic,^{8,9} 2-hydroxy-3-methylbutanoic,^{8,10} 2-hydroxypentenoic,¹¹ and 2-hydroxyhexanoic¹⁰ acids. One of the most prominent peaks in their spectra is at $M-117$ ($M-\text{CO}_2\text{TMS}$), and indicates the presence of an α -hydroxy group. Peaks of identical intensity at $M-15$ and $M-15-28$ are also characteristic. Other prominent peaks in the mass spectrum of 1 are observed at m/e 83 ($M-117-90$) and at m/e 103, which is also found in the mass spectra of 2-hydroxyhexanoic acids.¹⁰

For compound 2, a prominent $M-15$ peak at m/e 335 indicates $M=350$ for the TMS derivative and dideoxypentonic acid as a probable structure. The peaks at $M-117$ and $M-117-90$ show that the compound contains an α -hydroxy group. A very prominent peak at m/e 103 is typical of ($\omega-1$)-deoxyaldonic acids,^{8,12} and in this case its presence suggests a branched structure. Comparisons with the mass spectra of TMS derivatives of 3-deoxytetronic acid⁸ and 3,4-dideoxypentonic acid^{8,13} indicate that its structure must be 3-deoxy-2-*C*-methyltetronic acid.

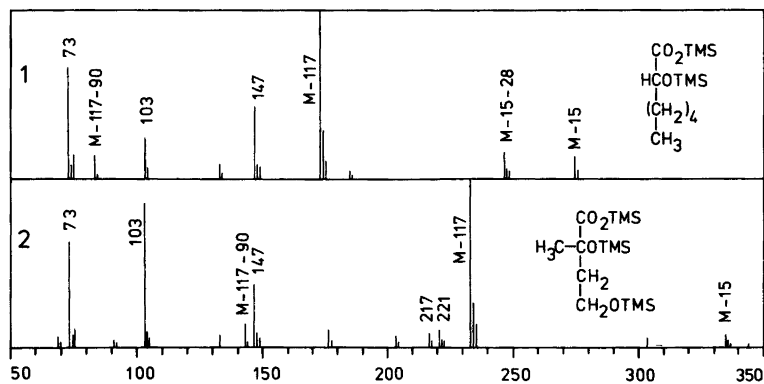


Fig. 1. The mass spectra at 70 eV of the TMS derivatives of 2-hydroxyheptanoic (1) and 3-deoxy-2-*C*-methyltetronic (2) acids.

The formation of 2-hydroxyheptanoic acid from carbohydrates during alkaline pulping is very unlikely. Similarly, the origin of C₅- α -hydroxy monocarboxylic acids in black liquors^{1,3,6} has remained unexplained because there exists no model experiments to indicate their formation from carbohydrates. An explanation might be their presence in wood in very small amounts.

The branched structure of 3-deoxy-2-C-methyltetronic acid is strong evidence for its formation by benzilic acid rearrangement of 5-hydroxy-2,3-pentandione (1,4-dideoxy-2,3-pentodiulose). It has been recently shown that appreciable amounts of 2-deoxy-3-C-methyltetronic acid are formed during nonoxidative alkaline degradation of pectic substances¹⁴ and alginates,¹⁵ most likely by benzilic acid rearrangement of 3,4-dioxopentanoic acid formed as an intermediate. The many obvious similarities between alkaline degradation of cellulose and pectic substances¹⁴ make plausible the formation of 3-deoxy-2-C-methyltetronic acid from cellulose as described. However, our attempts to identify this acid after alkaline treatment of cellulose and mannan have been unsuccessful. The corresponding straight-chain acid, 3,4-dideoxypentonic acid, is known to be formed from cellulose and mannan *via* 3-deoxypentulose.¹⁶

Experimental. Compounds 1 and 2 were identified in the spent liquors from sodium hydroxide pretreatment of pine wood.¹⁷ Compound 2 was also identified in kraft and kraft-antraquinone black liquors of birch wood.⁶ They amounted to less than 0.2 % of the hydroxy acids in the corresponding black liquors. The analytical procedures are described elsewhere.⁷ In the gas chromatograms the peak of compound 1 appeared just after C-methyltartronic acid, whereas compound 2 was eluted between 3-deoxytetronic and 2-deoxytetronic acids (*cf.* Ref. 7).

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