Identification of Novel Cellulose Degradation Products

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Several hydroxy monocarboxylic acids, C-alkyl-substituted tartronic acids, and other carboxylic acids were identified as novel polysaccharide degradation products by capillary GLC–MS after hot sodium hydroxide treatment of cotton cellulose. The mass spectra of the per(trimethylsilyl) derivatives of these compounds are reported. Their formation routes remain largely unexplained.

Some early investigations indicated that glucosiosaccharinic acid is formed by alkaline degradation of cellulose.¹-¹¹ Later, the application of various chromatographic techniques has revealed that many other hydroxy monocarboxylic acids, as well as some dicarboxylic acids, are generated during non-oxidative alkali treatment of cellulose and mannan.¹²-¹⁷

In recent work involving the treatment of cotton cellulose with hot sodium hydroxide solution, several carboxylic acids which has not been detected earlier were discovered as degradation products.¹⁸ The mass spectrometric identification of these compounds is now described and their formation routes are discussed.

Mass spectrometric identification

Hydroxy monocarboxylic acids. The prominent M-15 peak at m/z 247 in spectrum 1 (see Experimental) indicates a hydroxypentanoic acid. The relatively low intensities of the peaks for the ions at m/z 103, 117 and 131 (resulting from cleavage at C₄-C₅, C₃-C₄ and C₂-C₃, respectively) suggest the structure to be 5-hydroxypentanoic acid, which is confirmed by comparison of the spectrum with those of the trimethylsilyl (TMS) derivatives of 2-hydroxypentanoic,¹⁹ 3-hydroxypentanoic,¹⁹ 4-hydroxypentanoic¹⁹ and 4-hydroxy-3-methylbutanoic²⁰ acids. The m/z 204 ion is a rearrangement product²² which is often found in the mass spectra of the TMS derivatives of x-hydroxyalkanoic (x ≥ 3) acids²²,²³,²⁴ and long-chain alkanedioic acids.²²,²⁵-²⁷

Analogously, spectrum 2 refers to a hydroxyhexanoic acid (mol. wt. 276). The peaks at M-15–28 (233) and M-117 (159) are characteristic of an α-hydroxy acid.²⁸ The presence of an ethyl group is indicated by peaks for the M-29 (247) and M-29–90 (157) ions,²⁹ indicating 2-ethyl-2-hydroxybutanoic acid.

Spectrum 3 was recorded for two closely eluting compounds which can firmly be identified as diastereomeric 4-deoxy-2-C-methyltetronic acids (mol. wt. 350). A very prominent m/z 117 ion peak indicates²⁸ the α-deoxy structure, and the well-known McLafferty-type rearrangement³⁰ produces the m/z 306 ion. The identification is also confirmed by comparison with the spectra of the 4-deoxytetronic³¹ and 2-C-methyltetronic³² acid derivatives.

Finally, spectrum 4 corresponds to a dihydroxyhexanoic acid (or a hydroxypentanedioic acid, mol. wt. 364). The peaks at M-117 (247) and M-117–90 (257) show the presence of an α-hydroxy group. The 2-C-methyl-branched structure is indicated by the ion peaks at m/z 233 and 143, resulting from cleavage at C₃-C₄ and permitting identification as 3,4-dideoxy-2-C-methylpentonic acid. The corresponding dicarboxylic acid, 2,3-dideoxy-4-C-methylpentaric acid, shows an analogous fragmentation pattern.³³ The mass spectra of the TMS derivatives of the straight-chain²⁹ and branched-chain³⁴ 2-hydroxypentanedioic acids are quite different.

Tartronic acids. Structure determination of the C-alkyl-substituted tartronic acids as the TMS de-
derivatives can be based\textsuperscript{35} on the intense $M\text{-}15$, $M\text{-}44$, $M\text{-}117$ and $m/z$ 305 peaks, which were used in the identification of C-ethy1tartronic (mol. wt. 364) and C-propenyltartronic (mol. wt. 376) acids (spectra 5 and 6).

By analogy, spectrum 7 refers to a C-(hydroxypropyl)tartronic acid (mol. wt. 466). The conclusion that the hydroxy group is located at C\textsubscript{5} is based on the expectation\textsuperscript{19,20,36} that C-(2-hydroxypropyl)tartronic acid, being an $\eta$-hydroxy acid, should give rise to a very prominent $m/z$ 117 peak. The alternative possibility, C-(1-hydroxypropyl)tartronic acid, can be excluded (cf. Ref. 37). A very similar mass spectrum\textsuperscript{38} is obtained for 2-C-carboxy-3-deoxytetraric acid, which was also found after hot alkali treatment of cellulose.\textsuperscript{18}

Other carboxylic acids. Three mass spectra corresponded to the derivatives of triodeoxyheptaric acids (mol. wt. 480). The base peak at $m/z$ 129 in spectrum 8 is produced by cleavage at C\textsubscript{7}–C\textsubscript{6} (or C\textsubscript{8}–C\textsubscript{9}) following the loss of trimethylsilanol, and is consistent with the structure 3,4,5-trideoxyheptaric (2,6-dihydroxyheptanedioic) acid. Similar fragmentation gives the intense $m/z$ 129 peak also from the TMS derivatives of 2,3-dideoxyxypentaric,\textsuperscript{12} 2,3,4-trideoxyhexaric\textsuperscript{12} and 3,4-dideoxyhexonic\textsuperscript{17} acids. The large distance between the chiral centres prevents the separation\textsuperscript{18} of 3,4,5-trideoxyheptaric acid into the two peaks of the erythro and threo forms.

A very similar spectrum (9) was recorded for two diastereomeric compounds. The absence of the $m/z$ 129 peak and remarkably shorter retention times\textsuperscript{18} indicate branched isomers of 3,4,5-trideoxyheptaric acid, most probably 3,4-dideoxy-2-C-methylhexaric acids.

Several mass spectra recorded\textsuperscript{18} corresponded to branched hydroxyhexanedioic or ethanetricarboxylic acids (mol. wt. 378), of which 1,1,2-ethanetricarboxylic acid was tentatively identified on the basis of a very simple mass spectrum [$m/z$ (% rel. int.): 363 (15), 261 (M−117, 53), 217 (22), 147 (42), 143 (M−117−118, 100), 133 (7), 99 (6) and 73 (80). 2-Hydroxy-2-methylpropanoic, 2-hydroxy-2-methylbutanoic, 3-deoxy-2-C-methyltartronic, 3,5-dideoxy-erythro-pentonic, 3,5-dideoxy-threo-pentonic and methylsuccinic acids were also detected as novel polysaccharide degradation products. Their mass spectra have been reported in other connections (see Refs. 18 and 39).

Discussion

The products formed by the well-known endwise degradation mechanism\textsuperscript{11,13,17} constituted the major part of the carboxylic acids obtained.\textsuperscript{18} Evidently, however, the thermal degradation and recombination reactions give rise to the formation of many acids in minor quantities. It is thus not possible to outline complete formation routes for these compounds, although some suggestions concerning the most probable intermediates can be made.

Hydroxy monocarboxylic acids. The last step in the formation of α-hydroxy acids during alkali degradation of cellulose is usually a benzilic acid rearrangement of a dicarbonyl compound. Accordingly, 2-hydroxy-2-methylpropanoic, 2-hydroxy-2-methylbutanoic and 2-ethyl-2-hydroxybutanoic acids should be formed by rearrangement of 2,3-butanedione, 2,3-pentanedione and 3,4-hexanediene, respectively. Of these, 2,3-butanedione (biacetyl) has been identified as a product in the thermal alkaline degradation of 1,6-anhydro-β-D-glucopyranose\textsuperscript{40} and cellulose,\textsuperscript{41} and its formation route has been described. Also, 2,3-pentanedione is formed by thermal degradation of cellulose\textsuperscript{41} and D-glucose.\textsuperscript{42} 2-Hydroxy-2-methylbutanoic acid was the most abundant of these three compounds.\textsuperscript{18}

By analogy, the formation of 4-deoxy-2-C-methyltartronic, 3-deoxy-2-C-methyltartronic and 3,4-dideoxy-2-C-methylpentonic acids can be explained as arising from benzilic acid rearrangement of 4-hydroxy-2,3-pentanedione, 5-hydroxy-2,3-pentanedione and 6-hydroxy-2,3-hexanediene, respectively; however, the reactions producing these hydroxidiketones appear to be unknown. The formation paths of 5-hydroxypentanoic and 3,5-dideoxypentonic acids also remain unexplained. A possible route to 5-hydroxypentanoic acid involves hydrolysis of 6-hydroxymethyl-2-oxohexamal, but the more probable product from this intermediate, 6,6-dihydroxyhexanoic acid, could not be found.\textsuperscript{18}

Recently, 2-hydroxy-2-methylpropanoic, 2-hydroxy-2-methylbutanoic, 3,5-dideoxypentonic and 3-deoxy-2-C-methyltartronic acids have been
found in small amounts in alkaline pulping liquors\textsuperscript{33,34} although their origin was unknown. The present evidence shows that these acids are, at least to some extent, degradation products of cellulose or glucomannans.

\textit{Tartronic acids.} The conversion of 4-O-substituted 2-ulosonic acids into C-alkyl-substituted tartronic acids has been discussed by Petersson.\textsuperscript{35} The formation\textsuperscript{18} of several compounds of this type indicates, however, that other intermediates must also occur. In any case, a benzoic acid rearrangement of 2,3-dioxoalkanoic acids can be regarded as the final step in their formation.

Identification of C-(3-hydroxypropyl)tartronic acid as a product in the degradation of cellubiose\textsuperscript{44} and cellulose\textsuperscript{12} has been reported previously, but its mass spectrum has not been published. The observations that this acid is also formed by alkaline degradation of \(\beta\)-galacturonic acid\textsuperscript{45} and alginates\textsuperscript{46} have not helped to elucidate its formation route.

\textit{Other carboxylic acids.} The present results confirm the earlier reports\textsuperscript{47,48} that seven-carbon hydroxydicarboxylic acids are formed during hot alkali treatment of cellulose. The recombination reactions required for their formation are completely unknown. The presence of dicarboxylic acids with more than seven carbon atoms is also possible.\textsuperscript{18}

A very unexpected compound with a branched structure, viz. methylsuccinic acid, most probably originates from thermal degradation of cellulose. This acid has been found in alkaline pulping liquors\textsuperscript{49,50} and although its origin was attributed to lignin,\textsuperscript{49} the role of cellulose as its source seems to be obvious also under pulping conditions. Other investigators have identified (hydroxy-methyl)succinic acid\textsuperscript{12} and 2-hydroxy hexanoic, glutaric and adipic acids\textsuperscript{51} after hot alkali treatment of cellulose; however, these compounds could not be found in the work described here.

\textbf{Experimental}

Treatment of cotton cellulose with 1 M or 3 M sodium hydroxide solution at 170–190°C, and capillary GLC–MS investigations of the resulting mixtures were described in a previous paper.\textsuperscript{18} To our knowledge, the following mass spectra (carboxylic acids as their TMS derivatives) have not been published before [\(m/z\) (% rel. int.):]

- 5-Hydroxypentanoic acid (1): 247 (29), 204 (9), 197 (14), 157 (12), 147 (100), 131 (18), 117 (21), 103 (18) and 73 (85).
- 2-Ethyl-2-hydroxybutanoic acid (2): 261 (7), 247 (14), 233 (18), 217 (10), 171 (9), 159 (84), 157 (12), 147 (64), 133 (9) and 73 (100).
- 4-Deoxy-2-C-methyltetronic acid (3): 335 (11), 306 (38), 245 (7), 234 (29), 233 (25), 221 (13), 203 (10), 147 (60), 143 (26), 133 (10), 117 (80) and 73 (100).
- 3,4-Dideoxy-2-C-methylpentonic acid (4): 349 (10), 259 (8), 247 (24), 233 (17), 217 (14), 157 (68), 147 (44), 143 (62), 133 (14), 129 (9), 103 (10) and 73 (100).
- C-Ethyltartronic acid (5): 349 (23), 320 (32), 305 (12), 259 (21), 247 (68), 233 (9), 169 (14), 147 (100), 133 (20), 131 (15), 115 (24), 103 (16) and 73 (48).
- C-Propenyltartronic acid (6): 361 (25), 332 (40), 305 (10), 259 (52), 245 (12), 233 (9), 219 (8), 147 (100), 133 (18), 117 (34), 81 (23) and 73 (72).
- C-(3-Hydroxypropyl)tartronic acid (7): 451 (28), 422 (33), 361 (26), 349 (16), 305 (40), 259 (10), 221 (18), 217 (12), 147 (32), 133 (17), 129 (14), 117 (16), 115 (11) and 73 (100).
- 3,4,5-Trideoxyheptaric acid (8): 465 (12), 363 (28), 347 (14), 273 (18), 245 (13), 229 (12), 215 (10), 201 (18), 191 (22), 173 (14), 157 (36), 147 (64), 129 (100), 103 (9) and 73 (89).

A branched isomer of 3,4,5-trideoxyheptaric acid (9): 465 (11), 363 (52), 347 (15), 273 (55), 245 (14), 229 (10), 221 (10), 183 (13), 147 (54), 143 (17), 133 (13), 115 (11), 111 (14) and 73 (100).

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References


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