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## Note

# The formation of 3-hydroxytetrahydrofuran-3-carboxylic acid by the degradation of xylan with alkali

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Among the carboxylic acids formed from carbohydrates under alkaline or acidic conditions are the hydroxytetrahydrofurancarboxylic acids. The first compound of this type, 4-hydroxy-2-(hydroxymethyl)tetrahydrofuran-4-carboxylic acid (**1**), was tentatively identified after treatment of 2-acetoxy-hexa-*O*-acetylcellobial[1] and 2-acetoxy-tri-*O*-acetyl-D-glucal[2] with alkali.

Compound **1** (anhydroisosaccharinic or 1,4-anhydro-3-deoxypentitol-2-carboxylic acid) is an important product from the alkaline degradation of cellulose[3–10] and mannan[11,12] (including related model substances[13–16]), and is thus formed in considerable amounts during the alkaline pulping of wood[9,17–23]. Compound **1** is also known as an acid-catalysed dehydration product of glucose[24] and as an artifact from the hydrolysis of cellulosic materials[6,24–30]. Generation of **1** by acid-catalysed dehydration of α-D-glucoisosaccharinic acid has also been reported[31].

The two diastereomers of the corresponding dicarboxylic acid, *i.e.*, "anhydroisosaccharinaric" acid (**2**, 4-hydroxytetrahydrofuran-2,4-dicarboxylic or 2[1],4-anhydro-3-deoxy-2-*C*-hydroxymethylpentaric acid) were recently identified after treatment of pectic acid[32], D-galacturonic acid[33], and alginates[34] with alkali. The analogous five-carbon compound, 3-hydroxytetrahydrofuran-3-carboxylic acid (**3**), which is the main product from acid-catalysed dehydration of xyloisosaccharinic acid lactone[35], has now been obtained in small amounts by treatment of birch xylan with alkali. Another related compound of carbohydrate origin is (2*S*,4*S*)-4-amino-2-(hydroxymethyl)tetrahydrofuran-4-carboxylic acid (**4**), which was first isolated[36,37] from an acid hydrolysate of diabetic urine and was later shown[38,39] to be a product of an unexpected reaction between D-hexoses and urea.

The yield of **3** varied from 4–6 mg/g of the charge, corresponding to 1–1.5% of the non-volatile carboxylic acids. Such a low yield has restricted the detection of **3** after treatment of xylan with alkali[40–43]. The proportions of other carboxylic acids were as reported previously[43].

Analogously with the route postulated[7,34] to be responsible for the formation of **1** and **2**, the end-wise degradation ("peeling") reaction of xylan produces the

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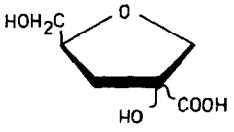

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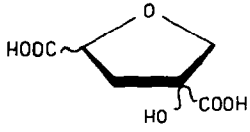

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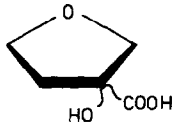

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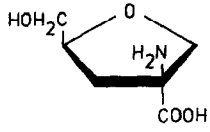

4

4-deoxy-2,3-pentodiulose intermediate (**5**), which is then dehydrated and rearranged to give **3** (Scheme 1). Under similar conditions, much higher amounts of **1** (from cellulose[3,9] and mannan[11,12]) and **2** (from pectic acid[32] and alginates[34]) are formed *via* the corresponding six-carbon intermediates. At present, no explanation can be given for the disfavoured formation of **3**.

5

Scheme 1

## EXPERIMENTAL

Samples (100 mg) of birch xylan[44] were treated for 90 min under nitrogen at 140°, 150°, and 160° with 0.6M sodium hydroxide (40 mL) in rotating autoclaves. The non-volatile carboxylic acids were per(trimethylsilylated) as their ammonium salts and analysed[45] with a Hewlett–Packard 5880 A gas chromatograph equipped with an SE-54 fused-silica capillary column (0.32 mm i.d. × 25 m) and a flame-ionisation detector.

The e.i. mass spectra were recorded[23] with a JEOL JMS-DX303 instrument (at 70 eV) combined with a Hewlett–Packard 5790 A gas chromatograph and the same column as above. The fragmentation pattern of the trimethylsilyl derivative

of **3** is typical of that of α-hydroxy acid derivatives and is analogous with the corresponding spectra[7,32] of **1** and **2**; *m/z* 261 ($M^+ - 15$, 7%), 233 (10), 171 (6), 159 ($M^+ - 117$, 100), 147 (36), 143 (5), 129 (5), 127 (5), 103 (5), 73 (67), and 69 (7). For the literature values, see ref. 35.

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