Carbohydrate Research, 69 (1979) 269–271

Note

Formation and further reaction of 3-deoxytetrulose during treatment of (1→4)-linked xylose oligomers with alkali

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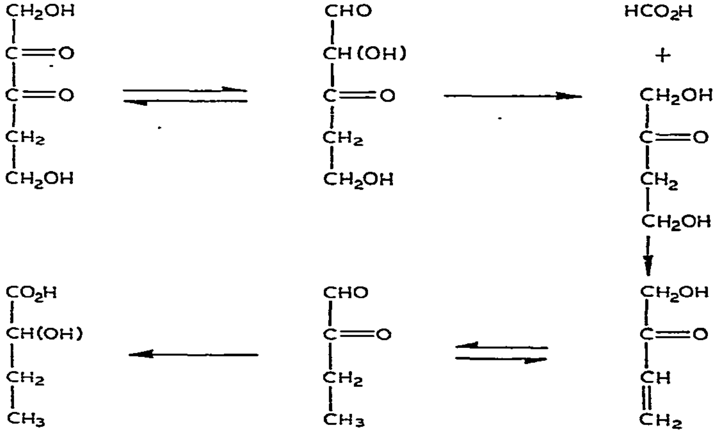
(Received December 21st, 1977; accepted for publication, March 14th, 1978)

3-Deoxypentulose has been isolated in appreciable amounts after heating hydrocellulose[1], cellobiose[2], and 4-deoxy-2,3-hexodiulose[3] in aqueous sodium hydrogencarbonate. The product composition after treatment in sodium hydroxide shows that 3-deoxypentulose is also an important intermediate in strongly alkaline solution. The nature of the final reaction products suggests that alkaline end-wise degradation of the (1→4)-linked xylopyranosyl residues in the xylan backbone proceeds by reactions analogous to those of cellulose[4]. The postulated 3-deoxytetrulose (1,4-dihydroxybutanone) has not been isolated previously. It has, however, been prepared from 2-butyn-1,4-diol and utilized in the preparation of histamine analogs[5].



Formation and further reaction of 3-deoxytetrulose

Scheme 1

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In the present work, a mixture of xyloheptaose and its lower oligomers gave 3-deoxytetrulose in 4% yield after treatment in aqueous sodium hydrogen carbonate at 80° for 28 h. It has previously been postulated[4] that 2-hydroxybutanoic acid, present in appreciable amount in the solution after alkaline treatments of xylan and wood, is formed *via* 3-deoxytetrulose. Accordingly, treatment of 3-deoxytetrulose with 0.15M sodium hydroxide at 90° for 40 min yielded 38% of the postulated acid. Other non-volatile monocarboxylic acids were not detected. The formation of 2-hydroxybutanoic acid is explained by a β-elimination of HO-4 followed by isomerization and benzilic acid rearrangement. The formation of 3-deoxytetrulose from the precursor 4-deoxy-2,3-pentodiulose and its further reaction are illustrated in Scheme 1.

EXPERIMENTAL

A mixture (1 g) of xyloheptaose and lower oligomers [obtained by mild hydrolysis of birch xylan with acid followed by removal of the mineral acid and uronic acids by treatment with the hydrogencarbonate form of a weakly cross-linked, anion-exchange resin (Dowex 1-X2)] was heated in 200 ml of 0.2M $NaHCO_3$ at 80° under a layer of paraffin oil for 28 h. The sugars were separated from the acids on an anion-exchange resin[6] and subjected to partition chromatography[7] in 92.4% (w/w) ethanol at room temperature on the sulfate form of an anion-exchange resin (Aminex A-28, 8–12 μm; 4 × 725 mm). The first 60 ml of the eluate were concentrated by evaporation, and the residue was re-chromatographed on the same column. A sugar (42 mg) that exhibited an adjusted retention-volume equal to 2.0 bed-volumes was isolated and identified as 3-deoxytetrulose.

The identity was established by g.l.c.[8,9] and g.l.c.–m.s.[9,10] (AEI Organic MS-20, EI, 70 eV) of the trimethylsilylated oxime and of the *O*-trimethylsilyl derivatives obtained after borodeuteride and borohydride reductions. Retention data from temperature-programmed analysis on two stationary phases (0.5% of OV-1 on 100/120 mesh Chromosorb G and 0.5% of OV-17 on 100/120 mesh Chromosorb G, respectively), given as "methylene unit" (MU) values, are 14.51 and 14.63 for the 3-deoxytetrulose, 13.84 and 13.68 for the 2-deoxytetritol, and 11.23 and 11.57 for the 2-hydroxybutanoic acid. The fragmentation patterns of the *O*-trimethylsilyl derivatives of the reduced samples clearly showed that the parent sugar was 3-deoxytetrulose. The most structure-specific ion from the 2-deoxytetritols obtained by reduction was that arising from α-cleavage between the vicinal Me_3SiO-groups (see Scheme 2).

Scheme 2 Mass-spectral fragmentation

After treatment of 3-deoxytetrulose with 0.15M NaOH at 90°, the reaction solution was passed through an anion-exchange resin in the acetate form. The resin was washed with water, and monocarboxylic acids were then eluted with 5M acetic acid (15 bed-volumes). 2-Hydroxybutanoic acid was the only non-volatile monocarboxylic acid found in this fraction.

The identity was obtained from gas-chromatographic[10] and mass-spectral[9] data which were compared with those of an authentic sample, as well as by ion-exchange chromatography in 0.08M sodium acetate (acetic acid added to pH 5.9) and in 0.5M acetic acid[11].

Mass-spectral data. — (*a*) Me_3Si derivative of 3-deoxytetrulose oxime: *m/e* 335, $M^{+\cdot}$ (2.2% of base peak at *m/e* 73), 320 (3.8), 246 (9.4), 230 (2.2), 216 (13), 202 (5.6), 191 (6.6), 172 (5), 158 (1.9), 157 (2.2), 156 (7.8), 149 (5.9), 148 (5.9), 147 (42), 133 (6.9), 131 (7.8), 129 (5.0), 128 (15), 118 (1.9), 117 (5.0), 116 (7.8), 103 (25), 101 (10), and 98 (16).

(*b*) Me_3Si derivative of borodeuteride-reduced 3-deoxytetrulose: *m/e* 308, $M^{+\cdot}-15$ (1% of base peak at *m/e* 103), 233 (3.3), 220 (38), 190 (11), 147 (38), 133 (10), 131 (7.9), 130 (15), 118 (3.9), 117 (3.3), 116 (2.6), 105 (4.6), 104 (11), and 103 (100).

(*c*) Me_3Si derivative of borohydride-reduced 3-deoxytetrulose: *m/e* 307, $M^{+\cdot}-15$ (1% of base peak at *m/e* 103), 232 (2.5), 219 (50), 189 (14), 147 (38), 133 (11), 131 (5.0), 129 (14), 119 (1.5), 117 (3.5), 115 (2.3), 105 (4.8), 104 (8.5), and 103 (100).

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