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Note

Epimerization and degradation of 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylitol in alkaline medium

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4-*O*-Methylglucuronoxylan is an important constituent of wood and wood pulps. An appreciable portion of the uronic acid moieties are split off during a kraft cook[1] by reactions which are still obscure. Moreover, other methylated uronic acid moieties formed[2] in the pulp during the cooking have been identified as 4-*O*-methyl-L-iduronic acid[3].

We now report on model experiments with 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylitol (**1**).

EXPERIMENTAL

Deaerated solutions of **1** in M sodium hydroxide (10 ml) were heated in Teflon-coated autoclaves for various times, then cooled, decationised, and analyzed by anion-exchange chromatography. The eluates were monitored automatically at 254 nm and by using a three-channel analyzer[4]. A typical chromatogram is shown in Fig. 1. The quantitative determinations were based on the response in the periodate–formaldehyde channel.

The products were isolated by preparative anion-exchange chromatography (Table I) and identified by g.l.c. and g.l.c.–m.s. of the trimethylsilyl (Me_3Si) derivatives[5]. The compound (X) eluted first was xylitol and the second was unreacted **1**. The product in peak **2** gave colour tests very similar to those of **1**, indicating it to be the epimerization product 2-*O*-(4-*O*-methyl-β-L-idopyranosyluronic acid)-D-xylitol. The mass spectra of **1** and **2** were almost identical, and **2** gave xylitol and 4-*O*-methyl-L-iduronic acid on acid hydrolysis.

The compound eluted last gave a weaker, relative response in the carbazole channel, but had very strong u.v. absorbance (λ_{max} 230 nm, ε 5910) characteristic of α,β-unsaturated uronic acids[6]. The acid was retained very strongly by the anion-exchanger, both in sodium acetate solution and in acetic acid. These data suggest the

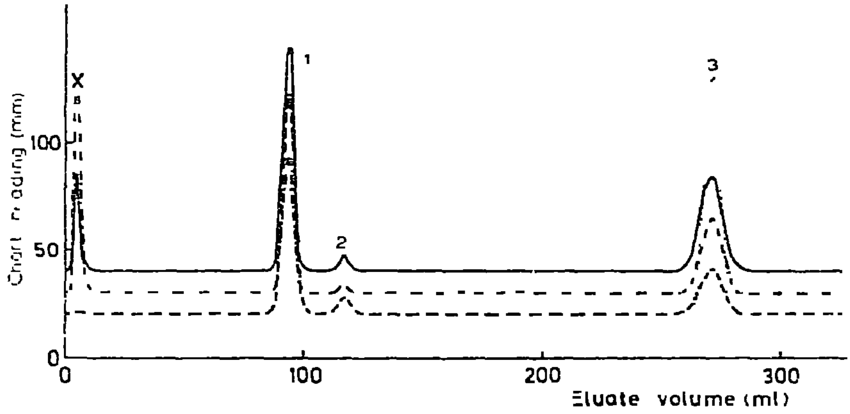


Fig. 1. Separation of products obtained after treatment of 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylitol (**1**) in M sodium hydroxide for 1 h at 150°. Column (4 × 820 mm) of Dowex 1-X8(AcO$^-$) resin (13–16 μm) eluted with 0.02M sodium acetate (with acetic acid added to pH 5.9) at a linear flow-rate of 1.1 cm/min. ——— chromic acid method, — —, periodate–formaldehyde method, – – – carbazole method, · · ·, u.v. absorption at 254 nm.

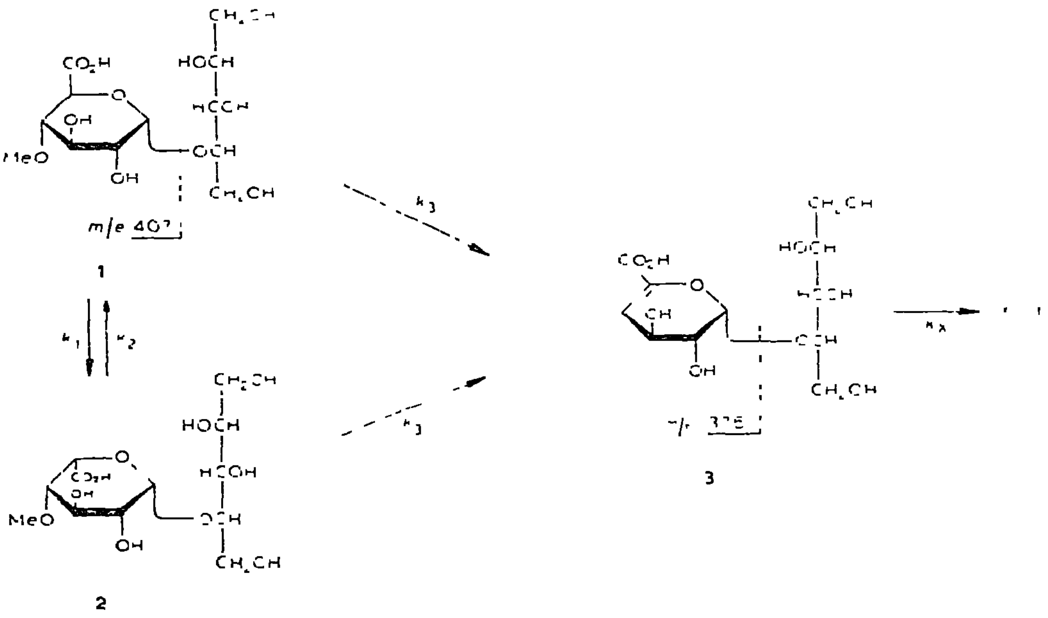
TABLE I

CHROMATOGRAPHIC DATA OF THE ACIDS PRESENT IN THE REACTION MIXTURE

	Volume distribution coefficient (D_v)			*Relative retention*[a]		
	0.02M NaOAc (pH 5.9)	*0.08M NaOAc (pH 5.9)*	*0.5M HOAc*	*OV-1 240*	*OV-17 240*	*SP-2401 200*
2-*O*-(4-*O*-Methyl-α-D-glucopyranosyluronic acid)-D-xylitol (**1**)	8.7	2.2	11.2	0.537	0.797	0.643
2-*O*-(4-*O*-Methyl-β-L-idopyranosyluronic acid)-D-xylitol (**2**)	10.9	2.7	9.3	0.415	0.600	0.515
2-*O*-(4-Deoxy-β-L-*threo*-hex-4-enopyranosyluronic acid)-D-xylitol (**3**)	25.9	6.5	33.8	0.403	0.616	0.502

[a] Retention times of the Me_3Si derivatives relative to those of the *O*-β-D-glucopyranosyl-(1→4)-D-glucitol derivative.

structure **3** which was confirmed by mass spectrometry of the Me_3Si derivative. The most prominent difference between the spectra of the Me_3Si derivatives of **1** and **3** was that the characteristic fragment ion (*m/e* 407) from the glycosyl moiety of **1** (see formula) was not recorded for **3** which gave a corresponding abundant ion with *m/e* 375.



The ¹H-n.m.r. spectra (D_2O, 270 MHz) of **1** and **3** contained doublets for H-1 at δ 5.17 (J 4 Hz) and 5.43 (J 2.7 Hz), respectively. A characteristic doublet for H-4 at δ 6.15 (J 3.2 Hz) was recorded for **3**

RESULTS AND DISCUSSION

The results given in Fig. 2 show that **1** was degraded rapidly in M sodium hydroxide at 150°. An appreciable amount of 2-*O*-(4-*O*-methyl-β-L-idopyranosyluronic acid)-D-xylitol (**2**) was formed rapidly by epimerization and both epimers were decomposed to give 2-*O*-(4-deoxy-β-L-*threo*-hex-4-enopyranosyluronic acid)-D-xylitol (**3**) and xylitol. The concentration of **3** reached a maximum after ~1.5 h and then decreased with increasing formation of xylitol. The formation of **3** from **1** or **2** presumably involves[7,8] β-elimination of MeO-4 following loss of H-5. It is therefore reasonable to assume that **1** and **2** are decomposed at the same rate.

No uronic or aldonic acids were detected in the reaction, but anion-exchange chromatography in 0.08 and 0.3M sodium acetate revealed small amounts of several fragmentation acids, mainly formic acid (0.7 mol per mol of degraded **3**). Condensation products held irreversibly by the ion-exchangers were also formed

If pseudo-first-order reactions apply for the depicted formulae scheme, then

$$-d[1]/dt = (k_1 + k_3)[1] - k'_2[2],$$

$$-d[2]/dt = k'_2[2] - k_1[1] + k_3[2],$$

$$d[3]/dt = k_3\{[1] + [2]\} - k_x[3],$$

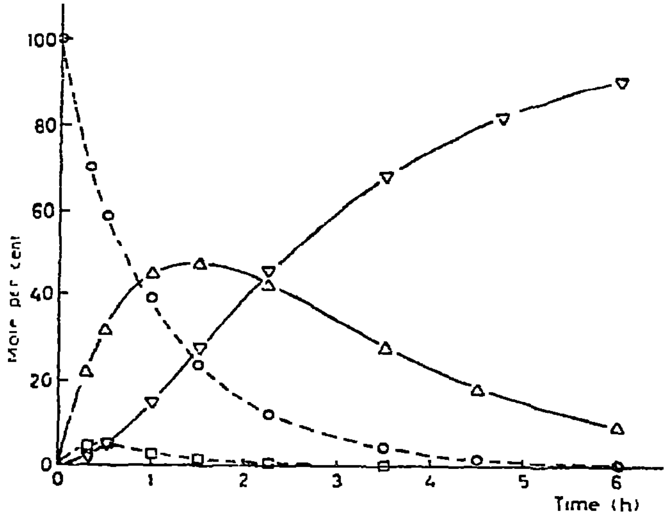


Fig. 2 Composition of the reaction mixture 2-*O*-(4-*O*-methyl-α-D-glucopyranosyluronic acid)-D-xylitol (—○—), 2-*O*-(4-*O*-methyl-β-L-idopyranosyluronic acid)-D-xylitol (—□—), 2-*O*-(4-deoxy-β-L-*threo*-hex-4-enopyranosyluronic acid)-D-xylitol (—△—), xylitol (—▽—)

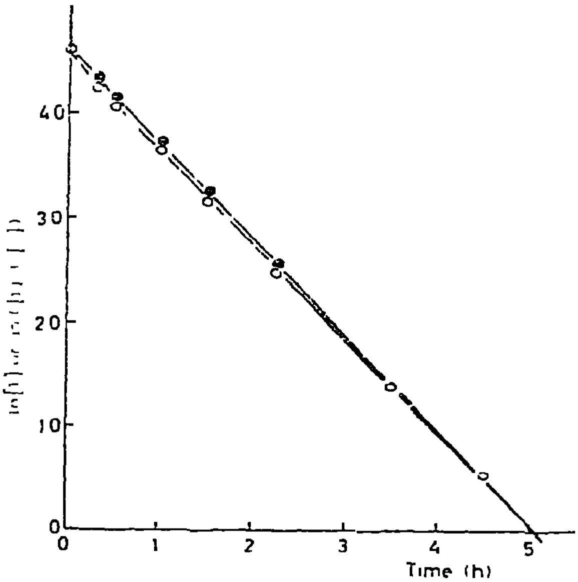


Fig 3. Relationship (—●—) between ln{[1]+[2]} and the time of reaction used for determination of k_3, ln [1] versus time (—○—) for comparison

and

$$d[X]/dt = k_X[3].$$

As predicted from the first two equations, a plot of ln {[1]+[2]} versus time (Fig. 3) gave a straight line. The pseudo-first-order rate constant k_3 was equal to 0.91 h^{-1}. The rate constant k_X for the formation of xylitol from 3 was calculated from the following equation,

$$[3] = \frac{k_3 \cdot [1]_0}{k_X - k_3}\left[e^{-k_3 t} - e^{-k_X t}\right],$$

which was obtained by integration. The full lines drawn in Fig. 2 represent the concentrations of 3 and xylitol (X) calculated by application of the rate constant $k_X = 0.52\ h^{-1}$. The results are in agreement with the postulated reaction scheme.

Most probably, a reaction scheme analogous to that discussed above is also responsible for the removal of 4-*O*-methylhexuronic acid moieties from xylan during a kraft cook. Hence, demethylation of the xylan should occur more rapidly than the loss of the uronic acid groups. This situation was observed by Clayton[8] in a study of the alkaline degradation of hardwood xylans. From the comparatively low degradation rate of 3, it must be concluded that 4-deoxy-L-*threo*-hex-4-enopyranosyluronic acid moieties are linked to the xylan present in kraft pulps. After acid hydrolysis of kraft pulps, large proportions of 4-*O*-methylglucuronic acid and appreciable proportions of 4-*O*-methyliduronic acid are present in the hydrolysate[2], whereas no unsaturated uronic acids have been observed. A plausible explanation is that the unsaturated uronic acid moieties are decomposed during the acid hydrolysis[9]. This was confirmed in experiments with 3, which showed that hydrolysis (2 and 3 h, 0.05M H_2SO_4, 130°) gave tar in addition to xylitol. No uronic acids were present in the hydrolysate. Hence, the above reaction scheme is valid for the epimerization and destruction of the 4-*O*-methylglucuronic acid moieties in xylan during alkaline pulping at high temperature.

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