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ALKALINE DEGRADATION OF MODEL COMPOUNDS RELATED TO (4-*O*-METHYL-D-GLUCURONO)-D-XYLAN

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ABSTRACT

The kinetics of alkaline degradation of eight model compounds related to (4-*O*-methyl-D-glucurono)-D-xylan in M NaOH in the temperature range 130–190° and under nitrogen have been studied. The first-order rate constants and activation parameters have been calculated. The alkaline degradation of pentose models requires less energy than the hexose models. The stability of the uronic acid models is lower than that of neutral models. The alkaline hydrolysis of glycosidic bonds of (4-*O*-methyl-D-glucurono)-D-xylan requires more energy than the peeling reaction.

INTRODUCTION

Alkaline hydrolysis of the glycosidic bonds of wood polysaccharides results in losses of pulp during alkaline cooking. Whereas the peeling reaction does not significantly change the d.p., alkaline hydrolysis has a marked effect on this parameter.

The kinetics of alkaline degradation have been studied only rarely on model compounds containing interglycosidic bonds[1]. After a study of the alkaline degradation of methyl β-D-cellotrioside[2], attention was paid to the kinetics of alkaline degradation of pentose models. These model compounds have no reducing end groups and the rate-determining step in the alkaline degradation will be the hydrolysis of the glycosidic bonds. The following model compounds were used: methyl β-D-xylopyranoside (**1**), methyl β-D-xylobioside (**2**), methyl β-D-xylotrioside (**3**), methyl 2-*O*-(methyl 4-*O*-methyl-α-D-glucopyranosyluronate)-β-D-xylopyranoside (**4**), methyl 4-*O*-[2-*O*-(methyl 4-*O*-methyl-α-D-glucopyranosyluronate)-β-D-xylopyranosyl]-β-D-xylopyranoside (**5**), methyl 2-*O*-(methyl 4-*O*-methyl-α-D-glucopyranosyluronate)-4-*O*-β-D-xylopyranosyl-β-D-xylopyranoside (**6**), (4-*O*-methyl-D-glucurono)-D-xylan (**7**), and reduced **7** (**8**).

EXPERIMENTAL

Compounds **1**–**6** were synthesised as described previously[3–8]. Polysaccharide **7**, prepared from beech sawdust[9], had $[\alpha]_D^{22}$ −70° (*c* 0.5, water), $\overline{M}_n$ 18,610 (deter-

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mined by osmometry), and contained 19.3% of uronic acid and 2.93% of methoxyl; the neutral portion of the saccharides formed on acid hydrolysis contained 98% of D-xylose. Reduction of **7** (1 g) in water (100 mL) with $NaBH_4$ (0.5 g) at room temperature for several days, followed by dialysis and lyophilisation, gave **8** which contained no reducing groups as determined by the method of Ströle[10]. Methyl 2,3,4-tri-*O*-methyl-β-D-xylopyranoside and methyl 2,3,2′,3′,4′-penta-*O*-methyl-β-D-xylobioside were used as standards in t.l.c.

The products of alkaline degradation were analysed by t.l.c. on Silica gel G (Merck), using ether–toluene (7:3) and detection by charring with sulphuric acid.

Solutions of substrate (1 mg) in M NaOH (1 mL) were sealed in ampoules and stored at temperatures (±1°) in the range 130–190°. After intervals (0.1–20 h), ampoules were cooled to room temperature and opened, and the contents were diluted with water to 25 mL. The concentration of saccharides in aliquots (1 mL) was determined spectrophotometrically, using the phenol–sulphuric acid method[11] and a Zeiss Specol 10 spectrophotometer at 480 nm on solutions which had been passed through a bacterial filter (Rasotherm, por. 1.6). The reference absorbance A_0 was that of the diluted solutions, and A_t was the absorbance after time t. The rate constants were calculated from the relationship $\ln A_0/A_t = f(t)$, using the linear regression method. Similarly, the activation energies and pre-exponential factors were calculated from the Arrhenius equation, using the modified programmes in AOS[12,13] and the programmable calculators TI-58C and TI-59 (Texas Instruments Inc.).

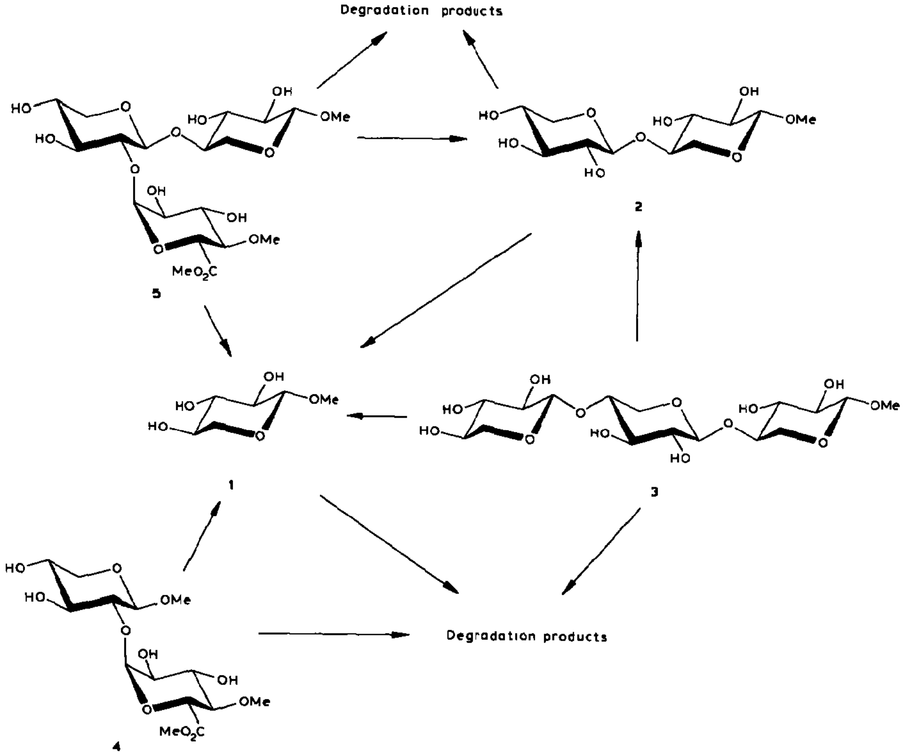
After quantitative determination of the saccharides, the samples were neutralised to pH 7 using Dowex 50-W X8 (H^+) resin, filtered, and concentrated to dryness. Each residue was methylated according to the method of Kuhn *et al.*[14].

RESULTS AND DISCUSSION

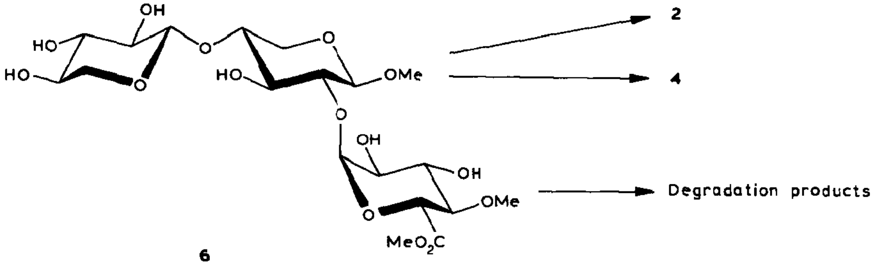
With the help of standards [methyl 2,3,4-tri-*O*-methyl-β-D-xylopyranoside (R_F 0.67) and methyl 2,3,2′,3′,4′-penta-*O*-methyl-β-D-xylobioside (R_F 0.52)], the methylated derivatives of **1** and **2** among the degradation products of trisaccharides **3**, **5**, and **6** were determined. By the same method, the methylated derivative of **1** was determined among the degradation products of disaccharides **2** and **4**. In the mixture of degradation products of oligosaccharides **4**–**6**, a substance was present with R_F 0.8, the structure of which was not determined because of its low concentration. Schemes 1 and 2 are proposed for the alkaline degradation of **1**–**5** and **6**, respectively. The term "degradation products" includes all compounds formed after alkaline hydrolysis of glycosidic bonds of the model compounds, except **1**–**6**. No attempt was made to analyse these products because of their low concentration.

The rate constants listed in Table I were determined for the degradation of **1**–**8** in M NaOH in the range 130–190° under nitrogen. All the rate constants fitted well the initial rates (the relation $\ln A_0/A_t$ *versus* time was a straight line with regression coefficient R = 0.95–1.0). After longer time intervals when consecutive reactions were evident, A_t values which lowered the regression coefficient were obtained, and these values were not used for the calculations of rate constants.

Comparison of rate constants for methyl β-D-glucopyranoside (**9**) studied previously[2] and **1**, obtained under similar conditions, shows that, in the absence of a primary hydroxyl group, the rate of alkaline degradation decreases (Table I). Thus, HO-6 in **9** may be involved in the rate-determining step of the degradation[1]. The pentose model compounds contain fewer nucleophilic groups that can participate in cleavage of glycosidic bonds. The activation energy (293.1 kJ.mol^{-1}) for the alkaline degradation of **1** was much higher than that (169.9 kJ.mol^{-1}) for **9**.



Scheme 1. Alkaline degradation of **1**–**5**.



Scheme 2. Alkaline degradation of **6**.

TABLE I

EXPERIMENTAL RATE CONSTANTS ($10^{-3}.h^{-1}$) FOR THE ALKALINE DEGRADATION OF **1–11** IN M NaOH UNDER NITROGEN

Temperature (degrees)	*Model*[a]										
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
130	—	—	1	14	14	36	311	145	—	—	—
140	—	1	3	25	42	83	433	211	—	—	—
150	—	2	8	42	116	186	591	337	2	2	2
160	—	5	12	83	313	401	795	598	6	4	5
170	2	12	37	88	771	836	1059	973	17	13	14
180	15	25	66	187	1958	1698	1389	1549	46	33	32
190	71	55	130	271	4560	3312	—	—	121	86	72

[a]Models **9–11** were studied previously[2].

The rate of alkaline degradation of **2** was greater than that for **1**. Comparison of the rate constants for methyl β-cellobioside (**10**), methyl β-cellotrioside (**11**), **2**, and **3** shows that the rate for the trimer is greater than that of the dimer, and that those of the pentose models are greater than those of the hexose models (Table I).

The activation energies were 134.2 and 118.2 kJ.mol^{-1}, respectively, for **2** and **3**. These values are lower than those for corresponding hexose models and represent the values for alkaline degradation of the saccharidic portion and probably reflect differences in the rigidity of the pyran ring of the pentosans compared to the hexosans. For the hexose models, it may be supposed, on the basis of activation energies for **1–3**, that the strength of glycosidic bonds in **3** decreases in the direction from the model bond to the true glycosidic bonds.

The rate constants for the xylouronides are at least one order of magnitude greater than for the pentose (Table I). The activation energies were 76.5, 149.7, and 117.5 kJ.mol^{-1} for **4–6**, respectively. The activation energies for **2** and **3** and **4–6** are not those of the individual glycosidic bonds but overall values. The value for **4** is lower than those of the trisaccharides **5** and **6**.

The activation energy for the trisaccharide **5** is higher than that of the trisaccharide **6**. Trisaccharides **5** and **6** differ in the xylose residue to which the glucuronic acid methyl ester is linked. The alkaline hydrolysis of the true β-glycosidic bond in **5** proceeds slower probably because of the presence of the α-glycosidic bond. In **6**, the internal β-glycosidic bond is not protected in this way and hence the activation energy is lower. It should be emphasised that conformational and steric effects, as observed for related compounds[15], cannot be excluded.

The rate constants for the polysaccharides **7** and **8** are an order of magnitude higher than those for **4–6** (Table I). The activation energy for **7** was 45.5 kJ.mol^{-1}. In **7**, the peeling reaction of uronic acids and the alkaline hydrolysis of the α and β linkages occur in parallel, and the consecutive reaction is secondary peeling.

The rate constants for **8** are lower than those for **7** (Table I). Since **8** contains

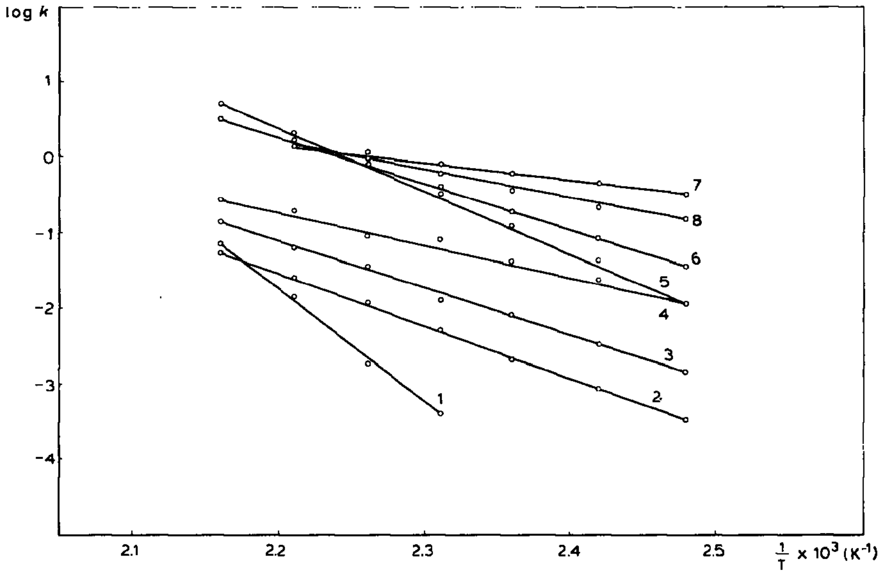


Fig. 1. Relation between log *k* and 1/T for alkaline degradation of models **1–8** in an inert atmosphere and M NaOH.

ionised uronic acid groups but no reducing groups, the rate-determining step is probably the alkaline hydrolysis of glycosidic bonds. The activation energy is 77.8 kJ.mol^{-1} and, because **7** and **8** differ only in the depressed primary peeling of **8**, it may be inferred that the activation energy of the alkaline hydrolysis of glycosidic bonds of (4-*O*-methyl-D-glucurono)-D-xylan is higher than that of the peeling reaction. The lower values of these activation energies compared to those for **1–6** could be due to the greater degree of motional freedom generally associated with polysaccharide molecules[16].

Table II contains the activation energies and the corresponding logs of the pre-exponential factors, the relationships of which are linear. From Fig. 1, the isokinetic temperature value of 174° for **5–8** was determined. Models **5** and **6**, which contain all of the types of glycosidic bonds present in (4-*O*-methyl-D-glucurono)-D-xylan (**7** and **8**), reflect the alkaline degradation of the macromolecule better than **1–4**.

The activation energies for cleavage of the glycosidic bonds in hemicelluloses during the delignification of wood chips could be influenced by the accessibility of

TABLE II

ACTIVATION ENERGIES AND LOG PRE-EXPONENTIAL FACTORS FOR **1–11**

Model	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
E (kJ.mol^{-1})	293.1	134.2	118.2	76.5	149.7	117.7	45.5	77.8	169.9	165.7	142.6
Log *A*	31.8	13.9	12.5	8.0	17.5	13.8	5.4	9.2	18.2	16.6	14.9

the polysaccharides in wood cells, as well as by inter- and intra-molecular hydrogen-bonds, or by covalent bonds with lignin. This situation probably contributes to the higher stability of (4-*O*-methyl-D-glucurono)-D-xylan during alkaline cooking in comparison with isolated hemicelluloses[17].

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