THERMAL DECOMPOSITION OF MODEL COMPOUNDS RELATED TO BRANCHED 4-*O*-METHYLGLUCURONOXYLANS*

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ABSTRACT

Methyl glycosides of xylo-oligosaccharides (linear and branched) and 4-*O*-methyl-D-glucuronic acid-containing oligomers closely reflecting the main structural features of native xylans were studied by thermal analysis and pyrolysis–gas chromatography. The number of monomeric residues in the oligosaccharides was found to affect markedly the course of active thermal decomposition. The thermal stability increases with increasing number of monomeric residues, but the ratio of the 2-furaldehyde formed to 3-hydroxy-2-penteno-1,5-lactone remains almost constant, the latter compound being formed from both xylopyranosyl and 4-*O*-methyl-D-glucuronic acid non-reducing residues in the molecule. A considerable difference in the course of thermal decomposition was observed on comparing reducing sugars to their glycosides, and when an ionic dehydrating catalyst was added to the pyrolyzed sample. The results suggest that the 4-*O*-methyl-α-D-glucopyranosyluronic acid linkage is the most thermally stable linkage in native (4-*O*-methylglucurono)xylans, and that the acetyl groups do not significantly accelerate the thermal decomposition of the polysaccharide.

INTRODUCTION

Thermal decomposition of (4-*O*-methylglucurono)xylan, the most thermally unstable component of hardwood, has been extensively studied[1-7]. The polysaccharide has been characterized thermoanalytically, and 2-furaldehyde and 3-hydroxy-2-penteno-1,5-lactone were found to be the main decomposition-products[4,5]. However, the chemistry of this thermal-decomposition process is not yet fully understood, and the mechanism of formation of the main products has not been elucidated in detail.

Reactions occurring during thermal decomposition of polysaccharides are highly complex, so that results obtained on polymeric materials are difficult to

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*Dedicated to Professor Roy L. Whistler.

interpret. Consequently, various model compounds such as D-xylose, lower xylo-oligosaccharides, and alkyl and aryl D-xylopyranosides have been studied[3,5]. Unfortunately, these compounds do not contain all of the structural features of the natural, title polysaccharide.

The present work, designed to yield more information on the thermal stability of (4-*O*-methylglucurono)xylan, utilizes synthetic, nonreducing oligosaccharide derivatives that closely reflect the main structural features of the native polysaccharide. The results have been compared with those obtained on related substances having the reducing, hemiacetal group unsubstituted, and are interpreted from the viewpoint of the effect of the main structural features of the native polysaccharide upon its thermal stability.

RESULTS AND DISCUSSION

The thermal analysis of methyl β-D-xylopyranoside (**9**) and the methyl glycosides **1**–**3** showed (Fig. 1, Table I) these substances to have different thermal stabilities, increasing with increasing number of monomeric residues in the molecule. This trend is manifested by the increasing initial temperature of weight-loss and by the rate of decomposition. Significant differences in the proportion of carbonaceous

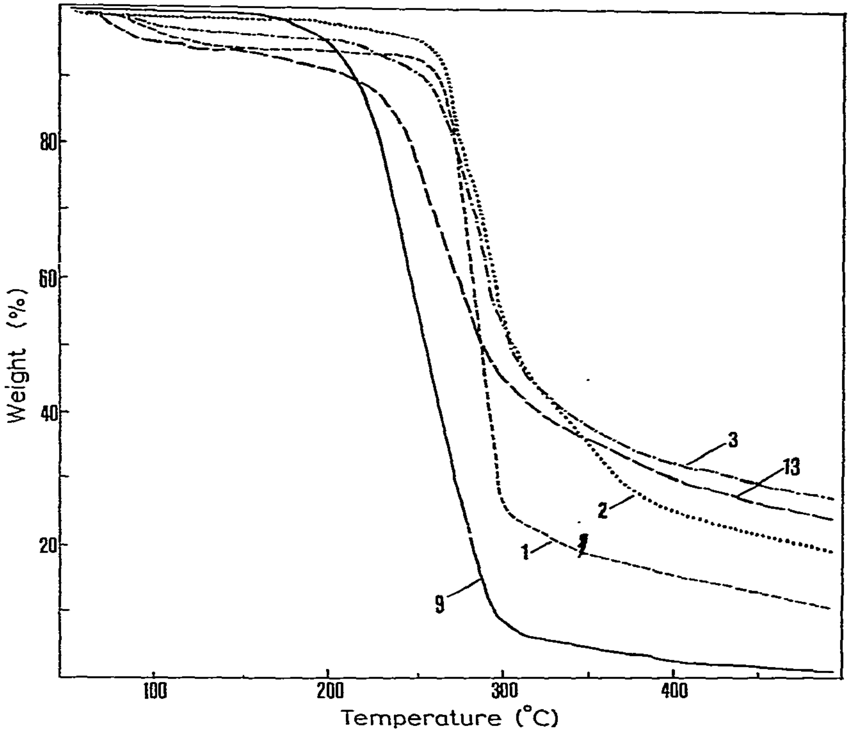


Fig. 1. Thermogravimetric analysis of methyl glycosides **1**–**3** and **9**, and of (4-*O*-methylglucurono)-xylan.

TABLE I

THERMAL-ANALYSIS FEATURES OF THE SAMPLES

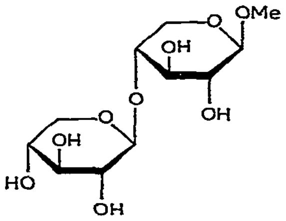
Sample	*M.p. (degrees)*	*D.t.a. peaks (degrees)*		*D.t.g. peaks*		*Residue at 500° (%)*	*A/B*[a]
		M.p.	*Dec.*	*(degrees)*	*maximum rate (mg/min)*		
1	103–104 148.5–149.0	103 148 171	280, 301[b]	287	0.76	10.8	1.2
2	216.5–217.5	218	272, 305[b]	291	0.55	21.2	1.3
3	—	—	280–310[b]	287	0.49	27.5	1.3
4	—	—	261	258	0.72	0.8	1.5
5	167–168	168	288, 303[b]	314	0.90	14.3	1.4
6	—	—	291, 310[b]	302	0.93	21.3	1.4
7	113.5–114.5	116	261	261	1.76	—	[c]
8	180–181	181	357	372	1.31	13.8	[c]
9	157	158	260	258	0.69	1.2	1.1
10	145	148	211, 290	210 283	0.22 0.38	10.7	—
11	185–186	190	238, 347[b]	235 285	0.35	13.8	0.3
12	205–206	207	236, 295[b]	235 286	0.32	14.2	0.5
13	—	—	270[b]	278	0.33	23.1	1.5

[a] Ratio of the peak area of 3-hydroxy-2-penteno-1,5-lactone (A) to the peak area of 2-furaldehyde (B). [b] Exothermic. [c] Not determined.

residue at 500° were determined for the derivatives **1**–**3** and **9**; for **3** this residue was even greater than that left by isolated hardwood xylan (Fig. 1). Also, the course of thermal decomposition of the glycosides **1**–**3** and **9** differs considerably from that of D-xylose and related, reducing oligosaccharides (compare also ref. 5). This result is not surprising, as it follows from previous work[7–10] that the process of dehydration at the reducing end commences at lower temperatures than that at which the glycosidic linkage of glycosides is cleaved with loss of the aglycon as the corresponding alcohol.

Ohnishi *et al.*[4,5] have shown that, although the major, volatile decomposition-product of xylan, xylobiose, and xylotriose is 3-hydroxy-2-penteno-1,5-lactone, none of the lactone is formed from D-xylose, whereas 2-furaldehyde is produced from all of the samples. In agreement with the Japanese authors, the ratio of the lactone formed to 2-furaldehyde found for glycosides **1**–**3** was observed to be almost constant (Fig. 2), and is higher than that found for the reducing oligosaccharides (Table I).

Although model compounds studied previously reflected some structural features of (4-*O*-methylglucurono)xylans, the thermal stability of compounds simulating the branching points and the simple, nonreducing 4-*O*-methyl-D-glucuronic acid residues attached to O-2 of some of the D-xylose residues have not been investigated thus far. As compared with the glycosides **1**–**3**, isolated samples of (4-*O*-methyl-



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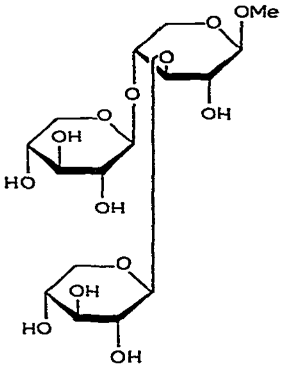

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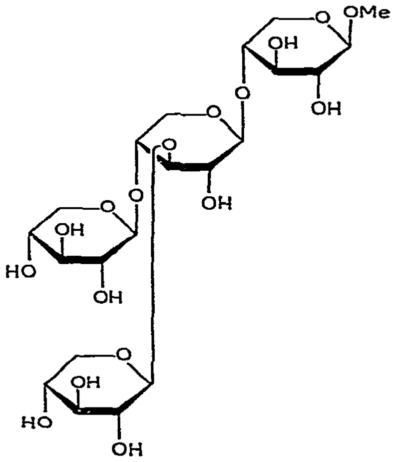

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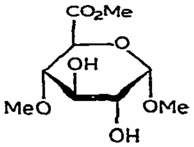

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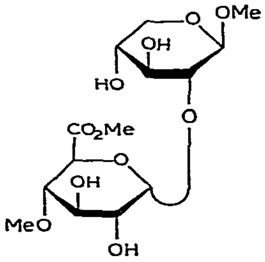

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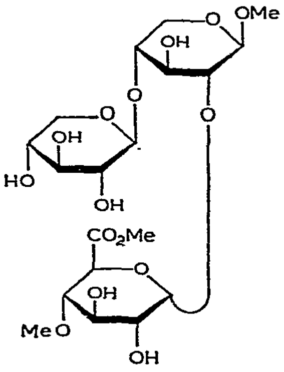

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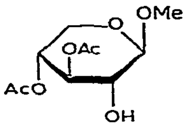

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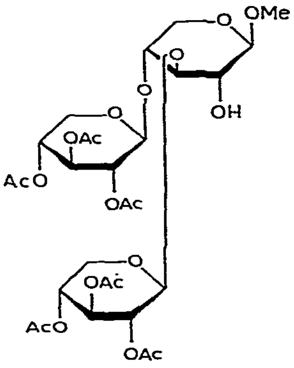

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Methyl β-D-xylopyranoside

9

D-xylose	xylobiose	xylotriose	(4-*O*-methylglucurono)xylan
10	11	12	13

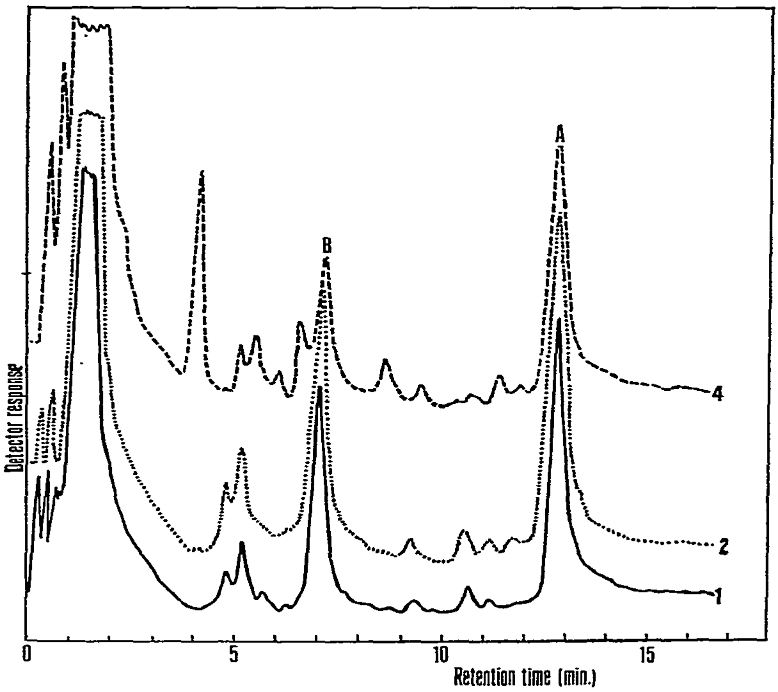

Fig. 2. Pyrolysis–g.l.c. scans of methyl β-xylo-oligosaccharides **1** and **2** compared with that of methyl (methyl α-D-glucopyranosid)uronate (**4**).

glucurono)xylan are thermally less stable, most probably because of the presence of the reducing end-units and free carboxyl groups in the macromolecule. Even more thermally labile are the xylo-oligosaccharides, although their stability increases slightly with increasing chain-length (Table I). The branching, the existence of which in native (4-*O*-methylglucurono)xylans appears to be indisputable[11,12], may be another stabilizing factor, as shown by the high thermal stability of the glycosides of the branched xylo-oligosaccharides studied herein.

At present, there are no literature data on the effect of uronic acid residues upon the thermal stability of native (4-*O*-methylglucurono)xylans. Although their state as they occur in wood is not known with certainty, there are indications that the uronic groups in the native polysaccharide are not present as carboxylate ions, but exist most probably as ester or lactone groups[12]. In order to furnish information on the contribution to the overall behavior of (4-*O*-methylglucurono)xylans upon heating, selected, esterified, alduronic acid derivatives (**4**–**6**) have also been studied.

Methyl (methyl 4-*O*-methyl-α-D-glucopyranosid)uronate (**4**) may be considered as the simplest model for the uronic acid side-chains of the title polysaccharide. Thermal analysis of **4** showed (Fig. 3) that the compound is quite thermally labile, leaving almost no residue after heating to 500°. The main products identified from its

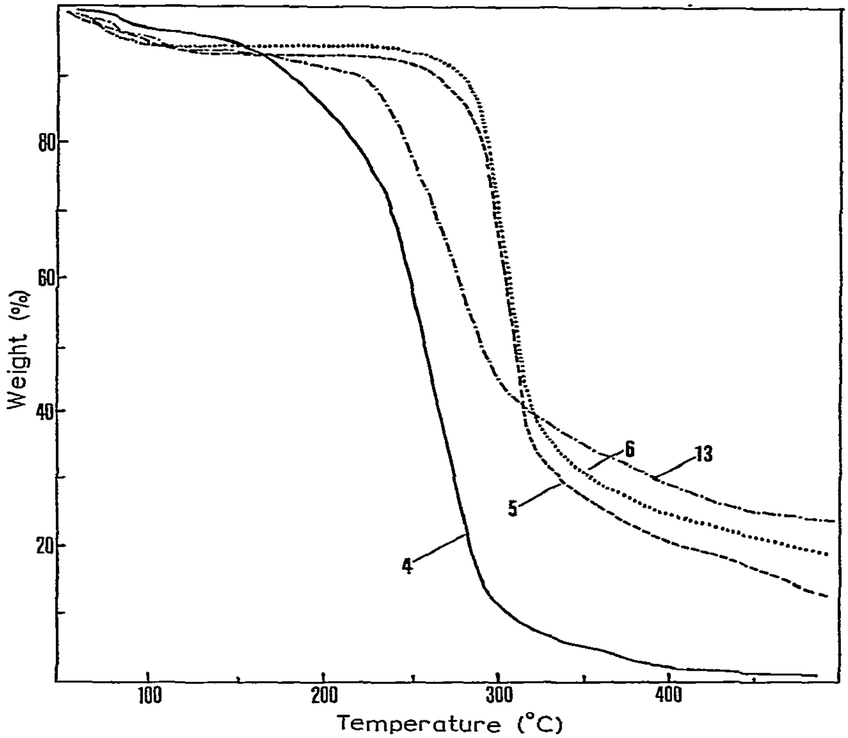

Fig. 3. Thermogravimetric analysis of alduronic acid derivatives 4–6 and of (4-*O*-methylglucurono)-xylan (13).

thermal decomposition are methanol, carbon dioxide, 3-hydroxy-2-penteno-1,5-lactone and 2-furaldehyde, as shown by pyrolysis–gas chromatography (Fig. 2). Compared with the monosaccharide derivative **4**, the alduronic acid derivatives **5** and **6** are considerably more stable on heating (Fig. 3). Compounds **5** and **6** are noticeably more thermally stable than methyl β-xylobioside (compare Figs. 1 and 3 and Table I), and it appears, taking into account the results of thermal analysis of **7** and **8** (see later), that the α-D-(1→2) glycosidic linkage present in **5** and **6**, constitutes the most thermally stable linkage present in native (4-*O*-methylglucurono)-xylan. This finding correlates well with the known resistance of the 4-*O*-methyl-α-D-glucopyranosyluronic acid linkage towards acid hydrolysis[13,14].

In order not to neglect the effect of the acetyl groups present in native (4-*O*-methylglucurono)xylans[12,13] and to gain information on their effect upon the course of thermal decomposition of the polysaccharide, the partially acetylated derivatives **7** and **8** were thermally analyzed. The thermal analysis of methyl 3,4-di-*O*-acetyl-β-D-xylopyranoside (Table I, Fig. 4) showed a more pronounced weight-loss over the whole range of the thermogravimetric curve, as compared with the non-acetylated compound **9**. This result is more probably attributable to the greater volatility of the partially acetylated monosaccharide derivative **7** (as compared with **9**) than to the

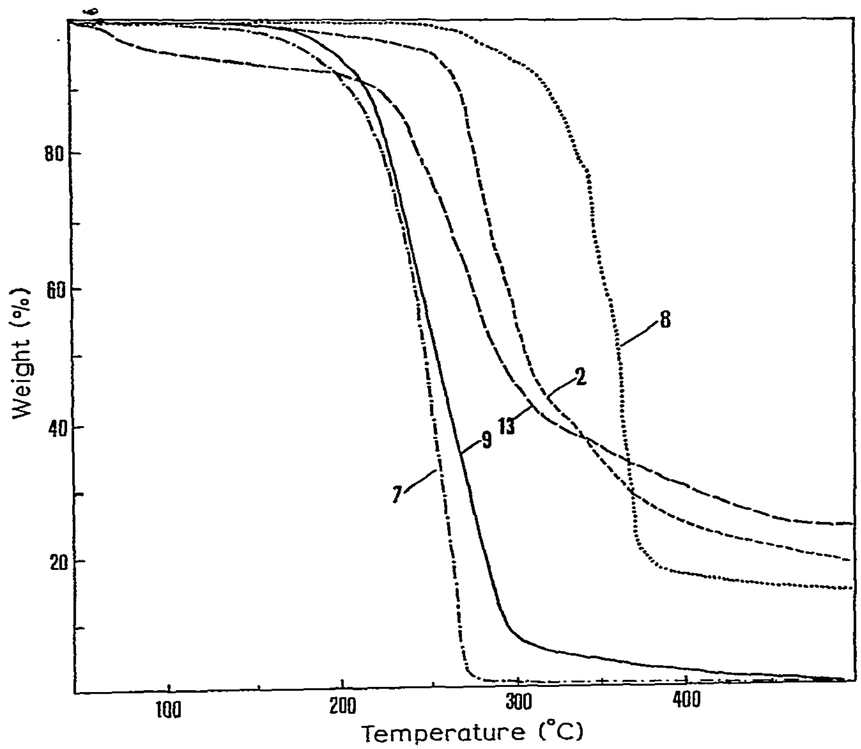

Fig. 4. Thermogravimetric analysis of methyl glycosides **2** and **9** compared with that of their partially acetylated analogs **8** and **7**, and with isolated (4-*O*-methylglucurono)xylan (**13**).

pyrolytic cleavage of acetyl groups. The partially acetylated, branched methyl β-xylotrioside **8** was found to be considerably more stable than either the corresponding non-acetylated derivative **2** or the isolated (4-*O*-methylglucurono)xylan. We are well aware that, as the ratio of *O*-acetyl to hydroxyl groups in **7** and **8** is not the same as that believed[12,13] to be representative of native (4-*O*-methylglucurono)xylans, these particular results must be considered as preliminary only. However, they indicate strongly that, contrary to a previous suggestion[15], the acetyl groups present in native xylans do not accelerate the thermal degradation of native xylans.

It is known[3,8] that the course of thermal decomposition of xylans and related compounds is altered markedly by the presence of small proportions of acids. For example, addition of zinc chloride to xylan has been shown to enhance pyrolytic decomposition and, at the same time, to promote the formation of 2-furaldehyde. Our results are in full agreement with this previous observation. Fig. 5 shows that the addition of zinc chloride to methyl β-xylobioside resulted in marked enhancement of the formation of 2-furaldehyde, whereas the proportion of 3-hydroxy-2-penteno-1,5-lactone formed did not decrease proportionally. The approximately fifty-fold increase in the proportion of 2-furaldehyde present among the volatile products of pyrolysis conducted in the presence of zinc chloride, as compared with that present

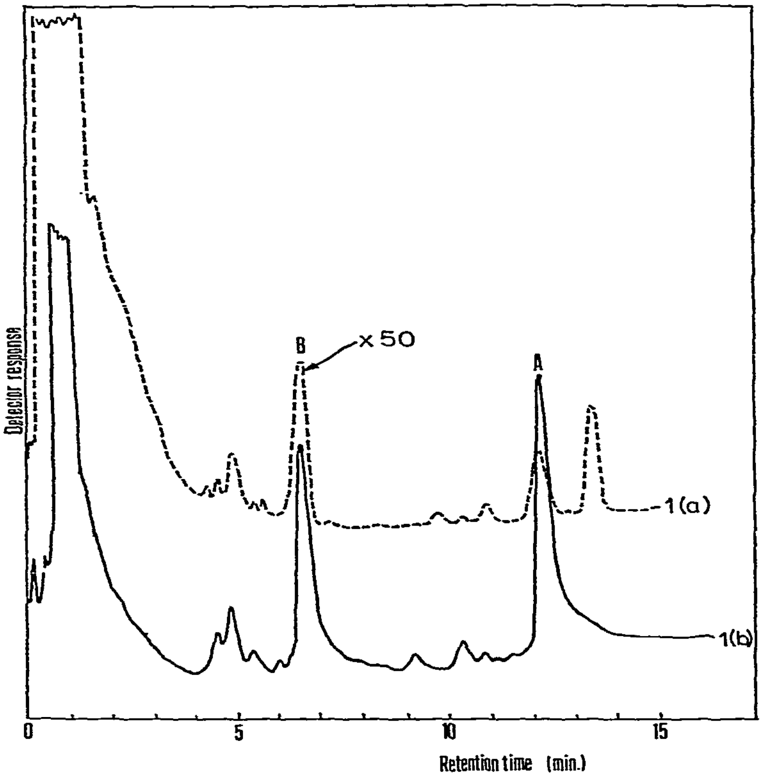

Fig. 5. Pyrolysis–g.l.c. scans of methyl β-xylobioside, (a) neat and (b) obtained after addition of zinc chloride.

among the volatile products resulting from pyrolysis of neat **1**, was not formed at the expense of the lactone (Fig. 5). This observation strongly supports the previous suggestion[5] that the lactone is formed independently from the formation of 2-furaldehyde.

Comparison of the results of thermal analysis of model compounds studied herein with those obtained with isolated (4-*O*-methylglucurono)xylans appears to suggest that native (*O*-acetyl-4-*O*-methylglucurono)xylan is more thermally stable than the isolated polysaccharide, and that a significant factor responsible for the lessening of its stability evident after its isolation is, for example, the ionized carboxyl groups and the increased number of free hydroxyl groups, both of which are liberated by saponification as a result of the alkaline extraction-process. The presence of *O*-acetyl groups in native xylans may be particularly important, as the increased stability of the acetates as compared with nonacetylated glycosides has already been established[16].

EXPERIMENTAL

Materials. — Synthesis of compounds **1–8** and **11** has been described previously[17–23]. Xylotriose was prepared according to Whistler and Tu[24]. Methyl β-D-xylopyranoside was prepared according to Hudson's method[25]. (4-*O*-Methylglucurono)xylan was obtained by extraction of beechwood holocellulose[2].

Thermal analysis. — The t.g., d.t.g., and d.t.a. data were obtained with a Mettler Thermoanalyzer 2, by using 7-mg samples in platinum pans. Platinum and rhodium–platinum thermocouples employing aluminum oxide as the reference were used for d.t.a. The samples were heated at the rate of 6°/min in a flow of nitrogen of 7 L/h.

Pyrolysis–g.l.c. — Samples (3 mg) were pyrolyzed in a Pyroprobe 150 pyrolysis unit (Chemical Data System, Inc.) preheated to 400° and connected directly to the carrier-gas stream of a temperature-programmed Chrom 4 gas chromatograph equipped with a column (3.7 m) of 15% of 20 M Carbowax. From the peak areas for 3-hydroxy-2-penteno-1,5-lactone (A) and 2-furaldehyde (B), the ratio A/B was calculated by a manner similar to that used by previous authors[5].

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REFERENCES

1 G. E. Domburg and V. N. Sergeeva, *Izv. Akad. Nauk Latv. SSR*, 6 (1966) 233–237.
2 M. Košík, V. Reiser, F. Kozmál, and R. Domanský, *Cellul. Chem. Technol.*, 2 (1968) 609–614.
3 F. Shafizadeh, G. D. McGinnis, and C. W. Philpot, *Carbohydr. Res.*, 25 (1972) 23–33.
4 A. Ohnishi, E. Tagaki, and K. Kato, *Carbohydr. Res.*, 50 (1976) 275–278.
5 A. Ohnishi, K. Kato, and E. Takagi, *Carbohydr. Res.*, 58 (1977) 387–395.
6 A. Ebringerová and M. Košík, *Chimija Drevesiny Riga*, (1977) 17–20.
7 F. Shafizadeh, *Adv. Carbohydr. Chem.*, 23 (1968) 419–474.
8 F. Shafizadeh, *J. Polym. Sci., Part C*, 36 (1971) 21–51.
9 D. Gardiner, *J. Chem. Soc., C*, (1966) 1473–1476.
10 M. Košík, V. Reiser, and P. Kováč, *Thermal Analysis*, Vol. 2, *Proc. Fourth ICTA*, Budapest, 1974, pp. 229–243.
11 M. Zinbo and T. Timell, *Sven. Papperstidn.*, 68 (1965) 647–662.
12 T. Timell, *Wood Sci. Technol.*, 1 (1967) 45–70.
13 S. C. McKee and E. E. Dickey, *J. Org. Chem.*, 28 (1963) 1561–1565.
14 R. L. Whistler and E. L. Richards, in W. Pigman and D. Horton (Eds.), *The Carbohydrates*, Vol. IIA, Academic Press, New York, 1970, pp. 447–469.
15 W. Sanderman and H. Augustin, *Holz Roh Werkst.*, 21 (1963) 256–264.
16 F. Shafizadeh, M. H. Meshreki, and R. A. Susott, *J. Org. Chem.*, 38 (1973) 1190–1195.
17 P. Kováč, J. Hirsch, and V. Kováčik, *Chem. Zvesti*, 32 (1978) 514–518.
18 P. Kováč, *Collect. Czech. Chem. Commun.*, 44 (1979), in press.
19 P. Kováč, *Carbohydr. Res.*, 31 (1973) 323–330.
20 P. Kováč and R. Palovčík, *Carbohydr. Res.*, 54 (1977) C11–C13.
21 P. Kováč, *J. Carbohydr. Nucleos. Nucleot.*, 4 (1977) 165–173.
22 P. Kováč and R. Palovčík, *Chem. Zvesti*, 31 (1977) 98–105.
23 P. Kováč, *Chem. Zvesti*, 33 (1979), in press.
24 R. L. Whistler and C. C. Tu, *J. Am. Chem. Soc.*, 74 (1952) 3609–3612.
25 C. S. Hudson, *J. Am. Chem. Soc.*, 47 (1925) 265–268.