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PYROLYTIC FORMATION OF 3-HYDROXY-2-PENTENO-1,5-LACTONE FROM XYLAN, XYLO-OLIGOSACCHARIDES, AND METHYL XYLOPYRANOSIDES

AKIO OHNISHI, KUNIO KATŌ, AND ERIKO TAKAGI
*Central Research Institute, The Japan Tobacco & Salt Public Corporation,
6-2 Umegaoka, Midori-ku, Yokohama 227 (Japan)*
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ABSTRACT

Xylan, xylotriose, and xylobiose were heated for 3 sec at 386 and 423° in helium as carrier gas The major, volatile decomposition-products of the foregoing compounds were 3-hydroxy-2-penteno-1,5-lactone and 2-furaldehyde Lactone formation also occurred on pyrolysis of methyl α- and β-D-xylopyranosides, although the yields of volatile products were very low, except for methanol, which was derived from the aglycon The relative yield of the lactone decreased as the number of non-reducing xylopyranosyl residues in the molecule decreased None of the lactone could be found in the pyrolyzate of D-xylose, whereas 2-furaldehyde was formed from all of the samples These results suggest that 3-hydroxy-2-penteno-1,5-lactone is formed independent from the formation of 2-furaldehyde, and that the lactone arises from the non-reducing xylopyranosyl residues in the molecule The results of dynamic thermal analyses of xylan, xylo-oligosaccharides, D-xylose, and methyl β-D-xylopyranoside are also reported

INTRODUCTION

3-Hydroxy-2-penteno-1,5-lactone (4-hydroxy-5,6-dihydro-2*H*-pyran-2-one) was first isolated by Miyazaki in 1975 from a vacuum pyrolyzate of beech xylan as very hygroscopic and labile, white crystals[1] In our previous paper[2], it was shown that a tobacco-stalk xylan, consisting almost exclusively of β-(1→4)-linked D-xylopyranosyl residues[3], also gave 3-hydroxy-2-penteno-1,5-lactone as one of the major, volatile decomposition-products, as determined by a c p p–g l c (Curie-point pyrolysis, gas–liquid chromatography) technique

In the present investigation, in order to obtain more information on formation of the lactone during the pyrolysis process, c p p–g l c and dynamic thermal-analyses of beech xylan, tobacco-stalk xylan, xylotriose, xylobiose, D-xylose, and methyl α- and β-D-xylopyranosides have been performed

RESULTS AND DISCUSSION

Dynamic thermal analysis. — The results of dynamic thermal analyses, in helium carrier-gas, of tobacco-stalk xylan, xylotriose, xylobiose, D-xylose, and methyl β-D-xylopyranoside are shown in Figs 1–5, respectively, and are summarized in Table I

As may be seen in Fig 1. the t g. (thermogravimetric) curve of the tobacco-stalk xylan shows a weight loss over the temperature range from 200–330°, followed by a slow, constant weight-loss (350–500°), leaving 27% of the residue at 400° This result is almost the same as that for cottonwood xylan (4-*O*-methylglucuronoxylan) as reported by Shafizadeh and McGinnis[4] The d t g (derivative thermogravimetric) curve (Fig 1) shows a peak at 299°, corresponding to the major thermal decomposition and subsequent volatilization In contrast, the d s c. (differential-scanning calorimetric) curve (Fig 1) does not show such a remarkable change in the temperature range from 130 to 500° The exotherm of the decomposition reaction and the endotherm of volatilization of the decomposition products probably overlap and cancel each other

The d t g curve of xylotriose (Fig 2) shows that the weight-loss starts at 191°, however, the curve is rather complicated The d s c curve (Fig 2) shows a significant endotherm peak in the temperature range 192–224° with a maximum at 219° However, this endotherm peak is not so sharp that it could not be explained by mere melting of the sample These facts suggest that not only the physical transition, but also chemical transformations of the molten material and further degradations, occur concurrently in this temperature region

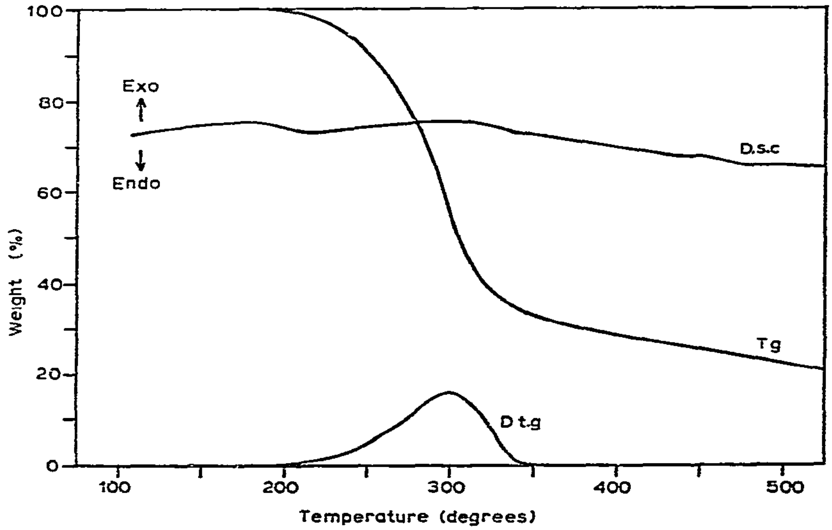

Fig 1 Thermogram of tobacco-stalk xylan

TABLE I

THERMAL ANALYSIS FEATURES OF THE SAMPLES

Sample	*D t g peak temperature (°)*	*T g residue at 400° (%)*	*D s c peak temperature (°)*	*ΔH (mcal/mg)*	*Notes*[c]
Tobacco-stalk xylan	200–[299][a]–330	26 9			
Xylotriose	191–[227[b], 241, 269, 286]–325	20 2	192–[219][a]–224	80 1	melt , trans
			224–[235]–268	34 2	decomp , vol
Xylobiose	173–[193, 226, 288[b]]–330	17 1	170–[195]–200	90 2	melt , trans
			200–[220]–242	61 9	trans , decomp , vol
			242–[297]–318	67 3	decomp , vol
D-Xylose	162–[210]–246	16 7	133–[153]–162	101 1	melt , trans
	246–[284]–339		162–[202]–258	198 0	trans , decomp , vol
			258–[290]–321	78 2	decomp , vol
Methyl β-D-xylopyranoside	135–[219]–237	0 5	133–[157]–160	110 6	melt
			160–[219]–231	266 2	decomp , vol

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[a]The bracket [ ] denotes the maximum temperature [b]The largest peak [c]All of the d s c peaks were endothermic melt = melting, trans = chemical transition such as isomerization, decomp = decomposition, vol = volatilization of the decomposition products

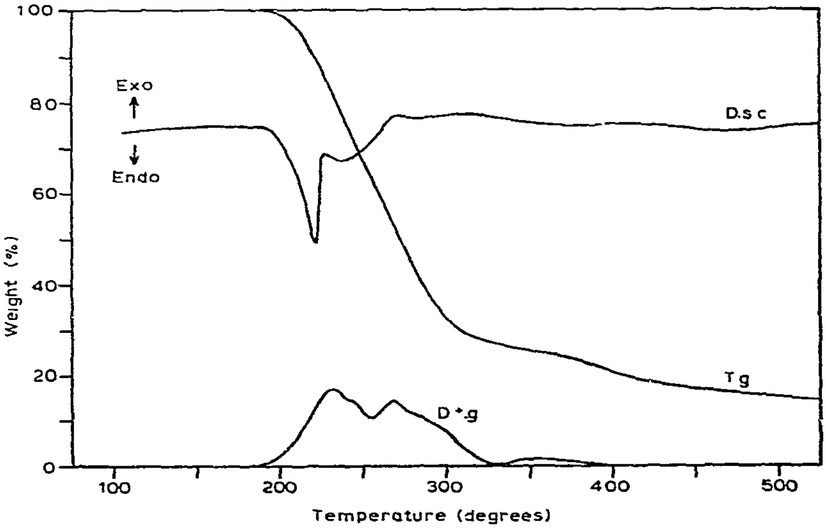


Fig 2. Thermogram of xylotriose

The profiles of thermograms of xylobiose (Fig 3) and D-xylose (Fig 4) resembled that of xylotriose (Fig 2), but the endotherm peak-temperatures (maxima at 195 and 153°, respectively) were lower than those of xylotriose (219°), and the t g and the d s c curves appear to be more complicated

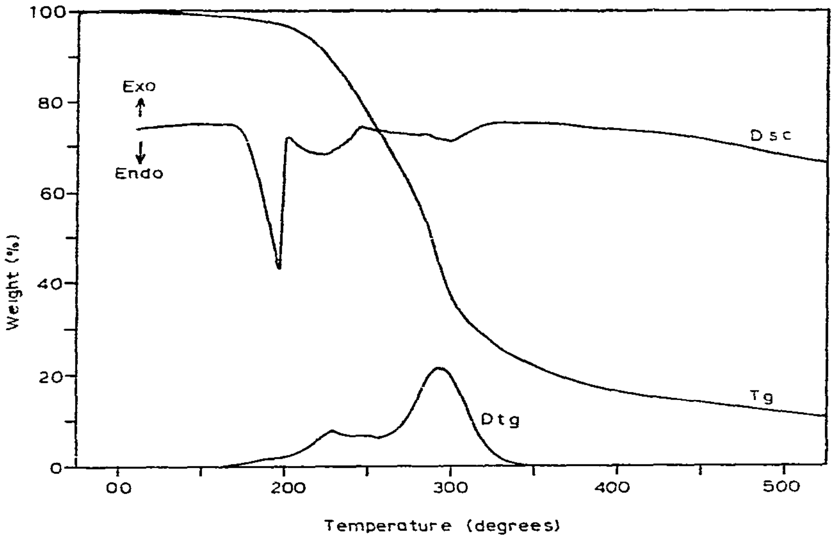


Fig 3 Thermogram of xylobiose

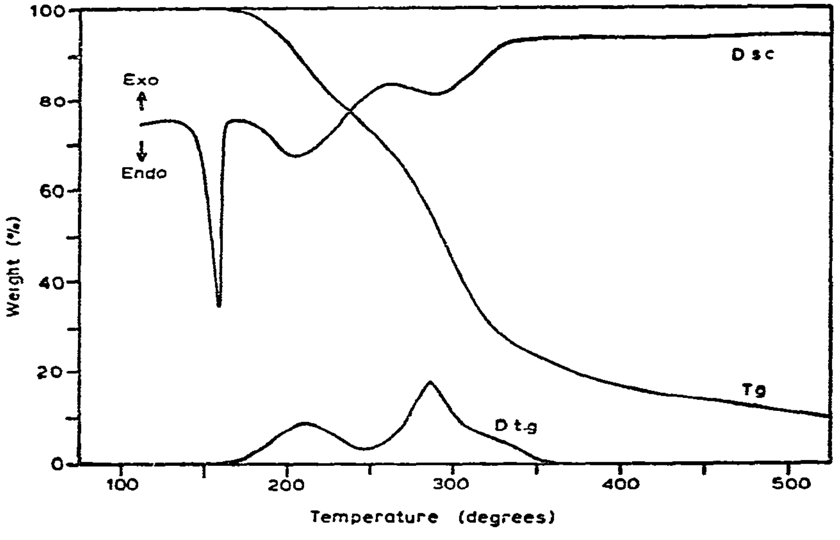


Fig 4 Thermogram of D-xylose

The d.s c curve of methyl β-D-xylopyranoside (Fig 5) shows two endotherm peaks The first peak, centred at 157° (lit.[6] 159°), is very sharp and corresponds to melting of the glycoside, whereas the secondpeak, having its maximum at 219°, is not so sharp It appears to correspond to volatilization of methanol evolved by the known thermal, intermolecular transglycosylation[5,6]

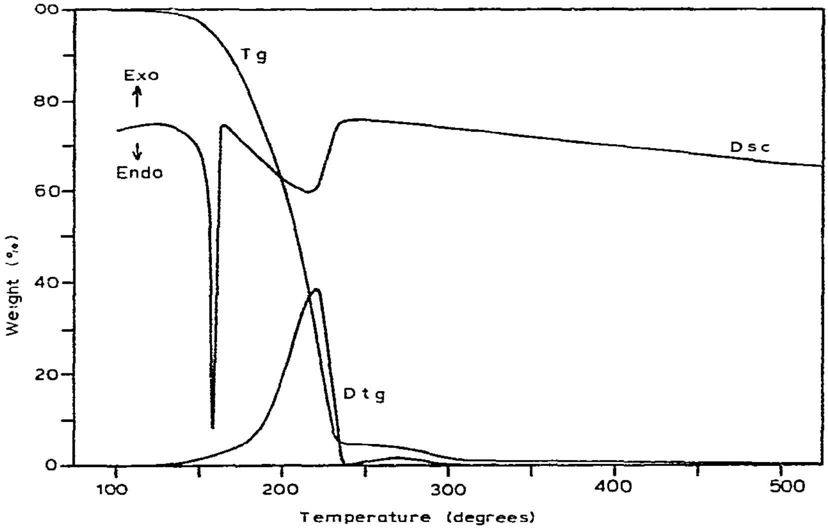


Fig 5 Thermogram of methyl β-D-xylopyranoside

TABLE II

COMPOSITION OF PYROLYZATES FROM THE CURIE-POINT PYROLYSIS OF SAMPLES

Sample	*Temperature* (°)	*Component* (%)		
		Volatile	*Tar*[a]	*Residue*
Tobacco-stalk xylan	386	18 8	26 2	43 3
	423	23 2	54 5	10 8
Xylotriose	386	11 4	45 9	34 7
	423	14 6	55 5	12 6
Xylobiose	386	13 4	36 7	47 7
	423	20 7	61 7	11 8
D-Xylose	386	12 5	56 4	31 0
	423	17 7	64 3	12 1
Methyl β-D-xylo-pyranoside	386	1 4	58 4	34 0
	423	1 6	87 9	6 5

[a] The tar component contained water produced by the thermal decomposition

Composition of the pyrolyzate — The composition of the Curie-point pyrolysis product of each sample was analyzed in a preliminary manner, and the results are summarized in Table II

The heating temperatures were 386 and 423° When the samples were heated at 358°, they showed no apparent change, no volatile product and no tarry substance were produced Under these low-temperature conditions, it is considered that the heating period is too short (3 sec) to decompose the samples into volatile and tarry substances, probably because of insufficient heat transfer

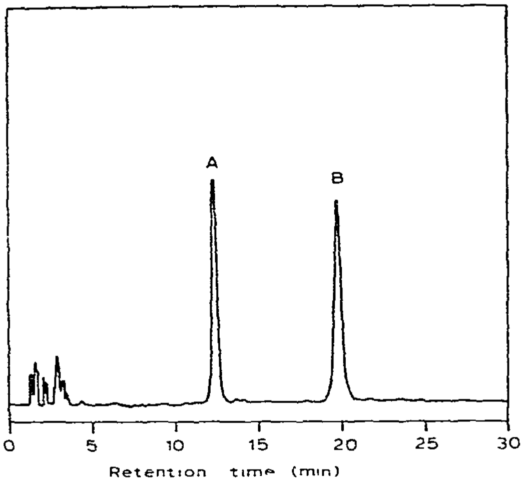
Table II suggests that the yields of volatile and tarry products are higher in the pyrolysis at 423° than at 386°, and that methyl β-D-xylopyranoside produced more tarry material than the other compounds did However, it should be noted that the net thermal events occurring in the Curie-point pyrolysis process and in the dynamic thermal analysis process are considerably different In the Curie-point pyrolysis of methyl β-D-xylopyranoside at 386°, the weight-loss was 1–8% (Table II), whereas in the dynamic thermal analysis process, the weight-loss was over 99% at 386° (Fig 5) The information given by the Curie-point pyrolysis procedure reflects the events occurring in the very initial stage of a high-temperature, thermal decomposition, whereas the d t a procedure gives information concerning the gradual thermal decomposition

Cpp–glc — The c p p –g l c chromatograms of tobacco-stalk xylan and D-xylose have been shown already in the previous paper[2] The xylan showed a very characteristic profile, displaying two principal peaks corresponding to 3-hydroxy-2-penteno-1,5-lactone and 2-furaldehyde, whereas the latter showed only one dominant peak corresponding to 2-furaldehyde and indicated no 3-hydroxy-2-penteno-1,5-lactone The c p p –g l c chromatogram of beech xylan was almost the same as that of the tobacco-stalk xylan

Figures 6–8 show c p p –g l c chromatograms obtained from xylotriose, xylobiose, and methyl β-D-xylopyranoside, respectively In these experiments, each sample was heated for 3 sec at 423° When the sample was heated at 386°, essentially the same c p p –g l c chromatogram was obtained as that at 423°

As may be seen in Figs 6 and 7, the profiles of both xylotriose and xylobiose are very similar to those of the xylans reported before[2] However, the relative yield of 3-hydroxy-2-penteno-1,5-lactone decreased as the number of non-reducing xylopyranosyl residues in the molecule decreased None of the lactone was produced at all from D-xylose[2] Table III shows this tendency more clearly The peak area corresponding to 3-hydroxy-2-penteno-1,5-lactone decreases in the order xylan, xylotriose, xylobiose, and D-xylose, whereas that corresponding to 2-furaldehyde remains almost constant throughout the series of compounds The ratio of peak area of the lactone to that of 2-furaldehyde at 423° is 1 3–1 9 with xylans, 0 8 with xylotriose, 0 2 with xylobiose, and 0 0 with D-xylose

Methyl β-D-xylopyranoside provided only a very small proportion of volatile products, as shown in Table II Figure 8 shows that the major volatile product is methanol, which is the aglycon of this pyranoside. Therefore, intermolecular trans-



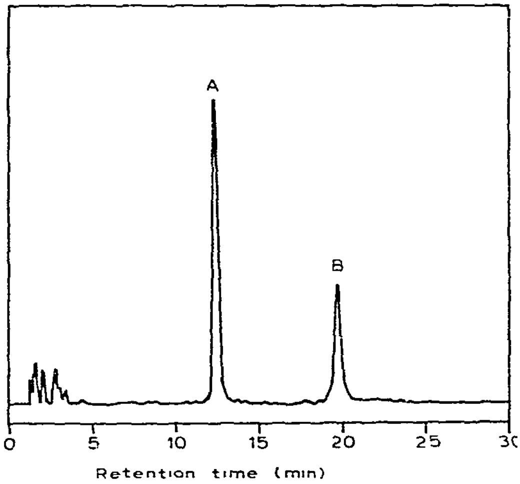


Fig 6 C p p -g l c chromatogram of xylotriose, A 2-furaldehyde, B, 3-hydroxy-2-penteno-1,5-lactone

Fig 7 C p p -g l c chromatogram of xylobiose

TABLE III

YIELDS[a] OF 3-HYDROXY-2-PENTENO-1,5-LACTONE AND 2-FURALDEHYDE FROM THE CURIE-POINT PYROLYSIS OF SAMPLES

Sample	*Temperature* (°)	*Peak-area* (*mm*^{2}/*µg*)		*Ratio A/B*
		3-Hydroxy-2-penteno-1,5-lactone (*A*)	*2-Furaldehyde* (*B*)	
Tobacco-stalk xylan	386	2 09	3 14	0 7
	423	2 20	1 67	1 3
Beech xylan	386	2 55	2 73	0 9
	423	2 84	1 53	1 9
Xylotriose	386	1 29	3 09	0 4
	423	1 22	1 65	0 7
Xylobiose	386	0 70	3 48	0 2
	423	0 54	2 53	0 2
D-Xylose	386	0 00	2 35	0 0
	423	0 00	2 08	0 0
Methyl β-D-xylopyranoside	386	0 41	0 39	1 1
	423	0 09	0 08	1 1

[a] Yield is indicated as peak-area of each component on the c p p -g l c chromatogram

glycosylation appears to be the principal process occurring during pyrolysis of the glycoside Nevertheless, the formation of some 3-hydroxy-2-penteno-1,5-lactone, together with 2-furaldehyde, from methyl β-D-xylopyranoside was clearly recognized, as may be seen in Fig 8 and Table III. The peak-area ratio of these two products is almost the same as that observed for xylans (Table III)

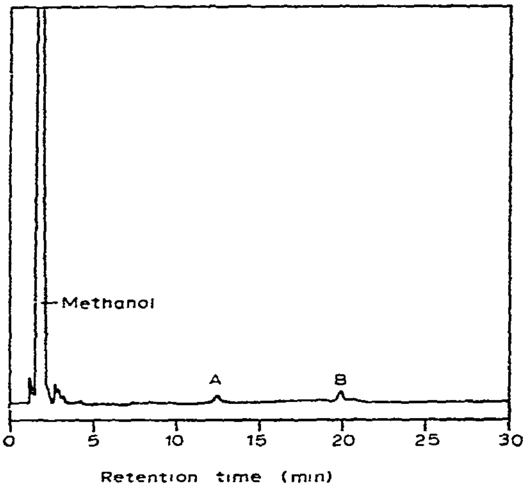


Fig 8 C p p -g l c chromatogram of methyl β-D-xylopyranoside

Methyl α-D-xylopyranoside showed the same c p p -g l c chromatogram as methyl β-D-xylopyranoside (Fig 8) No significant difference was observed between the two anomers in this regard

These results suggest that 3-hydroxy-2-penteno-1,5-lactone is produced from the non-reducing xylopyranosyl residues of the carbohydrate molecule, whereas 2-furaldehyde is derived from every xylopyranosyl residue These two reactions seem to be essentially independent of each other

EXPERIMENTAL

Materials — Tobacco-stalk xylan, containing no hexuronic acid, was isolated from stalks of *Nicotiana tabacum* (var BY) and purified by the procedure already reported[2 3] Beech xylan (Lot K-lot-17), donated by Sanyo-Kokusaku Pulp Co Ltd (Tokyo, Japan), was desalted before use by the method already described[2] Xylotriose and xylobiose, prepared by enzymic hydrolysis of hardwood xylan with a xylanase of *Streptomyces*[7], were kindly donated by Dr Kusakabe D-Xylose of reagent grade, purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan), was recrystallized from ethanol before use Methyl β-D-xylopyranoside was prepared and purified by Hudson's method[8] Methyl α-D-xylopyranoside was prepared by way of its 2,4-phenylboronate[8]

Dynamic thermal analysis — The tg, dtg, and dsc curves were recorded simultaneously with a Rigaku Thermoflex TG-DTG-DSC system, programmed at the rate of 10°/min The experiments were conducted with helium as the carrier gas (flow rate 40 ml/min) by using aluminum oxide as the reference and 5 mg of powdered samples For calibration of ΔH values, indium (99 999%) was used as the standard

Analysis of the pyrolyzate composition — The pyrolyzates were analyzed according to the procedure described in the previous paper[2]

Cpp-glc — The cpp-glc was performed as described in the previous paper[2,9] Three kinds of foil made of ferromagnetic alloys, whose Curie-point temperatures were 358, 386, and 423°, were used as the sample heater

The peak components A and B were identified as 2-furaldehyde and 3-hydroxy-2-penteno-1,5-lactone, respectively, in the manner described in the previous paper[2,9]

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