THERMAL DEGRADATION OF XYLAN AND RELATED MODEL COMPOUNDS

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ABSTRACT

Pyrolysis of *O*-acetyl-4-*O*-methylglucuronoxylan, 4-*O*-methylglucuronoxylan, and β-D-xylopyranosides involves thermal cleavage of the glycosidic groups. The resulting glycosyl units partly form random condensation products and are partly degraded to a variety of volatile products and char. Composition of the pyrolysis products changes with the introduction of additive or substituent groups. Addition of sodium hydroxide produces increased amounts of products of low molecular weight arising from carbonyl fragmentation and disproportionation, and zinc chloride promotes the formation of 2-furaldehyde, water, and char.

INTRODUCTION

In an earlier report on the pyrolysis and combustion of cellulosic materials, it was shown that the pyrolytic properties of a hardwood reflect the thermal behavior of its major components[1]. Among these compounds, cellulose and xylan contribute the bulk of the combustible, volatile materials which propagate the flame and fire[2]. Furthermore, xylan is thermally less-stable than other components and, as such, plays a significant role in the initiation of the pyrolytic reactions and propagation of fire. In subsequent studies, thermal analysis of α-D-xylose and several xylopyranosides, selected as model compounds, showed that heating of these molecules results in cleavage of the glycosidic group, polymerization of the glycosyl units, and decomposition of the sugar moiety within a narrow range of temperature[3,4]. It was also shown that addition of zinc chloride catalyses the cleavage and polymerization reactions and promotes dehydration and charring of the sugar residues[3,5].

In this study, the products formed on pyrolysis of α-D-xylose and several β-D-xylopyranosides have been analysed and compared with the pyrolysis products of 4-*O*-methylglucuronoxylan and *O*-acetyl-4-*O*-methylglucuronoxylan, in order to gain further information about the nature of the reactions involved.

RESULTS AND DISCUSSION

4-O-Methylglucuronoxylan and O-acetyl-4-O-methylglucuronoxylan were extracted from cottonwood[1] and pyrolysed under the same conditions as D-xylose and methyl β-D-xylopyranoside selected as model compounds. The pyrolysis was carried out before and after addition of 10% of zinc chloride, and the products were isolated as the charred residue, a tar fraction which condensed at room temperature, a liquid fraction (aqueous pyrolysate) that was collected in a dry ice–acetone trap, and carbon dioxide which was recovered as barium carbonate. The results obtained are shown in Table I and account for all the pyrolysis products except the remaining uncondensed gases (consisting of CO, H_2, and hydrocarbons). These data show that, in all cases, addition of zinc chloride has resulted in a decrease in the tar fraction and increased formation of char and aqueous pyrolysate. This is consistent with results obtained from dynamic thermal analysis of the model compounds[3], which indicated a change in the nature of the pyrolytic reactions and increased charring on addition of zinc chloride. The pyrolysis products were further analysed and investigated by several chemical methods.

TABLE I

FRACTIONATION OF THE PYROLYSIS PRODUCTS FROM O-ACETYL-4-O-METHYLGLUCURONOXYLAN, 4-O-METHYLGLUCURONOXYLAN, AND MODEL COMPOUNDS AT 300°

Product	Xylan		O-Acetylxylan		α-D-Xylose		Methyl β-D-xylopyranoside	
	Neat	+ZnCl₂	Neat	+ZnCl₂	Neat	+ZnCl₂	Neat	+ZnCl₂
Char (%)	31.1ᵃ	42.2	22.1	31.2	13.8	35.2	19.7	45.4
Tar (%)	15.7	3.2	33.1	10.0	50.2	15.2	45.0	4.0
Liquid condensate (%)	30.6	45.3	27.0	40.0	13.1	25.3	16.2	27.9
Carbon dioxide (%)	7.9	7.5	7.5	6.3	1.0	1.2	12.5	12.6

ᵃBased on the weight of the sample.

Tar fraction. — The tarry materials obtained from uncatalysed pyrolysis of 4-O-methylglucuronoxylan were fractionated by gel-permeation chromatography to give a fast-moving fraction of higher molecular weight which contained a mixture of oligosaccharides. These oligosaccharides could have been derived from random cleavage of the original polysaccharide or from recombination of sugar units formed by thermal cleavage of the glycosidic bonds. In the former case, they should still contain the (1→4)-β-D-links of the original polysaccharide and, in the latter case, they should show random links as observed in thermal polymerization of free sugars[6-8].

Fractionation of the tars derived from pyrolysis of α-D-xylose and methyl β-D-xylopyranoside also provided similar oligosaccharides. Acid hydrolysis of these products, as shown in Table II, gave an approximately 50% yield of D-xylose. The

partial yield of D-xylose can be accounted for by degradation of the pentose under conditions of acid hydrolysis[9] and by the presence of other units in the oligosaccharides.

TABLE II

ANALYSIS OF THE TAR FRACTIONS

Source	Component of high mol. wt. (%)	D-Xylose from hydrolysis (%)
Xylan	17[a]	54
α-D-Xylose	24	43
Methyl β-D-xylopyranoside		63

*Based on the weight of the starting materials.

Further evidence for the presence of other components was obtained from the infrared spectra of the tars which showed a carbonyl absorption band at $1710 \, cm^{-1}$. A similar absorption band, found for the products of the acid-catalysed polymerization of D-xylose, has been attributed to the presence of acyclic units[6,7]. However, in view of the considerable evidence for thermal dehydration and rearrangement reactions[3,10] and the isolation of a 3-deoxypentosulose from pyrolysis of xylan[11], it is reasonable to assume that the carbonyl absorption could be due to the incorporation of 3-deoxyaldosulose molecules in the oligosaccharides or to the dehydration and rearrangement of the glycosyl units.

End-group analysis, involving reduction and acid hydrolysis of the oligosaccharides, gave the D-xylose-to-xylitol ratios listed in Table III, indicating average degrees-of-polymerization of ~6–8.

TABLE III

PERIODATE OXIDATION AND END-GROUP ANALYSIS OF THE POLYMERIC TARS

Source	Periodate consumption[a]	D-Xylose–xylitol	
		Before oxidation	After oxidation
4-O-Methylglucuronoxylan	0.39	6:1	21:1
α-D-Xylose	0.46	5:1	11:1
Methyl β-D-xylopyranoside	0.11	7:1	

[a]Moles per D-xylose residue.

Periodate oxidation of the oligosaccharides, followed by reduction and acid hydrolysis, gave the low oxidation-values and high xylose-to-xylitol ratios shown in Table III. Analysis of the hydrolysis products also showed the presence of minor quantities of glycerol and ethylene glycol, but no glyceraldehyde or glycolaldehyde

could be detected. If the oligosaccharides contained only (1→4)-links, the amount of oxidant consumed should have been two moles for the terminal units and one mole for the internal units. The lower average-values of 0.11 to 0.46 indicate the presence of other links and/or branching which have protected the xylose residues from oxidation[8,12]. Thus, it could be seen that the oligosaccharides are derived from random condensation of xylosyl radicals. Furthermore, the increased ratios of xylose to xylitol, together with the formation of glycerol and ethylene glycol as the only other detectable products of the Smith degradation[13], indicate that much of the oxidation has taken place at the reducing end-groups.

Volatile pyrolysis products. — The composition of these products was determined by analysis of the liquid condensation product (aqueous pyrolysate) and by g.l.c. of the pyrolysis products. The former methods were used mainly for qualitative analysis, and the latter method for quantitative investigations. The results obtained for pyrolysis of α-D-xylose and methyl β-D-xylopyranoside at 500°, before and after treatment with zinc chloride, are shown in Table IV. These data show that the volatile pyrolysis products (other than methanol, derived from cleavage of methyl β-D-xylopyranoside) consist mainly of 2-furaldehyde and water, both of which are substantially increased by the addition of zinc chloride.

TABLE IV

VOLATILE PRODUCTS FROM PYROLYSIS OF α-D-XYLOSE AND METHYL β-D-XYLOPYRANOSIDE AT 500°

Product	α-D-*Xylose*		Methyl β-D-*xylopyranoside*		Method of identification[b]
	Neat	*+ZnCl₂*	*Neat*	*+ZnCl₂*	
Acetaldehyde	T[a]	T			c,d,e,f,h
Propionaldehyde	T	T	T	T	c,d,e,f,h
Methanol			15.1[c]	15.3	a,c
Unknown	T	T			
1-Hydroxy-2-propanone	T	T			c,d,e,f,h
Acetone			T	T	c,d,f,h
Acetic acid	T	T			a,c
2-Furaldehyde	5.8	13.3	2.4	4.9	a,b,c,d,e,f
Formic acid	T	T			a,c
Water	7.0	18.0	6.5	12.0	c

[a]T = trace amounts. [b]The letters refer to identification methods described in the experimental part. [c]Percentage yield based on the weight of the sample.

Pyrolysis of the tar fraction obtained from the condensation of α-D-xylose gave a more-complex mixture of volatile products containing large amounts of acetic acid and indicating a more-random breakdown and rearrangement of the molecule. Complex mixtures of volatile products were also obtained on pyrolysis of 4-*O*-methylglucuronoxylan and *O*-acetyl-4-*O*-methylglucuronoxylan as such, or on addition of zinc chloride or sodium hydroxide (see Table V and Figs. 1 and 2). The

TABLE V

PYROLYSIS OF 4-O-METHYLGLUCURONOXYLAN AND O-ACETYL-4-O-METHYLGLUCURONOXYLAN AT 500°

Peak number	Pyrolysis product	Xylan			O-Acetylxylan			Method of identification[b]
		Neat	+ZnCl₂	+NaOH	Heat	+ZnCl₂	+NaOH	
1,2[a]	Fixed gases	2.4[c]						c
3	Acetaldehyde	T	0.1	1.6	1.0	1.9	1.6	c,d,e,f
4	Furan		2.0	0.3	2.2	3.5	0.4	c
5	Acetone	} 0.3	T	3.3	} 1.4	T	} 5.8	c
6	Propionaldehyde		T	0.7		T		c,d,e,f
7	Methanol	1.3	1.0	2.1	1.0	1.0	1.8	c
11	2,3-Butanedione	T	T	T	T	T	} T	c,d,e,f
12	Ethanol	T		0.6	T		0.6	c
13	2-Butenal	T		1.2	T		1.4	c
14	1-Hydroxy-2-propanone	0.4	T	} 2.0	0.5	T	0.8	c,d,e,f,g
15	3-Hydroxy-2-butanone	0.6	T		0.6	T	0.6	c
16	Acetic Acid	1.5	T	3.1	10.3	9.3	3.4	a,c
17	2-Furaldehyde	4.5	10.4	1.6	2.2	5.0	0.6	a,b,c,d,e,f
	Char	10	26	21	10	23	23	
	Carbon dioxide	8	7	14	8	6	22	
	Water	7	21	26	14	15	19	c

[a]The numbers refer to the peaks in the chromatogram (Figs. 1 and 2). [b]The letters refer to identification methods described in the experimental part. [c]Percentage, yield based on the weight of the sample; T = trace amounts.
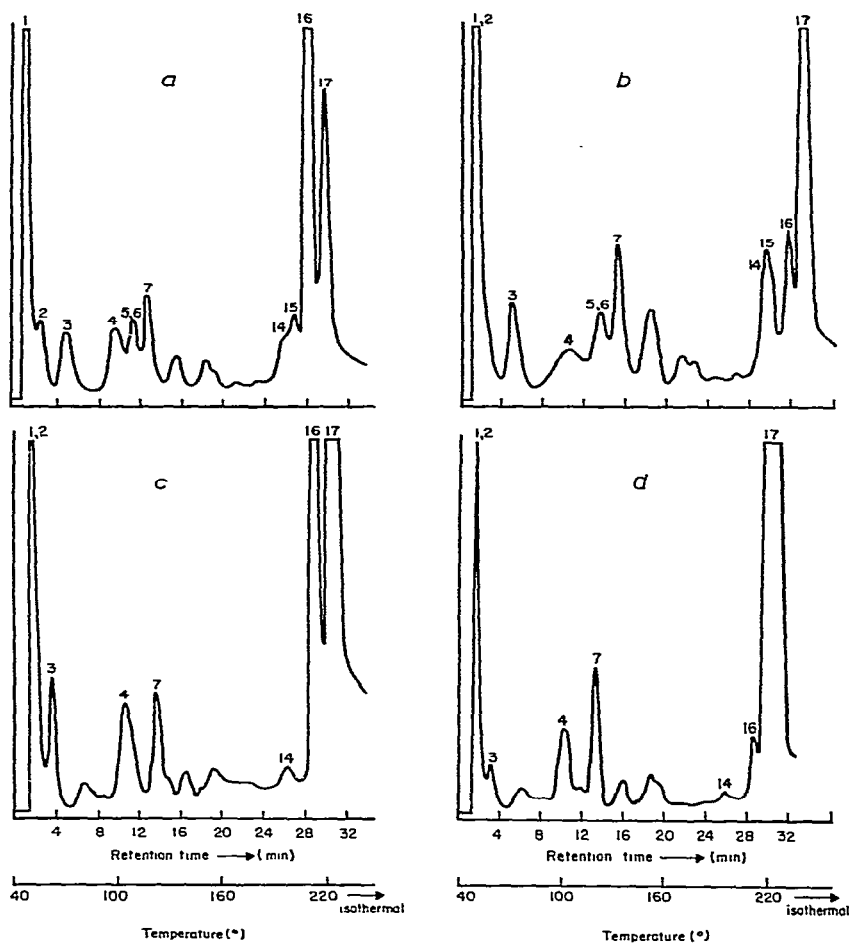
Fig. 1. Chromatograms of the pyrolysis products from: *a*, *O*-acetyl-4-*O*-methylglucuronoxylan; *b*, 4-*O*-methylglucuronoxylan; *c*, *O*-acetyl-4-*O*-methylglucuronoxylan+ZnCl₂; *d*, 4-*O*-methyl-glucuronoxylan+ZnCl₂.

formation of methanol and some of the products in these mixtures can be attributed to the pyrolysis of the 4-*O*-methylglucuronic acid residue in the xylan polysaccharides. Similarly, the high yields of acetic acid from *O*-acetyl-4-*O*-methylglucuronoxylan could be related to acetyl groups in the original material.

   The products formed from pyrolysis of 1,6-anhydro-β-D-glucopyranose (levoglucosan) under different conditions have been investigated by chromatographic analysis[5] and isotopic-tracing methods[10]. These investigations have shown that addition of zinc chloride results in the dehydration of the molecule, as in the acid-catalyzed decomposition of carbohydrates in aqueous solutions[14,15]. Whereas, under alkaline conditions, levoglucosan is degraded to a variety of two-, three-, and four-carbon fragments, which may be accounted for by base-catalysed reverse-aldol and
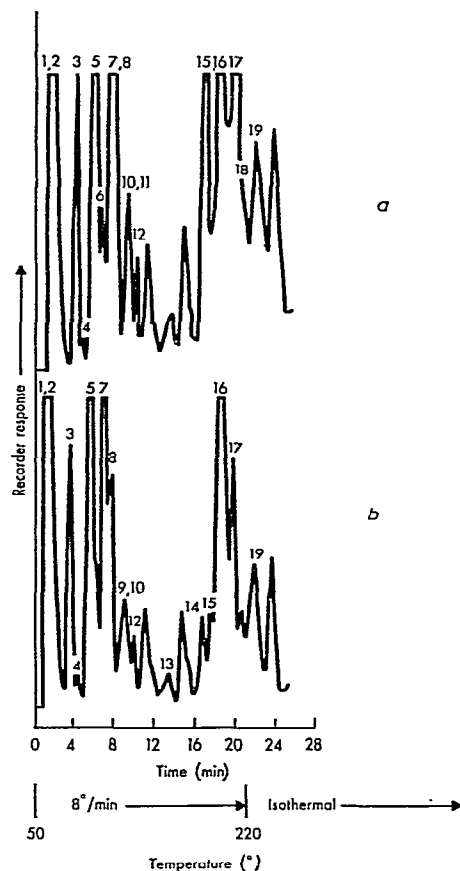
Fig. 2. Chromatogram of the pyrolysis products from a, 4-O-methylglucuronoxylan + NaOH and b, O-acetyl-4-O-methylglucuronoxylan + NaOH.

disproportionation reactions of the carbohydrates[16]. The data obtained from pyrolysis of xylan (Table V) also show that addition of zinc chloride has enhanced the formation of 2-furaldehyde, water, and char, and that addition of alkali has resulted in increased fragmentation of the molecule. However, comparison of the products formed from pyrolysis of levoglucosan and xylans indicate that the alkaline-fragmentation products of xylans are produced through more-extensive rearrangement or disproportionation reactions.

It has been proposed that the pyrolysis of carbohydrates proceeds through degradation of intermediate condensation products[17]. Re-pyrolysis of the tar obtained from 4-O-methylglucuronoxylan produced a chromatogram that was quite different from the chromatogram of the original polysaccharide. The tar chromatogram had a smaller peak for 2-furaldehyde and larger peaks for other compounds. A similar result was also obtained from the pyrolysis of pre-polymerized levoglucosan[5]. These data indicate that, although pyrolysis of carbohydrates results in cleavage of the

glycosidic bond and random condensation of the sugar units, the volatile products are not necessarily formed from the degradation of the condensation products and that some of the glycosyl units are decomposed directly. In other words, the glycosyl units could decompose directly to volatile pyrolysis products, or form condensation products, according to the prevailing conditions.

Isotopic tracing of the products formed from pyrolysis of levoglucosan has shown that fragmentation of the sugar moiety proceeds through competitive reactions which are initiated at different positions of the molecule[10]. By comparing the pyrolysis products of α-D-xylose, methyl β-D-xylopyranoside, xylans, and their random-condensation products, it can be seen that substitution of the xylosyl units produces a quantitative variation of the products by changing the reactivity of different positions and influencing the pattern of the competitive, pyrolytic reactions.

The correlation between cleavage of glycosidic groups and degradation of the glycosyl moiety was further explored by pyrolysis of several substituted phenyl β-D-xylopyranosides and analysis of the resulting, volatile products. As noted before, these products consist mainly of the free aglycon, 2-furaldehyde, and water. The yields of 2-furaldehyde, obtained before and after addition of zinc chloride, are given in Table VI. In the absence of zinc chloride, the yield of 2-furaldehyde varied from 1.5–5.5% with no obvious trend; however, after the addition of zinc chloride, it increased in reverse relationship with the electron density of the glycosidic oxygen[18]. These data indicate that addition of zinc chloride facilitates the competitive formation of 2-furaldehyde through a mechanism which involves concerted cleavage of the glycosidic group. The following scheme could account for the resulting rearrangements.
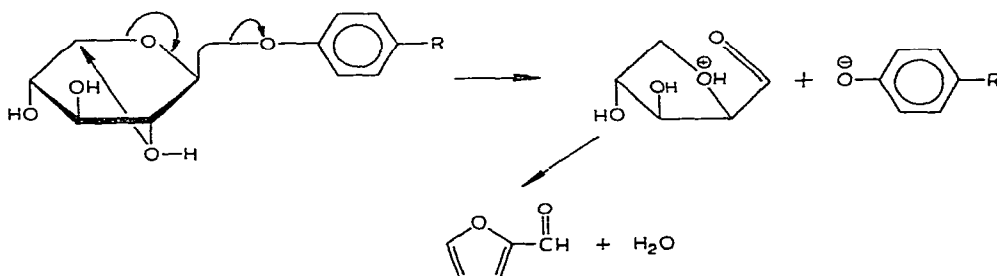
This study indicates that pyrolysis of the xylan polysaccharides and the related model compounds involves thermal cleavage of the glycosidic group. According to the prevailing conditions, the resulting glycosyl units can then condense randomly to form tarry products or are degraded to a variety of compounds through a combination of competitive dehydration, fragmentation, and disproportionation reactions. The dehydration reactions are catalysed by acidic conditions, and alkali promotes the fragmentation and rearrangements reactions. The pattern of the degradation reactions and composition of the products could be also altered by substitution of the glycosyl units.

TABLE VI

PYROLYSIS OF SUBSTITUTED PHENYL β-D-XYLOPYRANOSIDES AT 500°

Aglycon group	Hammett σ-value[18]	2-Furaldehyde(%)[a]	
		Neat	ZnCl₂
p-Aminophenyl	−0.66	1.5	
p-Methoxyphenyl	−0.27	3.4	18.2
p-Acetamidophenyl		3.7	13.6
Phenyl	0.00	5.5	20.8
p-Phenylphenyl	0.01	4.0	26.0
p-Bromophenyl	0.23	4.7	31.5
p-Chlorophenyl	0.23	3.1	35.0
p-Nitrophenyl	0.78 (1.27)	4.2	43.0

[a]Theoretical values.

EXPERIMENTAL

General methods. — Melting points were determined with a Fisher–Johns apparatus and are uncorrected. T.l.c. was conducted on silica 1B-F (Bakerflex), using 1-butanol–acetone–water (4:5:1), with detection by spraying with 10% sulfuric acid in methanol.

Analytical g.l.c. was performed with a Varian Model 1800 or an F and M Model 5750 instrument equipped with conductivity and flame-ionisation detectors. The column used to separate the carbohydrate compounds, after trimethylsilylation, was a 6 ft × 0.25 in. stainless-steel tube packed with Varaport 30 as the support and 3% SE-30 as the stationary phase. Decomposition products were analysed with a column containing 10% Carbowax 20M supported on Fluropak 80. Quantitative data were obtained by using a Varian Model 475-470 digital integrator calibrated with standard samples. Preparative g.l.c. was carried out with a Varian Autoprep Model A-700.

Sample preparation. — The procedure for the isolation of xylans has been described in an earlier publication[1]. Commerical α-D-xylose was recrystallized three times from ethyl alcohol: m.p. 149–151°; lit.[19] m.p.'s ranging from 141 to 154°. A mixture of methyl α- and β-D-xylopyranosides was prepared following the method of Hudson[20]. The β-D form, isolated by crystallization from the reaction mixture and purified by recrystallization from 1-butanol, had m.p. 156–157°; lit.[20] m.p. 156–157°.

The substituted phenyl β-D-xylopyranosides listed in Table VI were prepared by the method originally developed by Helferich and Winkler, and modified by De Bruyne and Van Wijnendaele[22].

The free sugars and the glycosides were ground to a fine powder prior to pyrolysis. Samples containing zinc chloride were prepared by adding 50 mg of the above compounds or the xylans to 5 ml of tetrahydrofuran containing zinc chloride

(1.11 mg/ml), mixing, and removing the solvent under vacuum at room temperature to produce a solid residue. The sodium hydroxide-treated samples were produced by a similar method using a methanolic solution of sodium hydroxide.

Pyrolysis apparatus. — A modified Sargent micro-combustion apparatus was used to pyrolyse large samples (500 mg) under vacuum (1.0 to 1.5 mmHg) at 300° for 10 min. The pyrolysis products were swept with a gentle stream of nitrogen through a series of condensers and fractionally collected downstream from the furnace. This gave a tar fraction condensed on the pyrolysis tube, an aqueous pyrolysate that was collected in a dry ice–acetone trap, some uncondensed gases, and a charred residue. The uncondensed gases were washed with a solution of barium hydroxide to recover the carbon dioxide as barium carbonate.

For direct analysis of the volatile products, samples were pyrolysed at 500° in a modified Perkin–Elmer pyrolysis unit, connected to a gas chromatograph. The resulting, volatile products were swept from the pyrolysis unit into the g.l.c. instrument by the carrier gas, without being condensed. A splitting device was used for taking out a side current and collecting a sample of different peaks or their reaction products, including 2,4-dinitrophenylhydrazones and barium carbonate.

Separation of the tar components. — The tar fraction condensed on the glass pyrolysis tube was dissolved in water, and the filtered solution was concentrated to dryness on a rotary evaporator. It was then separated on a column (25 × 4 cm) of Sephadex G-10 gel to give two bands, a fast-moving diffuse band containing the materials of high molecular weight (above 700), and a slow-moving band containing the materials of low molecular weight.

Analysis of the polymeric tar. — The polymeric material (10 mg) was hydrolysed in 2M trifluoroacetic acid[23] or in M hydrochloric acid containing 10 mg of D-glucitol hydrate as an internal standard, following the procedure of Laver and associates[9]. The solution was then neutralised and analysed by g.l.c. To obtain the ratio of the reducing end-groups, 6 mg of the tar and 10 mg of the D-glucitol hydrate were dissolved in 10 ml of water containing 30 mg of sodium borohydride. After 24 h at room temperature, the solution was concentrated to dryness, the residue was re-dissolved in acidic methanol, and the solution again concentrated to dryness. This procedure was repeated four times to remove the volatile boric ester. The reduced tar was then hydrolysed as before.

For periodate-oxidation experiments, samples of the polymeric material (9 mg) were dissolved in 10 ml of 15mM sodium metaperiodate and left in the dark. The periodate consumption was determined by using a spectrophotometric method[24] and reached a constant value after 4–5 days. The periodate-oxidation products were identified following the procedure of Alfes and Bishop[25].

Separation and identification of the volatiles.— The volatile pyrolysis products were resolved by analytical and preparative g.l.c. methods, and by t.l.c. of the mixed 2,4-dinitrophenylhydrazones (2,4-DNPH) using the procedure of Byrne[26]. The isolated products were identified by (*a*) mass spectroscopy with a Consolidated Electrodynamics mass spectrometer (Model 21-103C); (*b*) infrared spectroscopy;

(c) g.l.c. retention time; (d) R_F values of the 2,4-DNPH derivatives on silica gel; (e) R_F values on alumina; (f) color reactions of 2,4-DNPH derivatives with 2-aminoethanol; (g) melting point of the 2,4-DNPH derivatives; (h) the ultraviolet–visible spectrum of the 2,4-DNPH compounds.

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