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1,5-ANHYDRO-4-DEOXY-D-*glycero*-HEX-1-EN-3-ULOSE AND OTHER PYROLYSIS PRODUCTS OF CELLULOSE

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ABSTRACT

Uncatalyzed pyrolysis of cellulose provides a tar containing mainly 1,6-anhydro-D-glucose derivatives and some unsaturated products. The latter include a new enone that has been isolated by preparative, column chromatography in 1.4% yield and identified as 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose. This compound is also formed by pyrolysis of other carbohydrate polymers. A mechanism for its production from internal units has been deduced from the experimental data. The pyrolysis products of cellulose also contain 3,5-dihydroxy-2-methyl-4*H*-pyran-4-one, which appears to be an oxidation product.

INTRODUCTION

Renewed interest in the conversion of biomass residues into chemical feedstock and synthetic intermediates has promoted research into the application of pyrolytic methods for the depolymerization of cellulose and cellulosic materials[1–4].

We now report on the analysis of the pyrolysis products obtained from various carbohydrate compounds, and the isolation and characterization of 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose (**1**) as a significant, new product.

RESULTS AND DISCUSSION

Isolation and characterization of 1,5-anhydro-4-deoxy-D-glycero-*hex-1-en-3-ulose* (**1**). — A gas–liquid chromatogram obtained for a (trimethylsilyl)ated sample of tar from the pyrolysis of Whatman CF 11 cellulose powder is shown in Fig. 1. Component* *g*, which had previously been observed in this laboratory in condensates from the pyrolysis of cellulose, was isolated by column chromatography of the pyrolyzate, after initial removal of 1,6-anhydro-β-D-glucopyranose (levoglucosan) by crystallization from acetone. Component *g* was shown to be 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose (**1**). Although **1** could be crystallized in relatively pure form,

*Referred to as unknown *b* in ref. 5.

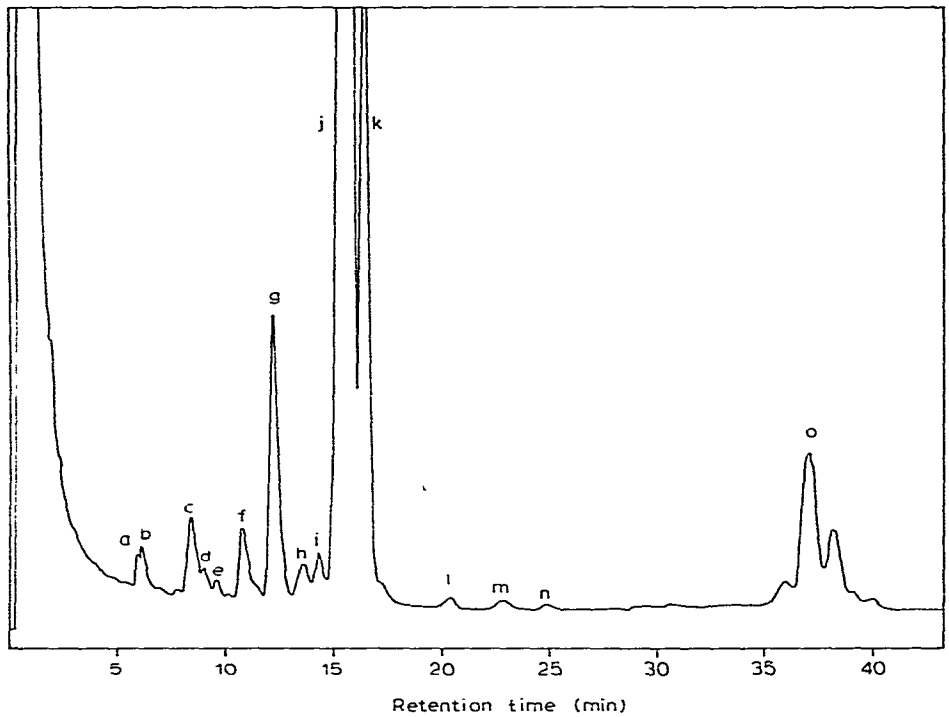


Fig. 1. G.l.c. of tar from pyrolysis of (trimethylsilyl)ated cellulose (column *2*, 110 to 275° at 4°/min). [a, 5-(Hydroxymethyl)-2-furaldehyde; b, 1,4:3,6-dianhydro-α-D-glucopyranose; c, 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (**5**); d, unknown; e, 3,5-dihydroxy-2-methyl-4*H*-pyran-4-one (**11**); f, unknown; g, 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose (**1**); h and i, unknown; j, levoglucosan; k, 1,6-anhydro-β-D-glucofuranose; l, α-D-glucose; m, β-D-glucose; n, 3-deoxy-D-*erythro*-hexosulose (ref. 5); and o, *O*-D-glucosyl-levoglucosans.]

it proved difficult to recrystallize. Benzoylation of **1** yielded the more readily crystallized dibenzoate **2**, and this procedure was used to increase the recovery of **1** from chromatographic fractions, affording an overall yield equivalent to 1.4% of **1** from cellulose.

Elemental analysis and mass spectral data (M^+, 144) indicated a molecular formula of $C_6H_8O_4$ for **1**, and strong absorptions in the i.r. spectrum at 1663 and 1616 cm^{-1}, and in the u.v. spectrum at 293 nm (ε_{mM} 5.80) suggested the presence of a conjugated enone function. Acylation respectively provided the crystalline dibenzoate **2** and a syrupy diacetate **3**.

Full interpretation of the n.m.r. spectrum of **1** (see Table I) was assisted by recording spectra of solutions thereof in Me_2SO-d_6 and Me_2CO-d_6, as, in each of these solvents, portions of the spectra are obscured by water and by undeuterated-solvent resonances. A singlet due to the uncoupled vinylic proton (H-1), and broad exchangeable resonances due to enolic (OH-2) and alcoholic (OH-6) protons, are readily recognized in the spectrum of **1**. The remaining multiplets correspond to the CH_2CHCH_2 residue of C-4, -5, and -6. In a decoupling experiment, irradiation of the

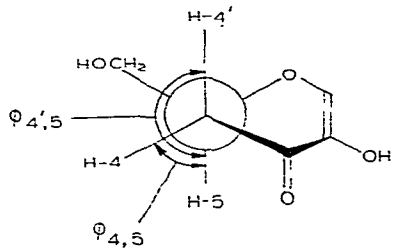
TABLE I

^{1}H-N.M.R. PARAMETERS (δ) AT 60 MHz FOR 1 AND ITS DERIVATIVES

Compound	*Solvent*	*H-1*	*H-4*	*H-4'*	*H-5*	*H-6,6'*	*Other*	$J_{4,4'}$	$J_{4,5}$	$J_{4',5}$
1[a]	Me_2SO-d_6	7.48s	2.74dd	2.33dd	4.35m[b]	3.6m[c]	5.02 br s, OH-6 7.79 br s, OH-2	17	5	13
1	Me_2CO-d_6	7.42s	2.85dd	2.42dd	4.46m[b]	3.8m	5.6 br, OH	17	5	13
2	$CDCl_3$	[d]	3.05dd	2.67dd	4.95m[e]	4.65m	7.3–7.9 *m*- & *p*-PhCO, H-1 7.9–8.4, *o*-PhCO	17	5.5	12
3	$CDCl_3$	7.47s	2.92dd	2.54dd	4.75m[e]	4.4m	2.18 s, OAc-6 2.29 s, OAc-2	17	5.5	11.5

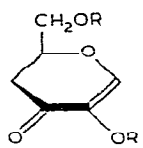
[a]Recorded at 60 and 100 MHz. [b]7-Peak m, width 30 Hz. [c]Overlaps resonance for water in solvent. [d]Merged with benzoate resonance. [e]8-Peak m, width 30 Hz.

multiplet at δ 3.6 (H-6,6') collapsed the multiplet at δ 4.35 (H-5) into a pair of doublets with residual $J_{4,5} = 5$ Hz and $J_{4',5} = 13$ Hz. These coupling constants show that the molecule adopts the $^4H_5$ conformation **1a**, as do related enones[6–9], in which one of the dihedral angles is large ($\phi_{4',5}$), while the other is small ($\phi_{4,5}$), and the 5-(hydroxymethyl) substituent is pseudo-equatorial.

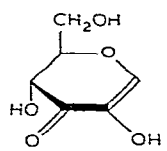


1a

Although the n.m.r. spectrum of **1** does not conclusively locate the enolic hydroxyl group on C-2 (*i.e.*, it could be on C-1), its position α to the 3-carbonyl group is suggested by the spectral and ionization characteristics. The u.v. absorption maximum of **1** at 293 nm was found to be reversibly shifted to 339 nm in basic solution (pH > 10), indicating the presence of an ionizable species. The 4-*C*-hydroxy analog of **1**, namely, 1,5-anhydro-D-*erythro*-hex-1-en-3-ulose (**4**), which has been isolated as an intermediate in the alkaline degradation of hexosiduloses[10], displays similar strong absorptions at 293 nm (pH 5) or ~340 nm (pH 12). The pKa of **1** was determined to be 9.5 by titration and spectrophotometric methods, showing that **1** is a slightly stronger acid than the enolic form of 1,2-cyclohexanedione (pKa 10.30)[11], but a significantly weaker acid than 1,3-cyclohexanedione (pKa 5.89)[11], in which the enolic hydroxyl group is β to the carbonyl group.



1 R = H
2 R = Bz
3 R = Ac



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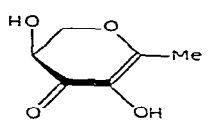
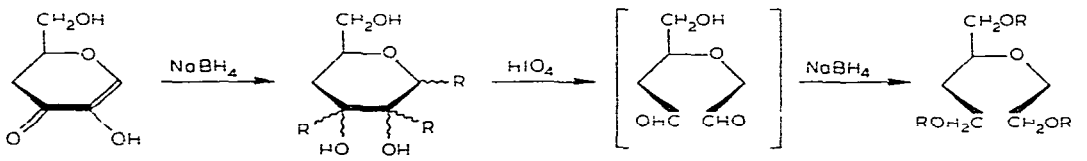


5

6

In addition, the u.v. absorption maximum due to the conjugated enone chromophore is found at longer wavelength (293 nm) for **1** than for its dibenzoate **2** (269 nm) or its diacetate **3** (268 nm). The absorption of these 2-*C*-acyloxy derivatives is in the range (260–270 nm) observed for 2-*C*-unsubstituted enones[12,13], and for related 2-*C*-acetoxy[8], -acetyl[12], and -carboethoxy[12] derivatives. Evidently, these substituents do not conjugate with the chromophoric group to any great extent. The bathochromic shift of ~25 nm caused by the 2-*C*-hydroxyl group in **1** and in the related enones **4** and 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one[9] (**5**), indicates that the 2-hydroxyl group participates in conjugation, presumably through hydrogen bonding to the carbonyl group. Consistent with this conclusion, the i.r. carbonyl absorption is shifted from 1680 and 1690 cm^{-1} for **2** and **3**, respectively, to 1663 cm^{-1} for **1**.

In view of the recently reported isolation of 5,6-dihydro-4-hydroxy-2*H*-pyran-2-one (**6**) from the pyrolysis of xylan[14], it was considered important that the position of the vinylic hydroxyl group on C-2 be established unequivocally: this was accomplished by conversion of **1** into the known[15] tris(*p*-nitrobenzoate) **9**, *via* the sequence of borohydride reduction, periodate oxidation, borohydride reduction, and (*p*-nitrobenzoyl)ation reactions outlined in Scheme 1.



1

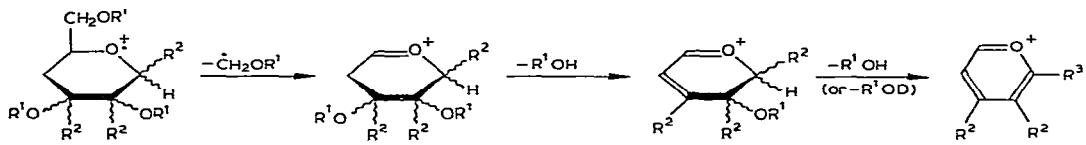
7 R = H
10 R = D

8 R = H
9 R = COC_6H_4N

Scheme 1

The initial reduction product **7** was characterized as its tri-*O*-(trimethylsilyl), -acetyl, and -methyl derivatives by g.l.c.–mass spectral studies. G.l.c. of these derivatives revealed that at least three of the four possible isomeric triols are present in the reduction product. Although none of the derivatives gave a molecular ion, the fragmentation pattern shown in Scheme 2, initiated by homolytic cleavage of C-5–C-6, satisfactorily accounts for significant ions in each spectrum. Many other ions, including the more-intense ones, could be rationalized as arising from the molecular ions by losses of simple units (see Experimental section).

The mass spectra of the per(trimethylsilyl)ated derivatives contained ions of similar intensity at *m/e* 203, 204, and 205. The ion at *m/e* 204 could be due to the $Me_3SiO\dot{C}H\dot{C}HOSiMe_3$ fragment, indicating a vicinal diol grouping[16] in **7**. In an attempt to obtain further evidence concerning the origin of this ion, **1** was reduced with sodium borodeuteride in deuterium oxide. Reduction could proceed by way of 1,2- or 1,4-addition to the enone. Either pathway should lead to the 1,2,3-tri-*C*-deuterio-triols **10**. The deuterio-reduction product was per(trimethylsilyl)ated, and the mass



R^1	R^2	R^3	*m/e* (rel. int)	*m/e* (rel. int)	*m/e* (rel. int.)
Me_3Si	H	H	261 (7)	171 (36)	81 (minor)
Me_3Si	D	H,D	264 (major)	174 (major)	83,84 (minor)
Ac	H	H	201 (0.8)	141 (16)	81 (76)
Me	H	H	145 (100)	113 (93)	81 (8)

Scheme 2

spectra of these derivatives were found to contain ions of similar intensity at *m/e* 205, 206, and 207. The ion at *m/e* 206 is consistent with the $Me_3SiO\dot{C}D\dot{C}DOSiMe_3$ fragment expected from the vicinal diol compound. However, as rearrangements are common in the mass spectra of trimethylsilyl ethers of carbohydrates[16], a definite conclusion cannot be drawn from this result alone. In other respects, however, the mass spectra were consistent with the structure of **10** and, hence, the proposed formula **1**. The ions expected for the major fragmentation pattern are shown in Scheme 2. According to this Scheme, loss of deuterium occurs only in the final step, and then only in part, which is consistent with the observed data.

Completion of the degradation outlined in Scheme 1, which is reliant upon oxidative cleavage of the vicinal diol grouping of **7**, led, without purification of the intermediates, to the isolation of the tris(*p*-nitrobenzoate) **9** in 34% yield following chromatographic purification. This compound had the expected n.m.r. spectrum, and m.p. and specific rotation consistent with those in the literature, providing final confirmation of the structure assigned to **1**.

Compound **1** was found to be stable under acid conditions, but to decompose in base. This is not unexpected, as its dicarbonyl form has been postulated as an intermediate in the formation of 1,4-anhydro-3-deoxypentitol-2-carboxylic acid in the alkaline degradation of cellulose[17].

Thermal analysis of **1** (see Fig. 2) revealed a slightly broadened m.p. at 98°, followed closely by an endotherm associated with most of the weight loss. An exotherm, beginning at ~200°, is associated with charring reactions that leave a 30% residue at 350°. The endotherm is most probably due, in part, to evaporation of **1**, as, in an attempted vacuum pyrolysis, it distilled unchanged. Similarly, distillation was the main result of an attempted vacuum pyrolysis of the dibenzoate (**2**) of **1**.

Other cellulose-pyrolysis products. — During the chromatographic fractionation of the cellulose pyrolyzate, a number of components were characterized in addition to **1**, and some were isolated. A small quantity of levoglucosenone, in a yield estimated by g.l.c. to be 0.4%, and larger amounts of 5-(hydroxymethyl)-2-furaldehyde and 1,6-anhydro-β-D-glucofuranose were detected, but were not isolated. Crystalline

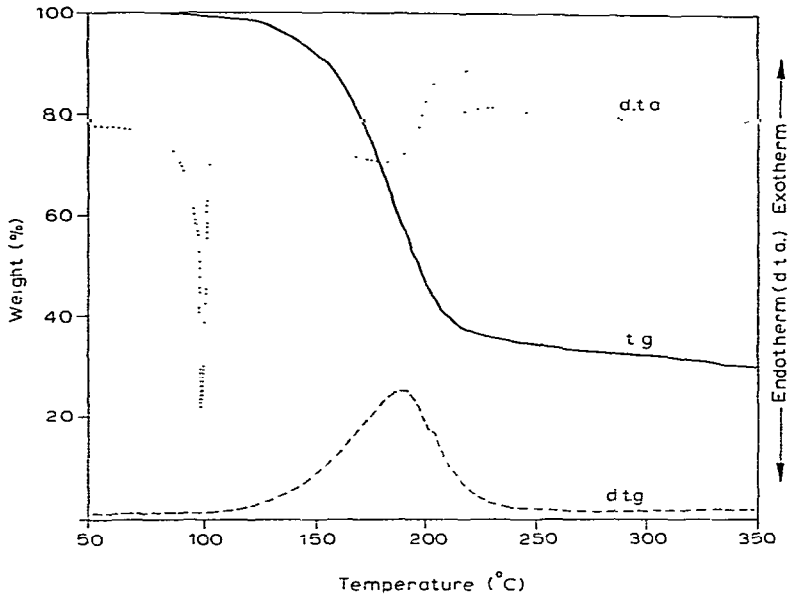
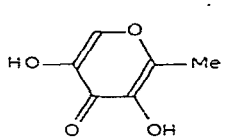


Fig. 2. Thermal analysis of 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose (**1**).

1,4:3,6-dianhydro-α-D-glucopyranose was obtained in 0.3% yield, which is comparable to the 0.5% yield isolable after pyrolysis of phosphoric acid-treated cellulose[18]. Isolation of this dianhydride from acid-catalyzed pyrolysis is experimentally simpler, however, due to its much higher concentration in the tar. In addition to the levoglucosan isolated in the initial crystallization, a further crop was obtained from chromatographic fractions, bringing the overall yield to 32.7%. The last five compounds have been reported from the pyrolysis of cellulose, and their yields have been quantified[19,20].

A small yield (0.1%) of a crystalline compound that could be readily purified by sublimation at atmospheric pressure was obtained following prolonged storage of the chromatographic fraction containing mainly 5-(hydroxymethyl)-2-furaldehyde: this compound was identified as 3,5-dihydroxy-2-methyl-4*H*-pyran-4-one (**11**) by comparison of its m.p. and i.r.-, u.v.-, and n.m.r.-spectral data with the reported values.



11

Pyrone **11** corresponds with only a very minor peak in the g.l.c. of (trimethylsilyl)ated cellulose tars. Any mechanism for its formation from a D-glucose unit of cellulose requires an oxidation step. A likely precursor of **11** is 2,3-dihydro-3,5-dihydroxy-6-methyl-4*H*-pyran-4-one (**5**), which is reported to be readily dehydrogenated to **11** during g.l.c.[21,22] and on standing in acetone solution open to the air[22]. In addition, it is possible to rationalize the formation of **5** from a reducing-sugar residue in cellulose in much the same way as its formation from reducing sugars in nonenzymic browning systems has been depicted[23,24]. An authentic sample of the dihydropyrone **5** was found to have the same retention time as component *c* in Fig. 1. Although **5** and **11** have not previously been reported as components of cellulose pyrolyzates, both have been observed in cigarette smoke[25] and as odorless products of Maillard reactions in model systems and in many foodstuffs[23,26,27].

Thus, a majority of the significant components of cellulose pyrolyzates that are revealed by (trimethylsilyl)ation–g.l.c. (see Fig. 1) have now been identified.

Quantitative analysis of pyrolysis products. — The tars obtained on pyrolysis of D-glucose, and a variety of polymers of D-glucopyranose, were analyzed by (trimethylsilyl)ation–g.l.c. for three of their major, monomeric constituents, namely, levoglucosan, 1,6-anhydro-β-D-glucofuranose, and 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose (**1**). The results are presented in Table II.

Temperatures were chosen to permit complete reaction in a reasonable period of time (5–30 min), and, in some cases, to avoid frothing. At these temperatures, much of the sample undergoes reaction during a warm-up period[28,29]; therefore, the temperatures given in Table II are those to which the pyrolysis oven was preheated. In agreement with previous observations[5], cellulose pyrolysis conducted in a vacuum (rather than at atmospheric pressure) led to an increased yield of tar and its major components, including enone **1**. Pyrolysis of other substrates was therefore performed under vacuum also.

The more "crystalline" cellulosic substrates gave more intramolecular transglycosylation products (the 1,6-anhydro-D-glucoses) and less of the unsaturated product **1**. Acidic catalysts are known to enhance dehydration and charring in the pyrolysis of cellulose[30], and, as expected, cellulose treated with increasing proportions of phosphoric acid yielded increasing proportions of char at the expense of the 1,6-anhydro-D-glucoses. The yield of **1** also decreased, indicating that any acid catalysis of the elimination reactions involved in its formation must be more than offset by enhanced decomposition. Pyrolysis both of α-D-linked D-glucans [amylose, amylopectin, cycloheptaamylose ("Schardinger β-cyclodextrin"), and nigeran] and β-D-linked D-glucans (cellulose and laminaran) gave similar yields of **1**, although nigeran, which consists preponderantly of alternating α-D-(1→3)- and α-D-(1→4)-linked units, and laminaran, which consists mainly of β-D-(1→3)-linked units, gave significant amounts of an as-yet-unidentified component not seen in the other pyrolyzates. Cycloheptaamylose, a cyclic polymer of seven β-D-(1→4)-linked D-glucosyl residues, gives typical yields of both **1** and the 1,6-anhydro-D-glucoses,

TABLE II

PYROLYTIC PRODUCTION OF 1,5-ANHYDRO-4-DEOXY-D-*glycero*-HEX-1-EN-3-ULOSE (1) AND THE 1,6-ANHYDRO-D-GLUCOSES

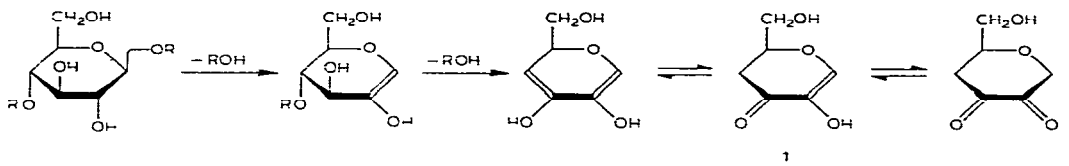
Substrate	*Temperature* (°C)	*Pressure* (torr)	*Sample weight* (g)	*Percent yield*[a]				
				Char	*Tar*	*Enone* **1**	*1,6-Anhydro-β-D-glucose*	
							Pyranose	*Furanose*
Cellulose								
Whatman CF 11	340	1.5	0.5	8	65	2.9	36	3.8
Whatman CF 11	325	~680	0.5	24	43	1.4	12	0.9
Avicel microcrystalline	390	1.5	0.5	3	84	2.3	49	4.8
Cotton hydrocellulose	390	1.5	0.5	2	85	1.3	58	6.0
Cotton linters	390	1.5	0.5	5	64	2.2	30	2.7
Whatman No. 41 ashless filter paper	390	1.5	0.5	5	69	2.7	38	3.6
Cellulose[b] + 0.1% of H_3PO_4	390	1.5	0.5	10	42	2.2	19	2.0
Cellulose[b] + 0.25% of H_3PO_4	340	1.5	0.5	19	37	1.2	15	1.0
Cellulose[b] + 1% of H_3PO_4	340	1.5	0.5	33	17	0.4	2.6	0.3
Amylose	315	1.5	0.15	11	57	1.8	26	1.9
Amylopectin	315	1.5	0.15	18	59	1.8	39	5.5
Cycloheptaamylose	315	1.5	0.15	11	66	2.3	40	4.0
D-Glucose[c]	315	1.5	0.15	11	56	trace	5.0	4.6
Laminaran[d,e]	315	1.5	0.15	10	64	1.4	19	1.4
Nigeran[d]	315	1.5	0.15	16	36	1.5	3.6	0.2

[a]Percent weight, based on the dry weight of substrate. [b]Whatman CF 11. [c]The tar contained α- and β-D-glucose in 8.2% yield. [d]These tars contained a major, unidentified component at slightly greater g.l.c. retention-time than the 1,6-anhydro-D-glucoses, in 3.1% and 3.8% yield from laminaran and nigeran respectively, using levoglucosan's response-factor. [e]Water-insoluble, ex *Laminaria cloustoni* fronds.

indicating that the processes involved in their production do not necessarily involve reducing end-groups.

Mechanism for pyrolytic depolymerization. — It is well established that the major reactions occurring during the uncatalyzed pyrolysis of carbohydrates are transglycosylations leading to anhydro sugars. A variety of competitive reactions, including dehydration, disproportionation, elimination, and polymerization, that operate on both the polymer and its monomeric depolymerization products, account for the minor pyrolysis products[4,5,19,31,32].

For the production of the enone **1** during thermal depolymerization of cellulose, a plausible mechanism that involves two sequential eliminations from a D-glucopyranosyl residue in the polysaccharide chain is shown in Scheme 3. The initial elimination, involving loss of the glucosidic substituent, creates a polymer chain having a terminal 2-hydroxy-D-glucal residue; a second elimination, involving the substituent on C-4, liberates the conjugated keto–enol, tautomeric mixture in which **1** preponderates. Such a mechanism is equally satisfactory for all of the α- or β-D-(1→4)-linked D-glucans.



1

R = polysaccharide residue

Scheme 3. Suggested mechanism for the pyrolytic formation of **1**

This elimination mechanism is supported by the typical yield of **1** from cycloheptaamylose, in contrast with the trace formed from D-glucose, which, as a reducing sugar, is more likely to undergo β-elimination to provide furan derivatives[3,2]. Because production of the enone **1** requires elimination of the substituent on C-4, which should be more rapid for carbohydrate residues (ROH) than for free hydroxyl groups, nigeran and laminaran, having glycosyloxy substituents on C-3, provide lower yields of **1**.

It is interesting that, whereas acid-catalyzed hydrolysis and elimination reactions of carbohydrates generally provide furan compounds, pyrolytic eliminations seem to favor pyran derivatives, leaving the original oxygen-ring intact.

EXPERIMENTAL

General methods. — T.l.c. was performed on silica gel; carbohydrates were detected by using a 3:5:95 anisaldehyde–sulfuric acid–ethanol spray-reagent and heating at 120°. Developing solvents employed were: *A*, 3:2 ethyl acetate–1,2-dichloroethane; *B*, 1:2 ethyl acetate–light petroleum ether; and *C*, 5:4:1 acetone–ethyl

acetate–water. Thermal analysis (t.g., d.t.g, and d.t.a.)[33] and pyrolysis[18] were conducted as previously reported. Moisture contents were determined by oven-drying samples for 30 min at 120–125°. N.m.r. spectra were recorded with a Varian EM 360, 60-MHz instrument, and mass spectra, with a Varian Mat III spectrometer at 80 eV.

G.l.c. analyses. — The following stainless-steel columns were employed: *1*, 1.8 m × 2.2 mm (i.d.), packed with 3% of Silar 5CP on 80–100 mesh GasChrom Q, with the injector at 250°; *2*, 1.8 m × 2.2 mm (i.d.), packed with 3% of SE-52 on 100–120 mesh Gas-Chrom Q, with the injector at 255°; and *3*, 1.2 m × 2.2 mm (i.d.), packed with 3% of ECNSS-M on 100–120 mesh Gas-Chrom Q, with the injector at 200°. All analyses employed hydrogen flame-ionization detection, digital integration, and nitrogen as the carrier gas. Pyrolyzates were analyzed, after (trimethylsilyl)ation, on column *2* as described before[18], but using methyl arachidate as the internal standard.

Isolation of products from the pyrolysis of cellulose. — Cellulose (Whatman CF 11, 180 g), having a moisture content of 3.8%, was pyrolyzed in five batches at 2–3 torr in a tube furnace preheated to 360–385°. The crude condensate was dissolved in methanol, evaporated to a syrup, and redissolved in acetone. On standing at −20°, this solution deposited light-brown crystals in two crops (34.4 g and 7.3 g) which were shown by trimethylsilylation–g.l.c. to be almost pure levoglucosan. The remaining liquors were then chromatographed on silica gel (600 g) eluted with mixtures of light petroleum ether–ethyl acetate–acetonitrile varying from 65:35:2 to 35:65:2. Fractions shown by t.l.c. (solvent *A*) to contain largely a component with R_F 0.22, which was detected as a blue spot, were combined, and evaporated to a dark syrup (7.0 g) that yielded 1,5-anhydro-4-deoxy-D-*glycero*-hex-1-en-3-ulose (**1**) from ethyl acetate–hexane as yellowish crystals (1.73 g, 1.1%), m.p. 91–96°, $[\alpha]_D^{25}$ +155° (*c* 1.1, water): ν_{max}^{KBr} 1663 and 1616 cm^{-1} (s, O=C–C=C–O); λ_{max}^{MeOH} 293 nm (ε_{mM} 5.80): *m/e* 144 (M^+, 100%), 126 ($M - H_2O$, 14), 115 (17), 113 ($M - CH_2OH$, 21), 102 (9), 98 (25), 97 (70), 87 (99), 85 (11), 80 (13), 73 (7), 71 (17), 70 (18), and 69 (38%).

Anal. Calc. for $C_6H_8O_4$: C, 50.0; H, 5.6. Found: C, 50.1; H, 5.7.

Although **1** could be isolated by crystallization in two further experiments similar to the foregoing, it proved difficult to purify by recrystallization, although a variety of solvents was tried; in general, only a small proportion of the dissolved material was recovered as a powdery solid. On a single occasion, recrystallization from ethyl acetate–toluene–hexane yielded a small quantity of well-formed, colorless needles, m.p. 98.5–99°, identical with **1** in t.l.c.

After removal of crystalline **1**, the filtrate, which still contained a considerable amount of **1** (t.l.c. evidence), was evaporated to a syrup which was dissolved in pyridine (25 ml). Benzoyl chloride (18 ml) was added at 0°, and the mixture was kept overnight at room temperature. Methanol (15 ml) was then added, and the mixture was partitioned between chloroform and water. The organic phase was successively washed with aqueous sodium hydrogencarbonate and water, and evaporated to a syrup; toluene (2 × 100 ml) and then water (2 × 100 ml) were added to, and evaporated from, this material under diminished pressure. The syrup (11.6 g) was now chromato-

graphed on silica gel (200 g) eluted with 80:20:1 light petroleum ether–ethyl acetate–acetonitrile, and fractions shown by t.l.c. (solvent *B*) to contain largely a component with R_F 0.28 were combined and evaporated to a syrup which yielded 1,5-anhydro-2,6-di-*O*-benzoyl-4-deoxy-D-*glycero*-hex-1-en-3-ulose (**2**)* in two crops from ethyl acetate–hexane as light-yellow needles (1.25 g, 0.33%). Recrystallization yielded colorless needles, m.p. 143–144°, $[\alpha]_D^{25}$ +125° (*c* 0.5, chloroform); ν_{max}^{KBr} 1730 (s, C=O, benzoate), 1680 and 1625 (s, O=C–C=C–O), and 1605 cm^{-1} (m, aromatic C=C); λ_{max}^{EtOH} 231 (ε_{mM} 30.50) and 269 nm (ε_{mM} 7.20); *m/e* 352 (M^+), 230 ($M-PhCO_2H$), 122 ($PhCO_2H$), 105 (PhCO, base peak), 77 (Ph), and 55.

Anal. Calc. for $C_{20}H_{16}O_6$: C, 68.2; H, 4.6. Found: C, 68.4; H, 4.7.

In addition to enone **1** [which eluted between (*iv*) and (*v*), described next], the following compounds were observed in other fractions during preparative chromatography, in order of elution. (*i*) Levoglucosenone was present in a yield of 0.4 g (0.3% from cellulose), as determined[18] by g.l.c., in a complex, syrupy mixture (4.6 g). (*ii*) 5-(Hydroxymethyl)-2-furaldehyde was the major component (t.l.c. and g.l.c. evidence) of a dark-red syrup (3.3 g). (*iii*) On storage at −20° for several months in ethyl acetate–hexane, the latter fraction yielded a small amount of crystalline 3,5-dihydroxy-2-methyl-4*H*-pyran-4-one (**11**) (0.20 g, 0.1%). Filtered off, washed with methanol, and purified by sublimation (140°, 1 atm.), it had m.p. 182–185° (sealed tube) [lit.[34] m.p. 156–156.5 and 184–184.5°]: ν_{max}^{KBr} 1650 (m), 1600 (m), and 1545 (s, broad) cm^{-1}; λ_{max}^{EtOH} 289 (ε_{mM} 8.90), 262 (ε_{mM} 5.50, shoulder), 217 (ε_{mM} 7.70, shoulder), and 204 nm (ε_{mM} 10.50); n.m.r. (Me_2SO-d_6): δ 9.06 and 8.89 (2 s, 1 H, enolic OH), 8.07 (s, 1 H, vinylic H), and 2.35 (s, 3 H, vinylic CH_3). The i.r. (including the fingerprint region), n.m.r., and u.v. data were consistent with those previously reported[34]. (*iv*) 1,4:3,6-Dianhydro-α-D-glucopyranose was obtained as crystals (0.46 g, 0.3%) from ethyl acetate–hexane, and, after recrystallization from the same solvent, it had m.p. and mixed m.p. 128–129°, $[\alpha]_D^{25}$ +66° (*c* 1.8, water) {lit.[18] m.p. 127.5–128°, $[\alpha]_D$ +67° (*c* 1.6, water)}. (*v*) Levoglucosan was obtained as crystals (15.0 g) from acetone, affording an overall yield of this compound, from cellulose, of 32.7%. (*vi*) 1,6-Anhydro-β-D-glucofuranose was present in the liquors (syrup weight, 13.4 g) following crystallization of the preceding component. T.l.c. and g.l.c. indicated that the 1,6-anhydro-D-glucoses were the only significant components of this fraction, in a pyranose to furanose ratio of 43:57.

2,6-Di-O-*acetyl-1,5-anhydro-4-deoxy*-D-glycero-*hex-1-en-3-ulose* (**3**). — A solution of compound **1** (0.33 g) in pyridine (3 ml) and acetic anhydride (3 ml) was kept overnight at room temperature. Methanol (3 ml) was added, and the solution was evaporated *in vacuo* at 50°, residual pyridine being removed by azeotropic distillation with toluene. A solution of the product in ethanol was decolorized with activated charcoal, and on evaporation, the diacetate **3** was obtained as a light-yellow syrup

Note added in proof.* — Lichtenthaler *et al.* have recently reported the following values for **2: m.p. 144–145°, $[\alpha]_D$ +124°. [F. W. Lichtenthaler, U. Kraska, and S. Ogawa, *Tetrahedron Lett.*, (1978) 1323–1326.]

(0.32 g, 61%). Vacuum distillation (0.5 torr) yielded a colorless syrup which was shown to be largely a single component by g.l.c. (column *1*) and t.l.c.: ν_{max}^{film} 1755 (s, C=O, acetate), 1690 and 1625 cm^{-1} (s, O=C–C=C–O); λ_{max}^{MeOH} 268 nm (ε_{mM} 7.05): *m/e* (g.l.c.–m.s.) 228 (M^+, weak), 186 (M − CH_2CO, 7%), 168 (M − HOAc, 3), 157, 144, 143, 126 (M − HOAc − CH_2CO, 40), 115, 113, 112, 110, 98, 97, and 43 (100%).

Reduction of **1**. — (*a*) *With sodium borohydride*. Compound **1** (0.60 g) was dissolved in 1:1 ethanol–water (35 ml), and a solution of sodium borohydride (0.60 g) in 1:1 ethanol–water (20 ml) was added. After 5 min at room temperature, the base was neutralized with an acid resin, the suspension filtered, the filtrate evaporated to dryness, and the residue evaporated four times with methanol, to yield a mixture of 1,5-anhydro-4-deoxy-D-hexitols (**7**) as a light-yellow syrup. A portion of this product was converted into its tris(trimethylsilyl) ether; in g.l.c. (column *2*, programmed from 100 to 275° at 8°/min), this was resolved into three components (retention times 10.5, 11.0, and 11.4 min, relative peak areas 1:7:17) having identical mass-spectral characteristics: *m/e* 349 (M − CH_3, 0.5%), 274 (M − $HOSiMe_3$, 0.5), 261 (M − CH_2OSiMe_3, 7), 247 (1), 243 (3), 235 (0.6), 231 (2), 217 (6), 205 (3), 204 (5), 203 (2), 191 (2), 189 (1), 185 (4), 184 (M − 2 $HOSiMe_3$, 2), 172 (8), 171 (M − CH_2OSiMe_3 − $HOSiMe_3$, 36), 169 (3), 147 (20), 145 (6), 143 (14), 133 (7), 129 (9), 117 (25), 116 (29), 103 (24), 101 (21), 75 (17), and 73 (100%).

A second portion of the reduction product was acetylated as already described, to yield a syrupy mixture of 2,3,6-tri-*O*-acetyl-1,5-anhydro-4-deoxy-D-hexitols that was resolved by g.l.c. (column *3*, programmed from 170 to 210° at 2°/min) into two components (retention times 11.0 and 11.9 min; relative peak areas 3:1) having identical mass-spectral characteristics: *m/e* 215 (M − OAc, 0.5%), 201 (M − CH_2OAc, 0.8), 173 (0.9), 172 (M − HOAc − CH_2CO, 1), 171 (2), 154 (M − 2 HOAc, 6), 141 (M − CH_2OAc − HOAc, 16), 129 (5), 112 (M − 2 HOAc − CH_2CO, 15), 94 (M − 3 HOAc, 38), 81 (M − CH_2OAc − 2 HOAc, 76), 69 (19), and 43 (100%).

A third portion of the reduction product was methylated with methyl iodide–sodium hydride in *N*,*N*-dimethylformamide, to yield a syrupy mixture of 1,5-anhydro-4-deoxy-2,3,6-tri-*O*-methyl-D-hexitols which was resolved by g.l.c. (column *2*, programmed from 80 to 275° at 8°/min) into three components (retention times 15.5, 16.3, and 17.6 min; relative peak areas 68:17:15) having identical mass-spectral characteristics: *m/e* 159 (M − OMe, 1%), 158 (M − MeOH, 2), 145 (M − CH_2OMe, 100), 113 (M − CH_2OMe − MeOH, 93), 88 (8), 87 (18), 85 (24), 81 (8), 69 (21), 59 (43), 58 (97), and 45 (70%).

(*b*) *With sodium borodeuteride in deuterium oxide*. Compound **1** (41 mg) was dissolved in deuterium oxide (15 ml), and a solution of sodium borodeuteride (42 mg) in deuterium oxide (5 ml) was added. After 1 h at room temperature, the solution was processed as in part (*a*), to yield a syrupy mixture of 1,5-anhydro-4-deoxy-D-hexitols-*1,2,3-C-d*$_3$ (**10**). Trimethylsilylation–g.l.c. revealed components having the same mobility, and the same peak-area ratio, as those in part (*a*), but giving the following mass-spectral data: *m/e* 352 (M − CH_3, weak), 264 (M − CH_2OSiMe_3),

245, 239, 232, 219, 218, 217, 207, 206, 205, 187, 174 ($M-CH_2OSiMe_3-HOSiMe_3$), 149, 147, and 73 (base peak).

(S)-*2-(2-Hydroxyethoxy)-1,4-butanediol tris*(p-*nitrobenzoate*) (**9**). — Compound **1** (0.10 g) was reduced with sodium borohydride (0.10 g) in water (20 ml) as already described. The syrupy product was sequentially oxidized with 0.1M periodic acid according to the procedure of Gorin[35], and the product reduced with sodium borohydride in water as just described, to yield syrupy (*S*)-2-(2-hydroxyethoxy)-1,4-butanediol (**8**); single component by t.l.c., R_F 0.36 (solvent *C*). This triol ether **8** was converted into its tris(*p*-nitrobenzoate) as described by Gorin[35]. This was purified by column chromatography on silica gel (50 g) eluted with 65:35:1 light petroleum ether–ethyl acetate–acetonitrile, and, on crystallization from ethyl acetate–hexane, **9** was obtained as pale-yellow needles (0.14 g, 34%), m.p. 100–102°, $[\alpha]_D^{25}$ −24° (*c* 1.4, chloroform) {lit.[15] m.p. 102–103°, $[\alpha]_D^{25}$ −28° (*c* 1.1, chloroform)}; n.m.r. ($CDCl_3$): δ 8.40 (12 H, aromatic), 4.4–4.9 (m, 6 H, CH_2-1,4,2′), 3.7–4.4 (m, 3 H, CH_2-1′ and H-2), and 1.9–2.5 (m, 2 H, CH_2-3).

Anal. Calc. for $C_{27}H_{23}N_3O_{13}$: C, 54.3; H, 3.9; N, 7.0. Found: C, 54.3; H, 4.0; N, 6.9.

pKa Determinations. — (*a*) *By pH titration*[36]. An aqueous solution of enone **1** was titrated against 0.08M sodium hydroxide. For molecular weight 144, the data indicated a monobasic acid with pKa 9.5.

(*b*) *By spectrophotometry*[36]. The pKa of **1**, determined at 289 and 339 nm, was 9.5 ±0.1. In aqueous solutions of pH 1.5–5.5, **1** has λ_{max} 289 nm (ε_{mM} 6.10) and is stable (no change in absorbance during 6 h at pH 3.15). In aqueous solutions of pH 11–12.5, the λ_{max} of **1** was shifted to 339 nm (ε_{mM} 4.90), and the compound was unstable: at pH 12.5, A_{338} decreased by 15% in 75 min, and by 50% in 5 h.

Attempted pyrolysis. — (*a*) *Of enone* **1**. Compound **1** (104 mg) was pyrolyzed under vacuum (1.5 torr) in a tube furnace preheated to 310°. T.l.c. and trimethylsilylation–g.l.c. analyses showed that the tar contained largely unchanged **1** (99 mg, 95%).

(*b*) *Of dibenzoate* **2**. Compound **2** (103 mg) was pyrolyzed under vacuum (1.5 torr) in a tube furnace preheated to 285°. Unchanged **2** (48 mg, 47%), identical with the starting material by t.l.c. and mixed m.p., was obtained by crystallization of the tar (98 mg) from ethyl acetate–hexane. The remaining liquors also contained mainly **2** (t.l.c.).

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