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MECHANISMS OF PYROLYSIS OF POLYSACCHARIDES: CELLOBIITOL AS A MODEL FOR CELLULOSE

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ABSTRACT

The pyrolysis of cellobiitol has been studied as a model for cellulose. The products were determined from pyrolysis at 350° *in vacuo* and at 350° and at 171° at atmospheric pressure. *In vacuo*, a 32% yield of 1,6-anhydro-β-D-glucopyranose (levoglucosan, **5**) and a 70% yield of D-glucitol and its anhydrides were obtained, but under atmospheric pressure these yields were much lower. A mechanism is postulated in which the first step in the pyrolysis is a heterolytic scission of the glucosidic linkage to produce a glucosyl cation and a glucitol anion. The former yields the volatile levoglucosan by intramolecular attack of O-6 on the C-1 cation and this reaction is favored *in vacuo* because of the resultant efficient removal of **5**. The glucitol is obtained predominantly as anhydrides, which are volatile in the vacuum pyrolysis. Lower temperature (171°) pyrolysis gave no **5**. The glucosyl cation under such conditions is believed to undergo intermolecular nucleophilic substitution with hydroxyl groups from unreacted starting material and from glucitol to produce oligosaccharides.

INTRODUCTION

Pyrolysis or thermal degradation of polysaccharides has been extensively studied and comprehensively and critically reviewed[1]. A great deal is known about the nature and yields of products of such pyrolysis, but there are still no exact conclusions concerning chemical mechanisms. In the specific case of (1→3)-glucopyranans, the pyrolytic formation of high yields of glucometasaccharinic acids[2] permits the conclusion that an "unzipping" mechanism is operative from the reducing end-groups, analogous to alkaline degradation, but no comparable conclusion is possible with any other type of polysaccharide. The most extensive studies have been carried out on the (1→4)-glucans, starch and especially cellulose, because of their abundance, and because the latter is the major component of biomass, for which thermochemical processing is a potentially viable approach to economic utiliziation.

For very pure cellulose, pyrolysis can yield >60% of a single product, namely, 1,6-anhydro-β-D-glucopyranose (levoglucosan, **5**)[3] and obviously a single

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mechanism with some type of "progressive" nature must exist for such high conversions. A progressive homolytic "unzipping" mechanism has been proposed by Kislitsyn *et al.*[4], which would fit such requirements, but the reactions involved lack any analogy in the wider field of carbohydrate chemistry, and their experimental justification may be considered flawed[3]. The most frequently cited speculations regarding mechanism of levoglucosan formation imply SN2CB displacements involving or following a mid-chain heterolytic glycosidic scission, and have been summarized by Shafizadeh and Fu[5]. Such mechanisms however are not compatible with high yields of **5** as a single product.

Recently[3], we posited that the heterolytic scission of a glucosidic linkage, analogous to acid hydrolysis, is the initial step in pyrolysis of pure cellulose. The concept of this scission and the subsequent reactions owe much to our detailed studies of the mechanism of thermolysis of sucrose[6]. The concept requires that the initial pyrolytic scission of cellulose results in the formation of two shorter cellulose chains, one with a short-lived, resonance-stabilized glucosyl cation in place of a "normal" reducing end-group. This glucosyl cation is then stabilized by intramolecular addition of O-6 to C-1, leaving a unit of levoglucosan at the new chain end. The predominant final pyrolysis product, namely **5**, is then liberated by any subsequent scission of the ultimate glucosidic linkage and, being relatively volatile, is able to leave the pyrolysis site. This latter scission becomes increasingly probable as the chain lengths are progressively shortened. Thus the initial reactive intermediate from the pyrolytic scission of the glucan (namely, the glucosyl cation) enters a "stability sink" by forming the 1,6-anhydride at the end of a shortened chain, and this is postulated as the key to the high-yield pyrolysis. As a test of this hypothesis, we now describe an investigation of the pyrolysis of cellobiitol (**1**), which we consider to be the simplest model compound for the study of cellulose pyrolysis mechanisms. In this and subsequent papers, we shall also consider the major types of competing polysaccharide pyrolysis mechanisms, such as those which can produce high yields of glycolaldehyde at the expense of **5**, especially in the presence of minute amounts of "neutral" salts[3].

RESULTS AND DISCUSSION

The purpose of selecting cellobiitol rather than cellobiose as a model for cellulose pyrolysis was to conserve the stereochemistry about the glycosidic group, while eliminating the relatively facile and complex pyrolytic reactions which would originate at the potential aldehyde group of cellobiose and which would have little relevance to polysaccharide pyrolysis.

Effect of pressure on pyrolysis. — In pyrolyzing the cellobiitol, relatively low-temperature conditions under vacuum were used in order to gain maximum information on the pyrolysis mechanisms. This is in contrast to the normal approach involved with development of processes to maximize yields of pyrolysis oils, where higher temperatures or flash pyrolysis are more usual. The yields of pyrolysis

fractions and components are shown in Tables I and II, together with gas chromatography (g.l.c.) retention times and relative detector-response factors of the tri-*O*-methylsilylated pyrolyzate components, using erythritol as the internal standard. All g.l.c. peaks were resolved from each other except for the furanose isomer of **5** and one of the 2,5-anhydrohexitols (either 2,5-anhydro-L-iditol or 2,5-anhydro-D-mannitol), which coincided. No attempt was made to determine which 2,5-anhydrohexitol corresponded with each peak. The mass spectrometry of the coincident peak (12.0 min in Table II) was compatible with a mixture of the two components. The amount of 1,6-anhydro-β-D-glucofuranose present was calculated as 10% of the amount of the pyranose isomer, a ratio determined previously[7]. The area thus calculated for the furanose was subtracted from the total area for the coincident peak and the remainder was assumed to be the anhydrohexitol.

Under vacuum-pyrolysis conditions, individual chemical components whose total yield corresponded to >70% of the pyrolyzate were identified, but obviously some major components of the pyrolyzate cannot be determined by g.l.c. of Me_3Si ethers, presumably because they do not pass through the g.l.c. column. Similar discrepancies, usually of much greater magnitude, occur in all previous studies of pyrolyzates from cellulose using similar techniques. In such cases it has been suggested that at least some of the pyrolyzate components not accounted for by g.l.c. are polysaccharides derived from the post-pyrolysis polymerization of levoglucosan[8].

The compounds found in the pyrolyzate appear to result from the scission of the glucosidic linkage to form a glucitol anion and the resonance-stabilized glucose cation (**2** in Scheme 1). Levoglucosan is then formed by intramolecular addition of O-6 to C-1. The resultant product (**5**) is sufficiently volatile *in vacuo* that it is removed from the pyrolysis furnace before nonspecific secondary reactions can occur. The lower volatility of the glucitol results in slower removal from the pyrolysis zone, thus creating opportunity for partial conversion into the anhydrohexitols. The formation of these products will be discussed in greater detail next.

The effects of pressure on this reaction may be seen in Table II. There is a dramatic decrease in yield of **5**, from 32 to 6% of theoretical, when the pyrolysis is carried out at atmospheric pressure rather than *in vacuo*, and the yields of the

TABLE I

YIELDS OF PYROLYSIS FRACTIONS FROM CELLOBIITOL PYROLYSIS AT 350°

Pyrolysis time (min)	*Pressure (torr)*	*Pyrolyzate (%)*[a]	*Pyrolyzate II (%)*[b]	*Char (%)*	*Recovery (%)*
30	1.5	65.8	10.8	5.0	81.6
60	1.5	62.7	10.3	2.8	75.8
60	760	36.7	24.5	22.6	83.8
30[c]	1.5	66.3	19.7	2.6	88.6

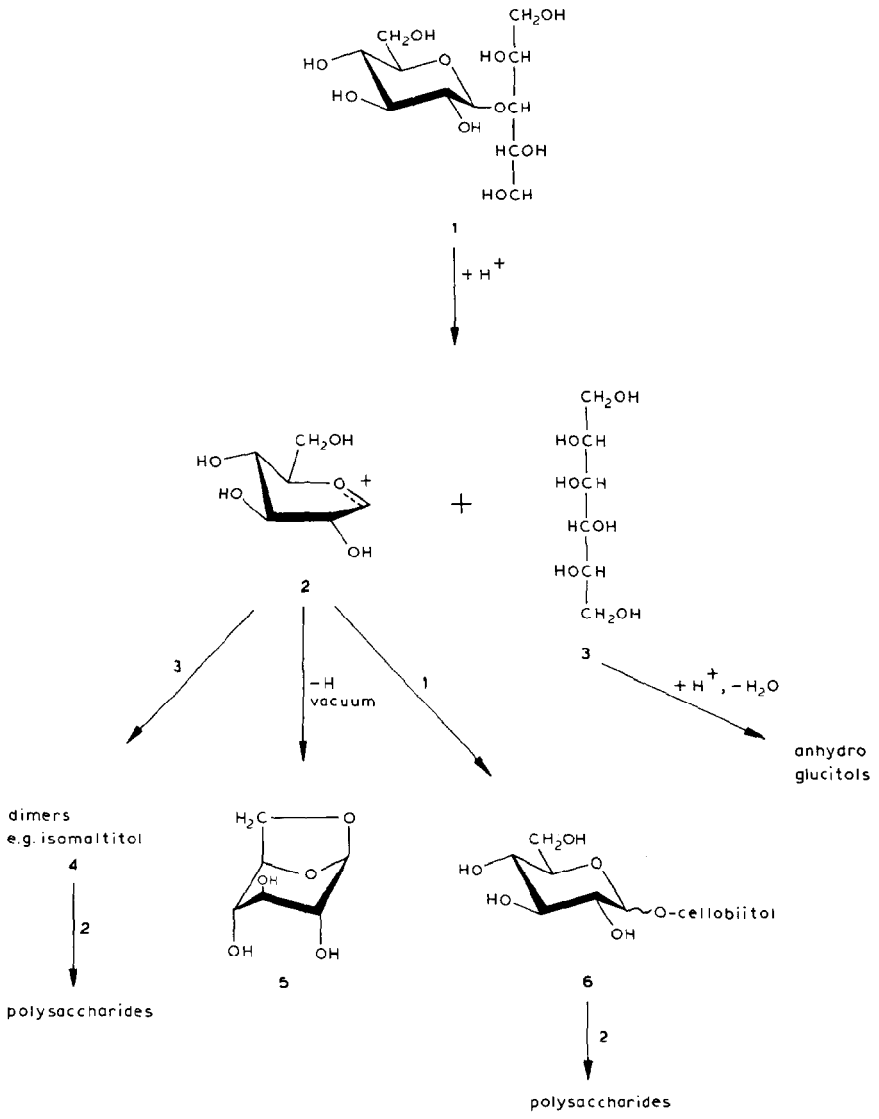
[a]Room-temperature condensation. [b]Condensation at 80°. [c]Sodium chloride (1%) added to cellobiitol.

TABLE II

MAJOR COMPONENTS OF PYROLYZATE I FROM CELLOBIITOL PYROLYSIS AT 350°

Pyrolysis time (min)	*Pressure (torr)*	*Levoglucosan*[a]	*% Theoretical yield (% of total pyrolyzate I)*					*Pyrolyzate I accounted for (%)*
			Glucitol	**7**	**8**	**9** *and* **10**	**11**	
30	1.5	32.0 (22.8)	16.1 (13.0)	23.7 (17.2)	4.9 (3.5)	25.0 (18.1)	[d]	74.6
60	1.5	31.0 (23.3)	21.7 (18.3)	16.5 (12.5)	3.6 (2.7)	18.0 (13.7)	[d]	70.5
60	760	6.0 (6.4)	0 (0)	8.8 (9.5)	0 (0)	22.4 (24.0)	14.2 (15.2)	55.1
30[c]	1.5	10.2 (7.2)	28.6 (22.8)	3.8 (3.2)	0.9 (0.8)	4.4 (3.7)	[d]	37.7
Response factor *vs.* erythritol		0.43	0.41	0.31	0.31	0.31	0.47	
Retention time (min)		11.1, 12.0	15.3	12.3	12.9	11.7, 12.0	6.7	

[a]Both pyranose and furanose isomers. [b]No attempt was made to differentiate between the two isomers. [c]1% sodium chloride in cellobiitol. [d]None detected.



monoanhydroglucitols are decreased whereas the other anhydrohexitols increase. All of these effects can be attributed to the fact that, at atmospheric pressure, the primary reaction-products are less volatile and hence more subject to secondary pyrolysis in the pyrolysis furnace. This secondary pyrolysis at atmospheric pressure appears predominantly as dehydration reactions leading to a major increase in carbonaceous char (Table I). The question must be considered as to whether these secondary pyrolyses proceed via intermediate formation of levoglucosan or *via* alternative pathways. Shafizadeh and co-workers have previously studied[10] the

pyrolysis of **5** under atmospheric pressure at 220 and at 600°. At the former temperature, **5** sublimed unchanged, while at 600° it was said to yield predominantly "tars", although the latter were not analyzed for unchanged **5**. In view of these results and of our very low yield of **5** in the atmospheric pressure pyrolyzates (6%, Table II), we conclude that the high conversion of cellobiitol to "char" does not proceed via initial formation of **5**. It therefore seems unlikely that there is any extensive formation of the glucosyl cation **2** at atmospheric pressure, as its conversion into **5** should not be pressure-sensitive. Accordingly, we postulate that, under atmospheric pressure, the cellobiitol undergoes complex dehydration reactions which compete with the reactions shown in Scheme 1 to yield carbonaceous char. Subject to the likely case that the conversion of **2** into **5** is reversible, the effect may operate via displacement of the equilibrium by rapid removal of **5** at low pressure, thus effectively accelerating formation of levoglucosan in comparison with the atmospheric-pressure pyrolysis. Similar conclusions should also be applicable to polysaccharide pyrolyses which will be the subject of future studies.

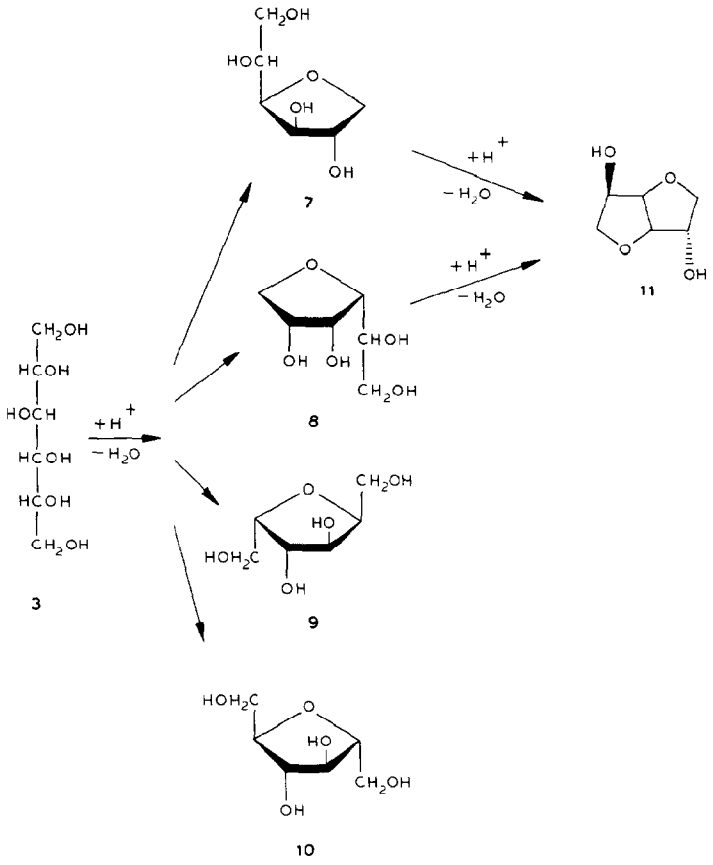
The effect of pressure on cellulose pyrolysis has previously been studied[11] and the results showed that higher pressures (>1 atm) during pyrolysis led to higher char formation. It should be noted however, that pressures lower than one atmosphere were not used, nor was any attempt made to characterize or quantify the pyrolysis products.

Detailed investigation of cellobiitol pyrolysis at 171°. — Thermogravimetry in nitrogen at 10°.min^{-1} from 110 to 400° showed a single derivative weight-loss peak at 325° and weight loss commencing (2%) at 270°. In order to obtain a more detailed understanding of the initial steps in the pyrolytic reaction, we investigated the reaction at 171°, a temperature significantly below the temperature of initial weight loss, because the initial reactions were not expected to involve weight loss.

The mechanism we propose for the pyrolysis is shown in Schemes 1 and 2. Some preliminary studies have confirmed that the addition of 1% of trichloroacetic acid dramatically accelerates the reaction (~90% loss of cellobiitol after 1 h at 171°). There is little doubt that this catalysis occurs by the protonation of the glucosidic oxygen atom and that the initial rate-determining step is the scission of this bond.

The glucosyl cation **2** is lost through several reaction channels. It may cyclize to form levoglucosan **5**, it may add to glucitol (most probably at O-1 or O-6 producing a disaccharide, or it may add to a cellobiitol molecule to produce a trisaccharide (analogous to the formation of kestoses in pyrolysis of sucrose)[12]. Subsequent addition of further glucosyl cations to di- and tri-saccharides will produce oligosaccharides and, at advanced reaction-times, polysaccharides.

The glucitol anion formed by the initial scission is likely to capture a hydrogen ion from water, which is simultaneously produced in competing reactions, to form D-glucitol **3**, which is relatively stable at short reaction-times. At longer reaction-times the glucitol undergoes dehydration to form the monoanhydrohexitols (**7–10**) and at very extended reaction-times the dianhydride **11** is formed.



Analyses were carried out by l.c. utilizing a solvent with relatively low resolving power, which eluted disaccharides and trisaccharides as "groups" in two distinct peaks in order to facilitate preparative chromatography. The rates of formation of the foregoing products, as well as the loss of cellobiitol, are shown in Fig. 1. The curves for diseappearance of cellobiitol and for formation of glucitol each show a brief lag-phase. In this respect there is an analogy with the pyrolysis of non-crystalline sucrose[12] in which it was concluded that the initial acceleration in rate or autocatalysis was due to formation of traces of acids by other minor, but competing non-specific pyrolytic mechanisms. Protonation of the glucosidic oxygen then accelerates the scission of **1** (see preceding). The apparent termination of cellobiitol loss at ~15% residual cellobiitol is due to the fact that disaccharide *products* are analyzed with cellobiitol by the l.c. procedure. The trisaccharides are secondary products, hence they show a more pronounced lag-phase and their yield passes through a maximum because they are themselves subject to pyrolytic scission and also because they can add to glucosyl cation. The maximum in yield of glucitol is due to reaction with glucosyl cation and to formation of anhydrohexitols.

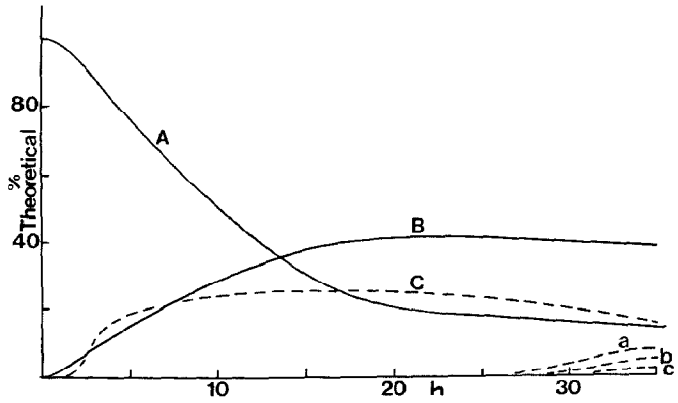


Fig. 1. Loss of cellobiitol and formation of major products at 171°: A, cellobiitol; B, glucitol; C, trisaccharides; a, 1,4-anhydro-D-glucitol; b, 2,5-anhydro-L-iditol and 2,5-anhydro-D-mannitol; and c, 3,6-anhydro-D-glucitol.

No levoglucosan was produced under these conditions. Previous studies[9] indicate that, during thermogravimetric analysis, levoglucosan begins to evaporate at 180°. We therefore measured the weight loss from the open vials used in our experiments and determined that no weight loss occurs until the anhydrohexitols are produced. It is clear therefore that, if any levoglucosan had been produced, it would have remained in the reaction mix, and would have been detected by the l.c. The absence of levoglucosan is most simply explained by the assumption that, in this system, the transglycosylation reactions of the glucosyl cation are more rapid than the intramolecular addition. This situation is reversed at higher temperatures and lower pressures because **5** is more efficiently removed from the **2**⇄**5** equilibrium (see preceding).

The production of trisaccharides in the early stages of the pyrolysis is expected to result predominantly from the addition of glucosyl cation **2** to unreacted cellobiitol. Accordingly, we found that hydrolysis of the trisaccharides, obtained by preparative l.c., produced glucose and glucitol in the ratio of 2:1. The presence of oligosaccharides having d.p. >3 was observed by l.c. as a number of small, broad peaks at retention times longer than trisaccharides. Additionally, t.l.c. of the reaction mixes at extended reaction times showed a long streak extending back to the starting line from a point corresponding to the trisaccharides, indicating the presence of larger oligo- and poly-saccharides.

The monoanhydrohexitols **7–10**, formed late in the reaction, consisted predominantly of 1,4-anhydro-D-glucitol (**7**), with smaller amounts of the 2,5-anhydro isomers (**9, 10**) and 3,6-anhydro-D-glucitol (**8**). 1,4:3,6-Dianhydro-D-glucitol (**10**) was also observed, though only in trace amount. The extent of formation of these anhydrides was smaller than in the higher-temperature pyrolysis (Table II), probably because of competition from char-forming reactions at the extended reaction-times. The same anhydrides have been found in the acid-

catalyzed dehydration of glucitol as studied by Bock *et al.*[13]. The formation of anhydro derivatives from alditols in general has been extensively studied and is the subject of two reviews[14,15]. Their formation directly from alditols generally involves an intramolecular SN2 displacement of a protonated hydroxyl group.

Effect of sodium chloride. — In our previous work on cellulose pyrolysis[3], we have shown that added "neutral" salts have a dramatic effect upon the pyrolysis products, even at extremely low levels. For example, during vacuum pyrolysis, the addition of 0.05% sodium chloride to cellulose decreased the yield of levoglucosan from 55 to 9% and increased the glycolaldehyde yield from less than 0.1 to 4.0%.

As demonstrated in Tables II and III, the same effect is seen when sodium chloride-treated cellobiitol is pyrolyzed. Under vacuum, the levoglucosan yield is decreased from 32 to 10%, while significant glycolaldehyde (1.67% yield) was obtained from pyrolysis in the presence of sodium chloride and none was detected in the absence of the salt. The formation of glycolaldehyde from cellulose pyrolysis has been investigated previously and while no definite mechanism has been established for its formation, some speculations exist[16,17].

When cellobiitol containing sodium chloride was pyrolyzed at 171°, there was a dramatic increase in the rate of disappearance of the cellobiitol. Thus after 3 h, there was a 90% loss of cellobiitol, while the untreated sample showed only ~10% loss. In previous investigations on sucrose melts[12], a similar effect has been noted, the catalytic effect of the sodium chloride being tentatively attributed to its ability to facilitate charge separation by raising the dielectric constant of the sucrose melt. A similar explanation may also apply in the case of cellobiitol.

Polymerization also appeared to occur much more rapidly in the presence of sodium chloride. Samples pyrolyzed for longer than 3 h all contained components that did not dissolve in the 95% methanol solvent, but rapidly dissolved in water. These components were assumed to be polysaccharide in nature, but were not further investigated.

TABLE III

MAJOR COMPONENTS (OTHER THAN WATER) OF PYROLYZATE II FROM CELLOBIITOL PYROLYSIS AT 350°

Pyrolysis time (min)	*Pressure (torr)*	*Yield (weight %)*		
		Glycolaldehyde	*Acetic acid*	*Hydroxyacetone*
30	1.5	[b]	[b]	[b]
60	1.5	[b]	[b]	[b]
60	760	[b]	0.27	[b]
30	1.5	1.6	0.14	0.52

[a]Sodium chloride (1%) added to cellobiitol. [b]None detected.

EXPERIMENTAL

Materials. — Cellobiitol (**1**) and anhydrides **7**, **8**, **9**, **10**, and **11** were prepared as described later. All other reagents were used as received in the purest commercially available grade.

General methods. — All ^{13}C-n.m.r. and ^{1}H-n.m.r. spectra were recorded at room temperature with a Jeol FX-90 instrument at 22.5 and 89.56 MHz, respectively. All gas chromatography (g.l.c.) was carried out on a Hewlett–Packard HP-1 capillary column (0.2 mm i.d. × 12 m) using helium as the carrier gas, flame-ionization detection, digital integration, and a temperature program of 170° isothermally for 7.5 min followed by a rate of 10°/min up to 245° and then isothermally at 245° for 2 min. Samples were converted into trimethylsilyl ethers by using bis(trimethylsilyl)trifluoroacetamide in pyridine after addition of erythritol as an internal standard. All l.c. analyses were done on a Waters bonded-amine radial-compression column at room temperature, using 19:1 methanol–water as the eluent at flow rate of 1.0 mL/min. Detection was by differential refractometry using authentic samples of individual compounds as external standards. Retention times were; glucitol (6.0 min), cellobiitol and other disaccharides (7.5 min), and trisaccharides (8.8 min). Vacuum pyrolyses were conducted on a 0.5-g scale at 266 Pa under a nitrogen flow (sufficient to decrease the original vacuum by 133 Pa) as described previously[18]. Atmospheric-pressure pyrolyses at 150–180° were conducted by heating a weighed amount (20 mg) of cellobiitol contained in a loosely capped vial in a thermostatted (±1°) air-oven. Atmospheric-pressure pyrolyses at 350° were conducted in the same apparatus as the vacuum pyrolyses under a nitrogen flow of 50 mL/min. Samples containing weighed amounts of sodium chloride were mixed by dissolution in a minimum amount of water followed by evaporation under vacuum. The pyrolyzate I products (room temperature condensates) from pyrolyses at 350° were analyzed as Me_3Si ethers by g.l.c. while pyrolyzate II products (−80° condensates) were analyzed by ^{1}H-n.m.r. in deuterium oxide as described earlier[18]. Lower-temperature pyrolysis products were analyzed by l.c. and g.l.c. of Me_3Si ethers.

Preparation of cellobiitol. — Cellobiose (13 g) was dissolved in water (150 mL) and $NaBH_4$ (3 g) added. After 1 h at room temperature, prewashed Amberlite IR-120 (H^+) ion-exchange resin (90 mL) was added and the solution stirred for 10 min to decompose excess borohydride. The solution was passed through a column containing an additional 90 mL of the same prewashed resin and the effluent, together with 300 mL of washings from the column, taken to dryness *in vacuo*. The solid residue was washed three times with MeOH (125 mL), with drying between each addition by rotary evaporation to remove methyl borate, the remaining solid was vacuum-dried overnight at 40° and then dissolved in boiling MeOH (450 mL). A portion did not dissolve and was filtered off and discarded. The solution was concentrated to half volume and allowed to crystallize, giving white crystals, m.p. 140–143° (lit. 142–143°). The ^{13}C-n.m.r. shifts and assignments in deuterium oxide

solution with 2-methylpropan-2-ol as internal reference (31.1 p.p.m.) are as follows (off-resonance coupling in parentheses): glucose moiety, 103.9 (d, C-1), 74.7 (d, C-2), 76.9 (d, C-3), 70.8 (d, C-4), 77.2 (d, C-5), 61.9 (t, C-6); glucitol moiety, 63.4 (t, C-1), 73.6 (d, C-2), 71.1 (d, C-3), 80.6 (d, C-4), 72.5 (d, C-5), 64.0 (t, C-6).

*Preparation of 1,4-anhydro-*D*-glucitol* (**7**), *2,5-anhydro-*L*-iditol* (**9**), *and 2,5-anhydro-*D*-mannitol* (**10**). — These compounds were obtained as a mixture, as reported previously[20], and were not separated.

*Preparation of 3,6-anhydro-*D*-glucitol* (**8**). — This compound was prepared by reduction of 3,6-anhydro-β-D-glucopyranose with $NaBH_4$ as for the preparation of **1**.

Preparation of 1,4:3,6-dianhydroglucitol (**11**). — This was as previously reported[17].

The authenticity of compounds **7**–**11** was confirmed by ^{13}C-n.m.r. analysis of the products with comparison to known chemical shifts[13].

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