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THE BEHAVIOR OF CELLULOSE, AMYLOSE, AND β-D-XYLAN TOWARDS ANHYDROUS HYDROGEN FLUORIDE*

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ABSTRACT

Cellulose, amylose, and D-glucose are converted into α-D-glucopyranosyl fluoride (3) when dissolved in anhydrous hydrogen fluoride. The fluoride subsequently undergoes condensation to afford a mixture of oligosaccharides, probably *via* an oxocarbonium ion. The fluoride 3 and the oligosaccharides are in an equilibrium, which was studied by ^{13}C-n.m.r. spectroscopy; in dilute solution in hydrogen fluoride, the D-glucosyl fluoride is the main product present, but when the hydrogen fluoride is evaporated, the equilibrium is shifted towards the oligosaccharides. These constitute a complex mixture which was studied by methylation and subsequent analysis of the methylated alditols derived therefrom. (1→4)-β-D-Xylan and D-xylose behave similarly to the D-glucose derivatives towards hydrogen fluoride.

INTRODUCTION

An important step in the utilization of photosynthetic biomass is the conversion of its carbohydrate components (cellulose and other, usually insoluble polysaccharides), often part of a difficultly accessible, lignocellulosic matrix, as in wood, into water-soluble products. Chemical degradation of cellulose and of wood polysaccharides has been performed with hydrochloric or sulfuric acid at various temperatures and concentrations[2–4]. This procedure is usually energy-consuming and, furthermore, leads to some furan decomposition-products, which may hamper further biotransformation. As early as 1910, preliminary work indicated the potential of hydrofluoric acid for the hydrolysis of cellulose with regard to its transformation into ethanol[5], but the major results were obtained around 1930, when Helferich *et al.*[6–8] showed that cellulose is readily soluble in anhydrous hydrogen fluoride (HF) at 0–20°, and that it is converted into water-soluble products by this treatment. Similar results were

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obtained by Fredenhagen and Cadenbach[9], who also found that polysaccharides could be extracted from wood by treatment with HF at room temperature. Later studies by Russian chemists[10-12] confirmed these results, and, quite recently, further work has been simultaneously undertaken in our laboratories and at Michigan State University[13] in order to reevaluate the procedure for the extraction of the carbohydrate components from the lignocellulosic matrix, with the objective of production of chemicals or energy.

From previous results, it appeared that the water-soluble products obtained by treatment of cellulose with HF contained only traces of fluorine[6,7], and they were found to be a mixture of oligosaccharides consisting mainly of α-D-linked D-glucopyranosyl residues[10]. Cellulose may also be dissolved in aqueous hydrogen fluoride, and carbohydrates may be separated from lignin in wood by this reagent. However, cellulose will only dissolve at a reasonable rate in highly concentrated (80–90%), aqueous hydrogen fluoride[9-11]. Treatment of amylose or D-glucose with HF was reported to give the same mixture of oligosaccharides as that obtained from cellulose[8,10,11,14]. In the present work, the reaction of cellulose, amylose, and D-glucose with HF has been reinvestigated, in order to secure more-detailed information about the course of the reaction and the structure of the products obtained. In addition, the behavior of one of the main hemicellulosic components, (1→4)-β-D-xylan, and D-xylose towards HF has been studied.

RESULTS AND DISCUSSION

Cellulose is readily soluble in HF, as already mentioned, and 40–50% solutions

TABLE I

G.L.C. ANALYSES[a] OF *O*-METHYLATED D-GLUCITOL ACETATES DERIVED FROM TREATMENT OF CELLULOSE, AMYLOSE, AND D-GLUCOSE WITH HF

Acetylated D-*glucitol*	*Retention time (min)*	*Cellulose + HF at 20°, HF evaporated (%)*	D-*Glucose + HF at 20°, HF evaporated (%)*	*Amylose + HF at low temp. (%)*
6-*O*-Me	56.4		0.6	
2-*O*-Me	53.1	0.6	0.7	0.5
2,3-Di-*O*-Me	48.8	10		9.2
3,4-Di-*O*-Me	48.7		6.3	
2,4-Di-*O*-Me	47.8	8.6	9.9	0.3
2,6-Di-*O*-Me	45.3			1.3
2,3,6-Tri-*O*-Me	41.7	5.4	3	61.5
2,3,4-Tri-*O*-Me	40.5	17.9	31.1	1.6
3,4,6-Tri-*O*-Me	38.3	8.7	5.6	0.8
2,4,6-Tri-*O*-Me	38.2	10	5.2	0.8
2,3,4,6-Tetra-*O*-Me	31.0	23.7	26.3	19.2

[a]The column temperature was 100 → 200° at 2° min^{-1}; injection temp. 250°; detection temp. 300°.

TABLE II

G.L.C. ANALYSES[a] OF *O*-METHYLATED XYLITOL ACETATES DERIVED FROM TREATMENT OF XYLAN AND D-XYLOSE WITH HF

Acetylated xylitols	*Retention time (min)*	*Xylan + HF at 20°, HF evaporated (%)*	*D-Xylose + HF at 20°, HF evaporated (%)*	*D-Xylose + HF + 10% of water at 20°, HF evaporated (%)*
5-*O*-Me	35.8	7.8		7.7
2-*O*-Me	30.2	17.7	9.3	18.2
2,3-Di-*O*-Me	23.5	18.7	23.5	20.8
2,4-Di-*O*-Me	21.8	17.2	14.4	15.7
3,5-Di-*O*-Me	19.8	3.3	1.3	3
2,3,4-Tri-*O*-Me	15.0	23.2	40.3	30.7
2,3,5-Tri-*O*-Me	13.2	1	1.4	1

[a]The column temperature was 125 → 220° at 2° min^{-1}; injection temp. 250°; detection temp. 300°.

may be prepared within a few minutes at temperatures ranging from −10 to +20° (the normal boiling point of HF); below −10°, solubilization is slow. The products formed from cellulose (or from other carbohydrates) and HF may be isolated either by evaporation of the HF, or by precipitation of the products by addition of diethyl ether[6]; in the present work, both procedures were used. The products obtained were studied by ^{13}C-n.m.r. spectroscopy, and by methylation analysis with g.l.c.–m.s. of the methylated alditol acetates (see Tables I and II).

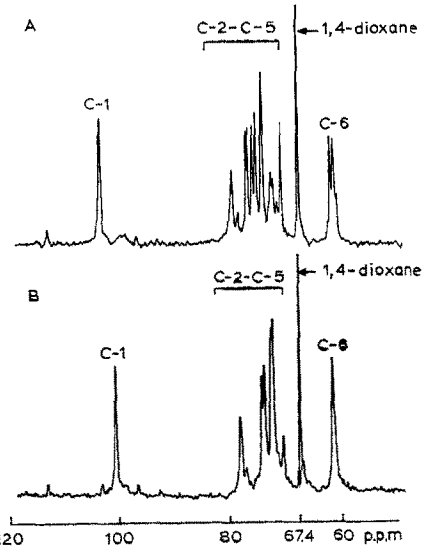


Fig. 1. ^{13}C-N.m.r. spectra in D_2O solution of A: cellulose treated with HF for 45 min at −5°; B: amylose treated with HF for a few minutes at low temperature.

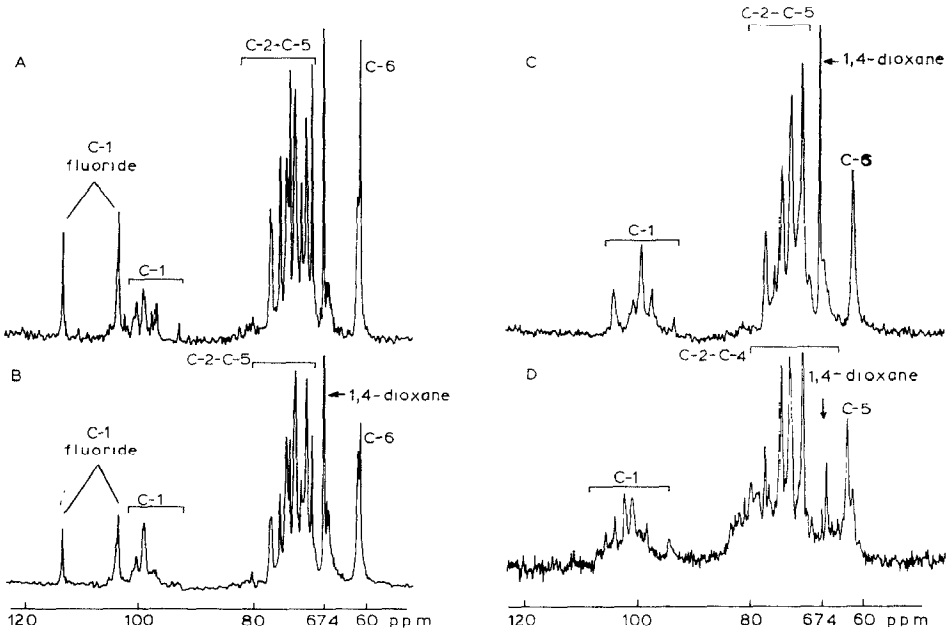


Fig. 2. ^{13}C-N.m.r. spectra in D_2O solution of A: cellulose treated with 8 parts of HF, precipitated with ether; B: cellulose treated with 1 part of HF, precipitated with ether; C: cellulose treated with HF, and the HF then evaporated; D: D-xylose treated with HF, and the HF evaporated.

Cellulose was treated with HF in a series of experiments in which the temperature and the concentration were varied. It did not dissolve at a detectable rate at $-78°$. At $-10°$, it went into solution rapidly, and a 20% solution was obtained within ~5 min. When this solution was immediately cooled to $-78°$ and diethyl ether was added, a product was precipitated that was largely insoluble in water, but soluble in dimethyl sulfoxide; the ^{13}C-n.m.r. spectrum (see Experimental section) showed that the water-insoluble part of this product was a β-(1→4)-linked glucopyranose oligomer. Treatment of cellulose with HF for 40 min at $-5°$, followed by precipitation with ether, gave a water-soluble product. Its ^{13}C-n.m.r. spectrum (see Fig. 1A) showed β-(1→4)-linked glucopyranosyl residues (C-1 at 103.4 p.p.m.) and weak signals from C-1 of the α and β anomers of the reducing glucose residue, at 92.9 and 96.8 p.p.m., respectively. Hence, both products described here constitute partially degraded cellulose. Of interest is the sharp, apparent doublet for C-6 at 61 p.p.m., ascribable to terminal and nonterminal, short-chain oligomeric glucose residues[15].

The nature of the products obtained when cellulose was kept in HF at 20° depended on the concentration of the solution and on the isolation procedure used. When a solution (~10%) of cellulose in HF was kept for 45 min at 20°, and then the product precipitated with ether, it was largely α-D-glucopyranosyl fluoride (**3**) as determined from its ^{13}C-n.m.r. spectrum (see Fig. 2A)[16]. When a 40–50% solution

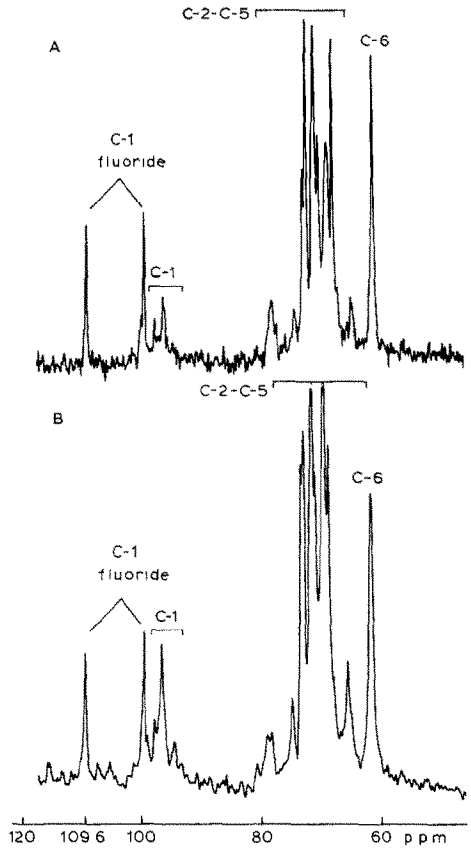


Fig. 3. ^{13}C-N.m.r. spectra in HF solution. A: 1 g of cellulose in 8 mL of HF. B: 1 g of cellulose in 4 mL of HF.

was treated in the same way, the product contained less glucosyl fluoride and more of a mixture of oligomers, as seen from the group of signals at ~98 p.p.m. (see Fig. 2B). When dilute or concentrated solutions of cellulose in HF were kept for 45 min at 20°, and then evaporated with a stream of air until most of the HF had been removed, and finally treated with diethyl ether, the product obtained contained no glucosyl fluoride, as demonstrated from its ^{13}C-n.m.r. spectrum (see Fig. 2C). The spectrum indicates that the complex product consists preponderantly of α-linked oligomers (broad C-1 signal at 98.6 p.p.m.) and smaller proportions of β-glucosides (C-1 at 103.7 p.p.m.), in agreement with previous results[10]. Methylation analysis (see Table I) showed a preponderance of (1→6)-linked D-glucopyranosyl units (~18% of 2,3,4-tri-*O*-methyl-D-glucitol) in the complex mixture. As l.c. showed that the product contained ~3% of free D-glucose (see Experimental section), the presence of ~24% of 2,3,4,6-tetra-*O*-methyl-D-glucitol indicated a high degree of branching, as also found previously[8,14].

The results described here were confirmed by measuring the ^{13}C-n.m.r. spectra of the products in HF solution. Thus, a 10% solution of cellulose in HF, prepared at −20° and measured after ~30 min, showed a spectrum similar to that in Fig. 1A, namely, partially degraded cellulose. When this solution was kept for a few h at 20°, it gave the spectrum shown in Fig. 3A, showing that the main product present is α-D-glucopyranosyl fluoride. No further changes took place when the solution was kept for several days. A 20% solution in HF, kept for a few h at 20°, gave a spectrum (see Fig. 3B) that indicated larger proportions of oligomers to be present, as seen from the group of signals at ~97 p.p.m.

When amylose was treated with HF at a temperature (~0°) just high enough to dissolve it, and then immediately cooled and precipitated with ether, it was possible to obtain a partially degraded product, whose ^{13}C-n.m.r. spectrum (Fig. 1B) showed almost only α-(1→4)-linked D-glucopyranosyl residues (C-1 at 100.7 p.p.m.)[15]. Methylation analysis indicated a d.p. of ~5, as seen from the 19% of 2,3,4,6-tetra-*O*-methyl-D-glucitol isolated (see Table I). Treatment of amylose with HF at −10° or at +20° gave the same products as those obtained from cellulose at 20° under otherwise identical conditions. The fact that amylose is completely converted into α-D-glucopyranosyl fluoride and oligosaccharides by treatment with HF for 1 h at −10° shows that it is degraded more rapidly than cellulose, which, under these conditions, yields only a partially degraded product.

Treatment of D-glucose with HF at 20° also yielded the same products as those obtained from cellulose or amylose. Thus, treatment with a large volume of HF followed by precipitation with diethyl ether gave mainly α-D-glucopyranosyl fluoride, having a ^{13}C-n.m.r. spectrum identical with that in Fig. 2A. When the HF was evaporated prior to treatment with ether, the product gave a spectrum identical with that in Fig. 2C, showing that it consisted of acid-reversion products and contained little D-glucose. The results of methylation analysis, shown in Table I, confirmed the similarity of the oligosaccharide mixture with that obtained from cellulose and starch under similar conditions.

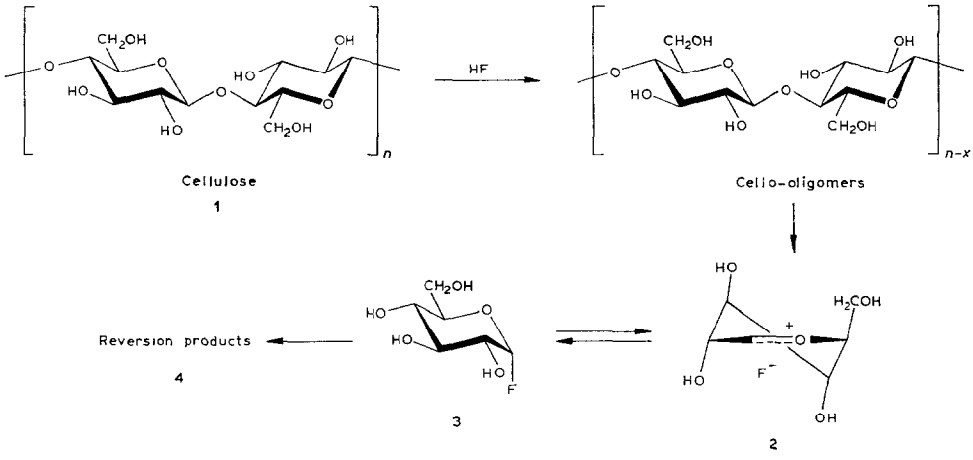
From these experiments, it is concluded that treatment of cellulose, amylose, or D-glucose with anhydrous HF primarily yields α-D-glucopyranosyl fluoride (**3**), a conclusion that Fredenhagen and Cadenbach[9] also reached (on the basis of conductivity measurements). The fluoride **3** is the main product isolated when dilute solutions of cellulose, amylose, or D-glucose in HF are precipitated with diethyl ether (see Fig. 2A). When more-concentrated solutions of HF are employed, the products contain less of fluorides and more of an oligomer mixture (see Fig. 2B), and if the HF is removed by evaporation, virtually only oligomers are obtained (see Fig. 2C). Therefore, an equilibrium is assumed to exist between the fluoride and the oligomers, and the position of this equilibrium depends on the proportion of HF present. Consequently, if cellulose, and, presumably, other polysaccharides, are to be degraded into non-fluorine-containing products by treatment with HF, the equilibrium should be shifted as far as possible towards the oligomers by evaporation of the HF.

As xylans are important components of lignocellulosic materials, it was of

interest to study the behavior of this compound and of xylose towards anhydrous hydrogen fluoride. D-Xylose and (1→4)-β-D-xylan gave, in all cases, identical products when treated with HF; almost independent of the reaction conditions and isolation procedure used, the material obtained was a complex mixture of oligosaccharides. When D-xylose was treated with a large proportion of HF, followed by precipitation with ether, the product obtained contained only traces of α-D-xylopyranosyl fluoride, as seen from a weak signal at 112.8 p.p.m. in the ^{13}C-n.m.r. spectrum, corresponding to the downfield peak of the C-1 doublet[16]. The product obtained by treating D-xylose or xylan with HF for 45 min at 20°, followed by evaporation of the HF, gave the ^{13}C-n.m.r. spectrum shown in Fig. 2D. Methylation analysis (see Table II) indicated that the product is a complicated mixture containing considerable proportions of furanoses. L.c. analysis showed that the products contained 4–5% of free D-xylose. Hence, xylan behaves analogously to cellulose; however, α-D-xylopyranosyl fluoride seems to be present in much smaller proportions than D-glucopyranosyl fluoride, even in dilute HF solution, probably because the equilibrium between xylosyl fluoride and the oligosaccharide mixture is shifted towards the latter.

Hydrolysis of polysaccharides with aqueous mineral acids often leads to the formation of furan derivatives, especially with pentose-containing polysaccharides. The products obtained in the present work, either by treating cellulose, D-glucose, β-D-xylan, or D-xylose with HF were all treated with diethyl ether, in order to obtain amorphous powders that could be readily filtered. In this procedure, any 2-furaldehyde or 5-(hydroxymethyl)-2-furaldehyde would be present in the ether solution; however, evaporation of the ether solutions left no detectable amounts of furan derivatives. Treatment of D-xylose with HF to which was added 10% of water gave a product similar to that obtained with anhydrous hydrogen fluoride, as may be seen from the methylation analysis (see Table II). The ether filtrate from this product was also devoid of furan derivatives.

Anhydrous HF dissolves and depolymerizes polysaccharides, especially cellulose



(**1**), more rapidly and at lower temperatures than any other acid that has been studied for this purpose. The easy dissolution of polysaccharides in HF may be explained by the strong tendency of the latter to form hydrogen bonds, which will lead to disruption of the intermolecular hydrogen-bonding of the polysaccharide molecules and, hence, to their dissolution. The subsequent degradation of polysaccharides to glycosyl fluorides probably takes place *via* protonation and formation of the conjugate acid and then of the oxocarbonium ion (**2**), in agreement with the accepted mechanism for acid-catalyzed hydrolysis of pyranosides[17]. Because other oxocarbonium ions, such as acetoxonium and benzoxonium ions, are stable in HF solution[18], it is likely that **2** would also be stable, and this would favor a displacement of the equilibrium toward this species. It should, however, be pointed out that, in the ^{13}C-n.m.r. spectra measured in HF solution (see Fig. 3), **2** has not been observed, but only the fluoride (**3**). Furthermore, it may be anticipated that the formation of hydrogen bonds between HF and the hydroxyl groups of the glycopyranosyl residues would modify the polarity of these hydroxyl groups, favoring the conjugate acid transition stage leading to the oxocarbonium ion (**2**).

The ready formation of oligomeric, reversion products (**4**) (which appear to be highly favored in this process of fluorolysis as compared to hydrolytic treatments using mineral acids) is, as expected, concentration-dependent and probably follows the classical pathway, *i.e.*, electrophilic reaction of an oxocarbonium fluoride intermediate with a polyhydroxylated carbohydrate residue. The high extent of formation of these reversion products leads to the anticipation that further biotransformation, using yeast fermentation, for example, will require a post-hydrolysis step involving either the use of mineral acid or of glycosyl-hydrolases.

It should furthermore be noted that the degradation of polysaccharides with HF, according to the mechanism proposed herein, is not a hydrolysis; therefore, comparison with reactions in aqueous acids is difficult.

EXPERIMENTAL

General methods. — The ^{13}C-n.m.r. spectra were recorded with a Bruker WH-90 instrument. Spectra of isolated products (see Figs. 1 and 2) were measured in D_2O solution, using 1,4-dioxane at 67.4 p.p.m. as the internal reference. The spectra of solutions in anhydrous hydrogen fluoride (see Fig. 3) were measured at 0° in a Teflon tube which fitted tightly in a 10-mm, glass sample-tube; acetone-d_6 was used for an external deuterium lock and reference.

The g.l.c.–m.s. analyses were conducted with an AEI MS 30 double-beam, mass spectrometer (Manchester), directly coupled to a Scot SP 2330 capillary column (25 m × 0.25 mm) fitted on a Girdel 3000 instrument (Paris). The electron-impact ionization mode was used with a source temperature of 150°, an ionization current of 100 μA, an ionization potential of 70 eV, and an acceleration potential of 3 kV.

The data were collected by using a Varian 100 MS computer system connected to the spectrometer.

The liquid chromatographic determinations for monosaccharide composition were performed with a Waters M 6.000 instrument fitted with a UK6 high-pressure injector and a differential refractometer detector (R401) connected to a Sefram servotrace recorder operating to 10 mV full scale. The column was a Waters (C_{18}) radialpack, with water (distilled, de-ionized, and filtered through 0.45-μm, Millipore membranes) as the eluant. The samples (100 mg) were dissolved in water (1 mL) and injected into the column. The percentage values were calculated by comparison with standard samples of D-glucose and D-xylose.

The anhydrous hydrogen fluoride (HF) was a commercial product, obtained in steel cylinders; prior to use, it was kept, in 50- or 100-mL portions, in polyethylene flasks at 0°. All reactions with HF were conducted in polyethylene bottles.

The cellulose was a CC 31 Whatman powder for chromatography. The amylose (Sigma) was from potato. The (1→4)-β-D-xylan was obtained as follows: commercial (1→4)-β-D-xylan (purum, Fluka) (20 g) was treated with M sodium hydroxide (2.000 L), and the insoluble part was filtered off. The solution was dialyzed for 48 h against tap water, and then for 10 h against distilled water (10 L). The nondialyzable part was concentrated to 500 mL, and freeze-dried, giving 15 g of (1→4)-β-D-xylan which was soluble in water and showed no acetyl groups in its ^{13}C-n.m.r. spectrum.

The methylation analyses of oligosaccharides were conducted according to the Hakomori technique, with the following adaptations. The oligosaccharide mixture (500 mg) was dissolved in Me_2SO (10 mL) by stirring at 60°. To the cooled solution was added sodium hydride (1 g) in Me_2SO (10 mL), and the mixture was stirred overnight. Two 3-mL portions of methyl iodide were added, at 1-h intervals, and, after being stirred overnight, the mixture was evaporated. The residue was extracted with chloroform (50 mL), and the extract was washed with water (2 × 10 mL), dried (Na_2SO_4), and evaporated. The residue thus obtained was dissolved in 72% sulfuric acid (2 mL) and kept overnight at room temperature. Water (56 mL) was then added, and the solution was boiled overnight, cooled, and made neutral by passage through Amberlite IR-45 (OH^-) ion-exchange resin. Sodium borohydride (250 mg) was added to the neutral solution, and, after 4 h, the excess of hydride was decomposed by addition of 10% acetic acid. The solution was evaporated, and traces of solvents were coevaporated with methanol (2 × 20 mL) and toluene (2 × 20 mL). The residue was kept overnight in pyridine (5 mL) and acetic anhydride (5 mL) and, after addition of methanol (5 mL), the solution was evaporated, and the residue dissolved in chloroform (100 mL). The solution was successively washed with saturated, aqueous potassium hydrogensulfate (20 mL), saturated sodium hydrogencarbonate (20 mL), and water (20 mL), dried, and evaporated, giving 5 to 600 mg of residue. The products thus obtained were analyzed by g.l.c.–m.s. under the conditions already described.

Treatment of cellulose, amylose, xylan, D-*glucose, and* D-*xylose with hydrogen fluoride, followed by recovery of the reaction products with diethyl ether.* — (*a*) *Reactions at room temperature and low dilution.* In a typical experiment, to each title

compound (5 g), cooled in ice, was added HF (5–6 mL) with shaking. The cellulose, as well as the other compounds, dissolved within a few min, and the clear, colorless solution was kept for 45 min at 20°. It was then cooled in Dry Ice–methanol, and cold diethyl ether (50 mL) was added. The mixture was stirred with a Teflon rod and, after a few min, the ether phase was decanted from the sticky precipitate. Several washings with ether at room temperature gave an amorphous solid which was filtered off, and dried *in vacuo* over potassium hydroxide. The yields were, from cellulose, 4.7 g; amylose, 5 g; xylan, 4.6 g; D-glucose, 4.5 g; and D-xylose, 4.2 g. The products were characterized through their ^{13}C-n.m.r. spectra, which were identical for cellulose, amylose, and D-glucose; a typical spectrum for the HF–cellulose sample is given in Fig. 2B. For xylan and D-xylose, the ^{13}C-n.m.r. spectra were also superposable; a typical spectrum for HF–xylan is given in Fig. 2D.

(*b*) *Reaction at room temperature and higher dilutions.* Cellulose, amylose, or D-glucose (5 g) was dissolved in HF (40 mL), and the solution was kept for 45 min at 20°. Precipitation with ether (250 mL) as just described gave, in all 3 cases, products (2.5 to 2.8 g) that mainly contained α-D-glucopyranosyl fluoride. The ^{13}C-n.m.r. spectrum of the product obtained from cellulose under these conditions is shown in Fig. 2A.

(*c*) *Reactions at low temperature.* Cellulose (10 g) was suspended in HF (50 mL) which was cooled to −78° in Dry Ice–methanol. The suspension was removed from the cooling bath, and shaken while the temperature was allowed to rise. The cellulose dissolved after a few min, and, as soon as a clear solution had formed, it was cooled to −78°. Precipitation with cold ether (400 mL), followed by washing with ether, filtration, and drying, gave 9.5 g of product. Extraction with boiling water, and subsequent drying, left 8 g of water-insoluble product that was soluble in Me_2SO; ^{13}C-n.m.r. data in Me_2SO-d_6: 102.6 (C-1), 79.8 (C-4), 75.1 (C-5), 74.7 (C-3), 73.2 (C-2), and 60.5 p.p.m. (C-6).

When cellulose (10 g) was mixed with HF (40 mL) at −5 to −10°, a clear solution was formed within 3–4 min. It was kept for 45 min at −5°, and then cooled to −78° and precipitated with ether as already described, yielding 9.5 g of a product that was readily soluble in water; for the ^{13}C-n.m.r. spectrum, in D_2O, see Fig. 1A.

Amylose (5 g) was suspended in HF (10 mL) at −78°. The mixture was then removed from the cooling bath, and shaken for a few min until a clear solution was formed. It was immediately cooled to −78°, and the product precipitated with ether, to give 4.2 g of material which was readily soluble in water; its ^{13}C-n.m.r. spectrum is shown in Fig. 1B, and the results of methylation analysis are given in Table I.

Treatment of cellulose, amylose, D-*xylan,* D-*glucose, and* D-*xylose with hydrogen fluoride, followed by recovery of the mixture by evaporation of the HF.* — In a typical experiment, the title compounds (5 g) were each dissolved in HF (5–6 mL, or alternatively, 40 mL) at 0°, and the solutions were kept for 45 min at 20°. A stream of air was then sucked over the solution for ~30 min at 20° by using a water aspirator. A syrup was left which, when stirred with diethyl ether (50 mL), turned into an amorphous solid that was filtered off, washed with ether, and dried over potassium

hydroxide. The yield was ~4.5 g for each compound. The ^{13}C-n.m.r. spectrum was recorded for each reaction mixture; the spectra were not affected by the amount of HF used. Typical spectra are given in Fig. 2C for the cellulose, amylose, or D-glucose reaction-products, and in Fig. 2D for D-xylan or D-xylose. Results of methylation analyses are given in Table I for the products from cellulose, amylose, and D-glucose, and in Table II for those from D-xylan and D-xylose.

In addition, the combined ether solutions from both the cellulose and the D-xylan treatment were separately evaporated in a stream of air, leaving ~25 mg of a residue in which no furan component could be detected by ^{1}H-n.m.r. spectroscopy of a solution in chloroform-*d*.

In a further experiment, D-xylan (5 g) was treated, as, already described, with HF (10 mL) to which was added water (1 mL). The product was subjected to methylation analysis (see Table II).

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