Journal of Analytical and Applied Pyrolysis, 19 (1991) 119–129
Elsevier Science Publishers B.V., Amsterdam

Thermal degradation of chitin and cellulose

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(Received July 27, 1990; accepted in final form February 6, 1991)

ABSTRACT

Dry chitin was thermally degraded under nitrogen. The main volatile degradation product was acetamide. Chitin and cellulose were depolymerized by thermal degradation in tetraethyleneglycol dimethylether as a high boiling and inert solvent to give water-soluble oligomers with a terminal anhydrosugar unit. In supercritical acetone, cellulose could be degraded to the extent of 98% and chitin to the extent of 85%. Monomeric anhydrosugars were formed with good yields and could be identified and isolated from the degradation syrups.

Cellulose; chitin; pyrolysis; polysaccharides.

INTRODUCTION

During the past several years we have been interested in methods that would allow controlled degradation of biopolymers to oligomers and low molecular weight compounds for further chemical treatment and usage. Our interest focused primarily on wood and its basic components hemicellulose, cellulose, and lignin [1–4], and secondly, on chitin [1,5], which forms the skeleton of crustaceans but is also part of the cell walls of moulds and mushrooms. These examples of biomass are readily available but are not used as food. Therefore, their chemical usage as renewable raw materials would not directly compete with food production.

Here some results on thermal degradation of the polysaccharides cellulose and chitin are reported.

EXPERIMENTAL

Thermal degradation of dry chitin under nitrogen

1 g of pulverized chitin (Sigma, practical grade, from crab shells, degree of acetylation = 0.62) was introduced into a two-necked flask equipped with an air condenser and heated at constant temperature in a stream of nitrogen for 15 h on an oil bath. The receiver was cooled in liquid nitrogen.

0165-2370/91/$03.50

TABLE 1

Thermal degradation of chitin *

T (°C)	200	205	210	228	232	238	252	280
Degree of acetylation **	0.57	0.53	0.49	0.48	0.41	0.36	0.27	0.06
Weight loss by deacetylation (%)	1.6	2.7	4.1	4.4	6.4	7.7	10.4	16.5
Total weight loss (%)	16.9	16.3	17.0	26.7	30.3	35.4	38.1	53.5

* Degradation time 15h. ** Degree of acetylation of charged chitin = 0.62.

The weight loss of the chitin was determined after cooling. Acetamide and acetic acid were identified in the condensate by HPLC. The degree of acetylation was determined by standard methods [6]. The results are given in Table 1.

The residue of chitin was treated with water, acetic acid (5%, 50%, and 100%), and 99% trifluoroacetic acid at room temperature and under reflux. The acids were removed in vacuo. The residue was suspended in water, heated and filtered off. The filtrate showed no sugars by HPLC or GPC.

High pressure–high temperature flow apparatus (HP–HT apparatus) (Fig. 1)

The solvent in reservoir 1 is pumped with a high pressure pump (Orlita DMPAE 10/MK) 2 into reactor 7, which is a preparative HPLC column (Knauer). Reactor 7 is charged with the polysaccharide and is heated in a GC-oven 12. The solvent is pre-heated in the heat exchanger 6 (stainless steel tube, o.d. 1.6 mm, i.d. 0.7 mm, 5 m). The extract is then quenched in heat exchanger 9 (as 6, 2 m), and collected in 11. The pressure against valve

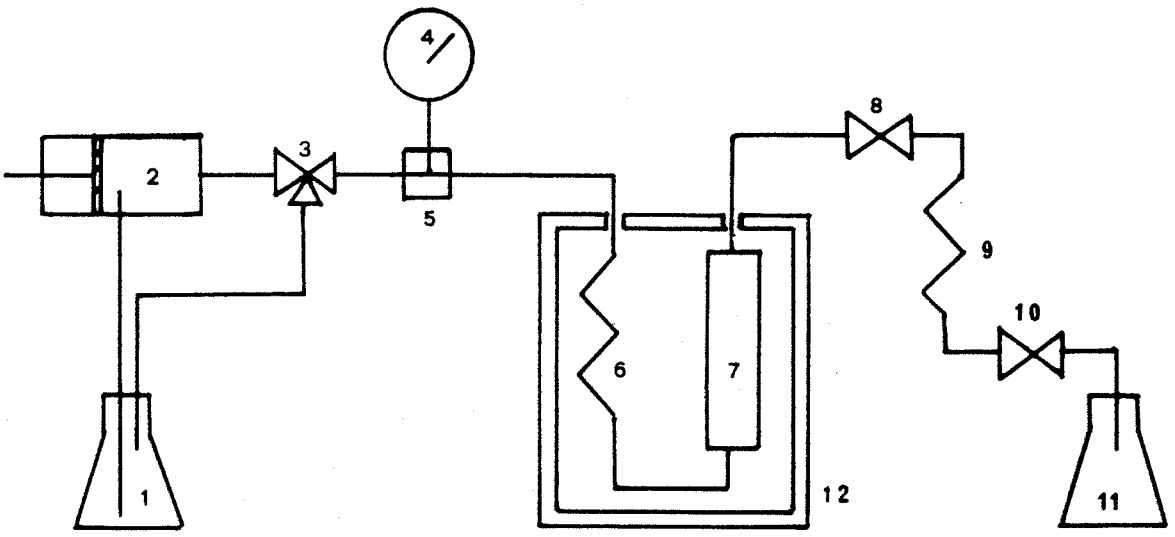


Fig. 1. High pressure–high temperature flow apparatus (HP–HT apparatus): (1), Solvent reservoir; (2), high-pressure pump for up to 600 bar; (3), excess-pressure valve; (4), manometer for up to 1000 bar; (5), T-piece; (6) and (9), heat exchanger (1.6 mm-diameter stainless steel tube); (7), reactor; (8) and (10), valve; (11), collector; (12), GC furnace.

8 is reduced in two steps with the valves 8 and 10. The same valves are also used to adjust the flow rate.

The HP–HT apparatus is operated as follows: First, at room temperature the solvent is pumped through the reactor. Then the flow rate and pressure are adjusted. Next the furnace 12 is heated to the extraction temperature. The flow rate and pressure have to be adjusted from time to time. The excess-pressure valve (Rheodyne) 3 helps to maintain a constant pressure.

Thermal degradation of cellulose in supercritical acetone

18 g of microcrystalline cellulose (Merck; dry weight 17.1 g) was transferred to reactor 7 (Fig. 1) and treated at a pressure of 25×10^6 Pa with acetone at an average flow rate of 4.5 ml/min. The temperature was slowly increased from 250 °C at the beginning of the experiment to 340 °C at completion of the degradation (after 10 h). There remained an extraction residue of 0.36 g (2.1%). Concentration of the acetone solution in vacuo gave 18.3 g of a dark syrup. The mass balance exceeded 100%, since small amounts of non-volatile condensation products of acetone are also formed during the reaction. The main products were identified as anhydrosugars by comparison with authentic materials. The following amounts (based on consumed cellulose) were determined by quantitative gas chromatography of the acetates (Carlo Erba Fractovap 2300, column 2m XE 60, $T = 473$ K, injection block 523 K, 20 ml He/min, triacetyl-1,6-anhydrogalactofuranose as internal standard): 38.8% 1,6-anhydro-β-D-glucopyranose **1a**, 4.3% 1,6-anhydro-β-D-glucofuranose **2**, 4.0% 1,4:3,6-dianhydro-α-D-glucopyranose **3**, ca. 1% 1,6-anhydro-3,4-dideoxy-β-D-glycero-hex-3-enopyranos-2-ulose **4**.

Thermal degradation of chitin in supercritical acetone

Chitin (Fluka, techn., ash content 5%; 15.0 g) was degraded in the same way as cellulose in the temperature range of 250–340 °C at 25×10^6 Pa by acetone at a flow rate of 5 ml/min over 7.5 h. The residue amounted to 2.3 g (15.3%). Concentration of the acetone solution by evaporation afforded 16.4 g of a mobile black oil, which was shown by combined GC/MS to contain acetamide and diacetamide. Thin layer chromatography showed the presence of 1,6-anhydro-3,4-dideoxy-β-D-glycero-hex-3-eno-pyranos-2-ulose **4**. Partition of the syrup between water and chloroform afforded 4.1 g of a water-soluble product and 12.3 g of chloroform extractables. The main sugar component 2-acetamido-1,6-anhydro-2-deoxy-β-D-glucopyranose **5** [7] could be recovered from the water-soluble product in 5.6% overall yield (0.8 g) by chromatographic separation on a silica gel column using acetone as the eluent.

Carboxymethylation of chitin

Chitin and the insoluble residue of chitin degradation, were carboxymethylated by standard procedure [8]. GPC was performed on Merck Fractogel TSK HW-40 (S); 8 × 360 mm; 0.2 ml H_2O/min; room temperature; RI detector (Knauer).

RESULTS

Thermogravimetric analysis of chitin revealed that this polysaccharide is thermally degraded in two steps (Fig. 2). The DTG-curve showed a first maximum at 290 °C and a second maximum at 360 °C. (The maximum at 66 °C represents the drying process). 85% of the charged chitin was volatilized up to 400 °C, and 25% was converted to char [5].

Online mass spectrometric analysis of the degradation process from 220 °C up to 260 °C showed mainly the mass spectrum of acetamide **6**. Quantitative determination of acetamide in the pyrolysate showed that 9.3 weight % of the charged chitin is converted to acetamide. This represents ca. 50% of the total amount of the acetamido groups of chitin [5]. The chitin had a degree of acetylation of 0.62.

Acetamide could be eliminated in a pericyclic cis-elimination to give products in the polymer residue as in Scheme 1. Both structures should allow for an easy hydrolysis of the chitin to give product oligomers. Unfortunately, heating of chitin under argon indeed gave acetamide in addition to acetic acid, water, and other minor degradation products.

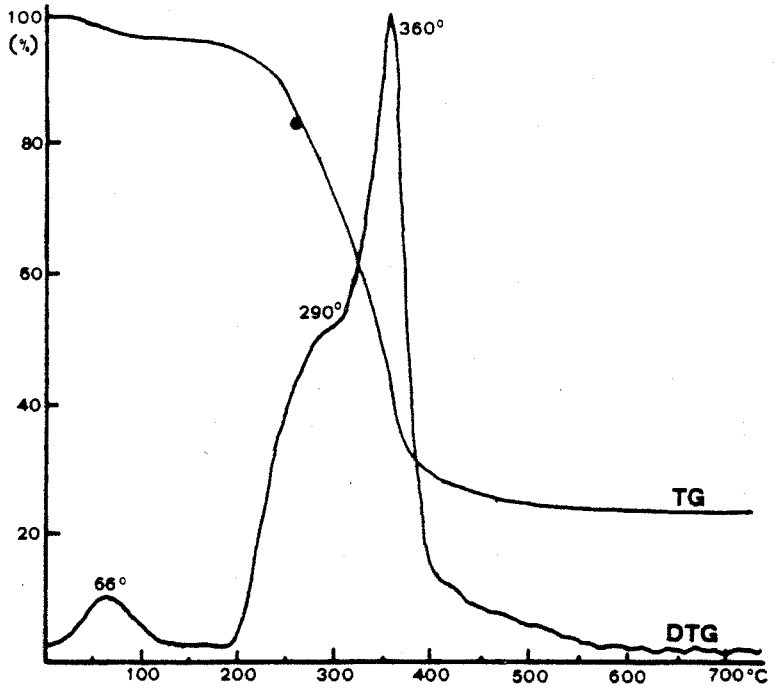
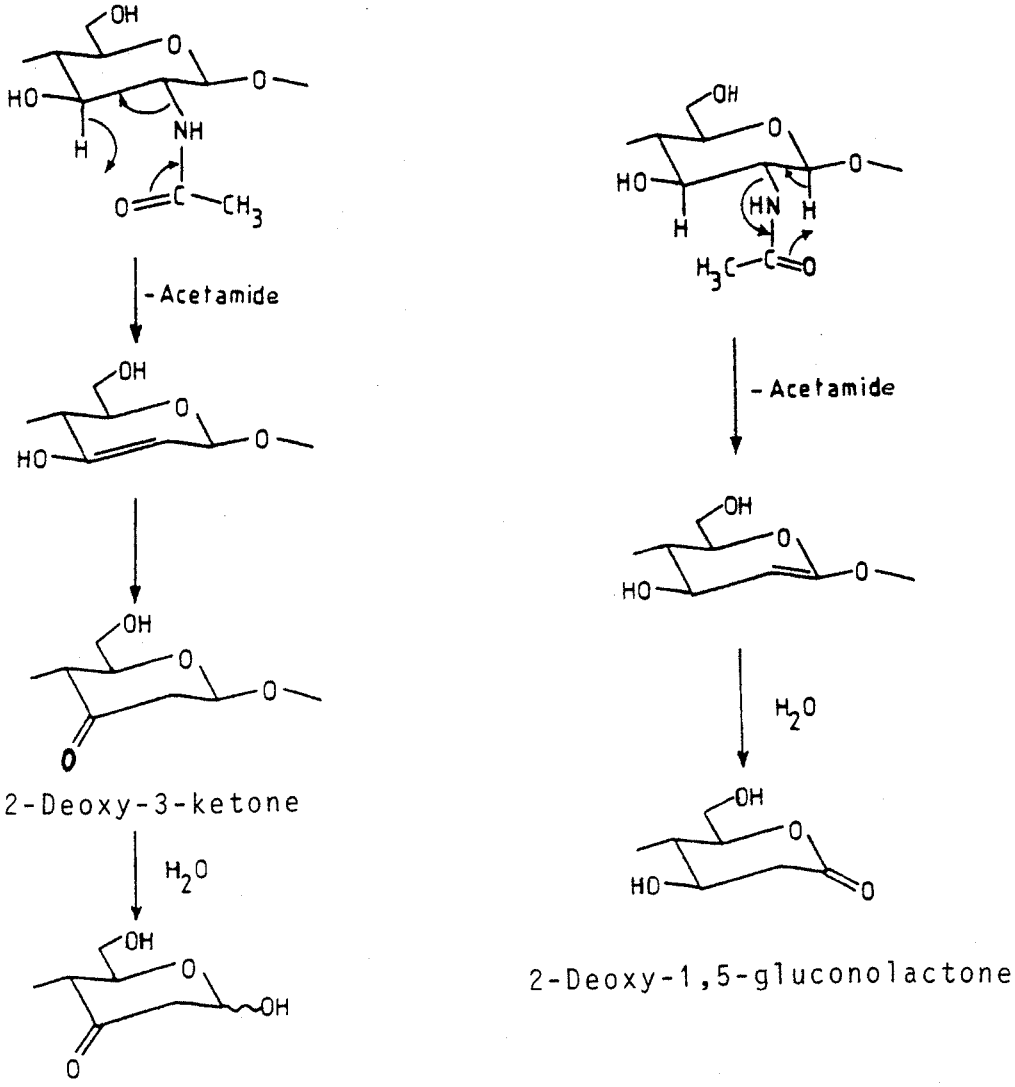


Fig. 2. Thermogram of chitin [5].



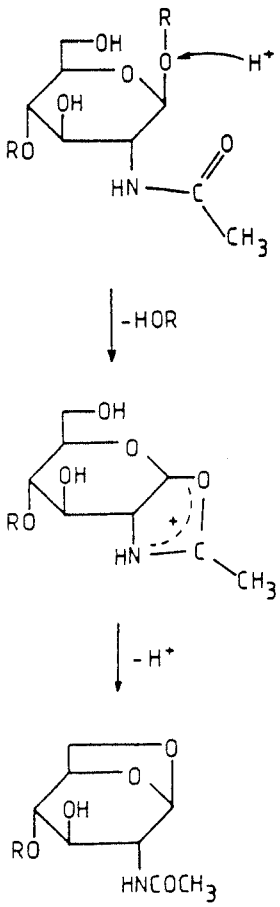
Scheme 1. Possible pericyclic elimination of acetamide from chitin.

However, the residue could not be hydrolysed with either water, acetic acid, or trifluoroacetic acid.

Quantitative correlation of the degree of acetylation and the total weight loss during thermal degradation showed that the elimination of acetamide is only a minor part of degradation (Table 1).

It was thought that the degradation process could be better controlled in the presence of a high boiling and inert solvent because of better heat transfer. Thus, chitin was suspended in tetraethyleneglycol dimethyl ether and heated to 210 °C. Acetamide **6** was found as a volatile degradation product, but again the residue could not be hydrolyzed by weak acids.

However, in this case very interesting water soluble degradation products were observed, i.e. oligomers of 2-acetamidoglucose with a terminal anhydro sugar unit **5**. ^{1}H-NMR spectroscopy provided an estimate of an average degree of polymerization (DP) ≈ 16. GPC showed well-resolved monomer **5a** and oligomers up to the hexamers **5b–5f**, plus higher unresolved oligomers. Preparative GPC yielded monomeric **5a** and oligomeric degradation products **5b–5e** which could be unambiguously characterized by ^{1}H-NMR,



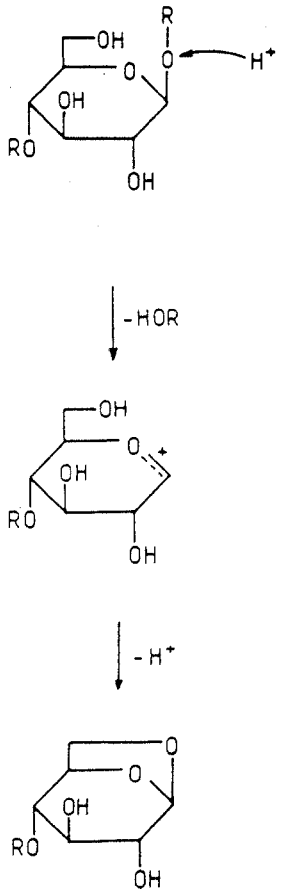
Scheme 2. Acid catalyzed and neighbour group assisted degradation of chitin to give a terminal anhydrosugar unit.

^{13}C-NMR, and FAB-MS. The best yield (18%) of water-soluble oligomers was obtained by degradation at 210 °C for 1 h [9].

We assume that the relatively easy depolymerization of chitin is induced by traces of acetic acid which can be formed from acetamide and water. The rate of depolymerization could be enhanced by the neighbour group activity of the acetamido group (Scheme 2).

Evidence for a neighbour group activity gives a comparison with analogous depolymerization of cellulose. Cellulose was depolymerized as chitin to give oligomers with a terminal anhydroglucose unit **1**, but the reaction rate is slower by some orders of magnitude, because a neighbour group assistance is not possible (Scheme 3). Thus, cellulose yielded after 4 h of degradation time at 250 °C only 4.5% of water soluble oligomers, whereas chitin yielded 18% of oligomers after 1 h at 210 °C [9].

The insoluble residue of chitin obtained by degradation in tetraethylene glycol dimethyl ether was carboxymethylated to allow a gel chromatographic investigation of the degree of depolymerization. Figure 3a gives the GPC of carboxymethyl chitin, and Fig. 3b of the carboxymethylated thermolysis residue. The DP was shifted to lower values, clearly demonstrating a depolymerization by the thermal degradation process.



Scheme 3. Acid catalyzed degradation of cellulose to give a terminal anhydrosugar unit.

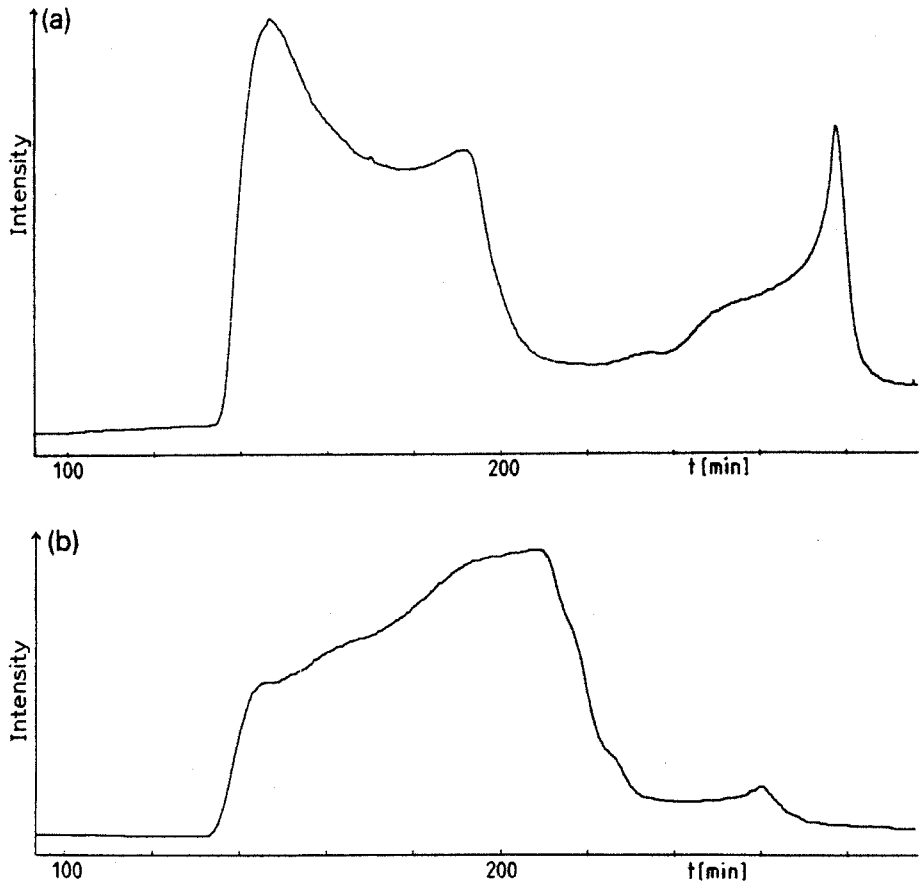
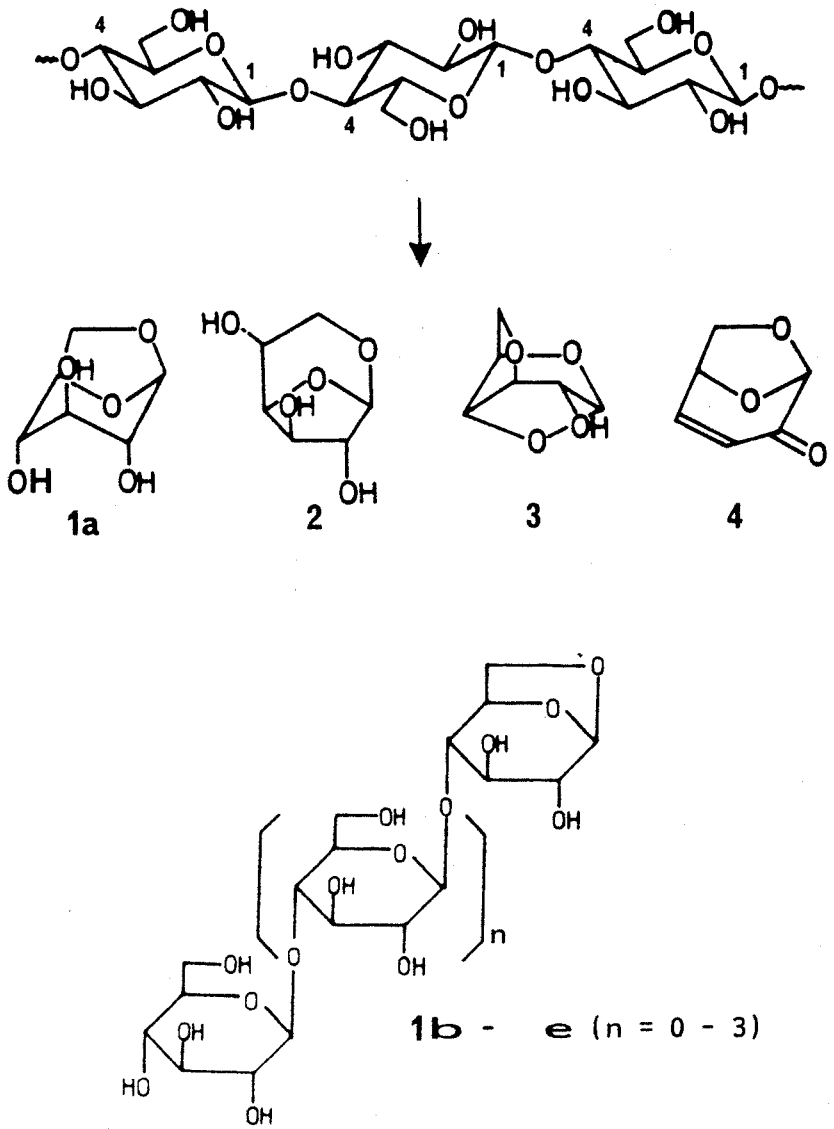


Fig. 3. GPC separation of (a) carboxymethylated chitin and (b) carboxymethylated residue of thermal chitin degradation in tetraethyleneglycoldimethylether as a high boiling and inert solvent.



Scheme 4. Anhydrosugars observed as degradation products of cellulose.

The decisive advantage of the degradation in a high boiling and inert solvent compared to the degradation of dry chitin under nitrogen or in vacuo is obvious. Oligomeric degradation products can be removed from the polymer matrix by dissolution in the solvent, however, they are not volatile enough to be removed with the nitrogen flow or in vacuo. But it is obvious that a more rapid removal of the primary degradation products from the matrix and the reaction zone should be of great advantage, thus avoiding secondary reactions of the oligomers.

To overcome this problem, the good dissolution properties of compressed gases in the supercritical state have been exploited. The apparatus used—a "high pressure–high temperature flow reactor" (HP–HT reactor)—was largely made up of HPLC equipment (Fig. 1) [1].

Thus, cellulose was degraded in supercritical acetone ($T_c = 508.5$ K, $p_c = 47$ bar) to yield 48% of monomeric anhydrosugars (Scheme 4). The yield of glucosan can be regarded as excellent when compared with the yields obtained with customary pyrolysis methods [10] (Table 2). Cellulose was

TABLE 2

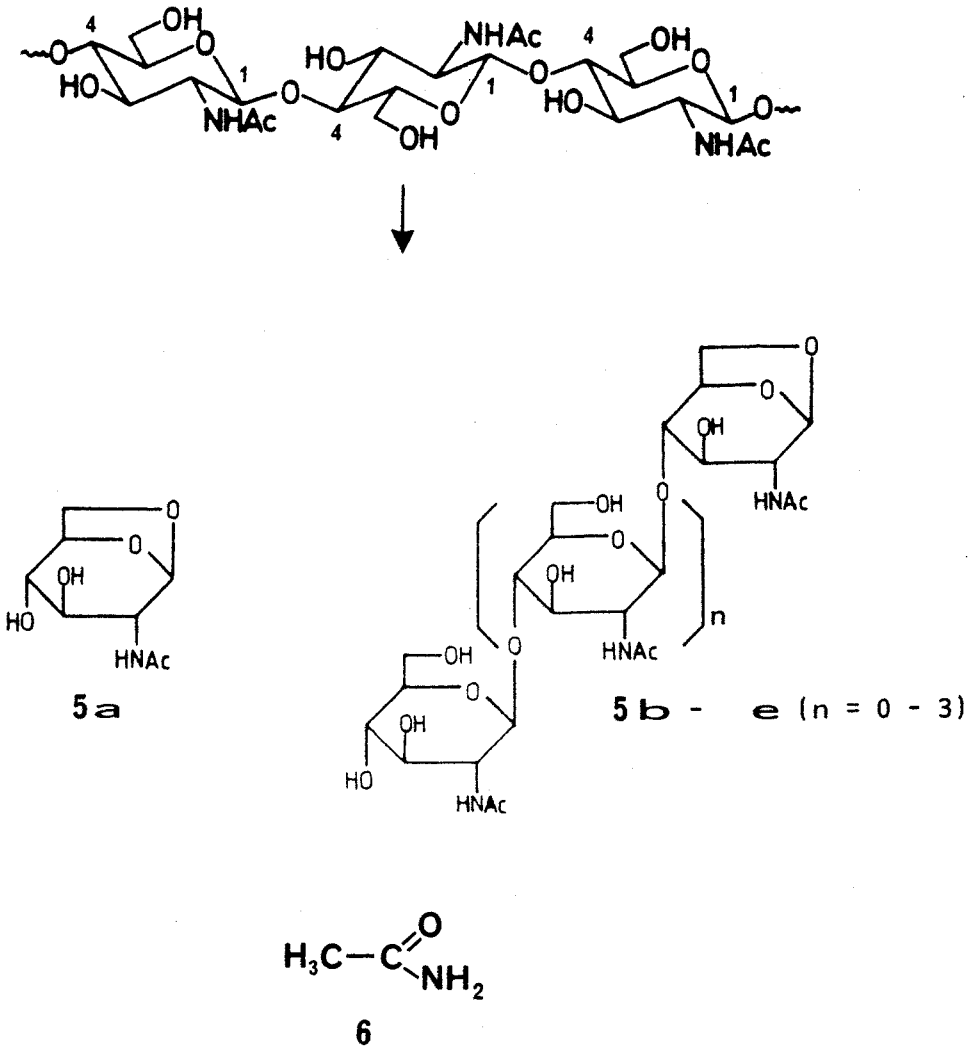
Products from thermal degradation of cellulose by different methods

Product	Conditions		
	Nitrogen 1 bar, 300 °C [a]	Vacuum 2 mbar, 300 °C [a]	Supercritical acetone 250–340 °C [b]
	yield (wt. %) [c]	yield (wt. %) [c]	yield (wt. %) [c]
Char	34.2	17.8	2.1
Tar	19.1	55.8	101
Glucosan **1a**	3.6	28.1	38.3
1,6-Anhydro-β-D-glucofuranose **2**	0.4	5.6	4.3
1,4:3,6-Dianhydro-α-D-glucopyranose **3**	– [d]	– [d]	4.0

[a] Data taken from [10]; [b] this work; [c] the percentages are based on the original amount of cellulose; [d] not observed.

almost quantitatively degraded; there remained an extraction residue of only 2%.

Unfortunately, the degradation syrups have not yet been analyzed with



Scheme 5. Anhydrosugars and acetamide observed as degradation products of chitin.

respect to oligomeric sugars. But it seems likely that an important part of the unidentified degradation products are oligomers, as suggested by the experiments of degradation in inert solvents.

Chitin was degraded in the same way as cellulose (Scheme 5). The residue amounted to 15.3%. The main monomeric sugar component 2-acetamido-1,6-anhydro-2-deoxy-β-D-glucopyranose **5** was recoverable from the water soluble extract of the syrup in 5.6% overall yield (based on the charged chitin) and in 9% yield (based on the available acetamidogroups; degree of acetylation 0.62). The actual amount of this sugar in the pyrolysate is higher, but further recovery by crystallization is rendered difficult by the degree of contamination with acetamide. From the chloroform extract of the degradation syrup numerous nitrogen heterocycles were identified in minor amounts by GC/MS, e.g. *N*-acetylpyrrole, *N*-acetylpyrrolidine, 2-formylpyrrole, and 2-formyl-5-methyl-pyrrole [11].

CONCLUSION

Monomeric and oligomeric anhydrosugars are primary degradation products of chitin and cellulose. The rate of depolymerization of chitin was enhanced due to the neighbour group assistance of the acetamido group in comparison to cellulose. Thermal elimination of acetamide from chitin was also observed. The yield was up to 50% of the available acetamido groups. The best way for thermal depolymerization of polysaccharides seems to be the degradation in a supercritical solvent, e.g. acetone, in a high pressure–high temperature flow apparatus. This method may also be applicable to other polysaccharides, allowing the isolation and separation of other monomeric and oligomeric sugars with a terminal anhydropyranose unit.

ACKNOWLEDGEMENT

The authors wish to express their thanks to the Deutsche Forschungsgemeinschaft for the financial support of this work.

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