



Fig. 1. Schematic diagram of the apparatus. 1) Solvent reservoir; 2) high-pressure pump for up to 500 bar (HPLC pump); 3) excess-pressure valve; 4) manometer for up to 600 bar; 5) T-piece; 6) pre-heater capillary (diameter 1.6 mm); 7) reactor ( $V=50$  ml), 8) valve; 9) heat exchanger (1.6 mm-diameter capillary); 10) collector; 11) GC furnace.

### Thermal Degradation of Cellulose and Chitin in Supercritical Acetone

By Peter Köll and Jürgen Metzger<sup>[\*]</sup>

In the thermal degradation of polysaccharides rapid removal of the primary products from the reaction zone is a decisive prerequisite for the use of this reaction on a preparative or industrial scale as regards obtaining a high-yield uniform product pattern. Customary pyrolysis methods lead, particularly on a large-scale, to secondary reactions accompanied by strong carbonization. This cannot be entirely avoided, even if the reaction is carried out *in vacuo*; moreover, the pyrolysis is then rendered difficult by the poor transfer of heat.

To overcome this problem, we have for the first time exploited the good dissolution properties of compressed gases in the supercritical state<sup>[1]</sup> in a flow apparatus. With this method we have been able to detect—to our knowledge for the first time—the primary product of the thermal degradation of chitin<sup>[2]</sup>, namely 2-acetamido-1,6-anhydro-2-deoxy- $\beta$ -D-glucopyranose<sup>[3]</sup>, an important amino sugar used as starting substance for the synthesis of physiologically active oligosaccharides<sup>[4]</sup>, and to isolate it on a preparative scale. Furthermore, cellulose could be degraded to the extent of 98%.

The apparatus used (Fig. 1) was largely made up of HPLC equipment; a GC furnace was used for heating. Acetone ( $T_c=508.5$  K,  $P_c=47$  bar) proved to be especially suitable as aprotic solvent. In a typical experiment, 18 g of microcrystalline cellulose (Merck; dry weight 17.1 g) was transferred to a preparative HPLC column and treated at a pressure of 250 bar with acetone at an average flowrate 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 only 0.36 g (2.1%). Concentration of the acetone solution *in vacuo* gave 18.3 g of a dark syrup, which was shown by thin-layer chromatography to consist mainly of low molecular products. The mass balance exceeded 100%, since small amounts of difficultly volatile condensation products of acetone are also formed during the reaction. However, since evolution of gases during the reaction is very slight, it can be assumed that approximately 98% of the cellulose is in fact liquefied. The main products could be identified, in particular, as anhydro-sugars 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 XE60,  $T=473$  K, injection block 523 K, 20 ml He/min, triacetyl-1,6-anhydrogalactofuranose as internal standard): 38.8% 1,6-anhydro- $\beta$ -D-glucopyranose ("glucosan"), 4.3% 1,6-anhydro- $\beta$ -D-glucofuranose, 4.0% 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose, ca. 1% 1,6-anhydro-3,4-dideoxy- $\beta$ -D-glycero-hex-3-enopyranos-2-ulose.

The yield of glucosan can be regarded as excellent when compared with the yields obtained on vacuum pyrolysis<sup>[5]</sup>. The cellulose is extraordinarily gently degraded by acetone,

[\*] Prof. Dr. P. Köll, Dr. J. Metzger  
Fachbereich 4 (Naturwissenschaften) der Universität  
Ammerländer Heerstrasse 67–99, D-2900 Oldenburg (Germany)

despite the high temperature. Thus, according to diffractometer measurements the residue still has the crystallinity of the starting cellulose even after 50 % degradation. Nor do scanning electron photomicrographs show any serious changes in the structure at this stage of the degradation.

Chitin (Fluka, techn., ash content 5 %; 15.0 g) was degraded in the same way as cellulose in the temperature range 250—340°C at 250 bar by acetone at a flow rate of 5.0 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. Additional thin-layer chromatography showed the presence of 1,6-anhydro-3,4-dideoxy- $\beta$ -D-glycero-hex-3-eno-pyranos-2-ulose. Partition of the syrup between water and chloroform afforded 4.1 g of water-soluble product and 12.3 g of chloroform extract. The main sugar component 2-acetamido-1,6-anhydro-2-deoxy- $\beta$ -D-glucopyranose<sup>[3]</sup> 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 eluent. 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. However, in view of the ready accessibility of the starting material and the relative ease with which the reaction and isolation can be carried out, the yield is nevertheless preparatively acceptable.

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Cellulose, 9004-34-6; chitin, 1398-61-4; 1,6-anhydro- $\beta$ -D-glucopyranose, 9012-72-0; 1,6-anhydro- $\beta$ -D-glucofuranose, 7425-74-3; 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose, 4451-30-3; 1,6-anhydro-3,4-dideoxy- $\beta$ -D-glycerohex-3-enopyranos-2-ulose, 37112-31-5; 2-acetamido-1,6-anhydro-2-deoxy- $\beta$ -D-glucopyranose, 37042-52-7

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