CHEMISTRY LETTERS, pp. 1361-1362, 1974. Published by the Chemical Society of Japan

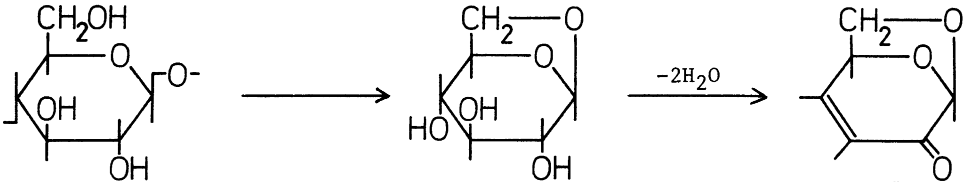
IDENTIFICATION OF 1,6-ANHYDRO-3-DEOXY-β-D-GLUCOPYRANOSEN AS A THERMAL DECOMPOSITION PRODUCT OF CELLULOSE

Akio OHNISHI, Eriko TAKAGI, and Kunio KATŌ
Central Research Institute, The Japan Tobacco & Salt Public Corporation
6-2 Umegaoka, Midori-ku, Yokohama 227

1,6-Anhydro-3-deoxy-β-D-glucopyranosen (I) was isolated from liquid pyrolysate of cellulose by GLPC and identified from IR, UV, mass and NMR spectra. It seems to be a thermal decomposition intermediate between levoglucosan (II) and levoglucosenone (III).

Thermal decomposition of cellulose has widely been investigated, and various decomposition products, such as furans, aldehydes, ketones, organic acids, lactones, phenols, aromatic and aliphatic hydrocarbons and water, have been identified by chromatographycal techniques1,2).

Recently, Halpern et al.3) have reported levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-pyranosen-2-one) (III) as a major product of acid-catalysed pyrolysis of cellulose and speculated the following scheme for the formation of III.



Cellulose II III

Levoglucosan (1,6-anhydro-β-D-glucopyranose) (II) has already been confirmed in 1918 as a thermal decomposition product of cellulose by Pictet and Sarasin4), so the identification of certain intermediate compound between II and III has been desired for the establishment of the mechanism of thermal decomposition of cellulose.

In the course of our studies on the pyrolysis of carbohydrates, a new volatile compound was observed as a thermal decomposition product of cellulose. The isolation and identification of the compound confirmed the structure to be 1,6-anhydro-3-deoxy-β-D-glucopyranosen (I), and this paper deals with the results.

A 10 g sample of microcrystalline cellulose (Avicel, for column chromatography, Asahi Chemical Industry Co., Ltd., Tokyo) was pyrolysed in a Pyrex glass tube (15 × 200 mm) at 300-360 °C for 1 hr under reduced pressure (1 mmHg), and the yielded dark reddish syruppy distillate was extracted with ethyl acetate repeatedly. The extract was concentrated and an aliquot of the concentrate was injected into a Hitachi model 063 gas chromatograph equipped with a flame ionisation detector using a 5 % Carbowax 20M on Chromosorb G AW (60/80 mesh) column (stainless steel, 3 mm × 3 m). Helium was used as a carrier (60 ml/min) and the column temperature was elevated from 80 °C to 230 °C at the rate of 7.5 °C/min. The chromatogram obtained is shown in Fig. 1. The fraction of the unknown peak (A) was collected using the same instrument with a

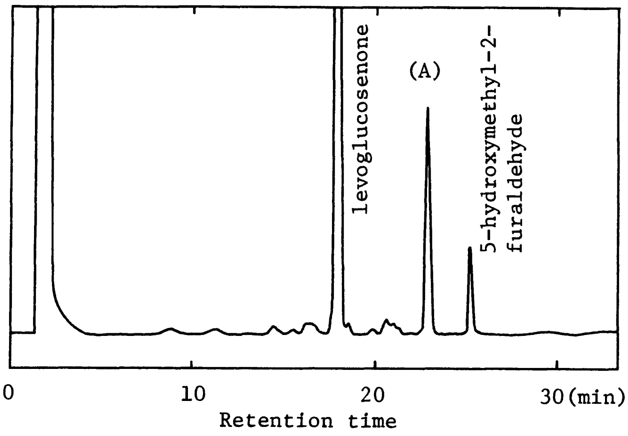
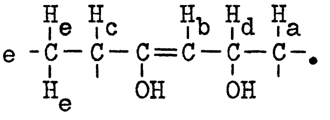


Fig. 1. Gas liquid phase chromatogram of ethyl acetate extract from cellulose pyrolysate using a Carbowax 20M column.

thermal conductivity detector, and further purified by recrystallization from ethyl acetate. The pure compound was obtained as water-soluble fine white crystals: mp 130-131 °C, $[\alpha]_D^{20} = +86^\circ$ (C_2H_5OH, c= 0.6).

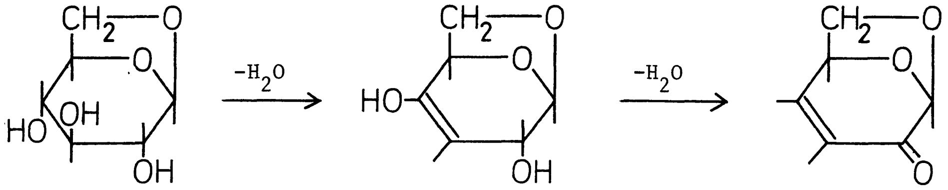
Anal. Found: C, 49.88; H, 5.57 %. Calcd. for $C_6H_8O_4$: C, 50.00; H, 5.59 %. IR (KBr) 3345 (ν_{O-H}); 3020, 2950, 2890 and 2870 (ν_{C-H}); 1060 (ν_{C-O}) cm^{-1}. UV_{max} (C_2H_5OH) 275 (ε 75) nm. Mass spectrum (70 eV) m/e 144 (M^+), 114, 99, 98, 86, 85, 73, 71, 70, 69, 60, 57, 55, 43, 42, 41, 39, 31, 29, 28, 27 and 18. NMR (CD_3SOCD_3) δ 5.36 (d,1; H_a), 5.23 (m,1; H_b), 4.18 (m,1; H_c), 4.05 (q,1; H_d), 3.91 (d,2; H_e) and 3.40 (m,2; $-O\underline{H}$) ppm; J_{ad}= 1.1, J_{bc}= 3.1, J_{bd}= 4.8 and J_{ce}= 1.6 Hz.

The IR spectrum suggested the existences of $-CH_2-$ and -C-O-C-, and the UV spectrum suggested the absence of any conjugated olefinic bonds. In the NMR spectrum, the addition of D_2O resulted in the disappearance of the signal at 3.40 ppm, indicating the existence of two -OH groups. These results in the mesurement of NMR spectrum suggested the structure



$$-\overset{H_e}{\underset{H_e}{C}}-\overset{H_c}{\underset{|}{C}}-\underset{OH}{C}=\overset{H_b}{C}-\overset{H_d}{\underset{OH}{C}}-\overset{H_a}{\underset{|}{C}}-.$$

These data satisfied the formula I, and any other configurations were found to be inconstructable by the use of molecular models. Heating of I in pyrolysis-GLPC showed a conversion to III. Thus the compound I seems to be the intermediate between II and III, and the following scheme will be presented for the formation of III.



II I III

The details of these related experiments and further studies will be published elsewhere in the near future.

References

1) F. Shafizadeh, Advances in Carbohydrate Chemistry, $\underline{23}$, 419 (1968).
2) F. Shafizadeh, J. Polymer Sci. Part C, $\underline{36}$, 21 (1971).
3) Y. Halpern, R. Riffer and A. Broido, J. Org. Chem., $\underline{38}$, 204 (1973).
4) A. Pictet and J. Sarasin, Helv. Chim. Acta, $\underline{1}$, 78 (1918).

(Received September 2, 1974)