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Curie-Point Pyrolysis of Cellulose*

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ABSTRACT: Microcrystalline cellulose was pyrolysed using a Curie-point pyrolyser, directly attached to a GLC apparatus, at 460°C for 5 sec under a neat condition without any additives. Although the total yield of organic volatile fraction was not so high, 2-furaldehyde and levoglucosenone were observed as the major components in this fraction. Another volatile product, 1,6-anhydro-3-deoxy-β-D-glucopyranosen, was also identified as the intermediate between levoglucosan and levoglucosenone. Levoglucosan could not be directly detected by the pyrolysis—GLC technique because of its low volatility, but it was thought to be one of the major components of the tar produced. Only slight amounts of these anhydro sugar homologues were observed in the Curie-point pyrolysis with D-glucose, cellobiose, cellotriose, cellotetraose, cellopentaose, and cellohexaose, though furans were abundantly observed in the volatile fractions. These results suggest the following two paths for the thermal decomposition reaction of cellulose at the initial stage:

Cellulose → Levoglucosan, 1,6-anhydro-3-deoxy-β-D-glucopyranosen, and levoglucosenone

Cellulose → 5-Hydroxymethyl-2-furaldehyde, 2-furaldehyde, and other furan compounds

KEY WORDS Cellulose / Cello-Oligosaccharide / Pyrolysis / Thermal Decomposition / Curie-Point Pyrolyser / Levoglucosan / 1,6-Anhydro-3-Deoxy-β-D-Glucopyranosen / Levoglucosenone / 2-Furaldehyde / 5-Hydroxymethyl-2-Furaldehyde /

Thermal decomposition of cellulose has been widely investigated by many workers.[1] Among the chemical approaches used to elucidate the mechanisms of the thermal decomposition reaction of cellulose, the isolation and the analysis of certain intermediate products may give the most valuable clues.

As early as in 1918, levoglucosan (1,6-anhydro-β-D-glucopyranose) (I) was reported as an important product in the pyrolysis of cellulose by Pictet and Sarasin.[2] This compound has also been recognised in the pyrolysis of starch[2] and D-glucose,[3,4] and has been believed for a long time to be a major intermediate product of the thermal decomposition of these carbohydrates.

Recently, Tsuchiya and Sumi[5] isolated a liquid compound, $C_6H_6O_3$, as a main component of the volatile fraction in the acid-catalysed pyrolysis of cellulose, and Halpern, *et al.*,[6] identified this compound as levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-glucopyranosen-2-one) (III). It thus becomes very interesting to discuss the thermal decomposition mechanism of cellulose, although these experiments were not carried out in a neat condition, because III can be formed by the elimination of two molecules of water from I.

On the other hand, Katō and Komorita[7] suggested 3-deoxyglycosulose (IV), as one of the significant decomposition intermediates which would lead to the formation of furan compounds, such as 5-hydroxymethyl-2-furaldehyde, furfuryl alcohol, and 2-furaldehyde.

However, most of these suggestions were based on the results obtained through a relatively long time exposure of the decomposition products in a hot furnace, which would bring about successive reactions of the primary products: such as dehydration, decarboxylation, depolymerization, condensation, and fragmentation. Accordingly,

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the GLC patterns finally observed would be considerably different from those of the primary product only.

To obtain the real primary decomposition products of cellulose and related compounds, the authors have applied a Curie-point pyrolysis—GLC (CPP—GLC) which was developed by Simon, *et al.*,[8] in 1967. In this procedure, samples are momentarily heated to a fixed temperature and kept at the temperature for a few seconds in an inert carrier gas atmosphere which is maintained at a relatively low temperature, so successive reactions of the primary products due to excess heating are almost totally avoided.

In this paper, III, II, 2-furaldehyde, and 5-hydroxymethyl-2-furaldehyde have been identified in the volatile fraction of the primary decomposition products in the Curie-point pyrolysis of cellulose, and the mechanism of the thermal decomposition reaction is discussed. Also the conventional methods for the preparation of II and III are described.

EXPERIMENTAL

Samples

Commercial microcrystalline cellulose powder (Avicel, for column chromatography, Asahi Chemical Industry Co., Ltd., Tokyo) was used as the standard cellulose sample after being treated with 1-*N* HCl at 85°C for 30 min, washed with water repeatedly, and dried over phosphorus pentoxide.

Levoglucosan (I) was prepared and purified by the usual method.[9]

Cello-oligosaccharides (cellobiose, cellotriose, cellotetraose, cellopentaose, and cellohexaose) were prepared as follows: The cellulose sample was acetolysed[10] at 40°C for 24 hr. The resultant acetolysate was saponified with 0.2-*N* $NaOCH_3$ in methanol, and the white precipitate was collected, dissolved in water, and deionised with Dowex 50W. A portion of the aqueous solution was charged on a Sephadex G 25 (fine) column (15×1450 mm) and the column was eluted with water. The fractions containing the individual oligosaccharide were combined, and each was evaporated to dryness. The individual residues were crystallised from methanol or water—methanol, respectively.

Instrumentation

The CPP—GLC was carried out by a Shimadzu model PYR-10 Curie-point pyrolyser directly combined with 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). A typical CPP—GLC was carried out under the following conditions:

Sample weight, 0.2—0.4 mg; pyrolysis temperature, 460°C; heating period (oscillation period), 5 sec; atmosphere, He (containing O_2 less than 2 ppm); flow rate, 40 ml/min; column oven temperature, 80—230°C (7.5°C/min).

A Shimadzu model PYR-2A furnace-type pyrolyser was also used as a reference for the Curie-point pyrolyser; in this procedure a 0.2-mg sample fixed on a sample holder was quickly inserted into the furnace kept at a fixed temperature, and as soon as the temperature of the sample reached 460°C the holder was taken out from the furnace.

For the preparative-GLC operation, a Hitachi model K 23 gas chromatograph equipped with a thermal conductivity detector was used under isothermal conditions; a 10-% Carbowax 20 M on Chromosorb W AW (60/80 mesh) column (stainless steel, 3 mm×2 m) was used.

The NMR, mass, IR, and UV spectra were measured using a JEOL model JNM-PS-100, a Hitachi model RMU-7, a JASCO model IR-G, and a Hitachi model 124, respectively. The optical rotations were measured on a Yanaco model OR-50D, and the elementary analyses were carried out on a Yanaco model MT-2.

Preparation of 1,6-Anhydro-3-Deoxy-β-D-Glucopyranosen (II)

The cellulose sample was pyrolysed in a Pyrex glass tube at 300—360°C for about 1 hr under reduced pressure (1 mmHg). The resultant dark reddish syruppy distillate was extracted with ethyl acetate repeatedly. The extract was concentrated and fractionated with a silicic acid column (15×150 mm) using ethyl acetate as eluant. The fraction corresponding to this compound was collected and treated with activated charcoal. After filtration the clear filtrate was concentrated to an yellowish crude material, which was purified by recrystallization from ethyl

acetate. The pure compound was obtained as water-soluble fine white crystals: mp 130—131°C, $[\alpha]_D^{20}=+86°$ (C_2H_5OH, $c=0.6$).

Preparation of Levoglucosenone (III)

The cellulose sample was treated with a 1-% (v/v) solution of 85-% H_3PO_4, as described by Tsuchiya and Sumi,[5] and pyrolysed by the above method. The resultant liquid pyrolysate was distilled with a microdistillation apparatus under reduced pressure and the fraction of bp 110—120°C (20 mm) was collected. The green-yellowish liquor obtained was almost pure levoglucosenone. For further purification, a preparative GLC was conducted using a 10-% Carbowax 20 M column. The pure compound was obtained as water-insoluble green-yellowish liquor: $[\alpha]_D^{20}=-524°$ (C_2H_5OH, $c=1.0$) [lit.[6] $-460°$ ($CHCl_3$, $c=1.0$)].

RESULTS AND DISCUSSIONS

CPP—GLC with Cellulose

Some typical results of CPP—GLC and furnace-type pyrolysis—GLC (FTP—GLC) with cellulose are shown in Figures 1 and 2, respectively. It is obvious that the chromatogram obtained from the use of a Curie-point pyrolyser (Figure 1) is extremely simple relative to that of the furnace-type pyrolyser (Figure 2). The peaks which appear within 5 min of the retention time correspond to the light gases derived from the primary decomposition products by their further fragmentations. As seen from the figures, both the members and contents of the light gases in the CPP—GLC are much less than those in the FTP—GLC. Moreover, it is very interesting to notice that in the case of CPP—GLC, only two components, peaks A and B, are particularly dominant in the volatile fraction. These two components seem to be the primary products of the thermal decomposition of cellulose detectable by the GLC technique. In the case of FTP—GLC, many components other than peaks A and B are observed: these seem to be derived from successive heat reactions of the primary decomposition products.

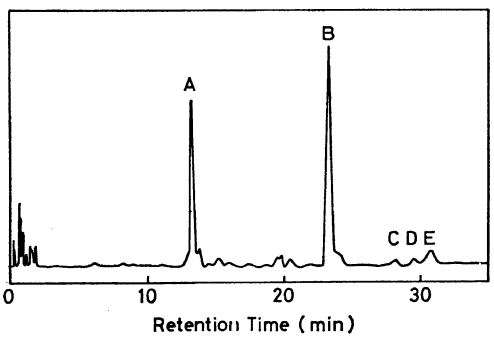


Figure 1. Profile of CPP—GLC with cellulose.

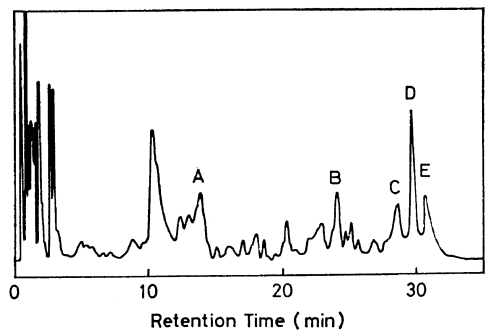


Figure 2. Profile of FTP—GLC with cellulose.

This indicates that in the Curie-point pyrolysis of cellulose, the primary decomposition products, such as the components corresponding to peaks A and B, were detectable without any further successive reactions.

Identifications of Peak Compounds

The compounds corresponding to peaks A, C, and E in Figure 1 were identified as 2-furaldehyde, levulinic acid, and 5-hydroxymethyl-2-furaldehyde, respectively, from their retention times and mass spectrum data.

The peak B compound was identified as levoglucosenone (III) after patient preparation using a preparative CPP—GLC instrument equipped with a thermal conductivity detector.

Anal. Calcd, for $C_6H_6O_3$: C, 57.14; H, 4.76%. Found: C, 57.13; H, 4.77%. IR (NaCl) 3050, 2950, 2880 (ν_{C-H}); 1718, 1690 ($\nu_{C=O}$); 1100 cm^{-1} (ν_{C-O}) (Figure 3). UV_{max} (C_2H_5OH) 217 (ε 6000), 273 (ε 378), 355 nm (ε 85) (Figure 4). NMR (CCl_4) δ 7.11 (q, 1, H_a), 5.96 (q, 1, H_b), 5.15 (d, 1, H_c), 4.89 (m, 1, H_d), 3.78 (m, 1, H_e), 3.96 ppm, (m, 1, H_f) $J_{ab}=10.0$, $J_{ad}=4.6$, $J_{bc}=1.3$, $J_{de}=1.0$, $J_{df}=4.1$, $J_{ef}=6.5$ Hz (Figure 6). Mass spectrum (70 eV) *m/e* 98, 97, 96, 81, 70, 69, 68, 55, 53, 52, 44, 43, 42, 41, 39, 29, 28, 27, 20, 18.

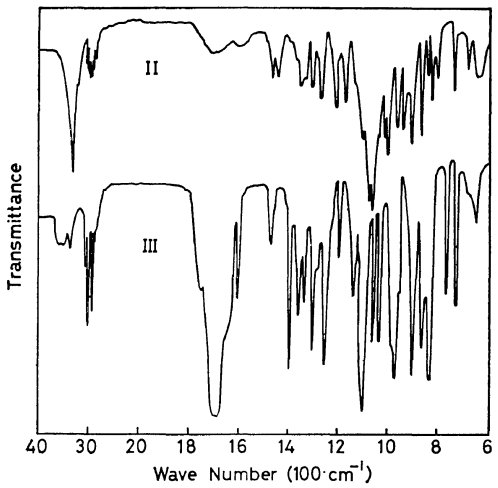


Figure 3. Infrared absorption spectra of (II) 1,6-anhydro-3-deoxy-β-D-glucopyranosen on KBr and (III) levoglucosenone on NaCl.

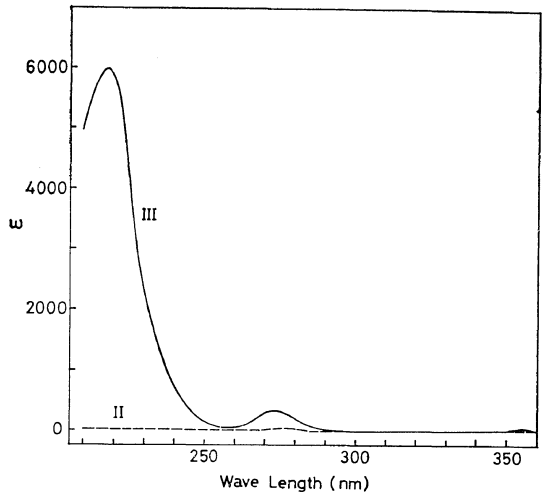


Figure 4. Absorption spectra of (II) 1,6-anhydro-3-deoxy-β-D-glucopyranosen and (III) levoglucosenone in ethanol.

These data precisely agreed with those of the compound prepared from the method mentioned in the experimental section, and seem to be essentially the same as those presented by Halpern, *et al.*[6]

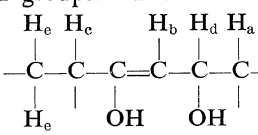
It should be noted that III was the dominant yield, together with 2-furaldehyde, in the case of CPP—GLC under the neat condition without any additives, as in the acid-catalysed pyrolysis of cellulose.[5,6]

The compound III had a smoky odor and made a purple chelate complex with ferric chloride through keto—enol tautomerization. The melting point of the 2,4-dinitrophenylhydrazone (reddish needles from $CHCl_3$) was 214°C (decomp).

The peak D compound was identified as 1,6-anhydro-3-deoxy-β-D-glucopyranosen (II) after the purification mentioned above.

Anal. Calcd, for $C_6H_8O_4$: C, 50.00; H, 5.59%. Found: C, 49.88; H, 5.57%.

In the IR spectrum (KBr), shown in Figure 3, the absorption bands at 3345 (ν_{O-H}); 3020, 2950, 2890, 2870 (ν_{C-H}); and 1060 (ν_{C-O}) cm^{-1} indicated the presence of $-CH_2-$ and $-C-O-C-$, and the absence of C=O. As shown in Figure 4 the UV spectrum (C_2H_5OH), shows no significant absorption except for a minor peak at 275 nm (ε 75) which may be due to the $n-\pi^*$ transition of a small amount of C=O induced by some keto—enol tautomerization, indicating the absence of any conjugated double bonds. The mass spectrum (70 eV), shown in Figure 5, indicated that the molecular weight was 144. The NMR spectrum (CD_3SOCD_3) is shown in Figure 6: signals at 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, OH) ppm; J_{ad}=1.1, J_{bc}=3.1, J_{bd}=4.8, and J_{ce}=1.6 Hz were observed. 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 suggested the structure



. The data precisely agreed with those of the compound

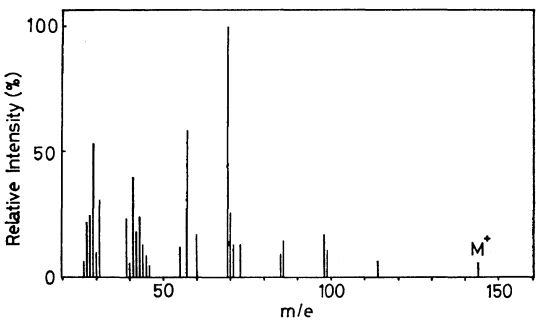


Figure 5. Mass spectrum of 1,6-anhydro-3-deoxy-β-D-glucopyranosen.

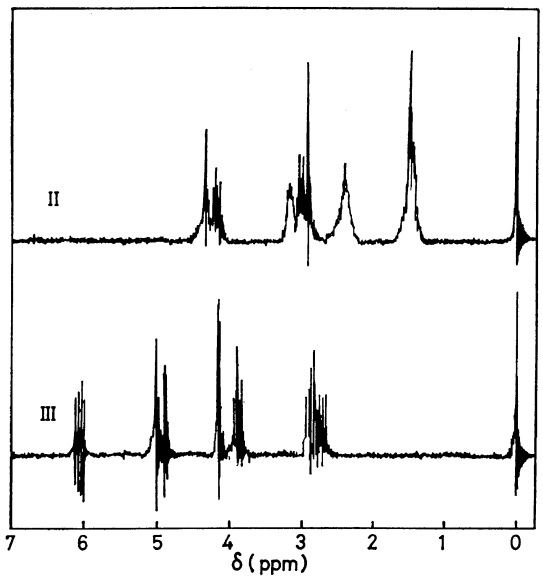


Figure 6. NMR spectra of (II) 1,6-anhydro-3-deoxy-β-D-glucopyranosen in hexadeutero-dimethylsulfoxide and (III) levoglucosenone in carbontetrachloride.

prepared from the method in the experimental section. These assignments satisfied formula II and all other configurations were found to be unconstructable by the use of molecular models.

The CPP—GLC of II showed the formation of III, and on the other hand II was formed from III by storage for several month in air. Accordingly, the compound II seems to be the intermediate between I and III.

The compound III has never been directly observed as the pyrolysis product of cellulose using other pyrolysis—GLC techniques than the CPP—GLC one. The reason for this may be that in the case of CPP—GLC the successive decomposition reactions of III which must occur very rapidly in the other cases were almost avoided by momentarily heating in the relatively low temperature inert atmosphere. Therefore the Curie-point pyrolysis system seems to be very superior to the other usual ones for studying the mechanisms of thermal decomposition reactions.

CPP—GLC with D-Glucose and Cello-Oligosaccharides

As shown in Figure 1, the primary products of thermal decomposition of cellulose were furans (2-furaldehyde and 5-hydroxymethyl-2-furaldehyde) and volatile anhydro sugar homologues (II and III). The result of CPP—GLC with D-glucose is shown in Figure 7. As seen in the figure, the primary decomposition products of D-glucose were mostly furans, and volatile anhydro sugar homologues were rarely observed. The next

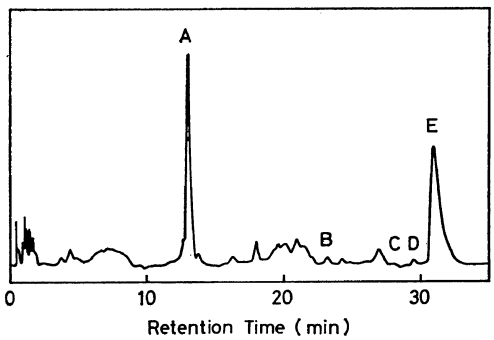


Figure 7. Profile of CPP—GLC with D-glucose.

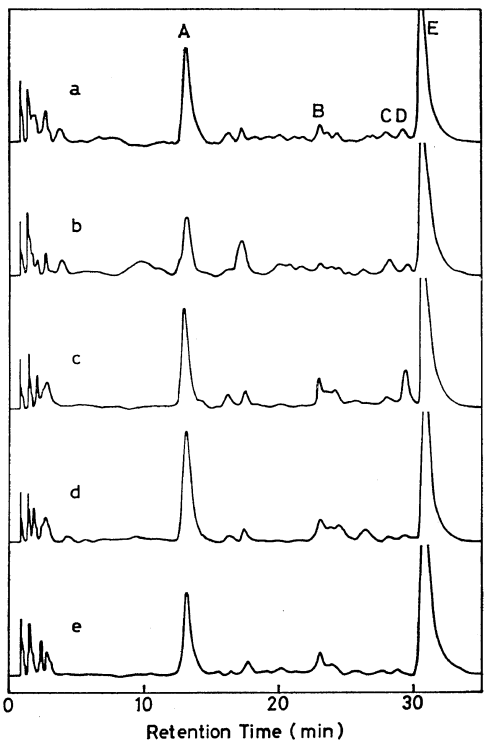


Figure 8. Profiles of CPP—GLC with cello-oligosaccharides: (a) cellobiose; (b) cellotriose; (c) cellotetraose; (d) cellopentaose; (e) cellohexaose.

problem presented was how many β-1,4-glucoside bonds in a molecule are, at the least, required for the formation of II or III as the primary pyrolysis products. To investigate this problem, cellobiose, cellotriose, cellotetraose, cellopentaose, and cellohexaose were prepared and their pyrolitic behaviors were examined.

The results of CPP—GLC with these cello-oligosaccharides are shown in Figure 8, in which the products were mostly furans, and II and III were rarely observed as in the case of D-glucose (Figure 7). Thus a higher degree of polymerization, above seven or more, and probably somewhat higher order conformations will be required for presenting the same decomposition profiles as in the case of cellulose.

Decomposition Mechanism

As shown in Figure 1, the primary products of thermal decomposition of cellulose were both furans and anhydro sugar homologues, whereas those of D-glucose and cello-oligosaccharides were almost exclusively furans, as shown in Figures 7 and 8. Although it has been reported[3,4] that I is produced from pyrolysis of D-glucose in a heated vessel or a glass tube, in most of those experiments D-glucose might first be polycondensated and certain polysaccharides thus formed subsequently decompose into these anhydro sugar homologues.

The result of CPP—GLC with I is shown in Figure 9. The main products were III and II, and no furans were observed. This indicates that I does not play an important role as an intermediate for the formation of furans during the thermal decomposition of cellulose. It is also assumed that whenever I is formed during the decomposition reaction, its homologous compounds II and III would be also produced. Accordingly, when II or III is observed in the volatile fraction of pyrolysates of cellulose, I should be also produced simultaneously although I can not be detected directly by the CPP—GLC method because of its lower volatility.

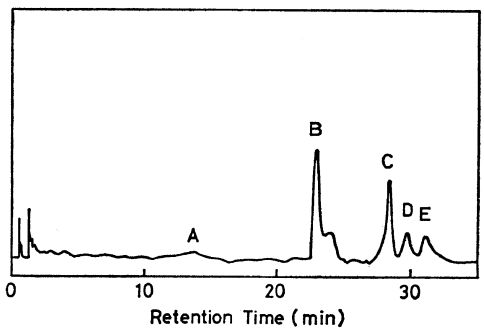
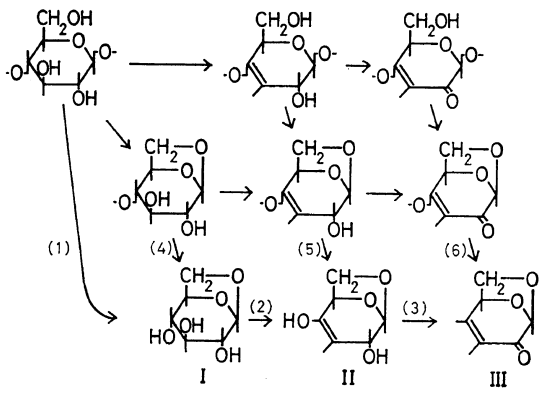


Figure 9. Profile of CPP—GLC with levoglucosan.

The pyrolysis yields of III and 2-furaldehyde were measured as approximately 3 and 2 wt%, respectively, under the conditions of this CPP—GLC technique. The yield of tar condensed on the inside wall of the instrument was approximately 55—75 wt%, in which the major components were thought to be I and such a precursor of 2-furaldehyde as IV. Those of water and the residual char were approximately 5—15 and 15—35 wt%, respectively.

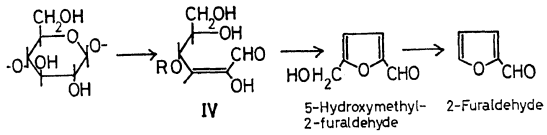
Thus the total yield of organic volatile fraction was not so great, but volatile compounds other than III and 2-fualdehyde were hardly observed at all as seen in Figure 1.

From the above observations the following reaction scheme was suggested for the formation of anhydro sugar homologues as the primary decomposition products of cellulose.



The compounds I, II, and III may be produced not only through the straight paths (1), (2), or (3), but also through the formation of a certain anhydro- and/or deoxy-saccharide moiety in a polymer chain such as the paths (4), (5), or (6). However, no direct evidence for the latter reaction process has been obtained yet.

On the other hand, the following mechanism has been suggested for the formation of furan compounds from cellulose.[7]



The intermediate compound 3-deoxyglycosulose (IV) was identified by Katō and Komorita.[7] The result of CPP—GLC with I (Figure 9), in which furans were only slightly observed, supports strongly the above reaction scheme.

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