

# Curie-point Pyrolysis of Cellulose in the Presence of Potassium Malate

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Finely powdered cellulose was pyrolysed in a Curie-point pyrolyser, which was directly attached to a gas chromatograph and mass spectrometer (CPP-GC/MS), at 358 °C for 5 sec in He (gas) without any additives. The Pyrolysis products were levoglucosenone as the main component, 2-furaldehyde, 1,4:3,6-dianhydro- $\beta$ -D-glucopyranose and 5-hydroxymethyl-2-furaldehyde. However, CPP-GC/MS of cellulose in the presence of potassium malate (5 % as potassium) gave 2-furanmethanol as the main component, and a number of low molecular compounds were formed; e.g., lactones, ketones and furans. A possible new reaction path for cellulose to 2-furanmethanol via D-xylose is presented.

It has been reported that the amount of CO evolved was reduced by about 20% (w/w) when cigarettes were burnt in the presence of potassium malate.<sup>1)</sup> In order to elucidate the effect of adding potassium malate, a pyrolytic study on cellulose was done.

Since the thermal decomposition temperature of cellulose is about 350 °C, an investigation of the conversion of pyrolytic compounds from cellulose was carried out at this temperature. A possible new pathway to the formation of 2-furanmethanol will be presented.

## Materials and Methods

*sample.* Powdered crystalline cellulose (avicel: Asilhi Chemical Industry Co., Ltd.) was used as the cellulose sample. Finely powdered potassium malate (Kanto Chemical Co., Ltd.) was used after having been dried at 80 °C for 1 hr. Levoglucosenone was prepared by the method described by Onishi et al.<sup>2)</sup>

3-Deoxy-2-xylosulose and 3-deoxy-2-glucosulose were obtained from D-Xylose and D-glucose by the method described by Kato.<sup>3)</sup> The other chemicals were of reagent grade and were used without further purification.

*Instruments* A Curie-point Pyrolyser (Nippon Analytical Industry Co., Ltd.: JHP-3) was directly combined with a gas chromatograph and mass spectrometer (Hewlett Packard 5890 GC and 5970 MS). A fused silica

column (0.25mm i.d.  $\times$  30m) was used with surface-bonded polyethylene glycol 20M (DB-WAX from J & W Scientific). Typical conditions for the CPP-GC/MS measurements were as follows: Sample weight .02 - 0.5mg; Pyrolysis temperature, 358 °C; heating period .5sec; atmosphere . He; flow rate of carrier gas, 1.0ml/min; injection temperature . 210 °C; temperature program, the column oven temperature was held at 50 °C for 5min, then raised to 200 °C at a rate of 2 °C/min, and finally held isothermally at 200 °C for 30min; El method, electron energy, 70eV.

*Trimethylsilyl derivatives and their analysis.* After the Curie-Point Pyrolysis was complete the non-volatile condensate on the quartz sample holder and the pyrolytic residue of cellulose with potassium malate in the pyrofoil were each extracted to a glass vial with 30  $\mu$ l of Pyridine. Thirty  $\mu$ l of N,O-bis-TMS-trifluoroacetamide (BSTFA) was added in the former case, and 50  $\mu$ l of BSTFA was added in the latter case. The vial was finally allowed to stand for 40 min at 80 °C so that the Trimethylsilyl(TMS) derivatives could be obtained. One  $\mu$ l of the solution was injected into the GC/MS the column oven temperature being held at 50 °C for 10 min then raised to 210 °C at a rate of 2 °C/min and finally held isothermally at 210 °C for 20min. The GC/MS conditions were the same as those already described except that a fused silica capillary column (0.25mm i.d.  $\times$  12.5m) was coated with dimethyl silicone (Hewlett Packard) and the mass spectrometer was run 10min after injecting the sample in order to avoid contamination of the ion source.

## Results and Discussion

Pyrolysis of cellulose in the presence or absence of potassium malate

A typical result from the CPP-GC/MS of cellulose is shown in Fig. 1. The pyrolytic products of cellulose were 2-furaldehyde (A), Levoglucosenone (1,6-anhydro-3,4-dideoxy- $\beta$ -D-glycero-hex-3-enopyranos-2-ulosic acid; a), 1,4:3,6-dianhydro- $\alpha$ -D-glucopyranose (C), and 5-hydroxymethyl-2-furaldehyde (D). In the case of cellulose alone, anhydro-sugar homologues such as a and C were formed in large quantities, these being the important products from the Pyrolysis of cellulose.<sup>4)</sup>

The CPP-GC/MS result for cellulose in the presence of potassium malate (as 5% potassium) is shown in Fig. 2. In this case, the main component was 2-furanmethanol, and a

number of low molecular compounds were also found: e.g., lactones, ketones and furans. It should be noted that only very small amounts of anhydro-sugar homologues were observed. The presence of potassium malate decreased the formation of anhydro-sugdr and accelerated the formation of various lower molecular compounds.

After the Curie-point Pyrolysis had been conducted, the tar left on the quartz sample tube was collected and converted to TMS derivatives. The GC/MS chromatogram of these TMS derivatives is shown in Fig 3. Levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose; A) and 1,6-anhydro- $\beta$ -D)-glucofuranose (B) were observed in the pyrolytic tar of cellulose, but no similar compounds were observed in the pyrolytic tar produced with potassium malate. similar results were also observed

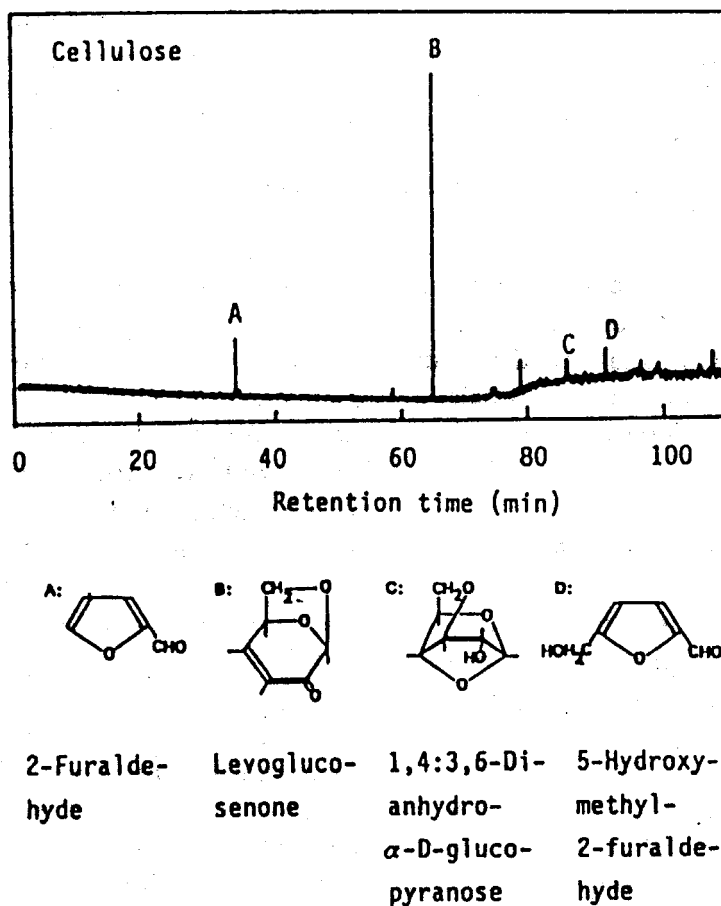
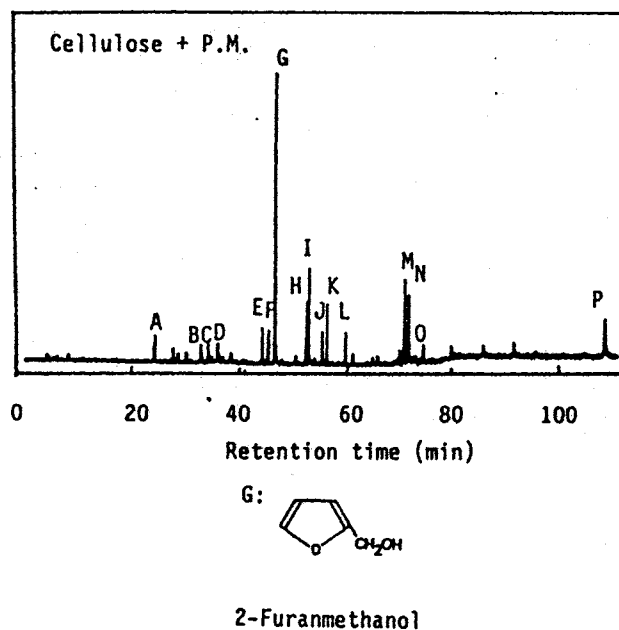


Fig. 1. GC/MS Results from Curie-point Pyrolysis of Cellulose Alone.

CPP conditions: 358°C, 5 sec. GC/MS conditions: column, 0.25 mm i.d. x 30 m fused silica capillary coated with PEG 20M; oven temperature, 50°C (5 min) → 200°C (30 min) at 2°C/min; carrier gas, He (1.0 ml/min) electron energy, 70 eV.



**Fig. 2.** GC/MS Results from Curie-point Pyrolysis of Cellulose in the Presence of Potassium Malate.

A, 1-hydroxy-2-propanone; B, acetic acid; C, 2-furaldehyde; D, unknown; E, propenoic acid; F,  $\gamma$ -butyrolactone; G, 2-furanmethanol; H, crotonolactone; I, cyclopentane-1,2-dione; J, 5-hydroxy-2-cyclopentenone; K, unknown; L, 2-hydroxy-3-ethyl-2-cyclopentenone; M, 2-hydroxy-4-butanolide; N, unknown; O, unknown; P, benzen-1,2-diol.

The CPP and GC/MS conditions are the same as those described in Fig. 1.

ed with the addition of the potassium salt of tartaric, citric, lactic, oxalic or malic acid.

These results suggest that alkaline substances such as potassium malate accelerate the fragmentation of cellulose and contribute to the generation of 2-furanmethanol.

#### *Elucidation of the generation mechanism for 2-furanmethanol*

Molton et al.<sup>5)</sup> reported the thermal degradation of cellulose with sodium carbonate, but they did not note the formation of 2-furanmethanol.

However, the addition of 0.1% by weight of potassium or sodium as the carbonate or hydroxide to cellulose led to furfural derivatives and low molecular weight compounds such as acetaldehyde and acetol.<sup>6)</sup>

When levoglucosan, levoglucosenone, 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde were pyrolyzed in the presence of potassium

malate, 2-furanmethanol was not detected.

The Pyrolysis of D-glucose and D-fructose produced only 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde as the major components. When potassium malate was added, they produced many compounds including 2-furanmethanol. In the case of the pyrolysis of D-xylose alone, 2-furaldehyde was the major product, but with potassium malate, the main product was 2-furanmethanol as shown in Fig. 4.

Kato has suggested that 3-deoxy-2-xylosulose and 3-deoxy-2-glucosulose become significant decomposition intermediates. Which, in turn, would lead to the formation of furan compounds such as 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde.<sup>7)</sup> The pyrolysis of these two intermediates with potassium malate, however, revealed that 2-furanmethanol was produced from 3-deoxy-2-xylosulose, but little was formed from 3-deoxy-2-glucosulose.

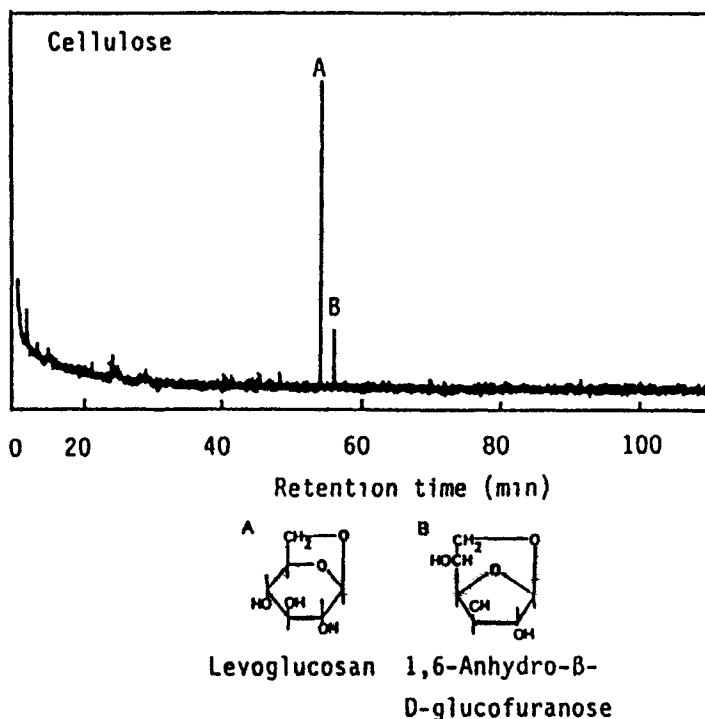


Fig 3 GC/MS Results of the Trimethylsilylated Tarry Pyrolyz ite of Cellulose

GC/MS conditions column 0.25mm i.d x 12.5m fused silica capillary coated with dimethyl silicone oven temperature 50 C (10 min)→210 C (20 min) at 2 C/min carrier gas He (1.0 ml/min) electron energy 70 eV MS was run after 10 min

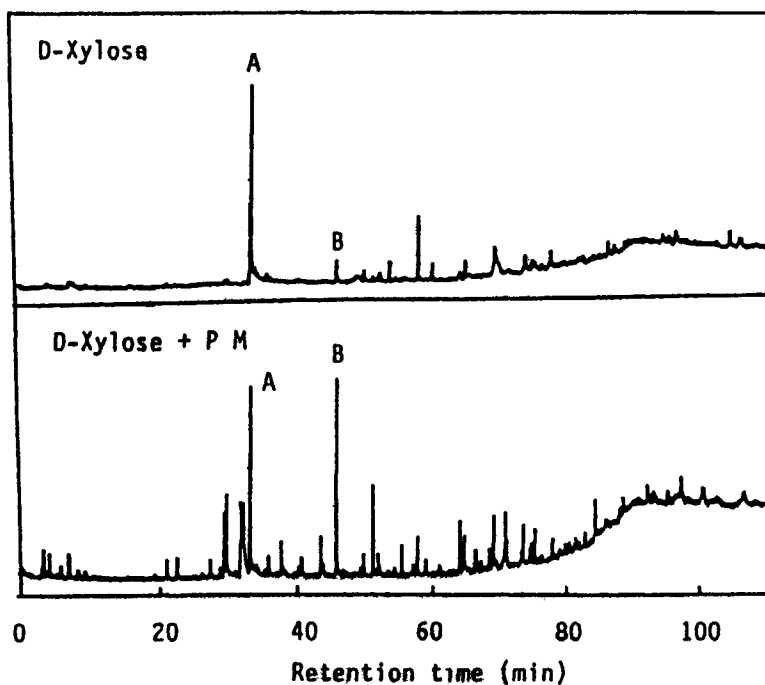


Fig 4 GC/MS Results from Curie point Pyrolysis of D Xylose and D Xylose in the Presence of Pot issium Malte

A 2 furaldehyde B 2 furanmeth inol

The CPP and GC/MS conditions are the same as those described in Fig 1

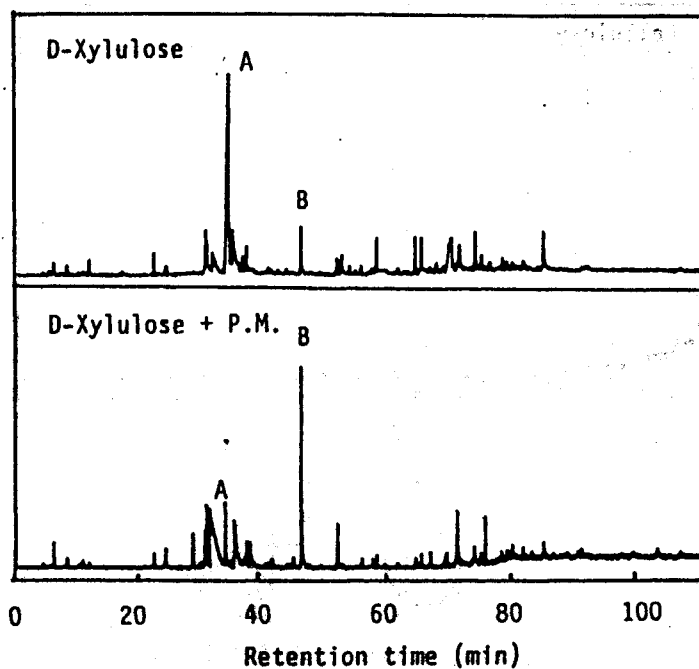


Fig. 5. GC/MS Results from Curie-point Pyrolysis of D-Xylulose and D-Xylulose in the Presence of Potassium Malate.

A, 2-furaldehyde; B, 2-furanmethanol.

The CPP and GC/MS conditions are the same as those described in Fig. 1.

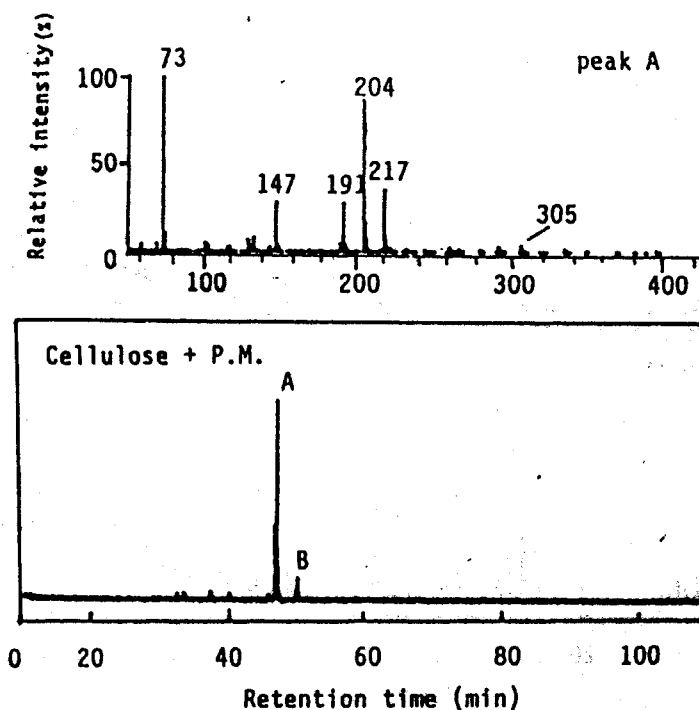


Fig. 6. GC/MS Results for the Trimethylsilylated Pyrolytic Residue of Cellulose in the Presence of Potassium Malate, and the Mass Spectrum of Peak A.

A, 1,2,3,4-tetrakis-O-(trimethylsilyl)-D-xylopyranose; B, unknown.

The CPP and GC/MS conditions are the same as those described in Fig. 3.

When D-xylulose, an Isomeric Compound of D-xylose, was pyrolyzed in the presence of Potassium malate. 2-furanmethanol was one of the main Compounds (Fig. 5) From Figs. 2 and 4. it is Considered that cellulose and D-xylulose would be degraded *via* similar pyrolytic paths in the presence or potassium malate

In general, 2-furaldehyde is converted into 2-furanmethanol and 2-furancarboxylic acid by Cannizzaro's reaction. However, in the present case, 2-furancarboxylic acid (82.9 min retention time) was not found, and the present reaction was assumed not to be a Cannizzaro case.

D-Xylose was detected in the pyrolytic residue of cellulose with potassium malate by a

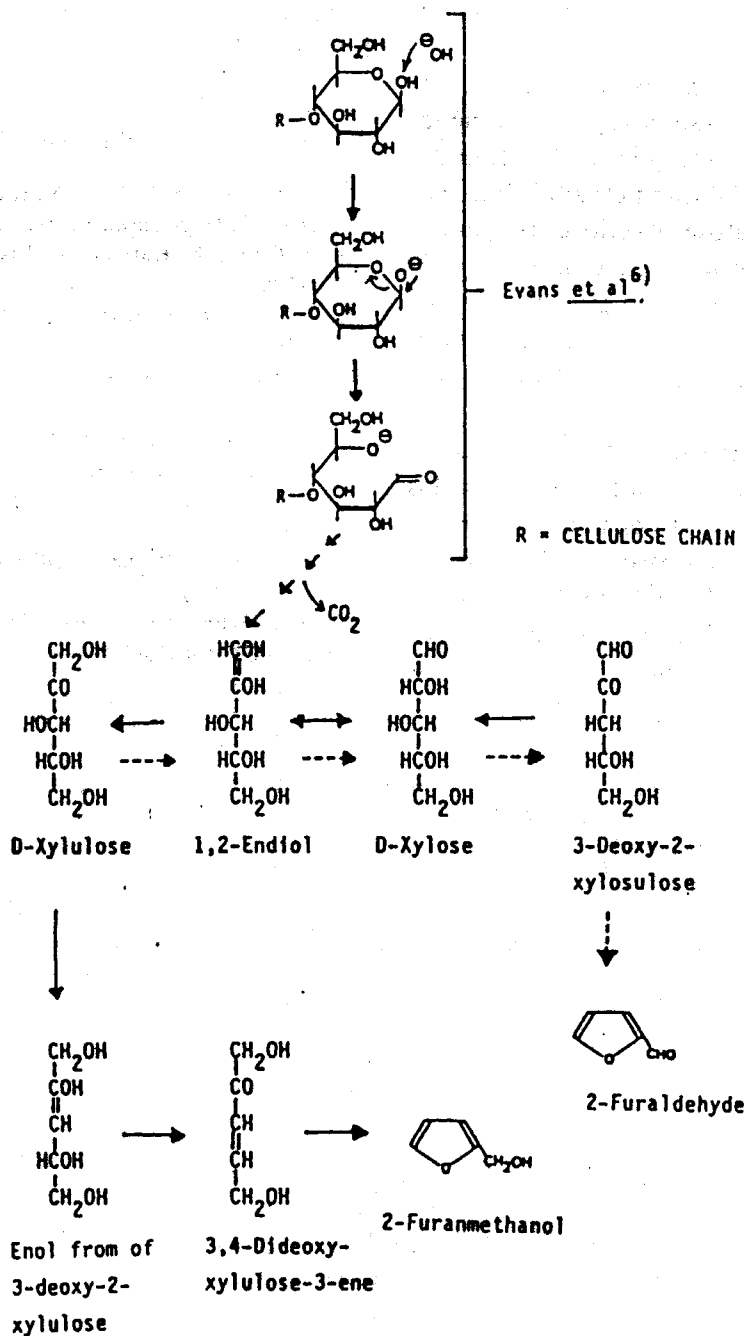


Fig. 7. Possible Formation Pathway for 2-Furanmethanol during the Pyrolysis Reaction. —, in the presence of potassium malate; ----, in the absence of potassium malate.

TMS derivative analysis. However, D-xylulose was not found by this method, as shown in

Fig. 6. which may have been due to the fact that D-Xylulose is not stable against heat.

#### *A possible formation pathway for 2-furan-methanol*

Evans et al.<sup>6)</sup> proposed that cellulose decomposes to form substituted furans with intermolecular dehydration in the presence of alkali-metal.

In the presence of potassium malate, the pyrolysis of levoglucosan, levoglucosenone, 5-hydroxymethyl-2-furaldehyde and 2-furaldehyde did not form 2-furanmethanol, but that of D-glucose, D-fructose, D-xylose, D-xylulose and 5-deoxy-2-xylosulose decomposed to 2-furanmethanol. However, D-glucose and D-fructose are not considered to have been precursors of 2-furanmethanol because it was not found in the pyrolytic residue (Fig. 6).

From these observations, the assumed reaction path for cellulose to 2-furanmethanol is presented in Fig. 7. It is considered that cellulose would be decomposed to 1,2-endiol by decarboxylation via dehydrated cellulose derivatives, and that 1,2-endiol would be transformed to D-xylose and/or D-xylulose by

aldose-ketose isomerization (Lobry deBruyn-Alberda von Ekenstein transformation).<sup>8)</sup>

When potassium malate was added, D-xylose could be transformed to D-xylulose, which makes 2-furanmethanol. Here, it has been taken into consideration that no aldehyde group would be necessary to form 2-furanmethanol. On the other hand, when no potassium malate was added, D-xylulose is liable to be transformed to D-xylose, which makes 2-furaldehyde.

#### References

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