

CHARACTERIZATION OF MONO- AND OLIGOSACCHARIDES PRODUCED
BY CO₂ LASER IRRADIATION ON CELLULOSE

Jun SUZUKI,[†] Jun-ichi AZUMA,^{*} Tetsuo KOSHIJIMA, Keizo OKAMURA,[†]
and Hajime OKAMOTO[†]

Section of Wood Chemistry, Wood Research Institute, Kyoto
University, Gokasho, Uji, Kyoto 611, and [†]Department of Wood
Science and Technology, Faculty of Agriculture, Kyoto University,
Kitashirakawa-Oiwake-cho, Sakyo-ku, Kyoto 606

The chemical structures of three mono-, two di-, and two tri-
saccharides (1~7) isolated from the pyrolysis products formed by
CO₂ laser irradiation on cellulose were investigated.

A unique characteristic of laser light lies in its coherence of waves unlike the waves from ordinal light source. It is also remarkably intense, directional and chromatically pure. The wavelength of CO₂ laser beam is in the infrared region at 10.6 μm .^{1,2)} Although metals are very highly reflective at this wave length, many other materials such as glass, quartz, plastics, wood and paper are capable of highly absorbing at this wave length, so that they can be cut, drilled or machined very effectively with CO₂ laser. Previous studies on paper cut by laser beam showed that fibrillar structure was apparently disappeared and bubbles of about 2~3 μm in diameter were appeared at the edge of the cut paper.³⁾ Although various chemical and mechanistic interpretations have been made on the conventional vacuum pyrolysis of cellulose,⁴⁻⁶⁾ little is known of the nature and mechanism of pyrolytic reactions caused by irradiation of laser beam. In this letter, we wish to describe the chemical structures of mono- and oligosaccharides produced by CO₂ laser irradiation on filter papers.

Toyo No. 7 filter paper (ash content 0.07%, basis weight 70 g/cm²) was cut by a CO₂ laser beam (Photon Sources Model 500 CO₂ laser) under the nitrogen stream (35 l/min) (Fig. 1). The cutting condition was chosen so as to obtain maximal yield of yellow pyrolysis products which adhered at the edge of the filter paper.

Power at the surface of the paper was 90~92 W, cutting speed 3.3 m/min, and defocus, distance between focus and paper, was 2.0 cm. The water soluble portion of the yellow pyrolysis products (about 15% of the original filter paper) was fractionated by carbon column chromatography. The samples eluted from the column with water (fraction I), 5% aqueous ethyl alcohol (fraction II), and 20% ethyl alcohol (fraction III) were collected and lyophilized; yields 2.8% (fraction I), 4.9% (fraction II), and 13.9% (fraction III) of the original water-soluble pyrolysis product. Three compounds (1, 2, and 3) were isolated from the fraction I by preparative TLC on Silica Gel 60 (Merk) with 1-butanol-2-propanol-H₂O (3 : 12 : 4, v/v) and their structures were respectively assigned to D-glucose (1), 1,6-anhydro-β-D-glucopyranose (levoglucosan) (2), and 1,6-anhydro-β-D-glucofuranose (3), respectively (Table 1). They were purified by TLC and characterized as their corresponding acetates.⁷⁾ Two sets of two compounds, (4 and 5) and (6 and 7), were similarly isolated from the fractions II and III, respectively, and they were identified as cellobiose (4), 1,6-anhydro-β-D-cellobiose (cellobiosan) (5), cello-triose (6), and 1,6-anhydro-β-D-celotriose (cellotriosan) (7) (Table 1), which were converted into acetates.⁸⁾ Figure 2 shows elution profiles of HPLC at 70°C by using an Aminex HPX-87P column (30 x 0.78 cm) (Bio Rad), monitored with a refractive index detector (Toyo Soda RI-8). Since all seven compounds were well separated, HPLC could be used for quantitative analysis (Table 1). The yield of 2 in water-soluble pyrolysis product was extremely low (2.7%) in the present study, in contrast to those reported in cases of high vacuum pyrolysis of cellulose above

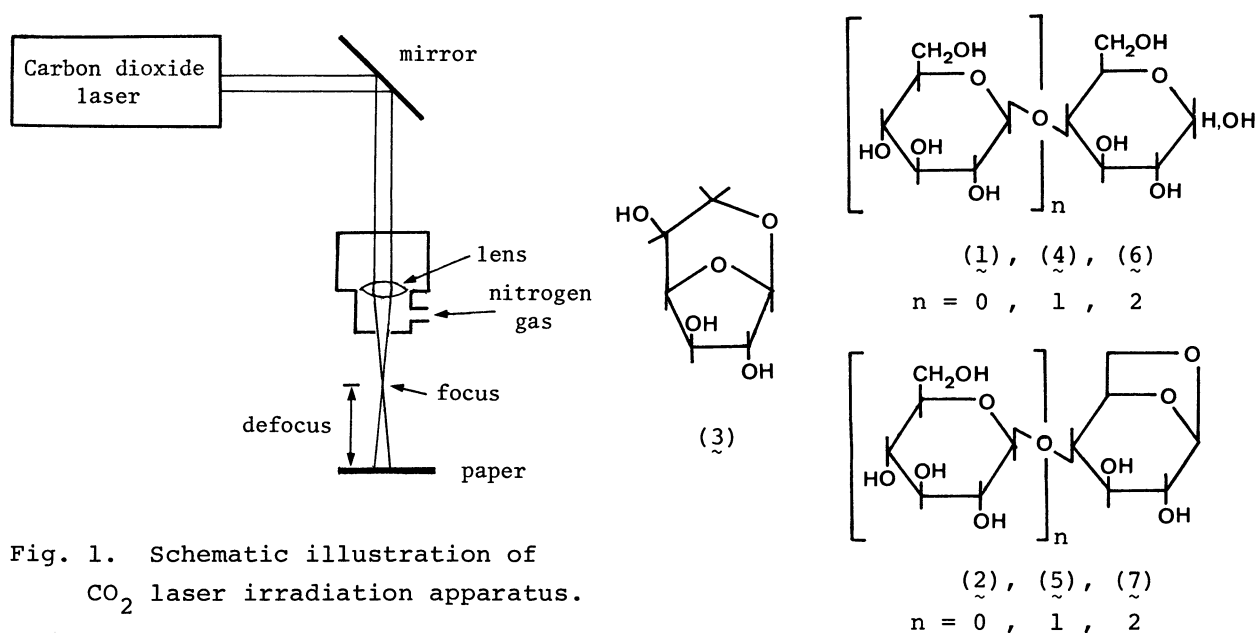


Fig. 1. Schematic illustration of CO₂ laser irradiation apparatus.

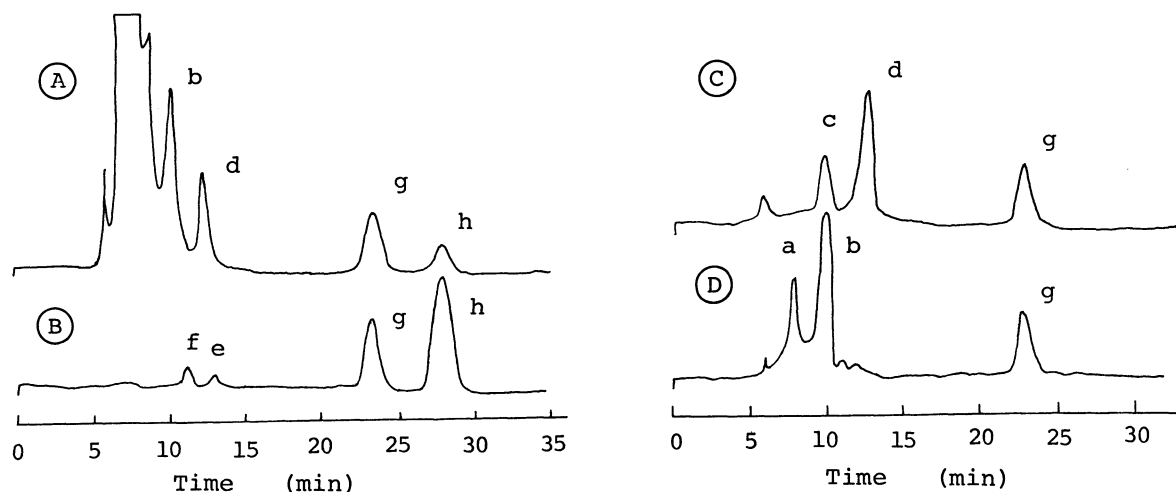


Fig. 2. HPLC elution profiles of water-soluble pyrolysis product of cellulose and of fractions obtained by carbon column chromatography. A, original pyrolysis product (7.3 mg/ml); B, fraction I (7.1 mg/ml); C, fraction II (6.1 mg/ml); D, fraction III (10.1 mg/ml). Peaks a to h indicate cellotriose (6), cellotriosan (7), cellobiose (4), cellobiosan (5), 1,6-anhydroglucofuranose (3), D-glucose (1), inositol (internal standard), and levoglucosan (2), respectively.

Table 1. Yields and characteristics of mono- and oligosaccharides produced by CO₂ laser irradiation on cellulose

Component	1	2	3	4	5	6	7
Yield ^a	0.18	2.80	0.13	4.39	1.24	7.65	1.84
Rf ^b	0.48	0.61	0.63	0.41	0.51	0.31	0.42
Rt (MG) ^c	2.00	0.47	0.65	-	-	-	-
Rt (I) ^d	0.51	1.20	0.57	0.42	0.54	0.36	0.44
Mp ^e	112 ~113	108 ~110	82 ~83	227 ~229	143 ~145	221 ~223	-
Degree of polymerization (DP) ^f	1	1	1	2	2	3	3
Methylated sugars ^g							
2,3,4,6-Tetra-O-methyl glucitol	1	-	-	1.0	1.0	1.0	1.0
2,3,4-Tri-O-methyl glucitol	-	1	-	-	-	-	-
2,3,5-Tri-O-methyl glucitol	-	-	1	-	-	-	-
2,3,6-Tri-O-methyl glucitol	-	-	-	1.0	-	2.1	0.9
2,3-Di-O-methyl glucitol	-	-	-	-	0.9	-	1.1

^aWeight per cent of the original water-soluble pyrolysis product determined by HPLC. ^bMobility (TLC) with 1-butanol-2-propanol-H₂O (3 : 12 : 4, v/v). ^cRetention time (GLC) relative to methyl β-D-glucopyranoside.¹¹⁾ ^dRetention time (HPLC, Fig. 2) relative to inositol. ^eMelting points as acetates. ^fDetermined by the graphical method (Rf/1-Rf vs. DP).¹²⁾ ^gMolar ratio of the partially methylated alditol acetates determined by methylation analysis (GLC and combined GLC-MS).¹³⁾

250°C.^{4,6)} This difference may be attributed to loss of $\tilde{2}$ probably because of its volatility. As regards formation of oligosaccharides, Wolfrom *et al.*^{9,10)} found that a mixture of 1,6-anhydro-oligosaccharides having (1 \rightarrow 4)- α (and β)- and (1 \rightarrow 2)- α (and β)- \underline{D} -glucosidic linkages and higher polymers having (1 \rightarrow 6)- α (and β)-, (1 \rightarrow 4)- α (and β)-, and (1 \rightarrow 2)- β - \underline{D} -glucosidic linkages and 1,6-anhydro- β -D-glucose end groups are formed when $\tilde{2}$ is heated at 235-250°C. In the present pyrolysis products, however, all the isolated oligosaccharides ($4\sim 7$) have solely (1 \rightarrow 4)- β - \underline{D} -glucosidic linkages, suggesting that these (1 \rightarrow 4)- β - \underline{D} -gluco-oligosaccharides produced from cellulose by CO₂ laser irradiation must be formed by cleavage of the glucosidic bonds in cellulose but not by polymerization of $\tilde{2}$. Thus, the present results may provide a useful information on the mechanism of laser-pyrolysis of cellulose.

The authors wish to thank Dr. Ken'ichi Takeo of Kyoto Municipal University for the gifts of cellobiosan hexaacetate and cellotriosan nonaacetate, Mr. Nobuaki Hattori of Kyoto University for the help of pyrolysis experiment, and Miss Haruko Tone for the preliminary work of the present study.

References

- 1) C. K. N. Patel, *Sci. Am.*, 219 (2), 22 (1968).
- 2) C. H. Miller, T. A. Osial, and A. Jagt, *Pulp Paper Mag. Can.*, 71, 63 (1970).
- 3) S. B. Nordin, J. O. Nyren, and E. L. Back, *Textile Res. J.*, 44, 152 (1974).
- 4) F. Shafizadeh, *Adv. Carbohydr. Chem.*, 23, 419 (1968).
- 5) A. Broido and F. J. Kilzer, *Fire Res. Abstr. Rev.*, 5, 157 (1963).
- 6) M. Černý and J. Staněk, Jr., *Adv. Carbohydr. Chem. Biochem.*, 34, 23 (1977).
- 7) M. Buděšinský, T. Trnka, and M. Černý, *Collect. Czech. Chem. Commun.*, 44, 1949 (1979). R. G. S. Titchie, N. Cyr, and A. S. Perlin, *Can. J. Chem.*, 54, 2301 (1976). K. Heyns, W.-D. Soldat, and P. Köll, *Chem. Ber.*, 104, 2063 (1971).
- 8) K. Takeo, T. Yasato, and T. Kuge, *Carbohydr. Res.*, 93, 148 (1981).
- 9) M. L. Wolfrom, A. Thompson, and R. B. Ward, *J. Am. Chem. Soc.*, 81, 4623 (1959).
- 10) M. L. Wolfrom, A. Thompson, R. B. Ward, D. Horton, and R. H. Moore, *J. Org. Chem.*, 26, 4617 (1961).
- 11) I. Kusakabe, Y. Kamiyama, and T. Yasui, *Nippon Nogei Kagaku Kaishi*, 51, 167 (1977).
- 12) D. French and G. M. Wild, *J. Am. Chem. Soc.*, 75, 2612 (1953).
- 13) B. Lindberg, *Methods Enzymol.*, 28, 178 (1972). H. Björndal, C. G. Hellerqvist, B. Lindberg, and S. Svensson, *Angew. Chem.*, 16, 643 (1970).

(Received January 24, 1983)