Carbohydrate Research, 50 (1976) 275–278

Note

Curie-point pyrolysis, gas–liquid chromatography of xylan

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(Received February 6th, 1976; accepted for publication in revised form, April 1st, 1976)

In our previous paper[1], some results of Curie-point pyrolysis, gas–liquid chromatography (c.p.p.–g.l.c.)[2] of cellulose and related carbohydrates were reported. In that report, 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (levoglucosenone)[3] and 2-furaldehyde were recognized as constituting almost all of the volatile products from cellulose. 1,6-Anhydro-3-deoxy-β-D-*threo*-hex-3-enopyranose[4] and 5-hydroxymethyl-2-furaldehyde were also found as minor products.

This paper deals with the results of c.p.p–g.l.c. of xylan isolated from tobacco stalks[5], and of D-xylose.

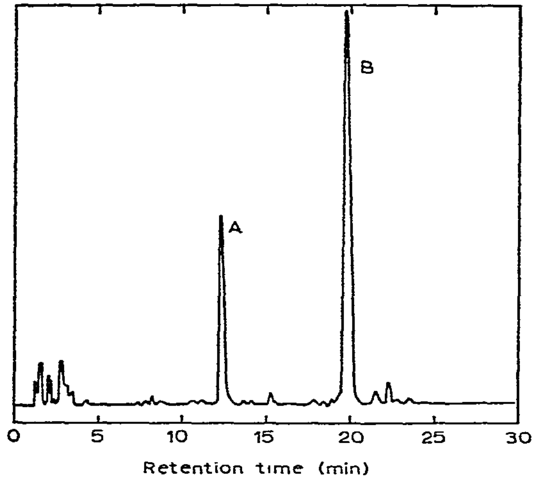
RESULTS AND DISCUSSION

A preliminary analysis of the composition of products from the Curie-point pyrolysis of tobacco-stalk xylan showed that the yield of total volatiles recovered was 21%, whereas tar and residue amounted to 47 and 13%, respectively. The gaseous products that could not be trapped at −72° were not measured.

The c.p.p.–g.l.c. chromatogram obtained with the xylan is shown in Fig. 1. As may be seen in that figure, the primary pyrolysis-products in the volatile, organic fraction are mostly composed of two components; peak A and B.

The compound corresponding to peak A was identified as 2-furaldehyde by comparing its retention time, and mass spectral data of the collected material, with those of authentic 2-furaldehyde. The formation of 2-furaldehyde during the pyrolysis of xylan has been well known[6] since 1913. Recently, Katō[7] and Miyazaki[8] suggested that 2-furaldehyde might be formed via 3-deoxy-D-*glycero*-pentos-2-ulose from both D-xylose and beech xylan. This intermediate would not be detected on the c.p.p.–g.l.c. chromatograms (Figs. 1 and 2) because of its lower volatility.

Peak B compound was originally obtained as a slightly yellowish syrup by repeated preparative c.p.p.–g.l.c. Several sublimations of the crude material at room temperature and 8–10 mtorr gave colorless plates. This pure compound was soluble in acetone, methanol, ethanol, 1,4-dioxane, and dimethyl sulfoxide, and insoluble in



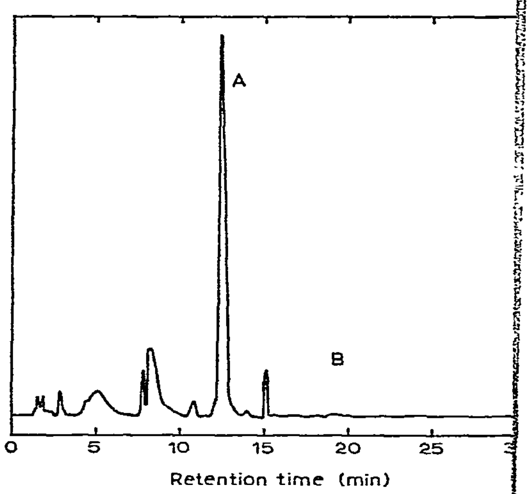
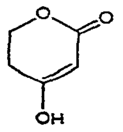


Fig. 1. C.p.p.–g.l.c. chromatogram of tobacco-stalk xylan.

Fig. 2. C.p.p.–g.l.c. chromatogram of D-xylose.

ethyl ether, benzene, and chloroform; m.p. 38°; no optical activity was observed. By high-resolution mass spectroscopy (70 eV) its formula was determined to be $C_5H_6O_3$ (found: 114.0316, calc.: 114.0315), *m/e* 114 (35), 58 (18), 57 (11), 55 (6), 44 (20), 43 (13), 40 (13), 32 (100), 30 (10), 29 (16), 27 (6); n.m.r. (acetone-d_6, 100 MHz): δ 2.63 (t, 2, H_A), 4.42 (t, 2, H_B), 6.42 (s, 1, OH), 7.33 (s, 1), J_{AB} 7.8 Hz; λ_{max}^{MeOH} 295 nm (log ε 4.756); ν_{max} (KBr) 3440 (O–H), 2950 (C–H), 1727 (C=O), 1630 (C=C), 1400 (C=C–H), 1178, 1100, and 1070 (C–O–C) cm^{-1}.

These data are essentially the same as those very recently reported by Miyazaki[9] for 3-hydroxy-2-penteno-1,5-lactone (4-hydroxy-5,6-dihydro-2*H*-pyran-2-one) (**1**), and in excellent accord with those of the authentic compound prepared by the modification of Miyazaki's method described in the experimental section.



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Miyazaki obtained **1** in 1.74% yield by heating beech xylan for 12 h at 180° under diminished pressure. However, his starting material contained a considerable proportion of hexuronic acid (~11.5%)[10], and so the possibility that 3-hydroxy-2-penteno-1,5-lactone may have arisen from the hexuronic acid could not be excluded. However, our tobacco-stalk xylan contained no detectable amount of such an acidic sugar (as reported in the earlier paper[5] and described in the experimental section of this paper), and we consider that 3-hydroxy-2-penteno-1,5-lactone definitely arises from a D-xylopyranosyl residue in the xylan molecule.

The result of c.p.p.–g.l.c. with D-xylose is shown in Fig. 2. As may be seen in that figure, no 3-hydroxy-2-penteno-1,5-lactone was present in the primary pyrolysis-products of D-xylose. The only major product in the volatile fraction was 2-furaldehyde. This may suggest that the formation of 3-hydroxy-2-penteno-1,5-lactone from D-xylopyranosyl residue requires a polymeric precursor.

Shafizadeh and Lai[11,12] have postulated the formation of such an intermediary rearrangement product as a 2-deoxy- or 3-deoxy-hexono-1,5-lactone or its free acid (or its derivatives) from the hexosyl residue to explain the pyrolytic evolution of carbon dioxide from C-1. According to their hypothesis[11,12], 2-deoxy- or 3-deoxy-pentono-1,5-lactone (or a derivative thereof) may be formed from the D-xylopyranosyl residue, and successive dehydration of this intermediate is considered to give 4-hydroxy-2-penteno-1,5-lactone instead of the 3-hydroxy-2-penteno-1,5-lactone that might result from a more-conventional mechanism. A precise mechanism that would account for the formation of 3-hydroxy-2-penteno-1,5-lactone from the pyranosyl skeleton cannot yet be given.

No anhydro sugar could be identified in the volatile fractions of the pyrolyzates from either tobacco-stalk xylan or D-xylose.

EXPERIMENTAL

Preparation and characterization of samples. — Tobacco-stalk xylan was isolated as a water-soluble polysaccharide from stalks of *Nicotiana tabacum* cv. MC (flue-cure type tobacco) by the procedure[5] previously reported. Before use, it was passed through a mixed-bed column of Dowex 1X and 50WX to remove ionic impurities that might affect the pyrolysis course. The sugar composition of its acid hydrolyzate was determined to be 91.1% of D-xylose and trace amounts of D-galactose and D-arabinose. No hexuronic acid (or its 4-methyl ether) or aldobiuronic acid could be detected in it by standard analytical methods[5]. Methylation analysis[5] showed no significant products other than 2,3,4-tri-*O*-methyl-D-xylitol diacetate (1.9%), 2,3-di-*O*-methyl-D-xylitol triacetate (89.7%), and 2- and/or 3-mono-*O*-methyl-D-xylitol tetraacetate (8.5%). This information indicates a linear chain structure of β-(1→4)-D-xylopyranosyl residues, with some branching, for the xylan. Molecular-sieve chromatography of the xylan on a column (10 mm × 1 m) of CPG-700, with a recording refractive-index monitor, and water as an eluant, showed only one sharp peak at the void volume, indicating the absence of any low-molecular-weight fragment. The number-average molecular weight was estimated osmometrically as 5700. The $[\alpha]_D^{23}$ value was $-52.1°$ (*c* 0.4, water).

Beech xylan (Lot. K-lot-17) was kindly donated by Sanyo–Kokusaku Pulp Co. Ltd. (Tokyo, Japan). It was not soluble in water and was treated with M hydrochloric acid for 30 min at 85° before use to remove basic impurities.

Preliminary analysis of the pyrolyzate composition. — A coil, path-type trap made of Pyrex-glass tube (inner diameter 1.0 mm, path-length 20 cm) was connected to an outlet pipe of a Shimadzu PYR-10 Curie-point pyrolyzer by a short silicon-rubber tube, and was kept at −72° by Dry Ice–ethanol. A 10-mg sample of tobacco-stalk xylan was heated for 3 sec at 423° in helium (flow rate 40 ml/min) with the foregoing pyrolysis system. The weight of total volatiles was given by weighing the trap before and after pyrolysis. The weight of tar was obtained by weighing the condensate on the quartz inner-wall of the pyrolyzer after having extracted it with methanol.

Curie-point pyrolysis, gas–liquid chromatography (c.p.p.–g.l.c.). — The c.p.p.–g.l.c. was performed as described in the previous paper[1], except for using a 2-m glass column containing 5% Carbowax 20M on Chromosorb GAW (100–120 mesh). The Curie-point temperatures of ferromagnetic conductors used (heating temperatures) were 423 and 386° for the xylan and D-xylose, respectively. The oscillation period (heating period) was 3 sec. The temperature of the column oven was programmed from 80° to 240° at a rate of 7.5°/min.

Isolation of pyrolysis products. — For collection of the peak components of c.p.p.–g.l.c., the preparative c.p.p.–g.l.c. technique was used as described before[1].

Preparation of 3-hydroxy-2-penteno-1,5-lactone. — The preparative, pyrolytic procedure reported by Miyazaki[9] was used, with some modifications. Beech xylan (5 g) was heated in a Pyrex-glass tube for 3 h at 200–220° under diminished pressure (1 torr). The resultant yellow-reddish, viscous distillate collected on an air-cooled trap was redistilled under somewhat higher pressure (8–10 mtorr). The crude crystals obtained were further purified by repeating sublimation to give fine, colorless plates. As reported[9], it was very labile and hygroscopic; yield 63 mg.

Instrumentation. — The n.m.r., high-resolution mass, i.r., and u.v. spectra were recorded with JEOL model JNM-PS-100, Hitachi model RMU-7, JASCO model IR-G, and Hitachi model 124 spectrometers, respectively.

ACKNOWLEDGMENTS

We thank Dr. K. Miyazaki of the Government Forest Experiment Station of Japan for his valuable comments in preparation of 3-hydroxy-2-penteno-1,5-lactone. We also thank Drs. M. Noguchi and S. Eda of this institute for their helpful advice.

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