Carbohydrate Research, 145 (1986) 348–350
Elsevier Science Publishers B V., Amsterdam – Printed in The Netherlands

Note

Isolation of a neutral linear xylan from guar seed husk

S UMADEVI SAJJAN AND PARAMAHANS V. SALIMATH*
Discipline of Biochemistry and Applied Nutrition, Central Food Technological Research Institute, Mysore-570013 (India)

(Received March 5th, 1985; accepted for publication, July 18th, 1985)

Studies of guar seeds have attracted much attention because of the presence of a galactomannan having high viscosity characteristics as the sole constituent of the endosperm[1]. Most of the studies have concerned the structure, modification, and rheology of guar gum (galactomannan)[2,3], but there has been no report of a systematic investigation of guar-husk carbohydrates, and hence this study.

When guar seeds were boiled with aqueous 2% Na_2CO_3, the husk was broken down into a fine powder, indicating cleavage of some of the alkali-labile components. The husk, thus obtained, was rich in sugars (90.1%) and contained mainly glucose (72.8%) and xylose (14.7%) together with traces of arabinose, rhamnose, galactose, and mannose.

The water-soluble fraction (2.0%) contained mainly arabinose (42.4%), galactose (16.4%), uronic acid (13.4%), and rhamnose/fucose (10.5%). The pectic-type polysaccharide (1.8%), on the other hand, was rich in uronic acid (40.8%) and also contained pentoses, deoxyhexoses, and hexoses in the ratios 4:2:3, and was probably a complex mixture[4].

After removing the water-soluble and pectic-type polysaccharides, the hemicelluloses were extracted with aqueous 10% NaOH. Since small-scale isolation of hemicellulose A yielded a xylan-type fraction, delignification was not considered to be necessary. In fact, the xylan-type fraction (96.6% xylose) is the second major polysaccharide (20.8%) after cellulose in guar husk. The hemicellulose B isolated (2.6%) still had a high content of xylose (60.7%), together with arabinose (13.6%), rhamnose (10.0%), glucose (9.6%), and galactose (4.9%). This may contain a small proportion of unextracted hemicellulose A and may be a composite aggregate of pentosans and hexosans.

The alkali-insoluble fraction (57.5%) was rich in glucose (98.2%) and was a true cellulose.

*To whom correspondence should be addressed

0008-6215/86/$ 03 50 © 1986 Elsevier Science Publishers B V.

Mannose was not present in significant amounts in any of the fractions. The presence of galactose in the water-soluble and pectic-type polysaccharides may be due to arabinogalactan- or rhamnogalacturonan-type polysaccharides and hence it appears that the galactomannan-type polysaccharide, which is the sole constituent of guar-seed endosperm, is not present in the husk.

The hemicellulose A fraction. — This fraction, which contains almost exclusively xylose, gave a sharp, symmetrical peak on ultracentrifugation, indicating its homogeneity. Methylation analysis gave derivatives of 2,3,4-tri-*O*-methyl-D-xylose (2.8%) and 2,3-di-*O*-methyl-D-xylose (97.2%), which indicated that hemicellulose A is mainly a (1→4)-linked linear xylan and that the residues are in pyranose form[5].

Partial hydrolysis of hemicellulose A yielded xylose and four oligosaccharides which were isolated by preparative p.c. Each oligosaccharide gave xylose on hydrolysis. A plot[6] of $R_M = \log [(1/R_F) - 1]$ versus d.p. was linear, indicating that the xylo-oligosaccharides comprised an homologous series. These results further indicated that hemicellulose A is a linear xylan.

The $[\alpha]_D$ value of $-20°$ (water) and the complete destruction of xylose by chromium trioxide oxidation indicated that the xylosyl residues were β-linked in accordance with reported xylan-type polysaccharides[7].

These structural features accorded with the consumption of 1.06 mol of periodate per mol of "anhydro sugar", and glycerol was formed on Smith degradation of hemicellulose A.

During the isolation of hemicellulose A, aqueous 2% Na_2CO_3 and aqueous 10% NaOH (N_2 atmosphere) were used. It is unlikely that β-elimination-type degradations of an "acidic xylan" occurred during extraction[8]. 4-*O*-Methylglucuronoxylan has been isolated using aqueous 10% NaOH (under N_2) at room and elevated temperatures[9].

Xylans and substituted xylans, such as arabinoxylans and 4-*O*-methylglucuronoxylans, have been described[6]. Amongst homoxylans, the xylan isolated from tobacco stalk[10] has one branch point per molecule, whereas that reported from groundnut is highly branched[11]. The xylan isolated from esparto grass[12] is a linear xylan and these are rare in Nature. The xylan from guar-seed husk belongs to the rare class.

EXPERIMENTAL

Most of the general methods employed have been reported[13].

Isolation of the husk and its fractions. — Guar seeds (100 g), variety Pusa Navsagar, obtained from the National Seed Corporation (Mysore, India), were washed with water 2–3 times and then treated[14] with boiling aqueous 2% Na_2CO_3 (200 mL) for 5 min. The separated husk (10.2 g) was neutralised with M HCl, washed free of salts with water, and dried. The hot water-soluble polysaccharides were extracted with water (90°, 2 h, ×3), and the pectic fraction was extracted from

the insoluble residue with aqueous 0.5% ammonium oxalate (85°, 2 h, ×3). Hemicelluloses (A and B) were then extracted[15] with aqueous 10% NaOH.

Methylation analysis. — Hemicellulose A (5 mg) was methylated by the Hakomori method[16] and the product was purified by dialysis followed by column chromatography on Sephadex LH-20. The methylated polysaccharide was hydrolysed, and the products were reduced ($NaBD_4$), acetylated, and subjected to g.l.c. and g.l.c.–m.s.[17,18].

Partial hydrolysis. — Hemicellulose A was treated with 0.1M trifluoroacetic acid for 4 h at ~100°. Excess of acid was evaporated by co-distillation with water, and the residual sugars were chromatographed with 1-propanol–ethanol–water (7:1:2) on Whatman No. 1 or 3 paper.

The conditions used for periodate oxidation, Smith degradation, chromium trioxide oxidation, and ultracentrifugation have been described[13].

ACKNOWLEDGMENTS

We thank Dr. R. N. Tharanathan (this Institute) and Dr. H. Mayer of the Max-Planck-Institut für Immunbiologie (Freiburg i. Br., West Germany) for the g.l.c.–m.s., Dr. M. R. Raghavendra Rao for his encouragement, and Dr. R. N. Tharanathan for critical reading of the manuscript.

REFERENCES

1 M. Glicksman, *Gum Technology in the Food Industry*, Academic Press, New York, 1969
2 A. M. Goldstein, E. N. Alter, and J. K. Seaman, in R. L Whistler and J. N. BeMiller (Eds.), *Industrial Gums*, Academic Press, New York, 1972, pp. 303–321.
3 G. K. Greminger and K. L. Krumel, in R. L. Davidson (Ed.), *Handbook of Water Soluble Gums and Resins*, McGraw-Hill, New York, 1980, pp. 6-1–6-19.
4 P. V. Salimath and R. N. Tharanathan, *Cereal Chem.*, 59 (1982) 430–435.
5 A. M. Stephen, in G. O Aspinall (Ed.), *The Polysaccharides*, Vol. 2, Academic Press, New York, 1983, pp. 98–193.
6 E. C. Bate-Smith and R G. Westall, *Biochim. Biophys. Acta*, 4 (1950) 427–440.
7 M. J. Song and T. E. Timell, *Cellul. Chem. Technol.*, 5 (1971) 67–71
8 G. O. Aspinall, in G O. Aspinall (Ed.), *The Polysaccharides*, Vol. 1, Academic Press, New York, 1982, pp. 19–131.
9 T. E. Timell, *Adv. Carbohydr. Chem.*, 19 (1964) 247–302
10 S. Eda, F. Watanabe, and K. Kato, *Agric. Biol. Chem.*, 41 (1976) 359–364.
11 D. B. Wankhede, R. N. Tharanathan, and M. R. Raghavendra Rao, *Carbohydr. Res.*, 74 (1979) 207–215.
12 S K. Chanda, E. L. Hirst, J. K. N. Jones, and E G V. Percival, *J Chem. Soc* , (1950) 1289–1297.
13 P. V. Salimath and R. N Tharanathan, *Carbohydr. Res.*, 107 (1982) 103–109.
14 S. Umadevi Sajjan, Ph.D. Thesis, University of Mysore, India, 1984.
15 R. L. Whistler and M. S Feather, *Methods Carbohydr. Chem.*, 5 (1962) 144
16 S. Hakomori, *J. Biochem. (Tokyo)*, 55 (1964) 205–208
17 H. Bjorndal, B. Lindberg, and S. Svensson, *Carbohydr. Res.*, 5 (1967) 433–440.
18 P. V. Salimath, R N. Tharanathan, J. Weckesser, and H. Mayer, *Eur. J. Biochem.*, 144 (1984) 227–232.