Note

Arabinosylxylotriose Mixedly Esterified with Acetic and Ferulic Acids from Sugar Cane Bagasse

Jun-ichi AZUMA, Atsushi KATO,*
Tetsuo KOSHIJIMA** and Keizo OKAMURA

Department of Wood Science and Technology,
Faculty of Agriculture, Kyoto University,
Sakyo-ku, Kyoto 606, Japan

* Wood Chemistry Division, Forestry and Forest
Products Research Institute, P.O. Box 16,
Tsukuba Norin Kenkyu Danchi-Nai,
Ibaraki 305, Japan

** Section of Wood Chemistry, Wood Research
Institute, Kyoto University,
Gokasho, Uji 611, Japan

Received March 26, 1990

The phenolic acids found in graminaceous plant cell-walls are esters with sugars and lignin.^{1–3)} Previously, we separated two feruloylated oligosaccharides from an enzymatic hydrolysate of the bagasse lignin-carbohydrate complex.^{4,5)} As an extension of the structural elucidation of phenolic-acid-containing oligosaccharides, we now describe the isolation and identification of a new tetrasaccharide mixedly esterified with acetic acid and ferulic acid **1** from sugar cane bagasse.

Extractive-free and depectinated bagasse from sugar cane (*Saccharum officinarum* L. NCo 310) was treated with a hemicellulase-cellulase mixture as described previously.⁵⁾

The 80% aqueous ethanol-soluble fraction of the hydrolysate was chromatographed on a Sephadex LH-20 column [eluant, water] to give a mixture of esterified oligosaccharides. A conjugate **1** having an *R_f* value of 0.41 was separated from the others by preparative TLC [irrigant, 1-butanol:acetic acid:water=62:15:23 (v/v)], and purified by preparative HPLC on an octadecyl column of YMC (SH-343-5, S-5 120A AQ) eluant, MeOH:water=1:1 (v/v); yield, 0.06% of the depectinated bagasse.

The FAB mass spectrum of **1** (*m/z* 787 [*M*+Na]⁺ and 765 [*M*+H]⁺) and the chemical composition analyses indicate that **1** is a tetrasaccharide (one mole of L-arabinose and three moles of D-xylose) substituted with 1 mol of *trans*-ferulic acid and one mole of acetic acid (Table I). The mode of linkages of these acids was deduced to be ester linkages by IR and UV spectroscopic data: **1** had characteristic absorption bands at 1735 cm⁻¹ (acetyl C=O), 1710 cm⁻¹ (conjugated C=O); the λ_{max} value of **1** at 325 nm in water shifted to 370 nm immediately after addition of sodium hydroxide to a final concentration of 0.1 M due to formation of sodium phenolate, and further shifted to 347 nm after incubation for 2 hr due to formation of sodium ferulate. By methylation and NMR spectroscopic analyses, the structure of the tetrasaccharide portion of **1** obtained by saponification with 2 M NaOH for 24 hr was found to be identical to 3'-L-arabinofuranosyl-D-xylotriose.⁵⁾ Further, on the basis of two dimensional H,H-, H,C-, and long-range H,C-COSY NMR experiments, all the ¹H and ¹³C signals of **1** could be unambiguously assigned (Table I). An acetyl group at C-2 of the arabinofuranose residue was identified by the connectivities between the acetyl carbonyl carbon (175.28 ppm) and protons of H-2 of arabinofuranose (5.00 ppm) and acetyl methyl (2.02 ppm) in the long-range H,C-COSY spectrum. Similarly, a feruloyl group at C-5 of arabinofuranosyl residue was identified by the connectivities between the feruloyl carbonyl carbon (171.27 ppm) and protons of H-7 of feruloyl residue (7.36 ppm) and H-5a of arabinofuranose (4.45 ppm). Based on these results, the primary structure of **1** was identified as *O*-β-D-xylopyranosyl-(1→4)-*O*-[2-*O*-acetyl-5-*O*-(*trans*-feruloyl)-α-L-arabino-furanosyl-(1→3)]-*O*-β-D-xylopyranosyl-(1→4)-β-D-xylopyranose.

The presence of arabinofuranose residues bearing alkali-labile substituents at both C-2 and C-5 was reported in wheat and barley straws and rye grass,^{6,7)} but their structures were not fully elucidated. According to our knowledge, the compound **1** represents the first identified mixed diester with arabinofuranose in the plant kingdom.

Table I. ^1H AND ^{13}C -NMR DATA FOR THE CONJUGATE 1

¹ H Chemical shifts (ppm) ^{a,b} and coupling constants (Hz)											
		H-1 (J _{1,2})	H-2 (J _{2,3})	H-3 (J _{3,4})	H-4 (J _{4,5a})	H-5a (J _{5a,5b})	H-6b (J _{4,5b})		H-2 (J _{2,6})	H-5 (J _{5,6})	H-6
X	α	5.19 (3.5)	3.56 (8.9)	3.77 (—) ^c	3.73 (—)	3.84 (—)	3.77 (—)	F	6.90 (2.0)	6.81 (8.1)	6.91
	β	4.58 (7.7)	3.26 (9.2)	3.54 (9.0)	3.75 (5.3)	4.03 (11.7)	3.35 (9.5)		H-7 (J _{7,8})	H-8	Me (OMe)
X'		4.42 (7.7)	3.45 (9.0)	3.73 (9.1)	3.80 (5.3)	4.11 (11.6)	3.35 (9.6)	F	7.36 (15.5)	6.13	3.73
X''		4.41 (7.7)	3.24 (9.2)	3.42 (9.1)	3.60 (5.2)	3.90 (11.7)	3.28 (9.4)	Ac			Me (OAc) 2.02
A		5.49 (1.8)	5.00 (3.3)	4.13 (6.1)	4.56 (3.3)	4.45 (12.3)	4.32 (6.0)				
¹³ C Chemical shifts (ppm)											
		C-1	C-2	C-3	C-4	C-5			OAc (Me)		OAc (C=O)
X	α	94.71	74.09	73.69	79.47	61.58					
	β	99.23	76.67	76.65	79.28	65.71					
X'		104.45	75.77	80.09	76.65	65.54					
X''		104.45	75.77	78.36	71.93	67.85					
A		108.11	85.77	78.36	85.29	65.91	Ac	23.02			175.28
F		129.19	113.57	150.22	150.69	118.13					
		C-6	C-7	C-8	C-9	OMe					
F		126.07	149.04	116.41	171.27	58.35					

^a In D₂O at 300.1 MHz and 25°C using acetone (2.218 ppm) as an internal standard.^b In D₂O at 75.5 MHz and 25°C using acetone (32.947 ppm) as an internal standard.^c Values not measured due to overlapping.

References

- 1) M. McNeil, A. G. Darvill, S. C. Fry and P. Albersheim, *Annu. Rev. Biochem.*, **53**, 625 (1984).
- 2) R. D. Hartley, *Modern Methods Plant Anal., New Series*, **5**, 92 (1987).
- 3) J. Azuma, *Modern Methods Plant Anal., New Series*, **10**, 100 (1989).
- 4) A. Kato, J. Azuma and T. Koshijima, *Chem. Lett.*, **1983**, 137.
- 5) A. Kato, J. Azuma and T. Koshijima, *Agric. Biol. Chem.*, **51**, 1691 (1987).
- 6) A. Chesson, A. Gordon and J. A. Lomax, *J. Sci. Food Agric.*, **34**, 1330 (1983).
- 7) J. A. Lomax, A. H. Gordon and A. Chesson, *Carbohydr. Res.*, **122**, 11 (1983).