Available online at www.sciencedirect.com

ScienceDirect

Carbohydrate Polymers 72 (2008) 382–389

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

A high-viscosity glycoglucuronomannan from the gum exudate of *Vochysia thyrsoidea*: Comparison with those of other *Vochysia* spp.

Ricardo Wagner [a], Fernanda F. Simas [a], Guilherme L. Sassaki [a], Marcello Iacomini [a], Maria Aparecida da Silva [b], Philip A.J. Gorin [a,*]

[a] *Departamento de Bioquímica e Biologia Molecular, Universidade Federa do Paraná, CxP 19046, 81531-980 Curitiba, PR, Brazil*
[b] *RECOR – Reserva Ecológica do Instituto Brasileiro de Geografia e Estatística, CxP 08.770, 70312-970 Brasília, DF, Brazil*

Received 20 April 2007; accepted 5 September 2007
Available online 14 September 2007

Abstract

The polysaccharide (VTh) extracted with water from the gum exudate of the trunk *Vochysia thyrsoidea* gave a solution of high viscosity and was homogeneous, with M_w 92.5×10^3 and $dn/dc = 0.212$. Partial hydrolysis gave a main chain of →4)-β-D-Glc*p*A-(1 → 2)-α-D-Man*p*-(1→ repeating groups. Since VTh contained 24% GlcA, neither its monosaccharide ratio (GC–MS of alditol acetates) nor methylation results were accurate. It was therefore carbodiimide-reduced to CR_3VTh, which contained Ara, Xyl, Man, Gal, and Glc in a molar ratio of 28:4:29:19:25: methylation analysis showed mainly nonreducing end-units of Ara*f* (25%), Ara*p* (8%), and Gal*p* (8%) and side-chain units of 3-*O*- (6%) and 3,4-di-*O*-subst. Gal*p* (12%). Main-chain units of Man*p* were 2,3-di-*O*-substituted (17%), showing that they were substituted at O-3 by side chains, but there was less side-chain substitution of Glc*p* units, which were mainly 4-*O*-substituted (12%). Most Ara*f* units in VTh and CR_3VTh were single nonreducing end-units, and were present in groups of α-L-Ara*f*-(1 → 3)-D-Man*p* and α-L-Ara*f*-(1 → 3)-[α-L-Ara*f*-(1 → 4)]-β-D-Gal*p*-(1 → 3)-α-D-Man*p*. Other degradation products derived from VTh agreed with this structure. The degree of side-chain substitution of the same main chain was greatest with the gum exudate polysaccharide of *V. tucanorum*, and progressively less with those of *V. thyrsoidea*, and *V. lehmannii*. High-viscosity aqueous solutions were formed by the gum of *V. thyrsoidea*, in contrast with those of *V. lehmannii* and *V. tucanorum*.

Keywords: *Vochysia thyrsoidea*; Gum glycoglucuronomannan; Structure; Chemotaxonomy

---

1. Introduction

Trees of the family Vochysiaceae are common in the sub-tropical and tropical regions of Brazil, often occurring in the transition zone between the savannah and Atlantic forest. Wagner et al. (2004) showed that the gum exudate, growing on the trunk of *Vochysia lehmannii*, contained a polysaccharide with a repeating →4)-β-D-Glc*p*A-(1 → 2)-α-D-Man*p*-(1→ group as its main chain, which was lightly *O*-substituted with complex side chains. The gum polysaccharide from *V. tucanorum* has a similar main chain, but with a much higher degree of *O*-substitution (Wagner et al., 2007). These structures are represented by their ^{13}C NMR spectra, that of *V. lehmannii* having predominant C-1 signals at δ 98.3 and 101.6 arising from the main chain (Fig. 1a). These were not evident in those of *V. tucanorum*, which were mostly from side chains (Fig. 1b), while those of the main chain were only revealed on partial hydrolysis. We now investigate the glycoglucuronomannan from the gum exudate of *V. thrysoidea*, which has been described by Almeida, Proença, Sano, & Ribeiro (1998). Its C-1 signals (Fig. 1c) indicated an intermediate degree of side-chain substitution.

---

[*] Corresponding author. Tel.: +55 41 3361 1670; fax: +55 41 3266 2042.
E-mail address: cesarat@ufpr.br (P.A.J. Gorin).

0144-8617/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2007.09.005

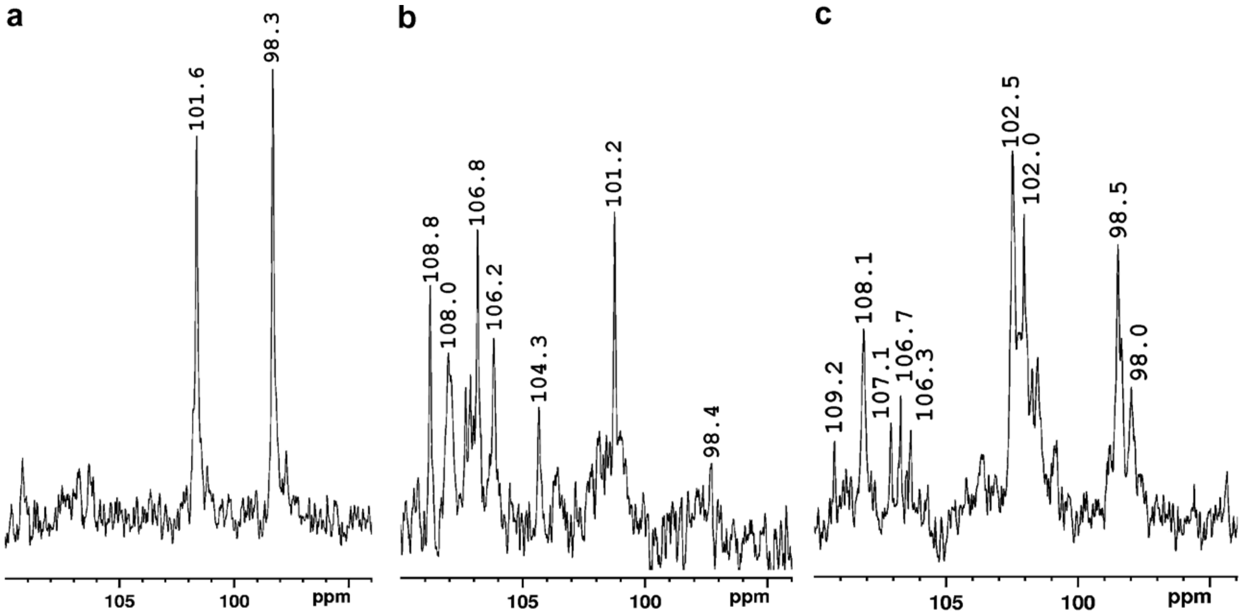

Fig. 1. C-1 regions of ^{13}C NMR spectra of polysaccharides from gum exudates of *V. lehmannii* (a), *V. tucanorum* (b), and *V. thyrsoidea* (c).

2. Experimental

2.1. *Vochysia thyrsoidea* gum

The gum was collected during January, 2005 from the trunk of a tree growing in the Ecological Reserve (RECOR) of the Brazilian Institute of Geography and Statistics, an affiliate of the Brazilian Institute of Geography and Statistics (IBGE). This is situated in a sub-tropical location 35 km to the south of the capital Brasília, in a region subject to frequent fires and dry periods, contributing to periodic tree stress.

2.2. Preparation of gum polysaccharide (VTh)

A sample of the original, dry gum was cleaned to remove manually charcoal arising from fires. A sample (110 g) dissolved almost completely in H_2O (1.0 L), and the viscous solution was evaporated to 450 mL, insoluble particles centrifuged off, and the supernatant added to EtOH (×3). The precipitated polysaccharide was dissolved in H_2O and the solution was dialyzed with a membrane having pores of 12,000–14,000, and then freeze-dried to give VTh (57 g).

2.3. Analytical methods

2.3.1. Monosaccharide composition of polysaccharides

The uronic acid contents of polysaccharides (1.0 mg) were determined using an *m*-hydroxydiphenyl colorimetric method, with which neutral, reducing sugars do not interfere (Filisetti-Cozzi & Carpita, 1991).

Samples (1.0 mg) were hydrolyzed with 2 M TFA for 8 h at 100 °C, and the products were reduced with $NaBD_4$ (Wolfrom & Thompson, 1963a) to give alditols, which were acetylated with Ac_2O–pyridine (Wolfrom & Thompson, 1963b). The resulting alditol acetate mixtures were analyzed by GC–MS (Jansson, Kenne, Liedgren, Lindberg, & Lönngren, 1970), using a Saturn 2000 model installed with a capillary DB-225 column (30 m × 0.25 mm i.d.), programmed from 50 °C (1 min) at 40 °C/min to 220 °C (then hold), with He as carrier gas.

The hydrolyzate of VTh was examined by silica gel TLC (solvent: *n*-PrOH–EtOAc–HOAc–H_2O, 2:4:2:1, spray:orcinol), to detect glucuronolactone with R_F 0.83. The mixture was treated with 0.5% aq. $NaHCO_3$ for 18 h at 25 °C to convert it to Na glucuronate, which does not afford glucitol on $NaBD_4$ reduction.

2.3.2. HPSEC analysis

The molecular weight distribution of VTh was determined using Wyatt Technology equipment incorporating ultrahydrogel columns 2000, 500, 250, and 120, connected to a differential refractometer (model 2410, Waters) and a laser light scattering detector, at 632.8 nm (Dawn DSPF model). The eluant was aq. 0.1 M $NaNO_2$ + 0.2 g/L NaN_3, at a flow rate of 0.6 mL/min. The samples were dissolved in aq. $NaNO_2$ (1 mg/mL) and filtered through a cellulose membrane with an average pore diameter of 0.2 μm: a volume of 100 μL was injected into the apparatus. Results were provided directly with the aid of ASTRA 4.70.07 computer software.

2.3.3. Methylation analysis of polysaccharides

Samples of polysaccharide (25 mg), when not soluble in Me_2SO, were partially *O*-methylated by the method of Haworth (1915), using Me_2SO_4/aq. NaOH, which rendered the product Me_2SO-soluble, and which was then per-*O*-