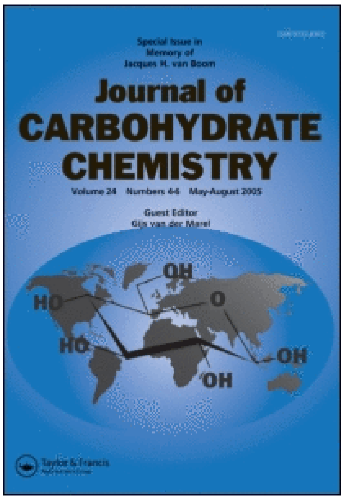

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Synthesis and Preliminary Characterization of New Uronans

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COMMUNICATION

SYNTHESIS AND PRELIMINARY CHARACTERIZATION OF NEW URONANS[1]

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It is of interest from both basic and applied research standpoints to widen the number of artificial uronans (polyuronic acids) starting from readily accessible non-ionic and/or ionic polysaccharides of vegetal or microbial origin. This especially if synthetic procedures leading to species of controllable charge density with minimal chain degradation can be adopted.

It appears that one such procedure was recently described in the literature by van Bekkum and coworkers[2] in which water soluble glycans (with the obvious exception of linear dextran) can be transformed into a polycarboxylate *via* selective C(6) oxidation in dilute aqueous solutions (0° C, pH 10) containing appropriate concentrations of NaClO, NaBr and catalytic amounts of the stable radical TEMPO (2,2,6,6-tetramethylpiperidine-1-oyl). Taking advantage of this route (and following closely the procedure previously described[2]) we have prepared and partially characterized a few new artificial uronans starting from pullulan, guar, scleroglucan, and gellan, respectively.[3] All polymer samples were purified by dissolution in water, precipitation with 2-propanol, redissolution in water, and extensive dialysis followed by freeze-drying. In the case of guar (having a mannose/galactose molar ratio close to 2) both the side-chain galactose residues and the main-chain mannose residues [not engaged in (6->1) glycosidic linkage with galactose] were oxidised. The resulting polycarboxylates have higher charge density than those

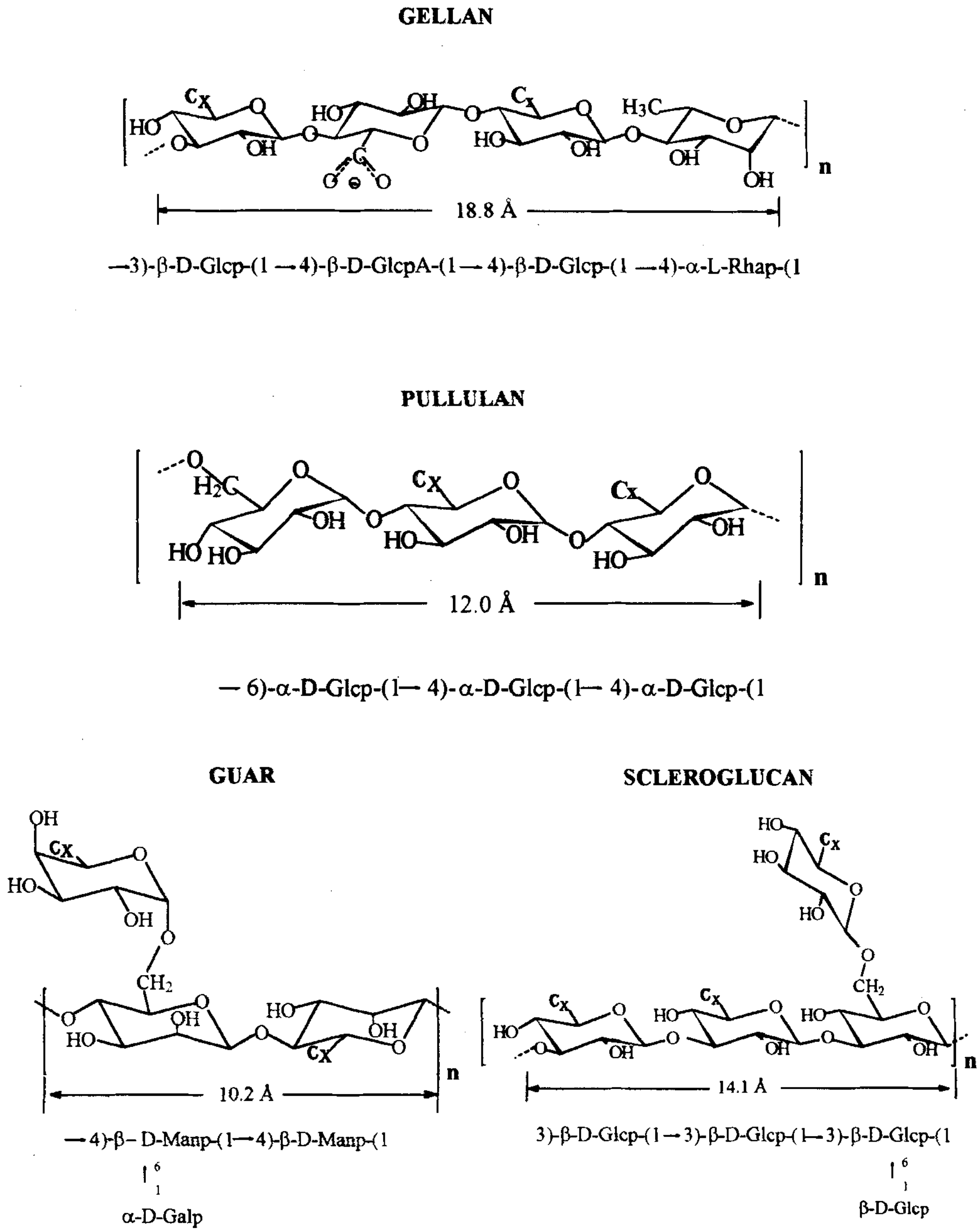

Figure 1: Primary structures of Gellan, Pullulan, Guar and Scleroglucan.
$Cx = -CH_2OH$ in native polymer;
$Cx = -COOH$ fully oxidized polymer.

Table 1. Polycarboxylates derived from gellan, pullulan, guar, and scleroglucan. Intrinsic viscosity and optical activity data.

Polymer	od[a]	[η][b]	[α][c]
gellan	0	800	-220
"	0.49	210	-192
"	0.78	290	-187
"	0.90	40	-207
pullulan	0	80	545
"	0.87	120	660
scleroglucan	0	1760	50
"	0.96	630	-150
guar	0	560	170
"	0.85	310	50

a. Oxidation degree expressed as the degree of conversion of -CH_2OH groups into -COOH groups (potentiometric equivalent weight data for the polyacids). See Fig. 1. b. Intrinsic viscosity data (mL/g) at 25 °C in 0.02 M NaCl for the native biopolymers and for the carboxylated derivatives (sodium salts). Native gellan chains are partially in double helical form in 0.02 M NaCl at 25 °C. Native scleroglucan is in triple helical form for the same conditions. c. Specific rotatory power at 365 nm and 25 °C. Readings taken in 0.1 M NaCl are either identical or differ by 1-2% from those reported above (with the exception of gellan). Native gellan is single-stranded in dilute salt-free aqueous solution while it is double-helical in 0.1 M NaCl and 25 °C with [α] = 180 at 365 nm. Polymer concentration: 0.1-0.2 % w/V.

obtainable by oxidation of the galactose residues only using galactose oxidase and aqueous I_2/KI.[4,5]

With scleroglucan, up to 96% of the primary alcoholic functions belonging to glucose residues in the side-chains and in the backbone were converted to -COOH groups with the formation of ionic species structurally different from those reported earlier and prepared by periodate/chlorite oxidation of the side-groups only.[6]

Gellan was considered mainly in order to compare the special conformational characteristics of the parent biopolymer in dilute aqueous solution[7] with those of a series of its derivatives in which increasing amounts of -COOH groups (partial to total oxidation of the glucose residues in the repeating units) were introduced along the polysaccharide skeleton.

Table 2. Sodium counterions activity coefficients in water, 25 °C, of the polycarboxylates derived from gellan, pullulan, guar, and scleroglucan.

Polymer(od)	b^a	n^b	ξ^c	$(\gamma^+\mathrm{exp})^d$	$(\gamma^+\mathrm{th})^e$
gellan (0)[f]	18.80	1	0.37	0.76	0.83
" (0.49)	12.79	1.47	0.56	0.78	0.76
" (0.78)	8.03	2.34	0.89	0.58	0.64
pullulan (0.87)	8.10	1.74	0.88	0.58	0.64
guar (0.85)	5.53	1.70	1.29	0.52	0.47
scleroglucan (0.96)	4.89	2.88	1.46	0.45	0.41

a. **b** = B/n (where B is the length of the repeating unit in Angstrom units) is the average distance, projected on the chain axis, between neighboring carboxylate groups (fully extend chain). The B values were estimated taking 4.7 angstroms as the average length of each sugar residue in the repeating units. (See Fig. 1). b. n is the average number of carboxylate groups per repeating unit (from the od data of Table 1). c. ξ is the linear charge density parameter defined as $\xi = 7.15/\mathbf{b}$ (water, 25 °C). d. potentiometric data obtained following the experimental procedure described in reference 8. Figures given are for the polymer concentration, C_p, range in which γ^+ resulted almost constant (C_p ca. 0.5-2.5 mquiv/L). e. theoretical values calculated according to Manning's theory (equations 51a and 51b of reference 9. f. gellan chains in water at 25 °C (C_p less than 10 mM) are assumed to be singly dispersed. γ^+ measurement for gellan was taken at $C_p = 2$ mquiv/L.

Most artificial uronans so far obtained starting from pullulan, guar, scleroglucan, and gellan behave in dilute aqueous solution as typical weak polyacids whose characteristic chirooptical properties gradually and regularly change with increasing degree of ionization (circular dichroism data not shown) and are practically independent of added NaCl concentration (see Table 1).

Only in the case of a gellan derivative with C(6) oxidation estimated around 2%, could evidence be detected of a salt (sodium) induced conformational change, much less pronounced, however, than that typical of the parent polymer[7] according to optical activity data.

In all cases, with the notable exception of pullulan, intrinsic viscosity data (Table 1) indicate that chain depolymerization took place to some extent during the oxidation process, the more so the higher the degree of oxidation (e.g., gellan). This, in our opinion, is the only weak point of a synthetic procedure[2] which is otherwise facile and allows for good yields.

Finally, it is worth mentioning that the sodium salts of all samples exhibit counterions "activity coefficient" (potentiometric data in water, 25 °C) values in line with qualitative predictions based on their respective "linear charge density" (see Table 2). Despite our approximate estimate of this parameter, the potentiometric data suggests that different considered uronans should exhibit single-stranded, expanded chains in water. Work is in progress in order to study in detail the physico-chemical properties of polyelectrolytes mentioned above as well as to explore their practical potentialities.

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REFERENCES AND NOTES

1. Presented at the *XVIII International Carbohydrate Symposium*, Milan, Italy, July 21-26, 1996.
2. A.E.J. de Nooy, A.C. Besemer, H. van Bekkum, *Carbohydr. Res.*, **269**, 89 (1995).
3. Origins of the biopolymers are: gellan ("Gelrite", KELCO Co., Lot 87063A); scleroglucan ("Actigum-CS-11", SANOfi BIO-INDUSTRIES, Lot 662); pullulan ("PI-20", HAYASHIBARA, Lot 01207), guar ("Gum Guar", SIGMA, Lot 566-0238). TEMPO and NaBr were SIGMA products. Aqueous NaClO (7% w/V) was a Carlo ERBA product.
4. M. Dentini, V. Crescenzi, *Carbohydr. Polym.*, **6**, 493 (1986).
5. E. Frollini, W.F. Reed, M. Milas, M. Rinaudo, *Carbohydr. Polym.*, **27**, 129 (1995).
6. V. Crescenzi, A. Gamini, R. Rizzo, S.V. Meille, *Carbohydr. Polym.*, **9**, 169 (1988).
7. V. Crescenzi, *Biotechnol. Progress*, **11**, 251 (1995), and references therein.
8. V. Crescenzi, M. Dentini, R. Rizzo in *Solution Properties of Polysaccharides*; D.A. Brant Ed.; ACS Symposium Series **150**, pp 331-347 (1981).
9. G.S. Manning, *J. Chem. Phys.*, **51**, 3 (1969).