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Composition and rheological properties of cashew tree gum, the exudate polysaccharide from *Anacardium occidentale* L.

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Anacardium occidentale gum from Brazilian plants has a higher galactose content and lower arabinose and rhamnose content than those gums from India and Papua. The other constituents (glucose, mannose and glucuronic acid) are similarly distributed. GPC of cashew gum detected the presence of 6% polysaccharide–protein complex, 42% polysaccharide of M_{pk} $1{\cdot}6 \times 10^4$. The whole gum is a low viscosity polysaccharide with an activation energy of flow for solution at 2 and 3% ($\sim$16 kJ mol^{-1}), characteristic of systems with little intra and intermolecular interactions. Experiments on the effects of NaCl, $CaCl_2$ and $AlCl_3$ on the reduced viscosity, as well as the effect of salt concentration on the specific viscosity, indicated that the affinity between *A. occidentale* gum and metal ions follows the order: $Al^3 > Ca^{2+} > Na^+$.

INTRODUCTION

Exudate gum from *Anacardium occidentale* L. is a branched acidic heteropolysaccharide employed locally as a substitute for gum arabic in pharmaceutical uses. Adhesive properties and insecticidal activity (Venkaiah, 1985), as well as emulsifier properties (Pontes, 1971), have been reported. The polysaccharide is produced in epithelial cells which border the gum ducts (Nair *et al.*, 1983) and is known to be part of the biochemical defences of the plant (Marques & Xavier-Filho, 1991). The gum from India and Papua has a galactan framework consisting of chains of β-(1–3)-linked D-galactose residues, branched and interspersed with β-(1–6) linkages (Anderson *et al.*, 1974; Anderson & Bell, 1975). D-galactose, L-rhamnose, D-mannose, D-glucuronic acid and 4-*O*-methyl-glucuronic acid are all present as end-groups. Xylose was identified in Indian species only. Brazilian gum contains arabinose, galactose and rhamnose (Rosenthal, 1955) and also glucose and glucuronic acid (Rodrigues *et al.*, 1993). The plant produces 178–2000 g/year, with an average value of 700 g/year (Bandeira, 1991). Nut production in trees older than 25 years increases after gum extraction. Given the importance of cashew tree culture to some regions of countries like Brazil (400,000–450,000 ha of plant) (Lima, 1988), India, Mozambique, Tanzania and Kenya, a study of the gum is of potential industrial interest. Polysaccharide gums find wide application because of their rheological properties. The effect of temperature and salts on the solution viscosity of *A. occidentale* gum will be discussed, as well as aspects of molecular heterogeneity and composition of this polysaccharide from Brazilian plants.

EXPERIMENTAL

Origin and purification of gum

Crude gum was collected as natural exudate from cultivated *A. occidentale* trees in the CNPCa-EMBRAPA experimental plantation, Pacajus, Ceará, Brazil, in September 1988. Common-type plants about 20 years old and yellow cashew producers were utilized. Clear nodules free of bark were selected to be purified as Na salts by use of the Rinaudo-Milas method as previously described (Rodrigues *et al.*, 1993).

Sugar composition

The samples (200 mg) were hydrolysed with 4 M trifluoroacetic acid (4 ml) for 2,.3, 4, 5 and 6 h at 100°C.

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To eliminate the excess of acid, MeOH was added (5 × 5 ml) and the solution was concentrated on a rotary evaporator after each alcohol addition. HPLC with refraction index detection was used to analyse hydrolysates. A cationic (Pb^{2+}) column (Phenomenex), with water as solvent at a flow rate of 0·6 ml/min and 80°C, was employed to determine glucose. The analysis of arabinose, rhamnose, galactose and mannose was performed with a NH_2-column (Spherisorb) and acetonitrile–water 85:15 (v/v) as the solvent system at flow rate of 1·5 ml/min and room temperature. Uronic acid content was determined as Na salt by conductometric titration with 0·01 M HCl (Rodrigues *et al.*, 1993).

Molar mass distribution

The peak molar masses (M_{pk}) were estimated with a liquid chromatograph FPLC System and UV-1 Detector (at 280 nm) from Pharmacia, interfaced with a density meter (PAAR-DMA-60/602). To overcome polyelectrolyte effects, all experiments were conducted in molar NaCl. Dextran samples and gum arabic were used as standards.

Viscosity measurement

Measurements were performed in dilute aqueous solution prepared by stirring for a period of 2 h, followed by filtration in a sintered-glass plate of grade fine (4–5·5 μm pore size). Total solubilization was achieved. An Ostwald capillary viscometer of 0·8 mm diameter and flow time for water of 150 s at 25°C was utilized. Intrinsic viscosity determinations were made in the presence of different salts while maintaining the same ionic strength: NaCl 1·00 M, $CaCl_2$ 0·334 M and $AlCl_3$ 0·170 M. Solutions of 2% concentration of gum with different salt contents (1×10^{-4} M–5×10^{-3} M) were prepared by addition of small aliquots of NaCl, $CaCl_2$ or $AlCl_3$ solution. The temperature was 25 ± 0·1°C in all experiments. To study the effect of temperature, solutions of 2 and 3% (w/v) concentration of gum were progressively heated from 25 to 70°C at a rate of 1°C/min. Measurements during cooling (70°C to 25°C) were also made. All flow times were averages of at least five replicates.

RESULTS AND DISCUSSION

A. occidentale gum from the northeast of Brazil has a higher content of galactose and a lower content of arabinose than those gums from India and Papua. The other constituents are similarly distributed (Table 1). This could reflect different hydrolysis conditions utilized with the former material as compared with those of other origins. If so, the lower values of arabinose and rhamnose could be due to the known greater lability of pentoses and 6-deoxyhexoses. Experimental procedure utilized by Anderson *et al.* (1974) was followed initially with the aim of comparison, but 32% of Brazilian gum remains unhydrolysed. The effect of hydrolysis time on the composition in other conditions was studied. Five hours represents the minimum necessary to hydrolyse all material without degradation of arabinose and rhamnose. Therefore, values in Table 1 reflect the correct composition of cashew gum from Brazil and noted differences between this polysaccharide and others from different origins are real.

Table 1. Composition of *A. occidentale* gum from different origins

Constituent sugar	Composition (%) of gum from India[a]	Papua[a]	Brazil[b]
Galactose	61	63	73
Arabinose	14	15	5
Glucose	8	9	11
Rhamnose	7	7	4
Mannose	2	1	1
Xylose	2	—	—
Glucuronic acid	6·2	5·7	6·3

[a] 0·5 M H_2SO_4 for 8 h at 100°C (Anderson *et al.*, 1974).
[b] 4 M trifluoroacetic acid for 5 h at 100°C (present work).

The GPC chromatogram of *A. occidentale* gum is shown in Fig. 1. Three main peaks, designated A, B, C, were detected by density measurements. This gum, therefore, behaves as a heterogeneous system similar to that of gum arabic (*Acacia senegal* gum from Sudan), from which three or four peaks have been obtained by size-exclusion chromatography (Vandevelde & Fenyo, 1985). Anderson and Bell (1975) found that *A. occidentale* gum, examined by zone electrophoresis, thin-layer electrophoresis and ion-exchange chromatography, is a one-component system. Preparative size-exclusion chromatography on Biogel P 300, however, as suggested by Anderson *et al.* (1965) for determining the

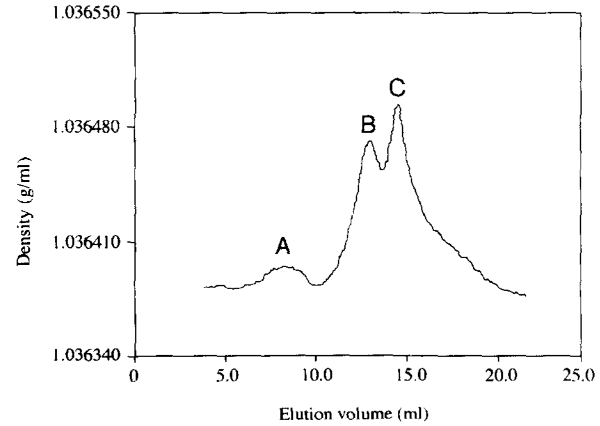

Fig. 1. GPC chromatogram of *A. occidentale* gum solution in 1 M NaCl.

molecular sizes of polysaccharides, also separated the cashew gum into three fractions.

Only one peak, corresponding to A, appeared when ultraviolet detection was used. This result suggests that fraction A is a polysaccharide–protein complex, probably an arabinogalactan–protein, as has been proposed for gum arabic (Fincher *et al.*, 1983). Peaks B and C are due to polysaccharide of different average molar masses.

To estimate M_{pk}, a calibration plot of elution volume was obtained by use of dextran fractions. Fraction A from cashew gum had a peak molar mass of about 9×10^5, the same order of magnitude as arabinogalactan–protein from *A. senegal* gum (10^6) (Vandevelde & Fenyo, 1985). Fractions B and C are low molar mass polysaccharides of M_{pk} $3{\cdot}2 \times 10^4$ and $1{\cdot}6 \times 10^4$, respectively. Anderson and Bell (1975) reported that *A. occidentale* gum has a M_w of $2{\cdot}6 \times 10^5$. The molecular self-aggregation of polysaccharide could explain the high molecular weight determined.

It is well known that separation in GPC is mainly governed by molecular size; i.e. both viscosity and molar mass, and so dextran is not an appropriate standard for a highly branched *A. occidentale* gum. The M_{pk} of *A. senegal* gum ($[\eta] = 14$ ml/g) was determined from the dextran calibration plot. Two peaks corresponding to molar masses of 5×10^5 and 1×10^5 were obtained, in agreement with M_w of $3{\cdot}5 \times 10^5$ calculated by the Mark–Houwink equation of the type $[\eta] = 1{\cdot}6 \times 10^{-2} M_w^{0{\cdot}53}$ (Vandevelde & Fenyo, 1985).

It is also interesting to evaluate the contribution of each fraction to whole gum. Assuming the density difference as proportional to the content of material, cashew gum comprises 6% polysaccharide–protein complex, 42% polysaccharide B ($M_{pk} = 3{\cdot}2 \times 10^4$) and 52% polysaccharide C ($M_{pk} = 1{\cdot}6 \times 10^4$).

RHEOLOGICAL PROPERTIES

General aspects

Polysaccharide gums find application as binding and suspending agents, film-forming materials, crystallization inhibitors, thickening agents, etc. These applications arise from the interesting rheology of these gums. A knowledge of their rheological properties, such as viscosity range, gel characteristics, temperature and salt effects, in addition to their availability and cost, play important roles in the industrial application of such gums.

Cashew gum is a low viscosity gum, comparable in many aspects to gum arabic. The absolute viscosities of 1% solutions of these gums are 1·0 mPa s (cashew gum) and 1·8 mPa s (gum arabic). Other industrial polysaccharide gums like methyl cellulose, CMC HV, karaya, sugar, locust bean and tragacanth have viscosities in the range of 1100–3400 mPa s at the same solution concentration (Meer *et al.*, 1975). Concentration has little effect on the viscosity of *A. occidentale* gum. A 3% solution has an absolute viscosity of 1·2 mPa s, not much greater than those of 2 and 1% solutions, which have 1·1 mPa s and 1·0 mPa s, respectively.

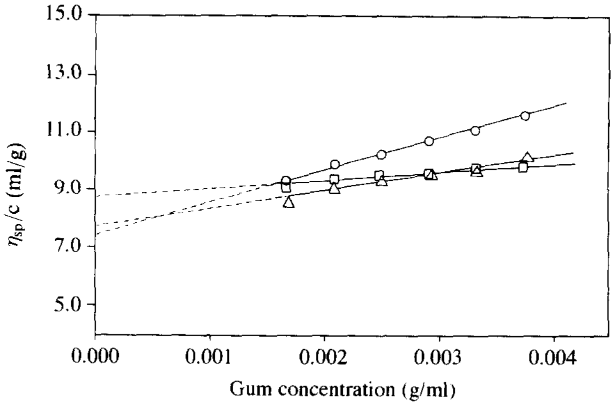

Fig. 2. Effect of salts on the reduced viscosity of *A. occidentale* gum in the presence of: (□) 1 M NaCl, (△) 0·334 M $CaCl_2$; and (○) 0·170 M $AlCl_3$. Temperature, 25°C.

The limit of the dilute regime is characterized by critical concentration $C_c^{\#}$. The average $C_c^{\#}[\eta]$ value proposed by Morris *et al.* (1981) for a random coil polysaccharide is 4. A smaller value (2·6) has been determined for a random coil galactomannan (Ganter *et al.*, 1992). A $C_c^{\#}[\eta]$ value near 1 has been obtained for stiff polysaccharides like xanthan (Milas *et al.*, 1990) and welan (Campana *et al.*, 1990). A value close to 4 was also determined for a semi-rigid polysaccharide (hyaluronate, $C_c^{\#}[\eta] = 3{\cdot}8$) (Fouissac *et al.*, 1993). The *A. occidentale* gum has $[\eta]$ of 8·8 ml/g in 1 M NaCl (Fig. 2). Taking an average $C_c^{\#}[\eta]$ value of 4, $C_c^{\#}$ is 0·45 g/ml. Even using the lowest value of 1, $C_c^{\#}$ is 0·11 g/ml. Thus, cashew gum behaves as in a dilute regime up to concentrations of 45%, or at least up to 11%. All measurements were performed in a very dilute regime (concentration less than 3%). Gum arabic, a similar polysaccharide, exhibits Newtonian behaviour as concentrations up to 40% (Meer, 1980). Although no η vs shear rate data are now available for cashew gum, the other factors suggest that this gum behaves like a Newtonian fluid under the present experimental conditions.

Effect of salts

Generally, viscosity of polyelectrolyte solutions decreases in the presence of electrolytes. If no specific interaction occurs (e.g., with monovalent metal ions) the added counter-ion is attracted towards the poly-ion domain, screens its charge and makes possible the contraction of the macromolecule. If site binding takes place (e.g. in the presence of multivalent ions) intermolecular and intramolecular interactions could occur in addition to the screening effects. The resultant viscosity depends on the relative contributions of these antagonistic effects. The viscosities of arabic and karaya gums decrease in the presence of NaCl (Meer, 1980); however, the addition of $CaCl_2$ and $AlCl_3$ increases the viscosities of karaya gum solutions (Meer, 1980).

The effect of NaCl, $CaCl_2$ and $AlCl_3$ on the reduced viscosity of *A. occidentale* gum solution was investigated (Fig. 2). The ionic strength was maintained at $I = 1$. The limiting value at $c = 0$ ($[\eta]$) decreases in the order: ${}^{[\eta]}\mathrm{NaCl} > {}^{[\eta]}\mathrm{CaCl_2} > {}^{[\eta]}\mathrm{AlCl_3}$, suggesting that the polysaccharide molecule at infinite dilution and in the presence of aluminium ions has a more contracted conformation than in the presence of calcium ions. Sodium ions induce the least chain contraction.

On increasing the concentration of gum ($> 0{\cdot}3$ g/dl) the order of reduced viscosity is reversed. Now, the interaction between the macromolecules is the most important factor. Different degrees of inter and intramolecular interactions are taking place. Aluminium ions are a more effective crosslinking agent than calcium ions. Sodium ions do not promote this kind of interaction.

The contribution of the shielding and crosslinking effects can be seen in the curve of specific viscosity vs salt concentration (Fig. 3). In the presence of NaCl, only the shielding effect occurs (η_{sp} decreases as salt concentration increases). Up to $2{\cdot}5 \times 10^{-4}$ M in $CaCl_2$, the shielding effect is predominant. In more concentrated solution, the crosslinking effect prevails. For $AlCl_3$, the crosslinking contribution is greater than the shielding one, at least at concentrations higher than 10^{-4} M.

The two experiments indicate that the affinity between *A. occidentale* gum and metal ions follows the order $Al^{3+} > Ca^{2+} > Na^+$. Rendelman (1978) proposed the same order of affinity of metal ions with carbohydrates containing carboxylate groups. The author suggests that the interaction is of electrostatic character, of inner sphere type and dependent on the charge/ionic radii ratios, which are 0·058, 0·020 and 0·009, for Al^{3+}, Ca^{2+} and Na^+, respectively. The order of the affinity for alginates (Matsumoto & Mashiko, 1990) and CMC (Matsumoto & Mashiko, 1988) is $Ca^{2+} > Na^+$, and for karaya gum (Meer, 1980) $Al^{3+} > Ca^{2+} > Na^+$, in agreement with the result found for cashew gum.

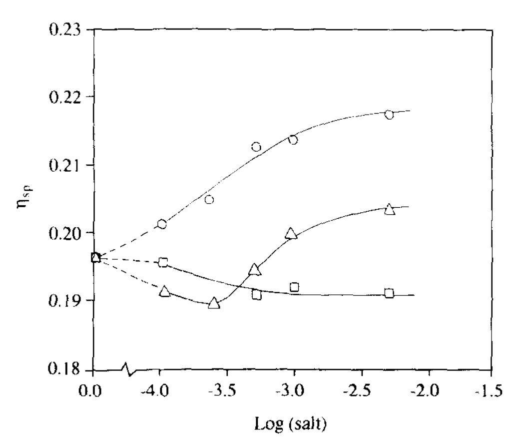

Fig. 3. Effect of salt concentration on the specific viscosity of 2% *A. occidentale* gum solution in the presence of: (□) NaCl; (△) $CaCl_2$; and (○) $AlCl_3$. Temperature, 25°C.

Effect of temperature

The viscosity of *A. occidentale* gum solution (2 and 3%) decreased with increasing temperature (Fig. 4). This may be attributed to: (a) the energy required to overcome the potential energy barrier (activation energy of flow) upon transition from one equilibrium to the next; (b) degradation of polymer; or (c) conformational (ordered–disorder) transition. No degradation occurs, since the temperature dependence at viscosity for a 2% cashew gum solution was the same on cooling from 70°C as during heating. A conformational transition, like the helix–coil in succinoglycan (Rinaudo, 1992) or in xanthan (Rinaudo *et al.*, 1979) does not occur. The *A. occidentale* gum is a highly branched heteropolysaccharide, with no ordered conformation.

An Arrhenius–Frenkel–Eyring equation ($\eta = B\exp(E/RT)$) (Vinogradov & Malkin, 1980) was applied to the η–T data. A simple linear dependence of ln η vs T^{-1} was observed for all gum solutions, as confirmation of no ordered–disorder transition. From the slope of the straight lines, the activation energy of flow (E) was calculated. Solutions at 2 and 3% exhibit E values of 15·6 and 16·2 kJ mol^{-1}, respectively.

It is well known that the value of E is affected by factors that determine the flexibility and interactions of macromolecules. Activation energy for flow of solution is also dependent on the solute concentration. For polymers of sufficiently high molar mass (10^4 or greater)

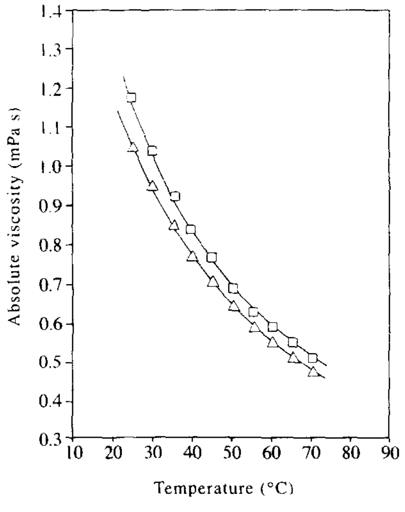

Fig. 4. Effect of temperature on the absolute viscosity of *A. occidentale* gum: (△) 2% sol.; and (□) 3% sol.

E is no longer dependent on molar mass (Vinogradov & Malkin, 1980).

Alginate and sodium carboxymethylcellulose (CMC-Na) exhibit, in 4% solution, *E* values of 23 and 27 kJ mol^{-1} (Narayan & Ramasubramanian, 1982), higher than that of *A. occidentale* gum in 3% solution (16·2 kJ mol^{-1}). They are, however, linear polymers strongly bonded by intra and intramolecular interactions involving hydrogen bonding and carboxylate–metal ions. In these cases, a high activation energy of flow is expected. The cashew gum is a branched polysaccharide with little possible interaction, similar to gum arabic, which has a comparable *E* value of 15 kJ mol^{-1} for a 2% solution (Varfolomeeva *et al.*, 1980).

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