

Solution Properties of Polysaccharides from *Anacardium occidentale*

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ABSTRAK

Kelikatan pecahan-pecahan polisakarida terlarut daripada *Anacardium occidentale* telah diukur. Kajian secara titratan potentiometri dan penentuan kandungan ion-ion logam yang biasa ditemui dalam gam menunjukkan bahawa perbezaan kelarutan dan kelikatan pecahan-pecahan itu mungkin disebabkan oleh perbezaan darjah pengasilan dan kandungan kation divalen. Pecahan dengan darjah pengasilan yang lebih tinggi membentuk gel, tetapi selepas pendeasilan separa, terserak di dalam air membentuk suatu serakan gel yang stabil. Kelikatan yang lebih tinggi yang diperlihatkan oleh pecahan terlarut mungkin disebabkan oleh kandungan ion divalen yang lebih tinggi.

ABSTRACT

The viscosities of fractions of polysaccharide obtained from *Anacardium occidentale* dissolved in aqueous solutions were measured. Investigation by potentiometric titration and determination of common metal ion contents in the gum indicated that the solubility and viscosity differences of the fractions may be attributable to the difference in the degree of acylation and the content of the divalent cations present in the fractions. The fractions with higher degrees of acylation form a gel, but when partially deacylated disperse in water to form a stable gel dispersion. The higher viscosity exhibited by the soluble fraction is attributable to the higher content of divalent cations.

Keywords: cashew gum, *Anacardium occidentale*, viscosity, solubility, metal ions contents, degree of acylation

INTRODUCTION

Anacardium occidentale [54577-58-1], or cashew, is a species of woody green trees widely grown in many tropical and subtropical countries, known for its nuts used as a food ingredient especially in oriental delicacies. Under certain conditions the bark of cashew exudates a gummy material known in general as cashew gum. It is a complex polysaccharide, comprising 61% galactose, 14% arabinose, 7% rhamnose, 8% glucose, 5% glucuronic acid and < 2% other sugar residues in a highly branched galactan framework consisting of chains of β -(1 \rightarrow 3)-D-galactose residues interspersed with β -(1 \rightarrow 6) linkage. The main aldobiuronic acid present is 6-O-(β -D-glucopyranosyluronic acid)-D-galactose

(Bose and Biswas 1970; Anderson *et al.* 1974; Anderson and Bell 1975). Gums exudated from many other related plant species are well known in the world, notably gum arabic from *Acacia* which is widely used as a conditioner in the food industry (Glicksman 1969). Although cashew gum has not found many industrial uses, its applications in the field of pharmacy have long been described (Howes 1949; Smith and Montgomery 1959). Current interest in *A. occidentale* centres on the various extracts from other parts of the plants, especially the apple juice and nutshell liquid which have been reported to show breast anti-tumour activity (e.g. Kubo *et al.* 1993; Toyomizu *et al.* 1993).

It was reported earlier (Zakaria and Rahman 1996) that cashew gum dissolves in water to give a soluble fraction (cold water dissolution) and the residue forms a stable gel dispersion when stirred in hot water. Since the gum is basically soluble in water, further detailed characterization is desirable in view of incorporating it into the preparation of porous films or beads of chitin and chitosan which are also natural polysaccharides currently being actively researched in our laboratory for agricultural applications. The present paper focuses on the solution properties of the polysaccharide.

MATERIALS AND METHODS

Origin of Samples

Samples of gum exudates were collected from the trees grown in the east coast of Peninsular Malaysia. No details of the botanical aspects of the species were noted. The gum was in the form of lumps with some contamination from tree bark debris. The appearance was colourless to light amber. The samples were ground to pass through a 2.5-mm sieve. The moisture content of the samples was 17.17%, determined by drying overnight at 105°C to constant weight.

Preparation of Solutions

Dried gum (10 g) was stirred in distilled water (250 ml) for 2-3 h at room temperature (RT). The supernatant was separated by centrifuge followed by decantation. The residue was washed with water and the washing water added to the separated supernatant. The procedure was repeated twice more and finally the supernatant was made up to 500 ml. Triplicate 10-ml aliquots were dried at 105°C to determine the amount of dissolved solids and hence the soluble fraction. The residue was treated similarly, but stirred on a hot water bath at 90-95°C. The dissolved solid obtained by this treatment is called gel dispersion. The whole gum solution was prepared by subjecting samples of raw gum to a combination of the preparation procedures of soluble fraction and gel dispersion.

Measurement of Viscosities

Viscosities were measured on a Haake Rotovisko RV3 using NV sensor head and two torsion springs of DMK 50 and DMK 500 g cm. Shear stress, τ (dyne cm⁻²)

and shear rate, D (s^{-1}) were deduced from the appropriate instrument readings to calculate the viscosities, η (cps) as the ratio of τ/D . All concentrations of solutions used for viscosity measurement (including the diluted solutions) were determined by the evaporation triplicate of aliquots. For the effect of pH, the pH values were adjusted by addition of 1M HCl or 1M NaOH prior to concentration determination. All measurements were made at RT ($30 \pm 2^\circ C$).

Potentiometric Titration

The potentiometric titrations were carried out on the two fractions as described elsewhere (Ashton *et al.* 1975; Jefferies *et al.* 1977, 1978; Phillips *et al.* 1980) at room temperature with potassium hydroxide 1M and hydrochloric acid 1M. For hydrolysis to determine the acetyl content, 100 ml of 1M NaOH was added to 100 ml of sample and left overnight. The mixture was then potentiometrically back-titrated against 1M HCl to determine the amount of KOH consumed.

Determination of Metal Ion Contents

Four metal ions (calcium, magnesium, potassium and sodium) commonly found in gums were determined for each solution (Selby and Wynne 1973). Solutions of each fraction (100 ml of known concentration) were evaporated on a hot plate, then transferred to a crucible and ashed in an oven at $650-700^\circ C$ overnight. Concentrated HCl (1 ml) was then added to the ash to dissolve the solid and the solution made up to 50 ml with distilled water. The metal contents were determined on a Varian Techtron AAS using solutions of chlorides of Ca, Mg, K and Na of AnalaR grade as standards.

RESULTS AND DISCUSSION

The viscosity of fractions of cashew gum are shown in *Fig. 1*, in which the soluble fraction clearly exhibits a higher viscosity than the gel dispersion, and in turn higher than the whole gum solution. The differences in the measured solubility and viscosity of fractions of gum solutions arise, in general, from the degree of acylation of the sugar units in the chains, which limits the solubility and promotes a higher viscosity (Phillips *et al.* 1980), and from the polyvalent cation content which also acts to promote a higher viscosity (Jefferies *et al.* 1978). Deacylation will thus allow the gel fraction to form a stable dispersion and, to some extent, lower the viscosity. The polyvalent cations may induce the chains of the polysaccharide to interact inter- or intra-molecularly, thus exhibiting a higher viscosity (Schweiger 1962). These interactions are suppressed under higher shear rates, as indicated by the lower viscosities of all the fractions at higher shear rates in *Fig. 1*. It seems that the viscosity of the whole gum solution under high shear rate is the limiting range of the viscosities of cashew gum fractions because (as will be discussed later) the solution is prepared and the viscosity is measured under conditions that promote a solution in which the higher viscosity is suppressed.

Detailed analyses of the potentiometric titration results are described elsewhere (Ashton *et al.* 1975; Jefferies *et al.* 1978; Phillips *et al.* 1980). The titre

with potassium hydroxide from natural pH to neutrality represents titration of the acid form of the polysaccharide. The titre with hydrochloric acid from natural pH to pH 2.5 represents titration of the salt form of the polyanion. Blank titres using distilled water were conducted and the equivalent weight and proportion of the polymer in the salt form calculated. The data for the cashew gum are presented in Table 1. The acid equivalent weight of 2944 for the soluble fraction and 3323 for the gel dispersion are relatively similar, and comparable to the value of 3368 calculated using the data of Anderson and Bell (1975) based on the glucuronic acid content and assuming other sugar residues to have a relative molar mass of 150. This result indicates that the difference in viscosities between the soluble fraction and the gel dispersion is not due to the difference in the acid form of the polysaccharide as in the case of acid gelling of algin (McNeely and Petitt 1973) and pectin (Towle and Christensen 1973). This is further supported by the fact that the variation of viscosities with pH of the solution (*Fig. 2*) is comparable with that in *Fig. 1*. The lower viscosities in the region of low pH (acid form) and high pH (salt form) and maximum in the vicinity of the natural pH is the normal behaviour of a polyelectrolyte solution (Katchalsky 1951).

The acyl group content of cashew gum determined by alkaline hydrolysis, expressed as % w/w acetyl group, is 4.75 for the soluble fraction and 6.50 for the gel dispersion. The corresponding figures for gum ghatti are 3.65 and 4.95 respectively (Jefferies *et al.* 1978). Gum karaya is a heavily acetylated polysaccharide (Money 1951; Jefferies *et al.* 1977), inducing insolubility by forming the gel, which is rendered soluble after deacetylation, when dispersed in water (Aspinall and Nasir-Ud-din 1965). Thus, the slightly higher value of acyl groups in the gel dispersion of cashew gum may have been responsible for the solubility behaviour observed (Zakaria and Rahman 1996). During the hot stirring, the gel is partially deacetylated and forms a stable dispersion which, however, has a lower viscosity than the soluble fraction. This is in contrast with the behaviour of gum ghatti solutions in which the gel dispersion has a higher viscosity (Jefferies *et al.* 1978).

TABLE 1
Potentiometric titration data of fractions of cashew gum

Parameter	Soluble fraction	Gel dispersion
Acid equivalent weight	2944	3323
Milliequivalent of ionic group per gram of gum	2.26	2.99
Sugar unit per anionic group	2.48	1.99
% Salt form	86.6	89.2
% Acid form	13.4	10.8
Sugar unit per acyl group	5.25	3.71
% w/w acetyl group equivalent	4.8	6.5
pK _a	3.5	3.3

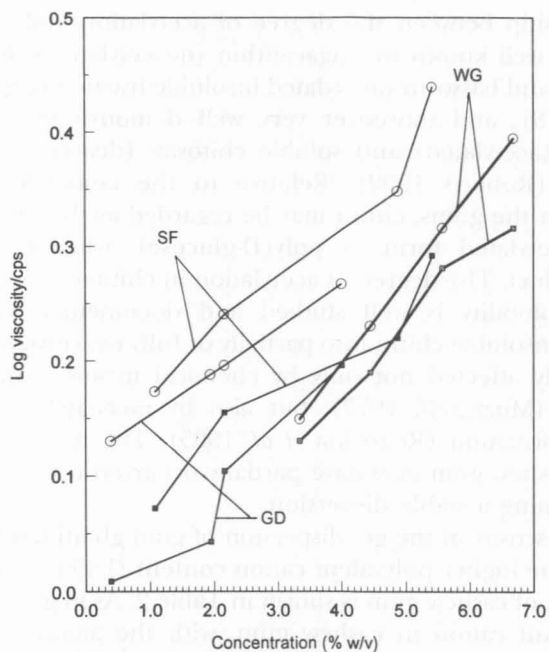


Fig. 1. Viscosities of soluble fraction (SF), gel dispersion (GD) and whole gum fraction (WG) of cashew gum at shear rates of (○) 340 s⁻¹ and (■) 3900 s⁻¹ (natural pH)

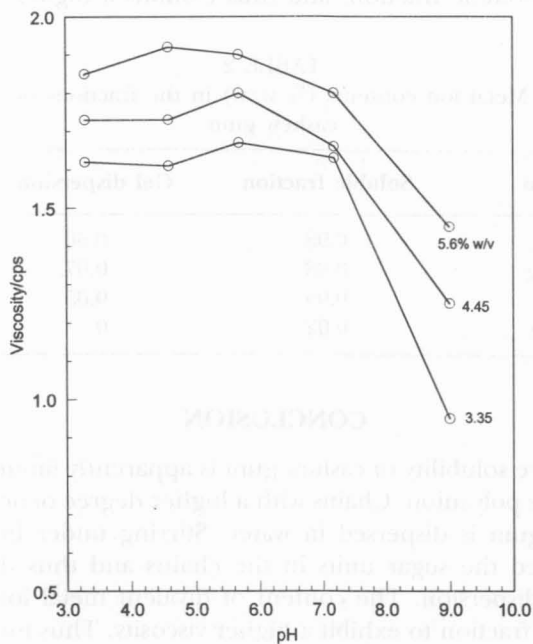


Fig. 2. The effect of pH on the viscosities of whole gum fraction of cashew gum at the concentration indicated (shear rate $D = 1.36 \times 10^3$ s⁻¹)

The relationship between the degree of acetylation and the solubility of polysaccharide is well known in tragacanthin (deacetylated soluble fraction of gum tragacanth) and bassorin (acetylated insoluble fraction of gum tragacanth) (Meer *et al.* 1973), and moreover very well demonstrated in the case of insoluble chitin (acetylated) and soluble chitosan (deacetylated) in aqueous solvent systems (Roberts 1992). Relative to the complex nature of the polysaccharides in the gums, chitin may be regarded as the model compound; chitin is the acetylated form of poly(D-glucose), whereas chitosan is its deacetylated product. The degree of acetylation in chitin-chitosan in relation to their aqueous solubility is well studied and documented (Roberts 1995). Deacetylation of insoluble chitin into partially or fully deacetylated product, e.g. chitosan is readily affected not only by chemical means, homogeneously or heterogeneously (Muzzarelli 1977), but also by mechanical means such as under shear deformation (Rogovina *et al.* 1995). The deacylation of the gel fraction of the cashew gum may have partially occurred under the hot stirring regime, thus forming a stable dispersion.

The higher viscosity of the gel dispersion of gum ghatti has been suggested as being due to the higher polyvalent cation content (Jefferies *et al.* 1978). The metal ion content of cashew gum is shown in Table 2. As in gum ghatti, calcium is the predominant cation in cashew gum, with the amount present in the soluble fraction being slightly higher than in the gel dispersion. This may explain the observed higher viscosity of the soluble fraction in parallel with the fact that in the case of gum ghatti, the gel fraction contains more divalent cations than the soluble fraction, and thus exhibits a higher viscosity.

TABLE 2
Metal ion contents (% w/w) in the fractions of
cashew gum

Ion	Soluble fraction	Gel dispersion
Ca	0.98	0.80
Mg	0.08	0.07
K	0.05	0.05
Na	0.02	0

CONCLUSION

Room temperature solubility of cashew gum is apparently limited by the degree of acylation of the polyanion. Chains with a higher degree of acylation will form a gel when the gum is dispersed in water. Stirring under heating may have partially deacylated the sugar units in the chains and thus the gum fraction formed a stable dispersion. The content of divalent metal ions bound to the chains causes the fraction to exhibit a higher viscosity. Thus for the gel fraction of the cashew gum, despite the insolubility due to the higher degree of

acylation, the viscosity of the dispersion obtained after partial deacylation is lower than that of the soluble fraction because of its lower polyvalent cation contents.

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