

# Synthesis and Characterization of Carboxymethylated Red Angico (*Anadenanthera macrocarpa*) Exudate Polysaccharide

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**ABSTRACT:** Red angico is a heteropolysaccharide (arabinogalactan) obtained from *Anadenanthera macrocarpa* trees. Carboxymethylation of angico gum (AG) with monochloroacetic acid (MCA) in alkaline aqueous medium resulted in samples which were characterized by <sup>13</sup>C nuclear magnetic resonance spectroscopy and gel permeation chromatography. The effects of reaction parameters, such as alkali concentration, MCA/AG ratio and temperature on the reaction yield and degree of substitution (DS) were investigated. The DS and MCA total efficiency values increase up to 2 h reaction time and then decrease. The DS varied from 0.11

to 1.10 depending on NaOH/MCA/AG ratio and temperature. The highest MCA total efficiency (0.57) was obtained for NaOH/MCA/AG molar ratio equal to 3:1:1, at 70°C. (DS = 0.63, yield = 91.0%). Nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) analysis shows that polymer degradation was observed in all samples. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2985–2991, 2007

**Key words:** red angico; *Anadenanthera macrocarpa* gum; arabinogalactan; NMR; GPC; carboxymethylation

## INTRODUCTION

*Anadenanthera macrocarpa* tree (*red angico*) is a plant from Northeast of Brazil.<sup>1</sup> Its bark is used as a tanning agent for leather and the wood as a construction material. The exudate gum is employed as an adhesive and alternative medicine in some regions of Brazil.<sup>2</sup> The gum is a polysaccharide (AG) composed of arabinose (67%), galactose (24%), rhamnose (2%) and glucuronic acid (7%).<sup>3</sup> Molecular characteristics of the whole polysaccharide and its fractions obtained by fractional precipitation have been investigated by static light scattering, dilute solution viscometry, and gel permeation chromatography (GPC). Hydrodynamic properties of polysaccharide fractions indicated a highly branched structure and a dependence of molar mass (M) on intrinsic viscosity [ $\eta$ ], expressed by the equation: [ $\eta$ ] = 0.0145M<sup>0.44</sup>, with intrinsic viscosity giving in mL/g. The gum was found to have a broad molar mass distribution with  $M_w = 3.7 \times 10^6$  g/mol and [ $\eta$ ] = 11 mL/g in 1M NaCl at 25°C.<sup>3</sup> "Angico" polysaccharide has low carboxyl content and so this study intend to introduce new carboxyl groups to make it

more useful for industrial applications as the formation of nanosphere by interaction with polycations or as adsorbent material for heavy metal adsorption, after crosslinking reaction. These investigations are already been carried out in our research laboratory.

Carboxymethylation is one of the most used reactions for chemical modification of polysaccharide because of the low cost of the chemicals, the nontoxicity of the products, and the ease of processing.<sup>4</sup> The obtained derivatives are usually polyelectrolyte that can be applied in the chemical, food, pharmaceutical, and cosmetic industries. The reaction is based on the Williamson synthesis, whereby the polysaccharide alkoxide is reacted with monochloroacetic acid (MCA) and the primary and secondary alcohol groups are substituted by carboxyl groups.

Reaction parameters (temperature, solvent, reaction time, and reagent concentration) and their effect on the degree of substitution (DS) and yield have been recently investigated for many polysaccharides, such as starch,<sup>5–9</sup> cellulose,<sup>10–12</sup> inulin,<sup>4</sup> cashew gum (CG),<sup>13</sup> *Cassia tora* gum,<sup>14</sup> *Cassia occidentalis* gum,<sup>15</sup> and Konjac gum.<sup>16</sup>

The aim of this work was to study the reaction parameter on the synthesis of carboxymethylated *A macrocarpa* polysaccharide (CMAG) with different degrees of substitution.

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## EXPERIMENTAL

### Origin and purification of the parent polymer

Crude polysaccharide samples were collected from *A. macrocarpa* native trees at Fortaleza, Ceará, Brazil. They were purified as a sodium salt using the method previously described.<sup>17</sup> Nodules free of bark were selected and dissolved in distilled water at room temperature to give a 5% (w/v) solution. The solution pH was adjusted to ~ 7.0 by addition of diluted aqueous NaOH. The clear solution was successively filtered through sintered glass and the purified polysaccharide precipitated with ethanol, after NaCl addition.

### Carboxymethylation reaction

The purified gum (4 g, ~ 0.027 mol) was mixed with volume of water in the range of 3.2–10 mL, until a homogeneous paste was formed. A 10M NaOH solution (volume in the range of 2.8–25.1 mL) was added and the mixture was kneaded for 10 min. After that, MCA (2.64–10.6 g) was mixed thoroughly with the paste. The mixture was heated at 35 and 70°C for 2 h. The reaction conditions applied to each sample are reported in Table I. The system was neutralized with 1M HCl and dialysed against distilled water until all remained reagents or added salt were eliminated (4–5 days). The solid carboxymethylated products (CMAG) were recovered by freeze-drying. The effect of reaction time on DS was investigated using reaction condition as described for sample 3.

### Degree of substitution

DS was determined by potentiometric back-titration. DS was calculated by the molar ratio of carboxymethyl acid groups to monosaccharide units, as following

$$\text{DS} = \frac{\text{mol of } -\text{CH}_2\text{COOH groups}}{\text{mol of monosaccharide unit}} \quad (1)$$

The molar mass of arabinose (168 g/mol), as the major constituent of angico polysaccharide,<sup>3</sup> was used to calculate the mols of monosaccharide units. A first value of DS was determined. The new molar mass of average monosaccharide units was then recalculated taking into account the addition of 58 g/mol (molar mass of CH<sub>2</sub>COOH) for each DS increase of 1.0 unity. The method of successive approximation was applied to obtain the final DS.<sup>13</sup>

### Reaction efficiency

Verraest et al.<sup>4</sup> proposed a parameter to measure the extent to which the carboxymethylation is favored compared with a competitive reaction, such as the hydrolysis of MCA into glycolate. This parameter is denominated MCA efficiency and is given by:

$$\text{MCA efficiency} = \text{DS/MCA} - \text{gum molar ratio} \quad (2)$$

Considering that the yield is also an important factor to measure the extent to which carboxymethylated macromolecular products are favored, Silva et al.<sup>13</sup> proposed another parameter, the MCA total efficiency, defined as:

$$\text{MCA total efficiency} = (\text{MCA efficiency}) \times \text{yield}/100 \quad (3)$$

### Gel permeation chromatography

Sample molar mass distribution was determined by GPC at room temperature using an Ultrahydrogel linear 7.8 × 300 mm<sup>2</sup> column and 0.1M NaNO<sub>3</sub> as solvent. A differential refractometer was used as detector. The GPC system was calibrated with pullulan standards from Showa Denko having molar masses ranging from 5.9 × 10<sup>3</sup> to 7.88 × 10<sup>5</sup>, for determination of parent polymer molar mass.

### Nuclear magnetic resonance spectroscopy

<sup>13</sup>C-Nuclear magnetic resonance (NMR) spectra of 5% w/v solutions in D<sub>2</sub>O at 80°C were recorded in a

TABLE I  
Carboxymethylation Reaction Conditions

CMAG sample	Volume of 10M NaOH (mL)	MCA mass (g)	Volume of H <sub>2</sub> O (mL)	[NaOH] (M)	Molar ratio NaOH/MCA/AG	Temperature (°C)
1	2.8	2.64	10	2.2	1:1:1	70
2	5.6	2.64	10	3.6	2:1:1	70
3	8.4	2.64	10	4.6	3:1:1	70
4	11.2	2.64	10	5.3	4:1:1	70
5	8.4	2.64	10	4.6	3:1:1	35
6	5.6	10.6	10	3.6	2:4:1	70
7	8.4	10.6	10	4.6	3:4:1	70
8	16.8	5.27	3.2	8.4	6:2:1	70
9	25.1	7.91	4.9	8.4	9:3:1	70

Mass of *angico* gum was maintained in 4 g and reaction time in 2 h.

Bruker DRX 500 spectrometer. Chemical shifts were given in values relative to internal acetone at 31.07 ppm. A distortionless enhancement through polarization transfer (DEPT) spectrum was recorded to determine the multiplicity of carbon peaks; the acquisition and delay times were 1.0 s. DEPT spectrum was obtained with final  $^1\text{H}$  pulse flip angle of  $135^\circ$  (DEPT 135). The signals in the  $^{13}\text{C}$ -NMR spectrum were assigned based on literature data for correlated compounds.<sup>18–20</sup>

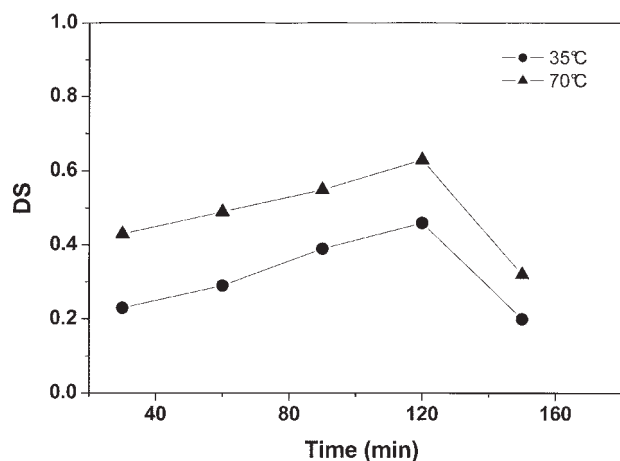
## RESULTS AND DISCUSSION

### Effect of reaction time and temperature on DS

The effect of reaction time and temperature on the DS (Fig. 1) of *Anadenanthera macrocarpa* polysaccharide was investigated keeping the NaOH/MCA/AG ratio at 3:1:1 (CMAG samples 3 and 5, Table I). Considering that MCA/AG ratio is equal to 1.0, MCA efficiency has the same numerical value of DS. The increase of reaction time up to 2 h seems to favor carboxymethylation reaction, however, after this time the side reaction in which MCA react with sodium hydroxide, leading to the formation of sodium glycolate, prevails with a consequent decrease in DS. The decrease in DS after 2 h reaction time was found to be independent of temperature. This behavior was also reported for *Cassia occidentalis* seed gum<sup>15</sup> and *Cassia tora* gum,<sup>14</sup> after 1 h of carboxymethylation reaction.

Assuming that the increase of DS with reaction time represents the carboxymethylation rate, it can be seen that between 30 and 120 min the rate seems to be the same at both temperature (30 and  $70^\circ\text{C}$ ).

In general, the DS increases with the increase of reaction time until a plateau is reached. This plateau depends on reaction condition and polysaccharide type. The carboxymethylation of inulin at  $95^\circ\text{C}$ , in aqueous medium and NaOH/MCA/inulin molar ra-



**Figure 1** Correlation between reaction time and DS at different temperatures.

tio of 4.2:2:1 reaches the plateau after about 60 min.<sup>4</sup> The DS for corn and amaranth carboxymethylated derivatives has no significant increase after 90 min of reaction in isopropyl alcohol at 65 and  $30^\circ\text{C}$ , respectively.<sup>8</sup> On the other hand, the plateau was not reached up to 8 h of carboxymethylation of potato starch in different alcohols at  $40^\circ\text{C}$ .<sup>6</sup> The enhancement of DS by prolonging the reaction time is considered to be a direct consequence of the favorable effect of time on swelling as well as the diffusion and adsorption of the reactants, with the ultimate effect of better contact between the etherifying agents and polysaccharide.<sup>8</sup>

The temperature effect on DS for CMAG samples is also depicted in Figure 1. It is shown that the increase of temperature leads to DS increasing. As the carboxymethylation reaction was carried out in high gum concentration ( $\approx 27\%$ ), the higher the temperature a decrease in the solution viscosity is observed with a better contact between reagents which increase the reaction efficiency. The maximal DS (0.63) and MCA total efficiency (0.57), as well as the yield (91.0%) were obtained at  $70^\circ\text{C}$ . Similar behavior was observed for granular potato starch in the range of  $30$ – $50^\circ\text{C}$ ,<sup>6</sup> *Cassia tora* gum from  $30^\circ\text{C}$  to reflux temperature,<sup>14</sup> corn starch in the range of  $30$ – $55^\circ\text{C}$  and amaranth starch from 45 to  $65^\circ\text{C}$ .<sup>8</sup>

### Effect of NaOH concentration on DS and product yield

The effect of NaOH concentration on DS and yield, for a given MCA/polysaccharide molar ratio and temperature is shown in Table II (CMAG samples 1–4). The DS and the yield increase with alkali concentration up to 4.6M NaOH and then decreases sharply. The latter is likely to be because of the occurrence of competitive reaction of sodium hydroxide with MCA, leading to a less substituted polymer.

For carboxymethylated CG an increase of DS was observed up to 6.2M NaOH.<sup>13</sup> The presence of a maximum DS in a particular NaOH concentration has also been found for starch from different sources.<sup>6,8,11,12</sup>

### Simultaneous effect of MCA and NaOH concentration on DS

The simultaneous effect of MCA and NaOH concentration on DS was investigated keeping temperature and solvent constant (CMAG samples 3, 8, and 9; Table II). The DS increases with MCA and NaOH concentration, and reaches the highest value (1.10) for NaOH/MCA/AG of 9 : 3 : 1 (Table II). On the other hand, the yield and the MCA total efficiency become insignificant (7.5 and 0.03, respectively). These effects may be due to polymer degradation caused by high NaOH concentration that led to lost of material and reduced reaction yield. For carboxymethylation of

**TABLE II**  
Efficiency of Reaction Conditions in the Production of Carboxymethylated AG Samples

CMAG sample	NaOH/MCA/AG molar ratio	Temperature (°C)	[NaOH] (M)	DS	Yield (%)	MCA efficiency <sup>a</sup>	MCA total efficiency <sup>b</sup>
1	1 : 1 : 1	70	2.2	0.28	53.0	0.28	0.15
2	2 : 1 : 1	70	3.6	0.43	86.0	0.43	0.37
3	3 : 1 : 1	70	4.6	0.63	91.0	0.63	0.57
4	4 : 1 : 1	70	5.3	0.38	44.0	0.38	0.17
5	3 : 1 : 1	35	4.6	0.42	71.3	0.42	0.23
6	2 : 4 : 1	70	3.6	0.42	44.0	0.21	0.09
7	3 : 4 : 1	70	4.6	0.11	71.0	0.02	0.01
8	6 : 2 : 1	70	8.4	0.71	3.1	0.35	0.01
9	9 : 3 : 1	70	8.4	1.10	7.5	0.37	0.03

<sup>a</sup> MCA efficiency is calculated by eq. (2).

<sup>b</sup> MCA total efficiency is calculated by eq. (3).

CG<sup>13</sup> similar effects were observed, although resulting in higher DS value (2.21) and MCA total efficiency not so low (0.23) for NaOH/MCA/CG of 6 : 3 : 1. The differences in DS and MCA observed between CG and *A. macrocarpa* polysaccharide may be because of composition. As *A. macrocarpa* polysaccharide has higher arabinose content, which is more labile than galactose, the main monosaccharide present in CG.<sup>18</sup>

DS values obtained by increasing MCA concentration, keeping NaOH/AG constant to 2 : 1 (CMAG samples 2 and 6, Table II) were only slightly affected. On the other hand for 3 : 1 NaOH/AG ratio an increase in four times of MCA concentration led to a DS dropping (CMAG samples 3 and 7) from 0.63 to 0.11. For *Cassia occidentalis* gum increase MCA concentration keeping NaOH/Gum ratio of 3.33 : 1 led to an increase of DS for MCA : G ratio of 1.76 : 1 (DS = 0.46).<sup>15</sup> For higher MCA concentration, a DS decrease was observed.<sup>15</sup>

### Comparison of carboxymethylation reaction parameters of different polysaccharides

Optimized reaction conditions (temperature and time of reaction, concentration of NaOH and MCA and also solvent) used for different polysaccharide are

compared in Table III.<sup>4,6,8,13–16</sup> The most efficient reactions were obtained at different temperature, depending on the polysaccharide, and varied from 30 to 95°C. In general, solvents are alcohols/water mixtures. The optimum NaOH/polysaccharide molar ratio ranged from 1.7 to 8 times. The amount of MCA necessary to a more efficient carboxymethylation reaction varied from 1 to 4 times the amount of polysaccharide. The highest NaOH/MCA molar ratio is 3. In most cases, reaction time of 3 h or less are enough to produce the optimized carboxymethylated product. Wheat and potato starch presented DS larger than 1.<sup>6</sup> *Cassia tora* polysaccharide showed the smallest DS value.<sup>14</sup>

The reaction condition employed for the *A. macrocarpa* carboxymethylation, such as short reaction time, low amount of MCA, low cost solvent (water), and high yield (91%), in comparison with other polysaccharide reaction parameters, indicate that this process exhibit some advantages over others.

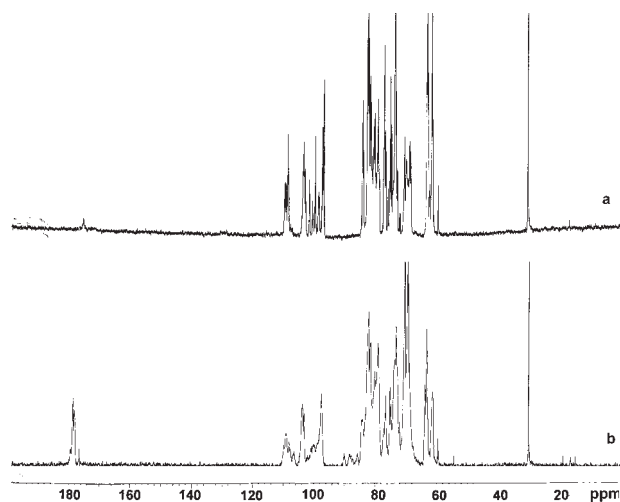
### <sup>13</sup>C-Nuclear Magnetic Resonance

The <sup>13</sup>C-NMR spectrum of *A. macrocarpa* gum [Fig. 2(a)] is rather complex. The polysaccharide shows a low intensity signal at the highest extreme field

**TABLE III**  
Comparison of Carboxymethylation Reaction Efficiency in Optimized Condition for Different Polyssaccharides

Polysaccharide (P) origin	Polysaccharide (P) type	Reaction temp (°C)	Reaction time (h)	NAOH/MCA/P mol ratio	DS	MCA eff	Solvent	Ref
<i>Cassia occidentalis</i>	Galactomannan	80	1	3.3 : 1.8 : 1	0.46	0.26	MeOH/H <sub>2</sub> O	15
<i>Cassia tora</i>	Glucomannan	Reflux	1	4.2 : 2.8 : 1	0.099	0.035	MeOH/H <sub>2</sub> O	14
<i>Amorphophallus konjac</i>	Glucomannan	50	40	2.4 : 1.6 : 1	0.32	0.20	MeOH/H <sub>2</sub> O	16
Starch	Wheat	55	5	1.7 : 1.7 : 1	1.40	0.82	IsopOH/H <sub>2</sub> O	6
Starch	Potato	40	8.3	2.5 : 2.5 : 1	1.30	0.55	IsopOH/H <sub>2</sub> O	6
Starch	Corn	65	1.5	2.5 : 2.0 : 1	0.24	0.11	CycloH/H <sub>2</sub> O	8
Starch	Amaranth	30	1.5	7.9 : 3.1 : 1	0.34	0.15	CycloH/H <sub>2</sub> O	8
Inulin	Fructan	95	5	8 : 4 : 1	0.99	0.25	H <sub>2</sub> O	4
<i>Anacardium occidentale</i>	arabinogalactan	55	3	3 : 1 : 1	0.90	0.90	H <sub>2</sub> O	13
<i>Anadenanthera macrocarpa</i>	arabinogalactan	70	2	3 : 1 : 1	0.63	0.63	H <sub>2</sub> O	This work

IsopOH, isopropyl alcohol; CycloH, cyclohexane.



**Figure 2**  $^{13}\text{C}$ -NMR spectrum of AG (a) and CMAG 3, DS = 0.63 (b).

(17.5 ppm) because of methyl groups of rhamnose residues.<sup>19–20</sup> In the anomeric region (90–110 ppm), 19 peaks were observed. Since only four monosaccharide residue units were identified by HPLC,<sup>3</sup> this point out to a highly branched structure, where the sugar residues seems to be subjected to different environments. This finding is in good agreement with results obtained by viscometric studies.<sup>3</sup> *Anadenanthera colubrina*  $^{13}\text{C}$ -NMR spectra have also been found to be complex, with 20 C-1 signals.<sup>20</sup> Peak due to C=O of glucuronic acid of *A. macrocarpa* gum was not detected by NMR [178 ppm, Fig. 2(a)], however, its presence was determined by potentiometric titration being calculated as 5.0%.

The presence of anomeric carbons from (1 $\rightarrow\alpha$ -arabinofuranose (110.3 ppm), (1 $\rightarrow$ 3)  $\alpha$ -arabinofuranose (108.5 ppm), (1 $\rightarrow$ 3) linked  $\beta$ -galactopyranose (104.3 ppm), glucuronic acid (103.6 ppm), (1 $\rightarrow\alpha$ -rhamnopyranose (101.6 ppm), (1 $\rightarrow\beta$ -arabinopyranose (100.5 ppm), and (1 $\rightarrow$ 4)  $\alpha$ -galactopyranose (99.4 ppm) were inferred based on model compounds<sup>17–18,20–23</sup>. The high intensity signals in the anomeric region (97.8–98.5 ppm) were assigned to C-1 of  $\beta$ -arabinopyranose from (1 $\rightarrow$ 2) linked  $\beta$ -arabinopyranose side chains, based on the chemical shift of  $\beta$ -arabinopyranose and taking into account the known displacements due to the O-substitution in sugar residues.<sup>21,22</sup>

The presence of the 4-*O*-methyl derivative of glucuronic acid was investigated by a DEPT 135 experiment [Fig. 3(a)], taking into account the fact that the resonances of the monosaccharide's primary group are very similar to the methoxyl groups which show signals in the 60–65 ppm region.<sup>23</sup> In this experiment the methylene carbons show opposite amplitude to methyl and methine carbons. The DEPT 135 spectrum of *A. macrocarpa* gum shows a resonance at 60.7 ppm characteristic of methyl carbons from methoxyl

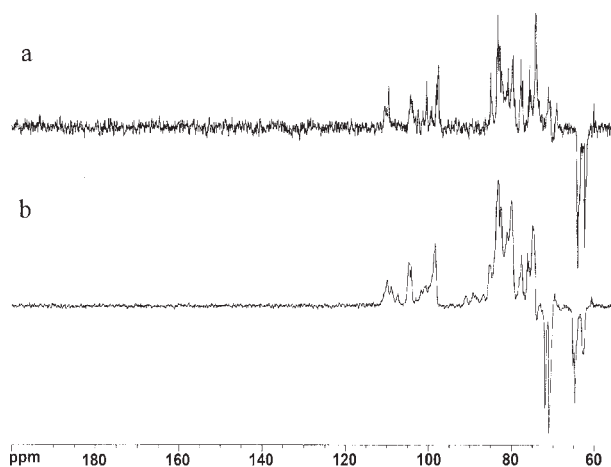
groups, confirming the presence of 4-*O*-methyl-glucuronic acid in the structure of the polysaccharide, in contrast to gum from *A. colubrina* (white angico).<sup>20</sup> By NMR data the main structure of *A. macrocarpa* polysaccharide seems to be composed by a main core of (1 $\rightarrow$ 3) linked  $\beta$ -D-galp and several different side chain of arabinose, galactose, and glucuronic acid, the structure is similar to that of *A. colubrina* polysaccharide.<sup>20</sup> The presence of 4-*O*-methyl glucuronic acid in the *A. macrocarpa* gum could possibly be used to differentiate the two species of *Anadenanthera* trees widely spread in Brazil.

NMR spectrum of CMAG-3 (DS 0.63) [Fig. 2(b)] shows an intense group of peaks because of carbonyl groups at 178.9, 178.4, and 178.7 ppm, as evidence of carboxymethylation reaction.<sup>13</sup> A decrease in the number of signals of anomeric carbons (98–110 ppm) of carboxymethylated samples suggests an elimination of monosaccharide units. An increase of peak intensities between 85 and 70 ppm, attributed to carbons from C-2 to C-5 of monosaccharide residue, may be due to insertion of CH<sub>2</sub> groups of  $-\text{CH}_2\text{COOH}$  of MCA in AG backbone and also to the shift of primary carbons (C-6) from region around 60 ppm to 71–69 ppm, after substitution of  $-\text{CH}_2\text{COOH}$  group on primary carbon.<sup>13</sup> New peaks in the regions of 84–89 ppm can be attributed to C-2 and C-4 substitutions, as observed for carboxymethyl pullulan.<sup>19</sup>

DEPT spectra of AG and CMAG [Fig. 3(b)] reveal an increase of CH<sub>2</sub> peak intensities, in the regions of 70–74 ppm, assigned to galactose primary carbon substituted in C-6 position, and to CH<sub>2</sub> groups from CH<sub>2</sub>COOH of MCA linked to polysaccharide.

### Molar mass distribution

The effect of NaOH concentration on molar mass distribution is shown in Figure 4. The curve for unmodi-

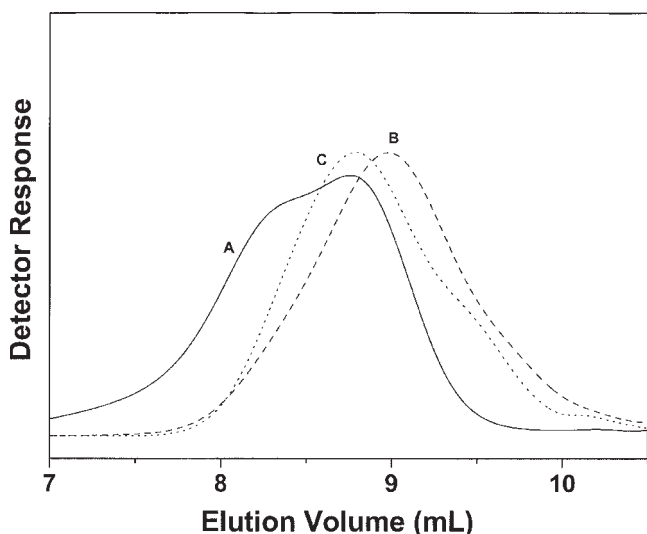


**Figure 3** DEPT spectra of AG (a) DEPT spectra of carboxymethylated samples: CMAG 3, DS = 0.63 (b).

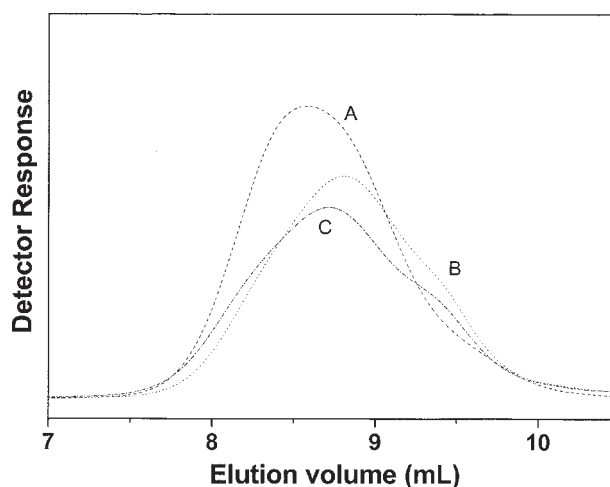
fied gum is very broad and multimodal. The two peaks, eluted at 8.3 and 8.7 mL, correspond to peak molar masses of  $1.4 \times 10^5$  and  $5.3 \times 10^4$  g/mol respectively, lower than previous results ( $1.6 \times 10^6$  and  $3.7 \times 10^5$  g/mol).<sup>3</sup> Change in GPC calibrants, period of gum extraction, age of the plant and also soil characteristics could be the cause of the observed difference.

The carboxymethylated polysaccharide is expected to elute at a lower volume than the starting polymer, if no chain length degradation occurs. This is because of repulsion of charged carboxylic groups of carboxymethyl moieties.<sup>4</sup> Another contribution is the higher molar mass of CM product, introduction of  $-\text{CH}_2\text{-COOH}$ /monosaccharide unit at each 1.0 unit increase in DS. The GPC curve for CMAG samples prepared with the lowest and highest NaOH concentration, respectively, samples 1 and 4 (curves B and C), was shifted to higher elution volume than unmodified AG (curve A), which seems to suggest that chain scission occurred during the carboxymethylation. A peak shoulder at elution volume 9.4 mL appears when NaOH concentration is 5.3M (curve C). The observed bimodal distribution indicates that there are two different carboxymethylated products being formed which could differ in the DS or in the average molar mass.

The simultaneous effect of increasing NaOH and MCA ratio, at same gum concentration (CMAG samples 3, 8, and 9) could be verified in Figure 5. As NaOH and MCA rate increase (curves B and C) a shoulder at volume elution higher than 9 mL appears, indicative of a high degree of chain degradation. This is consistent with very low yield (3.1 and 7.5%) observed for these samples (Table II).



**Figure 4** Elution profiles from GPC (RI detection) of AG (a) carboxymethylated samples: CMAG 1, DS = 0.28, NaOH/MCA/AG molar ratio = 1 : 1 : 1 (b), and CMAG 4, DS = 0.38, NaOH/MCA/AG molar ratio = 4 : 1 : 1 (c). Reaction temperature = 70°C.



**Figure 5** Elution profiles from GPC (RI detection) of carboxymethylated samples of angico gum : CMAG 3, DS = 0.63, NaOH/MCA/AG 3 : 1 : 1 (a), CMAG 8, DS = 0.71, NaOH/MCA/AG 6 : 2 : 1 (b), and CMAG 9, DS = 1.10 NaOH/MCA/AG 9 : 3 : 1 (c). Reaction temperature = 70°C.

Increasing reaction temperature from 35 to 70°C (samples 3 and 5) shifts the GPC curve to lower elution volume (data not shown). Peaks or shoulders at higher elution volume were not observed, suggesting that high temperature do not promote intense chain scission, at least for the 2 h reaction time, as verified for samples 8 and 9 (Fig. 5).

## CONCLUSIONS

Red angico gum was carboxymethylated with MCA in alkaline aqueous medium resulting in CMAG samples. The DS varied from 0.11 to 1.10 depending on NaOH concentration, MCA/AG ratio and temperature. The DS increases with alkali concentration up to 4.6M NaOH and then decreases sharply. DS increases with temperature up to 70°C. Taking into account the MCA efficiency towards production of carboxymethylated macromolecules from angico gum, the best resulting sample material is CMAG 3 (DS = 0.63), obtained with NaOH/MCA/AG molar ratio equal to 3 : 1 : 1, temperature at 70°C. The reaction condition employed, such as short reaction time, low amount of MCA, low cost solvent (water), and high yield indicates that this process is a potential candidate to industrial applications.

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