

Carboxymethylation of *Cassia occidentalis* Seed Gum

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ABSTRACT: The seeds of *Cassia occidentalis*, an annual weed occurring throughout India, are a rich source of galactomannan gum. The gum derived from seed endosperm can be utilized in a number of industries to replace conventional gums. With a view to utilize the gum for broader applications, carboxymethylation of *Cassia occidentalis* seed gum was carried out. The reaction conditions were optimized with respect to concentration of monochloroacetic acid, so-

dium hydroxide, solvent ratio, reaction time, and reaction temperature. Rheological studies of carboxymethyl gum exhibited relatively high viscosity and stability vis-a-vis unmodified *Cassia occidentalis* gum. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1606–1611, 2004

Key words: *Cassia occidentalis* gum; carboxymethylation; polysaccharides; modification; viscosity

INTRODUCTION

Cassia occidentalis gum (COG) is derived from the seeds of *Cassia occidentalis* Linn. (Kasondi), a common herbaceous annual weed occurring throughout India up to an altitude of 1,500 m.¹ Every part of the plant is used in different applications in the Indian Ayurvedic system of medicine.¹ The pods are 10–13 cm long and up to 0.8 cm in diameter and contain dark olive green seeds. The *Cassia occidentalis* seeds are a rich source of galactomannan (~30% endosperm).² The structure of the backbone of the seed polysaccharide, β -(1→4) linked D-mannopyranose and random distribution of α -(1→6) linked D-galactopyranose units in side chain (M/G : 3.1), was established by partial hydrolysis,³ permethylation,⁴ and NMR studies.⁵

Galactomannans are important industrial products used in various industries such as paper, food, cosmetics, pharmaceuticals, paints, well-drilling, mining, and explosives, etc.⁶ *Cassia occidentalis* seed gum has potential on account of its wide availability and can be utilized to replace the conventional gums such as guar and locust bean. With a view to prepare value added products, chemical modification of different seed gums containing galactomannans/xyloglucans has been carried out in our laboratory.^{7–16} *Cassia occidentalis* seed gum has a few drawbacks such as low solubility in cold water, dull color of gum solution, and

fast biodegradability. The present work was undertaken to overcome these drawbacks and make it more useful/industrially exploitable.

The present work attempts to study the optimization of the process for the preparation of the carboxymethyl derivative of *Cassia occidentalis* gum (CM-COG). Carboxymethylation can be performed in water as a solvent^{17–20} or in water-miscible organic solvents containing small amounts of water.^{13,21–25} The main reaction parameters, which influence the carboxymethylation process, are the solvent system, solvent composition, gum solvent ratio, concentration of sodium hydroxide and monochloroacetic acid (MCA), temperature, and duration of reaction.^{13,17–19,21,22}

In the present work, carboxymethylation was performed in a methanol/water system, and the reaction parameters with respect to degree of substitution were studied.

EXPERIMENTAL

Materials

Cassia occidentalis seed gum was obtained from M/S Shri Nath Gums and Chemicals (Jodhpur, India). Monochloroacetic acid, sodium hydroxide, methanol, acetic acid, and ammonium acetate were of laboratory reagent grade (S.D. Fine Chem. Ltd., Mumbai, India) and J acid (6-amino-1-naphthol-3-sulfonic acid) and glycolic acid were of Sigma grade (USA).

Methods

The synthesis of CM-COG was carried out as follows: COG (0.03 mol, 100 mesh) was dispersed in alkaline

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TABLE I
Reaction Parameters Used in the Carboxymethylation of COG

Figure	Experiment no.	Methanol (%) in solvent medium ^a	Time (min)	Temperature (K)	NaOH : MCA : COG, ^b (mol)	Gum : liquor (g/cm ³)	DS
1	a				2.5 : 1.76 : 1		0.278
	b				3.33 : 1.76 : 1		0.464
	c	80	60	353.15	4.16 : 1.76 : 1	1 : 10	0.393
	d				5 : 1.76 : 1		0.298
	e				5.83 : 1.76 : 1		0.229
	f				6.66 : 1.76 : 1		0.179
2	a				3.33 : 0.33 : 1		0.086
	b				3.33 : 0.66 : 1		0.140
	c				3.33 : 1.06 : 1		0.276
	d	80	60	353.15	3.33 : 1.42 : 1	1 : 10	0.385
	e				3.33 : 1.76 : 1		0.464
	f				3.33 : 2.1 : 1		0.341
	g				3.33 : 2.46 : 1		0.277
3	a			303.15			0.023
	b			323.15			0.118
	c	80	60	343.15	3.33 : 1.76 : 1	1 : 10	0.322
	d			353.15			0.464
	e			373.15			0.407
4	a		30				0.310
	b		60				0.464
	c	80	90	353.15	3.33 : 1.76 : 1	1 : 10	0.392
	d		120				0.390
	e		150				0.387
	f		180				0.381
5	a	0					0.152
	b	20					0.205
	c	40	60	353.15	3.33 : 1.76 : 1	1 : 10	0.222
	d	60					0.308
	e	80					0.464
	f	100					0.028
6	a					1 : 5	0.328
	b	80	60	353.15	3.33 : 1.76 : 1	1 : 10	0.464
	c					1 : 15	0.348
	d					1 : 20	0.337

^a Solvent medium : Methanol : Water (vol/vol).

^b In all experiments 0.03 mol (5 g) of COG (as AGU) was used.

aqueous methanol varying the gum : liquor ratio from 1 : 5 to 1 : 20 (Table I). To the above solution MCA (0.010 to 0.074 mol) was added in solid form with continuous stirring for 10 min. At this end, the flask was immersed in a thermostatic water bath keeping a specific temperature (303.15 to 373.15 K) at which the reaction was allowed to proceed for the desired duration (30 to 180 min). The flask contents were occasionally shaken during the course of the reaction. The reaction product was filtered on a G-3 sintered glass crucible, dissolved in water, and neutralized with dilute acetic acid (1 : 1, vol/vol). The reaction product was precipitated in ethyl alcohol and washed twice with aqueous methanol (2 × 100 mL, methanol : H₂O :: 80 : 20) followed by pure methanol. The products were initially dried at room temperature and then in an electric oven at 333.15 ± 2 K for 2 h.

Analysis and measurement

Determination of the degree of substitution

Determination of degree of substitution (DS) was based on the principles given by Sawicki et al.²⁶ by a colorimetric method using J acid.^{22,27}

Determination of rheological properties of CM-COG

The rheological properties were determined using a Brookfield Digital Viscometer model RVT D (Stoughton, MA) by adopting the following experimental conditions: range of shear rate between 2.8–34.0 s⁻¹ and temperature of 298.15 ± 1 K.

RESULTS AND DISCUSSION

The carboxymethylation of COG proceeds by a two-step consecutive reaction and is accompanied by an

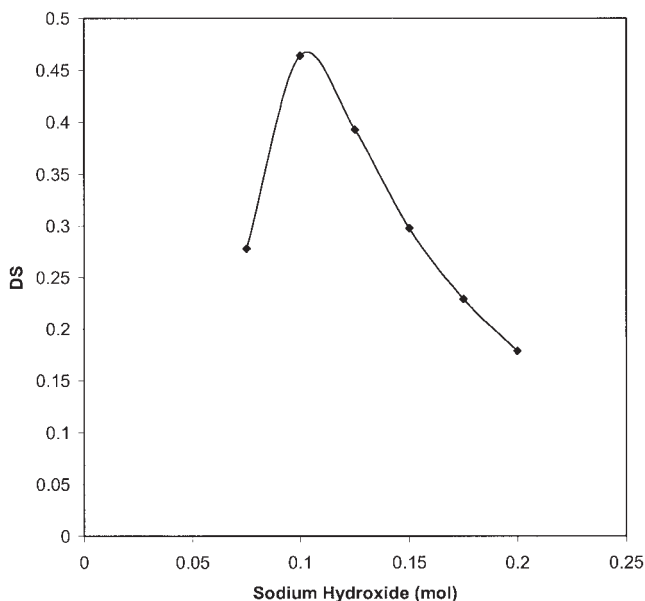
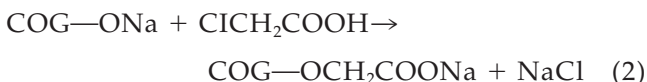
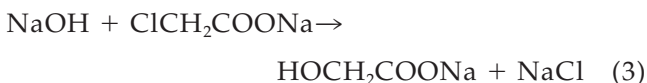


Figure 1 Dependence of DS on sodium hydroxide concentration. Reaction conditions as shown in Table I.

undesired side reaction. In the main reaction the sodium hydroxide reacts first with the hydroxyl groups of the gum to give alkoxides groups. The carboxymethyl groups are then formed in a S_N2 reaction between the gum alkoxide and MCA. The main reaction is given by



The side reaction takes place in both the liquid bulk and the gum phase,²³ and results in the formation of sodium glycolate from MCA and sodium hydroxide.



The optimization of the process of carboxymethylation was performed by varying the process parameters such as concentration of NaOH and MCA, gum-solvent ratio, water-methanol ratio, temperature, and duration of the reaction. Each parameter was varied keeping the others constant as shown in Table I.

Effect of sodium hydroxide concentration

The effect of variation of sodium hydroxide concentration from 0.075 to 0.200 mol at 353.15 K on DS was studied and the results are shown in Figure 1. It was observed that, as sodium hydroxide concentration in-

creases up to 0.100 mol, the DS also increases and then levels off. The increase in DS with increase in NaOH concentration up to 0.100 mol suggests that the carboxymethylation reaction shown by eq. (2) prevails over its competitive reaction [eq. (3)]. Above 0.100 mol concentration of NaOH, the glycolate formation increases^{13,17,22,28-30} and, consequently, a lower value of the DS of the CM-COG sample was obtained. This was confirmed by the estimation of glycolate formed^{13,27} in the case of the products obtained with DS values 0.278, 0.464, and 0.179 and was found to be 0.0008, 0.0010, and 0.0015 mol, respectively. Therefore, the 0.100 mol concentration of NaOH constitutes the optimum concentration for carboxymethylation of COG.

Effect of monochloroacetic acid concentration

The MCA concentration was varied from 0.010 to 0.074 mol at 353.15 K and the results are shown in Figure 2. Results showed the distinct pattern of the increase in DS on increasing the concentration of MCA, which gets optimized at 0.053 mol. However, a further increase in concentration of MCA beyond 0.053 mol on using the optimum dose of NaOH concentration (0.100 mol) favors the side reaction [eq. (3)]. Similar observations are reported for *Cassia tora* gum, starch and *Leucaena glauca* seed gum.^{13,17,29}

Effect of reaction temperature

Carboxymethylation of COG was performed at different temperatures (i.e., 303.15 to 373.15 K). The depen-

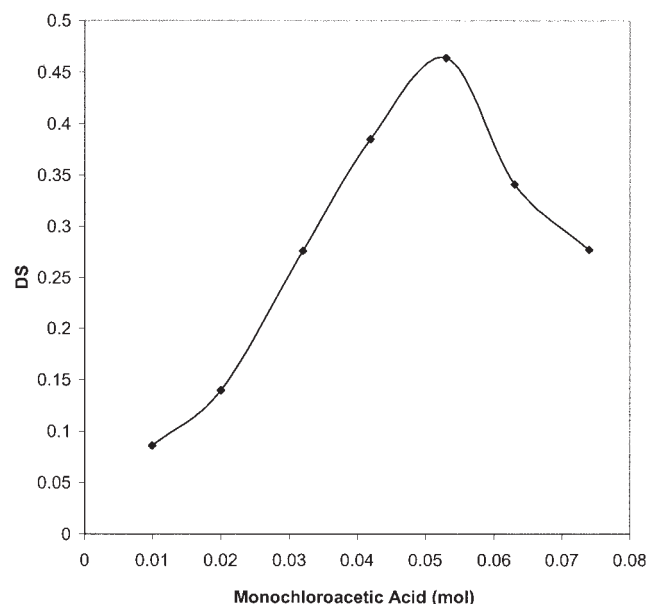


Figure 2 Dependence of DS on monochloroacetic acid concentration. Reaction conditions as shown in Table I.

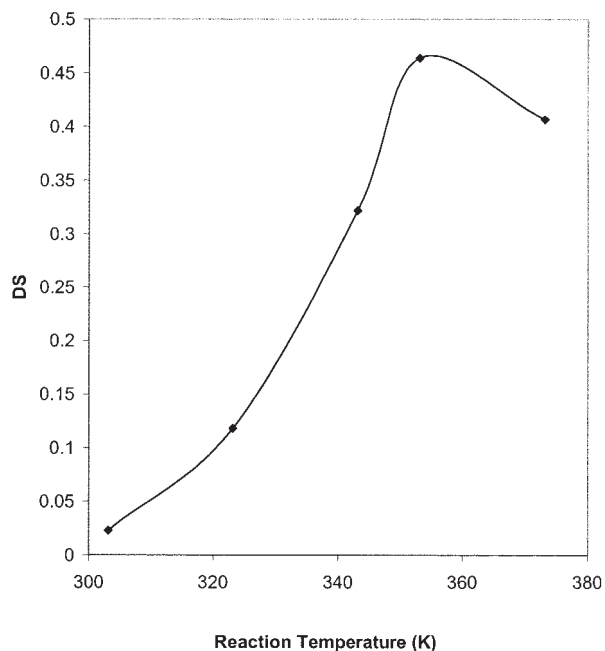


Figure 3 Dependence of DS on reaction temperature. Reaction conditions as shown in Table I.

dence of DS on reaction temperature is shown in Figure 3. It is observed that DS increases from 0.023 to 0.464 prominently as the reaction temperature increases from 303.15 to 353.15 K and decreases thereafter. It is due to the favorable effect of temperature on swellability of COG as well as diffusion and adsorption of reactants with the ultimate effect of inducing

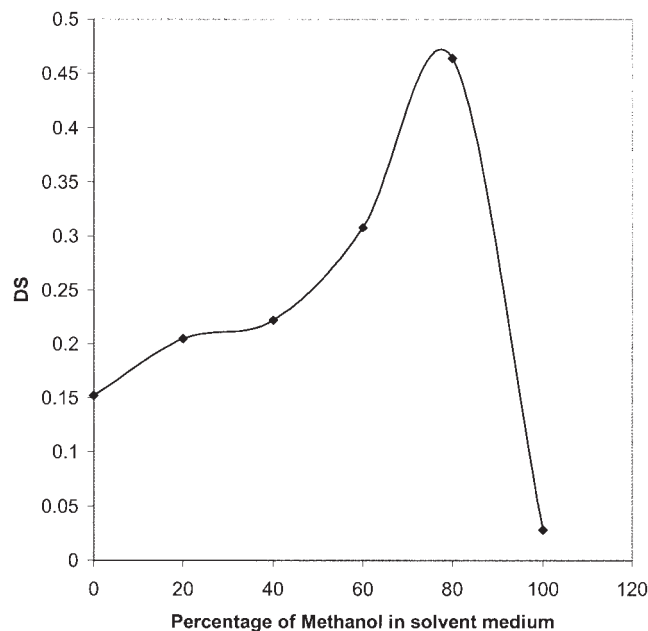


Figure 5 Dependence of DS on percentage of methanol in solvent medium. Reaction conditions as shown in Table I.

better contacts between etherifying agents and COG. The value of DS decreases at 373.15 K, due to higher glycolate formation^{13,29} [eq. (3) prevailing over the carboxymethylation [eq. (2)]].

Effect of reaction time

Figure 4 shows the effect of reaction time on DS at

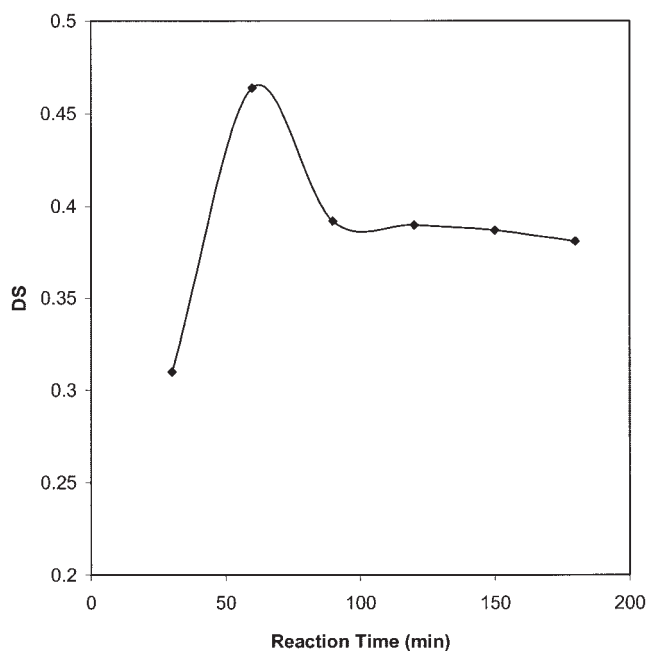


Figure 4 Dependence of DS on reaction time. Reaction conditions as shown in Table I.

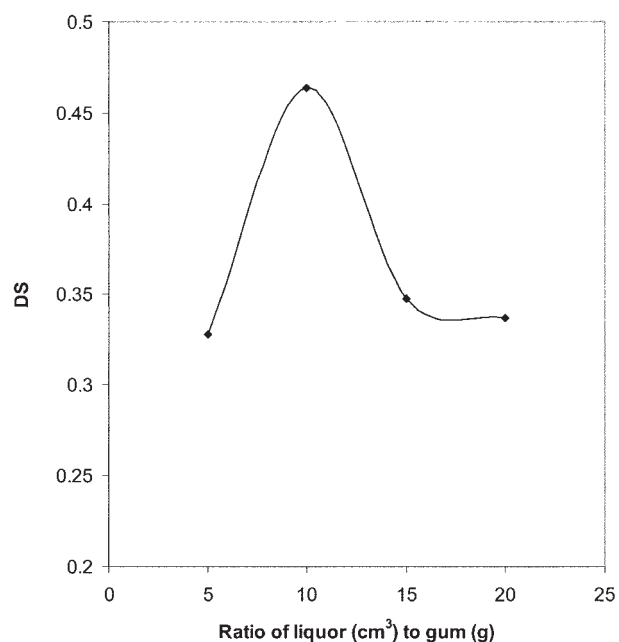


Figure 6 Dependence of DS on liquor (cm³)/gum (g) ratio. Reaction conditions as shown in Table I.

TABLE II
Rheological Studies of *Cassia occidentalis* Seed Gum

Apparent viscosity (cps) 2% solution							
Unmodified gum (COG)			Modified gum, DS (0.464)				
Shear rate (s ⁻¹)	3 h	24 h	Shear rate (s ⁻¹)	3 h	24 h	48 h	120 h
3.4	250.0	Degradation	2.8	9,650	8,250	7,750	6,300
6.8	212.5		5.6	7,625	6,850	6,425	5,400
17.0	175.0		14.0	5,030	4,830	4,580	4,050
34.0	162.5		28.0	3,180	3,145	3,010	2,805

353.15 K. The DS increases with the increase in reaction time and reaches a maximum in 60 min and a significant decrease was observed on increasing the time thereafter. The enhancement of DS by prolonging the duration of reaction from 30 to 60 min is a direct consequence of the favorable effect of time on swelling of COG as well as the diffusion and adsorption of the reactants with the ultimate effect of better contacts between the etherifying agents and COG. Similar observations were made earlier by different workers.^{13,17,18,22,30}

Effect of solvent medium

The effect of solvent medium on the extent of reaction is related to the miscibility, the ability to solubilize the etherifying agents and to swell the biopolymer and create an environment that favors carboxymethylation rather than glycolate formation [eq. (3)]. The results (Fig. 5) reveal that increasing the percentage of methanol in the mixture (CH₃OH-H₂O, vol/vol) enhances DS up to a maximum, after which it decreases, reflecting the negative effect of pure methanol on the carboxymethylation reaction. The maximum DS is obtained at a methanol : water ratio of 80 : 20. The above implies that solvent medium determines the extent of reaction.^{13,22}

Effect of gum and liquor ratio

The results obtained by investigating the effect of gum and liquor ratio on DS are shown in Figure 6. The amount of gum and reactants used during these experiments was constant, but the concentration of the gum and reactants was decreased by increasing the amount of solvent. The optimum DS (0.464) at gum : liquor ratio 1 : 10 signifies the role of volume of liquor medium. A critical amount of liquor helps the COG to swell and aids the diffusion and adsorption of etherifying agents on COG molecules. A decrease in the DS at higher liquor volumes was observed, which can be attributed to the reduced probability of collision of the reactants or a decrease in collision due to dilution. At a gum : liquor ratio lower than 1 : 10, it was difficult to

stir the reactants due to high viscosity; ultimately the low DS was observed. Similar results were observed during the carboxymethylation of starch.²²

Rheological studies

To assess the importance and feasibility of any gum or hydrocolloid in food and other industries, the viscosity profile is generally considered to be one of the parameters to decide the performance of said gum in a particular industry. The solutions of COG and CM-COG (DS 0.464) were prepared in 2% concentration at room temperature and their rheological properties were studied. It is seen (Table II) that CM-COG solution is highly viscous compared to COG solution and is characterized by a non-Newtonian pseudoplastic behavior. Results also indicate the effect of storing the CM-COG solution up to 120 h at various rates of shear. The apparent viscosity decreases only about 35% on storing up to 120 h, whereas unmodified gum degraded completely within 24 h. This indicates the stability of CM-COG paste toward microorganisms, since the presence of carboxymethyl groups makes the molecule resistant toward enzymatic attack.^{13,31}

CONCLUSION

Carboxymethylation of *Cassia occidentalis* seed gum was carried out with monochloroacetic acid in the presence of alkali as a catalyst under heterogeneous conditions. The optimum DS 0.464 was obtained by using the *C. occidentalis* seed gum (0.03 mol as AGU), NaOH (0.100 mol), MCA (0.053 mol), methanol-water ratio (4 : 1), solid-liquor ratio (1 : 10), temperature 353.15 K, and duration 60 min. The paste quality and microbial resistance of CM-COG was much better than that of native gum. The viscosity of CM-COG in 2% solution was about 38 times greater compared to native gum. Rheological studies showed the non-Newtonian pseudoplastic nature of CM-COG.

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