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Physicochemical characterization of grewia polysaccharide gum: Effect of drying method

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ABSTRACT

Grewia polysaccharide gum, a potential pharmaceutical excipient was extracted from the inner stem bark of *Grewia mollis*, thereupon drying was achieved by three techniques: air-drying, freeze-drying and spray-drying. Analysis of the monosaccharide composition including ^{1}H and ^{13}C NMR spectroscopic analysis of the polysaccharide gum was carried out. The effect of the drying methods on the physicochemical properties of the gum was evaluated by Fourier transformed infra-red (FT-IR) spectroscopy, solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis, differential scanning calorimetry and gel permeation chromatography. Monosaccharide sugar analysis revealed that the gum is composed of glucose, rhamnose, galactose, arabinose and xylose as the main neutral sugars. These were supported by the results from ^{1}H and ^{13}C NMR spectroscopic analysis. FT-IR and solid-state NMR results indicated that drying technique has little effect on the structure of the polysaccharide gum but XPS showed that surface chemistry of the gum varied with drying methods. Thermogravimetric analyses showed that oxidation onset varied according to the drying method. The molecular weight was also dependent on the drying technique. For industrial extrapolation, air-drying may be preferable to spray-drying and freeze-drying when relative cost, product stability and powder flow are required, for example in tablet formulation.

1. Introduction

Natural polysaccharide gums represent a group of polymers which swell to form highly viscous solutions or dispersions in aqueous media. They have found wide application in the pharmaceutical industry as polymer matrices in sustained release solid dosage forms (Bhardwaj, Kanwar, Lal, & Gupta, 2000; Huber & Christenson, 1996; Sujja-areavath, Munday, Cox, & Khan, 1996; Talukdar & Vercammen, 1993; Varshosaz, Tavacoli, & Eram, 2006), binders in tablets (Udeala & Chukwu, 1985), stabilizers or suspending agents in liquid dosage forms (Bilany, 2007), and in bioadhesive drug delivery systems (Middleton, Leung, & Robinson, 1990). They have the advantage of biocompatibility, low cost and relatively abundant availability (Vendruscolo et al., 2009) compared to their synthetic counterparts.

Grewia polysaccharide gum is obtained by extraction from the inner stem bark of the edible plant *Grewia mollis*, Juss (Family, Tiliaceae). In Nigeria, grewia polysaccharide gum grows abundantly in the middle belt region of the country where it is found growing wild or cultivated and is used as a delicacy by the local people.

The polysaccharide is isolated from the cell wall of the plant and has been reported to consist of glucose and rhamnose as the main monosaccharide components (Nep & Conway, 2010; Okafor, Chukwu, & Udeala, 2001). Although the binding (Emeje, Isimi, & Kunle, 2008), bioadhesive (Nep & Okafor, 2006) and mechanical (Muazu, Musa, & Musa, 2009) properties of the gum have been reported, information regarding its application is limited. A more detailed understanding of the physicochemical characteristics of the gum will help to understand and guarantee the behaviour of the material during formulation phases of drug development (Vendruscolo et al., 2009).

The drying process has been shown to have a significant effect on the physico-chemical properties and formulation characteristics of materials (York, 1983). Several techniques have been employed for the drying of materials. These include freeze-drying, oven-drying, spray-drying, and vacuum-drying and more recently, microwave drying. As the intended application of grewia gum is as an excipient for both solid and liquid dosage forms in its countries of origin, conventional drying techniques that would normally be available and widely accessible were evaluated in this study. The aim of this study therefore is to evaluate the effect of air-drying, freeze-drying or spray-drying on the physico-chemical characteristics of grewia polysaccharide gum from *G. mollis*.

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2. Materials and methods

2.1. Materials

Ethanol, sodium hydroxide and hydrochloric acid were procured from Sigma–Aldrich, UK. Pullulan polysaccharide was from Polymer Laboratories, UK. Pulverized crude inner stem bark of *G. mollis* was obtained from Nigeria after authentication by the forestry commission. All equipments used are as cited in the text.

2.2. Extraction and purification of grewia gum

Grewia polysaccharide gum was extracted as detailed previously (Nep & Conway, 2010). Briefly, the dried and pulverized inner stem bark of *G. mollis* shrub (2000 g) was dispersed in 0.1% w/v sodium metabisulphite and allowed to hydrate for 48 h. After this time the mixture was stirred for 2 h and passed through muslin to remove extraneous solid matter. The filtrate was treated with 20 mL of 0.1 N NaOH to precipitate and isolate alkali insoluble impurities, and centrifuged at 3000 rpm for 10 min. The supernatant was then treated with acidified ethanol, (containing 10 mL of 0.1 N HCl) to isolate acid insoluble impurities, and centrifuged again as described. The supernatant was treated with absolute ethanol and the resultant precipitate washed several times until only clear absolute ethanol was recovered. The precipitate was wet-milled and then passed through muslin before air-drying the product, or the precipitate was redispersed in water and thereupon spray-dried or freeze-dried. The air-dried product was dry-milled before further drying at 50 °C in an oven for 24 h. Spray-drying was carried out using a B-290 mini spray drier (Buchi Corporation, Switzerland) at inlet temperature of 160 °C while aspirator and pump were set to 85% and 5% respectively and the resultant powder was stored in an air-tight container until use. Freeze-drying was carried out using an Edwards Modulyo freeze dryer (Thermo Fisher Scientific Inc., UK) at −40 °C for 72 h. The freeze-dried and air-dried products were dry milled and passed through a 1.0 mm sieve, weighed and stored in air-tight containers until use.

2.3. Moisture content

The moisture content of the grewia polysaccharide samples was determined using a moisture analyzer (MA 40 Sartorius, Germany) according to the formula:

$$\text{Moisture content}\,(\%) = \frac{\text{initial weight} - \text{final weight}}{\text{initial weight}} \times 100 \qquad (1)$$

2.4. Angle of repose

Air-dried or freeze-dried grewia polysaccharide gum powder (10 g) was accurately weighed and carefully introduced into a funnel clamped to a stand with its tip 10 cm from a plane paper surface. The powder was allowed to flow freely unto the paper surface. The height of the cone, H, formed after complete flow and the radius of the cone, R were measured and used to calculate the angle of repose using the equation:

$$\text{Angle of repose}\,(\tan\theta) = \frac{H}{R} \qquad (2)$$

2.5. Bulk and tapped densities

Air-dried or freeze-dried grewia polysaccharide gum powder (10 g) was accurately weighed into a 100 mL measuring cylinder and, without disturbing the cylinder the volume was read to give the bulk volume of the powder. The measuring cylinder was then clamped to the USP I tapper of a USP tap density tester (Sotax TD2, Switzerland). The volume of the powder was read after every 50 taps up to a total of 300 taps when volume of powder was constant. This represents the tapped volume of the polysaccharide gum powder. The bulk or tapped density was calculated as the ratio of the weight of powder to the bulk or tapped volume respectively.

2.6. Compressibility index

The compressibility index of grewia polysaccharide gum was determined according to the Carr's compressibility index percentage:

$$\text{Compressibility}\,(\%) = \frac{\text{Bulk density} - \text{Tapped density}}{\text{Bulk density}} \times 100 \qquad (3)$$

2.7. Total ash and soluble ash

The AOAC, 1990, method was adopted. The gum samples (1.0 g) were weighed into a pre-ignited and pre-weighed crucible, and transferred into a furnace (Carbolite, Sheffield, England). The ignition temperature was 550 °C for 24 h. The recovered ash was transferred into a desiccator to equilibrate to room temperature before weighing.

The resultant ash from the above was mixed with distilled water, boiled, filtered and the filter was rinsed. Both filter paper and residue were transferred into the crucible and ignited for 24 h until a constant weight was reached. Thereafter, cooling was carried out in a desiccator and the product weighed.

Percent total ash was calculated from the formula:

$$\%\text{Total ash} = \frac{\text{Ash weight}}{\text{Original sample weight}} \times 100 \qquad (4)$$

Percent soluble ash was calculated from the formula:

$$\%\text{Soluble ash} = \%\text{Total ash} - \%\text{Insoluble ash} \qquad (5)$$

2.8. Viscosity and flow behaviour

The viscosity of a 1.0% w/v dispersion of the air-dried or the freeze-dried polysaccharide gum was read at shear rates between 0.1 and 2.0 s^{-1} at 23 °C using a Brookfield DV – 1+ viscometer version 5 (Brookfield Engineering Labs, Stoughton, USA). Spindle 2 was used and 3 min was allowed for stabilization of the readings before the viscosity was read.

2.9. FT-IR spectroscopy

The air-dried, freeze-dried or spray-dried grewia polysaccharide gum in KBr (1:10) was blended and compressed on an IR press. FT-IR spectra were generated using a Mattson Galaxy 3020 FT-IR spectrophotometer (Unicam, England).

2.10. Solid-state NMR

Samples of the air-dried, freeze-dried or spray-dried grewia polysaccharide gum were analysed on a solid-state ^{13}C NMR spectrometer (Varian VNMRS Polymer Laboratories Scientific Instruments, UK) operating at 102.56 MHz for ^{13}C with an acquisition time of 20.0 ms. Samples were run without modification and the spectra were referenced with respect to tetramethylsilane.

2.11. X-ray photoelectron spectroscopy

The air-dried, freeze-dried or spray-dried samples of grewia polysaccharide gum were analysed in an electron spectrometer (ESCALAB 250 Thermo Fisher Scientific Inc., UK) equipped with a hemispherical sector energy analyzer. A monochromatic Al Kα X-ray source was used at a source excitation energy of 15 keV and emission current of 6 mA. Analyzer path energy of 20 eV with step size of 0.1 eV and dwell time of 50 ms was used throughout the experiments.

2.12. Thermal analysis

Thermal degradation of the polysaccharide gum samples was studied on a Thermo-gravimetric Analyzer (Pyris 1 TGA, Perkin Elmer, USA). Approximately 1 mg of sample was introduced into the sample pan and heated at 10 °C per minute up to 500 °C under nitrogen atmosphere. DSC (Diamond DSC Perkin Elmer, USA) was also used to study the thermal properties of the polysaccharide gum samples. Exactly 4 mg of sample was weighed into the sample pan. Temperature was held at 30 °C for 1 min then the sample was heated to 200 °C at a rate of 10 °C per minute under nitrogen atmosphere.

2.13. Gel permeation chromatography

A GPC system calibrated using pullulan polysaccharide calibrants and 0.2 M $NaNO_3$, 0.01 M NaH_2PO_4 at pH 7.0 as eluent was equipped with PL aquagel Guard Plus two mixed OH (30 cm 8 μm) columns and a refractive index detector (with differential pressure and light scattering) and used to analyse samples of the polysaccharide gum at a nominal flow rate of 1.0 mL per minute and a temperature of 35 °C. The samples were prepared by adding 10 mL of eluent to 20 mg of sample and leaving overnight to hydrate. The solutions were warmed at 40 °C for at least 20 min and after cooling, the solutions were thoroughly mixed and filtered through a 0.45 μm PVDF membrane. Data were analysed using Polymer Laboratories 'Cirrus' software.

2.14. Monosaccharide sugars analysis and ^1H and ^{13}C NMR

Before GC and NMR analysis of the sample, the gum was hydrolysed according to the method of Tamoda, Satoh, and Suzuki (1977). The hydrolysed gum and sugar standards were converted to the alditol acetate derivatives and thereupon monosaccharide analysis was done on an ATI-Unicam 610 GC, (Unicam, UK) with a flame ionization detector (FID). The conditions were: Column-Supelco SP-2380 (30 m, 0.25 mm id and 0.2 μm film thickness), detector temperature – 280 °C, injector temperature – 260 °C, column temperature – 250 °C, split injection volume – 1 μL, split ratio – 50:1, helium flow – 1 mL/min, and 15 min isothermal run. The standard sugars used were L-rhamnose monohydrate, D-(+)-galactose, DL-arabinose D-xylose and D-(+)-glucose. ^{13}C and ^1H NMR spectroscopy was done on an AC 250 NMR spectrometer (Bruker, UK) in D_2O and analysed using Iconnmr and Topspin (Bruker) software.

2.15. Scanning electron microscopy

Scanning electron micrograph of the grewia gum samples was carried out (StereoScan 90, Cambridge instruments) after gold coating using an Enscope SC500 gold sputter coater.

2.16. Statistical analysis

The data was subjected to one-way ANOVA using the software Instat (GraphPad, San Diego, CA).

Table 1
Effect of drying method on some physicochemical properties of grewia polysaccharide gum.

	Air-dried	Freeze-dried	Spray-dried
Yield (%)	32.4	32.4	3.1
Solubility (mg/mL)	0.2 ± 0.01	0.1 ± 0.04	0.1 ± 0.03
Soluble ash (%)	3.4 ± 0.20	3.4 ± 0.10	3.8 ± 0.10
Total ash (%)	6.1 ± 0.36	6.1 ± 0.40	6.3 ± 0.40
pH	5.7 ± 0.03	5.7 ± 0.10	5.7 ± 0.04
Moisture content (%)	10.6 ± 2.00	15.4 ± 1.20	18.8 ± 2.60
Viscosity at 0.1 Hz (Pa s)	0.32 ± 8.70	0.29 ± 8.60	0.2 ± 6.70
Angle of repose (°)	30.4 ± 0.50	32.6 ± 1.03	–
Bulk density (g/mL)	0.16 ± 0.00	0.14 ± 0.00	–
Tapped density (g/mL)	0.20 ± 0.01	0.17 ± 0.01	–
True density (g/cm^3)	2.0 ± 0.01	1.7 ± 0.01	2.0 ± 0.10
Compressibility (%)	20.2 ± 1.20	21.4 ± 0.84	–

3. Results and discussion

3.1. Physicochemical properties of grewia gum

The solubility, total and soluble ash, and pH of the air-dried, freeze-dried or spray-dried grewia polysaccharide gum samples were not significantly different ($P > 0.05$) (Table 1). However, there was significant variation between the moisture content of the samples ($P < 0.05$) with the spray-dried grewia polysaccharide sample showing the highest moisture content.

Aqueous dispersions of all samples of grewia gum give an acidic pH. There is no significant difference in pH between the samples ($P > 0.05$). This suggests that grewia gum is not a neutral polysaccharide. The acidic nature of the gum indicates that the polysaccharide contains a uronic acid (sugar acid) in its structure (Cui, 2005).

The variation in total ash between the gum samples is not significant ($P > 0.05$). The spray-dried sample of the gum has more soluble ash compared to the air-dried and freeze-dried samples. This may be attributed to the effect of particle size on solubility, the spray-dried gum sample having smaller particle size compared with samples of the air-dried or freeze-dried gum.

The higher density values obtained for the air-dried fractions may be attributed to the increased propensity for shrinkage exhibited by the sample after the oven-drying process. This is in contrast with freeze-dried particles are light with a lower particle density than the relatively solid air-dried particles.

The powder flow properties which are necessary to consider industrial application of an excipient were evaluated for the air-dried and the freeze-dried polysaccharide samples. The results show that the freeze-dried fraction had a higher angle of repose than the air-dried fraction. This however does not allow important differences to be established between the two fractions as both fractions showed an angle of repose indicating 'good' to 'passable' flow behaviour (Wells & Aulton, 2007). However, the compressibility value of greater than 23% indicates that the flow of the gum samples is poor but may be improved by glidant (Staniforth, 2002; Wells & Aulton, 2007). The higher bulk and tapped densities of the air-dried sample indicate that the sample is packed together more closely than the freeze-dried sample. As should be expected the fluffy, fibrous and irregular shape of the freeze-dried sample will obstruct the close packing of the sample.

The loss on drying of the air-dried gum sample was 10.6 ± 2.00 (Table 1), lower than the 15% limit established in US Pharmacopeia (2007) for natural polysaccharide gums. However, the freeze-dried and spray-dried samples contained more water than the air-dried samples. Low moisture content is desirable for polysaccharide gums as residual water may enhance deterioration of the product. Consequently, following preliminary investigations, the drying conditions employed must target a residual moisture content. Air-drying appears to achieve optimal drying of the polysaccharide

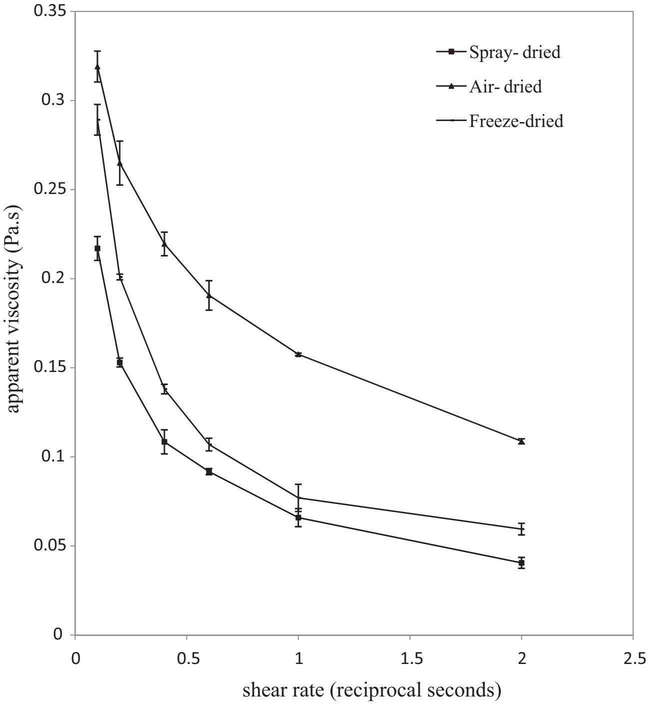

Fig. 1. Effect of drying method on viscosity and flow behaviour of grewia polysaccharide gum ($n = 3$, mean ± s.d.).

gum, and spray-drying or freeze-drying techniques should be further optimized to achieve lower moisture content.

The higher total ash content for spray-dried gum fraction compared with the air-dried and freeze-dried fractions can be attributed to the effect of the drying method on the thermal behaviour of the polymers. The US Pharmacopeia (2007) specified a value of 1.5% for guar gum. Grewia polysaccharide is composed of a high proportion of insoluble cell wall materials (Nep & Conway, 2010), which may also account for the high total ash content of the gum as compared with guar gum. A total ash content of >6% for grewia polysaccharide gum has been reported elsewhere (Okafor et al., 2001).

3.2. Viscosity and flow characteristics of aqueous dispersions

The impact of drying method on the viscosity of a 1.0% w/v aqueous dispersion of the polysaccharide gum is shown in Table 1. The flow behaviour of the samples of grewia polysaccharide gum is shown in Fig. 1. The viscosity of the gum dispersions decreases with an increase in shear rate. This is indicative of pseudoplastic flow behaviour (shear-thinning), as a decreasing number of chain entanglements at high shear rates accounts for the decrease in viscosity with increasing shear (Cui, 2005). The drying method is shown to have effect on the apparent viscosity of the gum dispersions and consequently the suspending ability of the gum samples may vary. It has been shown that drying method may have significant effect on the viscosity of materials (Jimoh, Olurin, & Aina, 2009). The viscosity of polysaccharide gums is a physical property largely influenced by their molecular weight (Wang & Cui, 2005). For a given polysaccharide, the molecular weight will vary depending on a number of factors such as the pathway and environment of synthesis, and the prevailing conditions under which the polysaccharide was extracted (Wang & Cui, 2005). The different temperatures under which drying was performed may have an impact on the molecular weight of the polysaccharide which may in turn affect the viscosity of the gum dispersions.

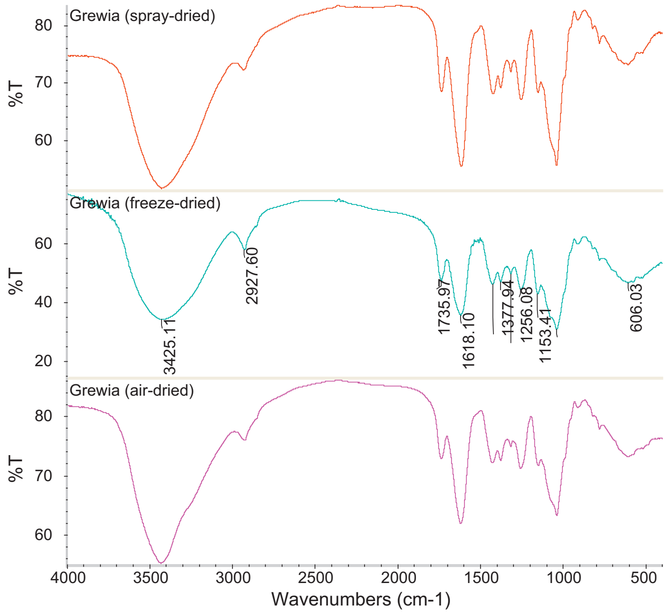

Fig. 2. Impact of drying method on the FT-IR spectra of grewia polysaccharide gum.

3.3. FT-IR spectroscopy

Fig. 2 shows the effect of drying method on the FT-IR scan of grewia polysaccharide gum. No visible differences could be observed between the spectra of the different gum samples. The band and peak characteristics of the spectra have been reported (Nep & Conway, 2010). The broad band at 3425 cm^{-1} indicates the presence of hydroxyl (–OH) groups due to moisture but could also arise from the hydroxyl of sugar rings. The peak at 2927 cm^{-1} results from stretching modes of the C–H bonds of methyl groups ($-CH_3$) or the C–H bond of methylene and methine groups. Absorption bands around 1618 and 1377 cm^{-1} may be due to carboxylate groups of galacturonic acid residues (Figueiro, Goes, Moreira, & Sombra, 2004). The wave numbers between 800 and 1200 cm^{-1} represent the finger print region for carbohydrates (Cui, Phillips, Blackwell, & Nikiforuk, 2007; Fillippove, 1992).

3.4. Solid-state NMR

Carbon-13 spectra from grewia polysaccharide gum samples are shown in Fig. 3a–c. The carbon-13 spectra from air-dried grewia polysaccharide gum have previously been reported (Nep & Conway, 2010). There were no major differences in the spectra obtained following the different drying methods. Each shows a broad band signal between 64 and 90 ppm which arises from the bulk of the ring C–OH carbons. The C4 carbon accounts for the high frequency shoulder. The line widths are typical of amorphous natural polymers. The C1 anomeric carbons give the signal between 90 and 110 ppm. The shape of this band suggests it is composed of multiple signals but the low resolution suggests the contrary. The low intensity signal at about 62 ppm is attributable to the $-CH_2OH$ group of the glucose. The high frequency signal at about 174 ppm is consistent with the –COOH group from a uronic acid and corroborates an earlier report (Okafor et al., 2001) that grewia polysaccharide contain galacturonic acid. The remaining signals at about 18 and 22 ppm can be attributed to the methyl groups of rhamnose. The two signals seen suggest that grewia polysaccharide gum may contain at least a fourth component. The closeness of the signal suggests that this fourth component may be similar to rhamnose.

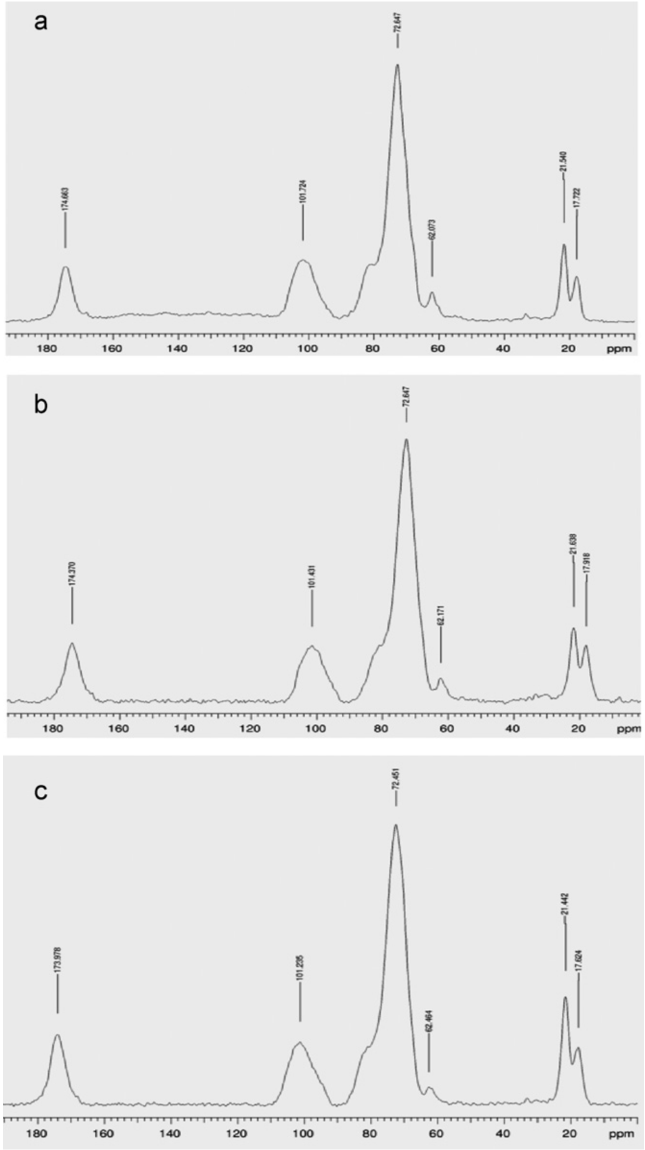

Fig. 3. Solid-state NMR of (a) air-dried, (b) freeze-dried and (c) spray-dried grewia polysaccharide gum.

3.5. X-ray photoelectron spectroscopy

XPS is capable of giving information on the relative elemental composition of all elements on a material's surface except hydrogen. The technique was employed to establish the relative composition of elements and to establish the effect of the drying method on the surface chemistry of the polysaccharide gum samples. Fig. 4a shows the effect of drying method on the synthesized carbon 1s spectra of the unprocessed (crude pulverized inner stem bark) and treated (purified and air-dried, freeze-dried or spray-dried) samples of grewia polysaccharide gum. These spectra indicate that some variation exists between the grewia polysaccharide samples. The information derived from the survey scan and the synthesized carbon 1s scans is shown in Fig. 4b and c.

Differences were observed in the relative composition of C or O in the air-dried and the freeze-dried samples ($P < 0.05$) but there were no significant variations in the composition of the other elements ($P > 0.05$). There is also no significant difference ($P > 0.05$) between the air-dried and freeze-dried, air-dried and spray-dried, or between the freeze-dried and spray-dried samples in terms of the C-components (i.e. C–C/C–H, C–O, C═O, and O–C═O) (Fig. 4c).

The variability seen with surface scans (Fig. 4a) may be attributed to differences in the composition of elements and C-components. This relative variation in elemental composition (Fig. 4b) was however only significant for C and O composition of the air-dried and the freeze-dried samples. Significant differences in chemical composition of materials as a consequence of drying technique employed have been reported in other polysaccharide gums (Mishra, Srivastava, Verma, Chauhan, & Rai, 2009). It can be seen that the differences between the unprocessed and the processed samples are greater than observed variations between the processed samples themselves.

3.6. Thermal analysis

The results showed that heating at a rate of 10 °C per minute from 30 °C to a maximum of 500 °C results in two mass loss events for the grewia polysaccharide gum samples. Table 2 summarises the details of thermal behaviour and thermal stability data according to the primary thermograms and derivative thermograms for the gum samples.

The first mass loss, taking place between 30 and 140 °C, may be attributed to the loss of adsorbed and structural water of biopolymers (Kittur, Harish Prashanth, Udaya Sankar, & Tharanathan, 2002; Vendruscolo et al., 2009) or due to desorption of moisture as hydrogen bound water to the polysaccharide structure. The second weight loss event, with an onset of over 250 °C, resulted in a weight loss of about 60%, can be attributed to thermal decomposition of the polysaccharide (Varma, Kokane, Pathak, & Pradhan, 1997) and is described by a weight loss onset and oxidation temperature. The air-dried, freeze-dried and spray-dried fractions show no variation in their oxidation temperatures ($P > 0.05$). These however have an oxidation temperature which is significantly lower than the unprocessed (crude and pulverized inner stem bark) grewia polysaccharide gum ($P < 0.05$). The reduction in impurities in the air-dried, freeze-dried and spray-dried samples compared with the unprocessed sample significantly alters the thermogravimetric parameters of the polysaccharide gum. The lower values of oxidation temperature, oxidation onset and residual mass of the spray-dried sample may not be unconnected with the fact that spray-drying (a thermal process) may have initial degradation effect on the polysaccharide structure thereby making it more susceptible to subsequent thermal degradation compared to the other samples.

The DSC traces of grewia polysaccharide gum (not shown) showed an endothermic event between 50 and 150 °C. This is attributable to moisture desorption and agrees with the results from TG analysis.

Table 2
Thermogravimetric parameters from grewia gum samples.

	Air-dried	Freeze-dried	Spray-dried	Unprocessed
Oxidation temperature (°C)	318 ± 2.5	313 ± 0.5	310 ± 1.0	330 ± 10.5
Weight loss onset (°C)	267 ± 6.2	270 ± 0.3	251 ± 6.5	264 ± 6.0
Residual mass (%)	22.1 ± 5.4	16.5 ± 5.8	11.4 ± 4.2	36.6 ± 3.7

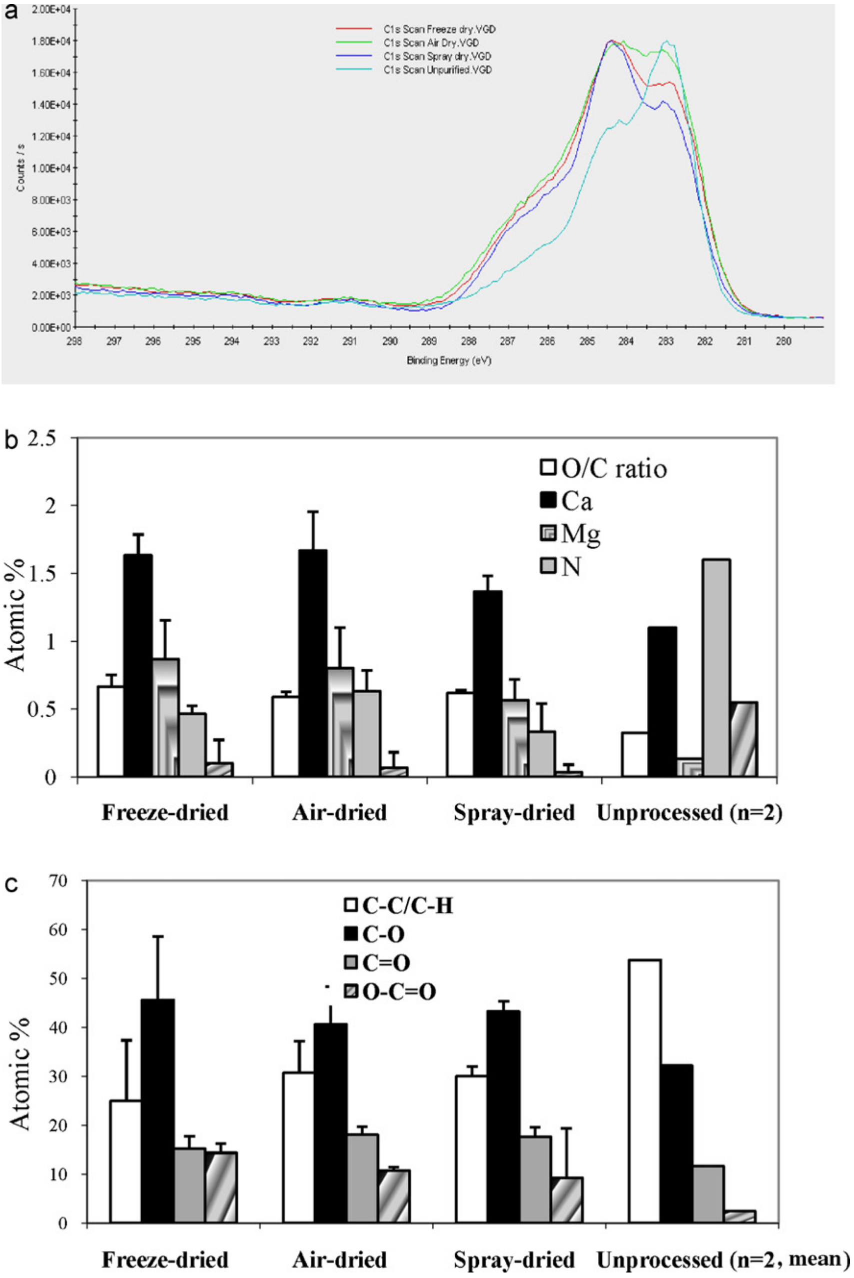

Fig. 4. Effect of drying method on (a) synthesized carbon 1s scans (b) elemental composition and (c) synthesized carbon 1s components of grewia polysaccharide gum samples ($n = 3$, mean ± s.d).

3.7. Gel permeation chromatography (GPC)

The molecular weights of the samples were expressed as the ‘pullulan polysaccharide equivalent’ molecular weight and are reported in Fig. 5a as the computed average molecular weight (Mw), number average molecular weight (Mn), and polydispersity index (Mw/Mn) shown in Fig. 5b.

The results showed that the molecular weight varies with the drying method. Cui (2005) has reported that the variation of molecular weight distribution of a material is dependent on a number of factors which include: pathway of synthesis, environment of synthesis and extraction conditions used to isolate the polysaccharide. The varying temperatures at which drying was carried out may account for the variation in the molecular weight of the polysaccharide gum. Thermal degradation caused by spray-drying or differences in soluble fractions may have some effect on molecular weight and polydispersity of a material.

3.8. Monosaccharide composition by GC analysis

The monosaccharide composition of grewia polysaccharide gum has been reported previously (Nep & Conway, 2010). Briefly, grewia polysaccharide gum is composed of five neutral sugars: glucose, rhamnose, arabinose, xylose and galactose. The mean relative concentration of these sugars in the polysaccharide is glucose (67.14%), rhamnose (6.2%), xylose (2.72%), galactose (9.61%) and arabinose (12.71%).

3.9. ^{1}H and ^{13}C NMR of grewia polysaccharide gum

The ^{1}H and ^{13}C NMR spectra of grewia polysaccharide gum have also been reported previously (Nep & Conway, 2010). Briefly, the ^{1}H NMR spectrum is crowded in a narrow region between 3 and 5 ppm typical of polysaccharides indicating the presence of many similar sugar residues (Cui, 2005). The spectrum shows the

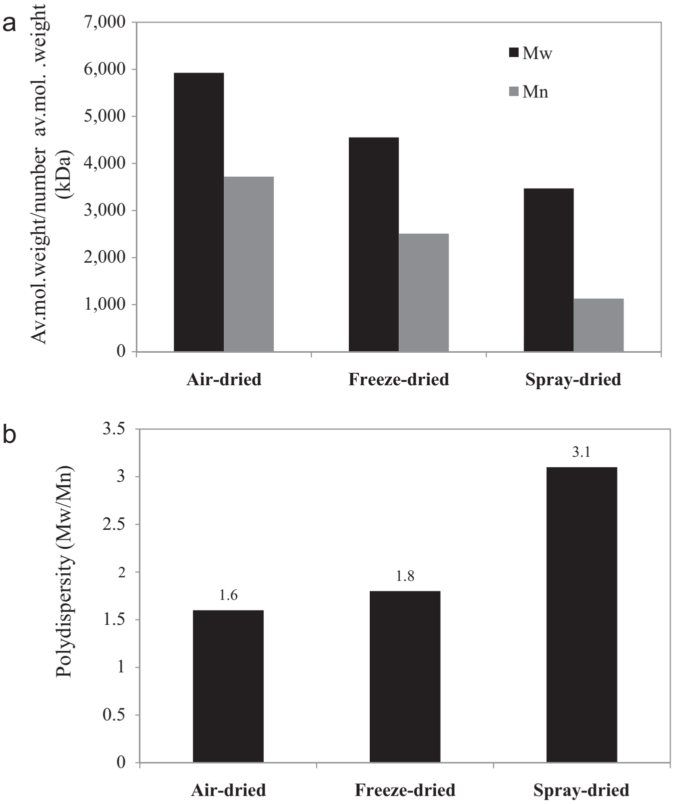

Fig. 5. Effect of drying method on (a) average molecular weight (Mw) and number average molecular weight (Mn) of grewia polysaccharide (b) polydispersity index (Mw/Mn) of grewia polysaccharide gum samples ($n = 2$, mean).

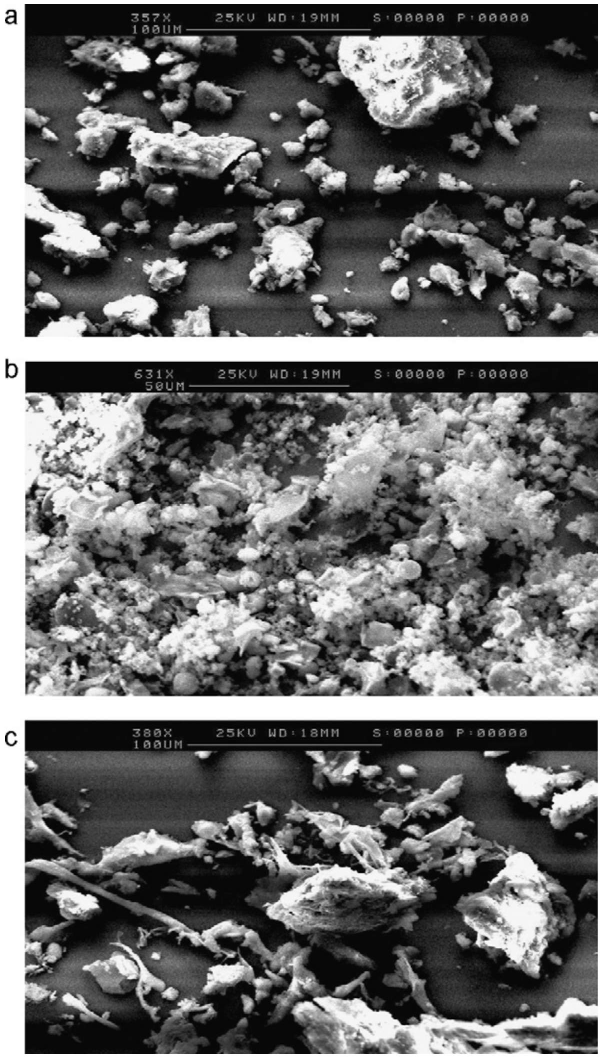

Fig. 6. Scanning electron micrographs of (a) air-dried (b) spray-dried and (c) freeze-dried grewia polysaccharide gum.

presence of a C–CH_3 group with signal at 1.15–1.21 ppm and further down field, the signal at 1.82 ppm is attributable to $COOCH_3$ (Cui, 2005). The signals between 3.1 and 4.3 ppm can be assigned to non-anomeric protons (H_2–H_6) while signals between 4.3–4.8, and 4.9–5.5 ppm arise from β-anomeric and α-anomeric protons respectively (Glicksman and Schachat, 1959). The signals between 3.0 and 3.8 ppm have also been assigned to –O–CH_3. Again, the –CH_3 indicates the presence of methylated sugar (rhamnose).

Evidence for the presence of deoxygenated sugar (rhamnose) was supported by the ^{13}C NMR with –CH_3 signals appearing in the much higher field 15–20 ppm (Cui, 2005). This –CH_3 is attributable to the methyl group of the rhamnose sugar unit. The signal between 20 and 30 ppm is thought to be a –CH_2 linked to OH which pushes the signal slightly downfield. The CH_2OH may be attributable to the glucose sugar unit. Signals from anomeric carbons of the monosaccharide components appear in the 90–110 ppm (Cui, 2005). The α-anomeric carbons are seen in the region of 95–103 ppm showing about 5 anomeric carbons which may be attributable to the five neutral sugar components of the polysaccharide while the signals due to non-anomeric carbons C_2–C_5 appear between 60 and 85 ppm.

3.10. Scanning electron micrograph of grewia polysaccharide samples

The scanning electron micrographs of grewia polysaccharide gum showing the effect of drying technique on particle morphology of the polysaccharide gum powder are shown in Fig. 6a–c. The micrographs show that spray-drying produced grewia polysaccharide gum powder that is smaller in size and with a more uniform size distribution than the freeze-dried or air-dried polysaccharide gum samples. The more spherical shape and smoother surface texture of spray-dried materials have been attributed to the turbulences in the spray-drying process which cause some erosion in the particle surface (Vendruscolo et al., 2009).

Aggregation of particles evident in the spray-dried sample is probably due to the presence of adsorbed moisture. Although this may also be the case for the freeze-dried and the air-dried samples, the fact that these samples were powdered by use of mortar and pestle also mean that size-reduction by this method may not be effective enough to effect uniform size distribution. Further processing will therefore be required before its application as an excipient.

4. Conclusion

Grewia polysaccharide gum is a novel polysaccharide gum with little published information on its characterization. The drying method had little impact on some physicochemical properties of the polysaccharide gum such as ash content, pH and flow characteristics of gum dispersions. The viscosity of a 1% w/v dispersion of the gum samples however varied according to the drying method and only the air-dried and freeze-dried samples exhibit satisfactory powder flow properties for application in tableting.

FT-IR and solid state ^{13}C-NMR results were typical of amorphous polysaccharides, with no variations between the spray-dried, freeze-dried and air-dried samples. XPS studies, however, showed that drying technique can have an effect on the surface chemistry of the polysaccharide gum.

The spray-dried product has a lower oxidation temperature, weight loss onset, and residual mass compared to the air-dried and freeze-dried samples, implying improved thermal stability of the air-dried and freeze-dried versions. Also, the molecular weight was determined to vary with the drying technique. Although further optimization of the drying techniques may be required to establish uniformity, nevertheless, present results indicate that air-drying, a low cost processing method, may be preferable to spray and freeze-drying when industrial extrapolation is indicated.

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References

Bhardwaj, T. R., Kanwar, M., Lal, R., & Gupta, A. (2000). Natural gums and modified natural gums as sustained-release carriers. *Drug Development and Industrial Pharmacy*, *26*(10), 1025–1038.

Bilany, M. R. (2007). Suspensions and emulsions. In M. E. Aulton (Ed.), *Pharmaceutics: the design and manufacture of medicines* (3rd ed., pp. 383–405). Philadelphia: Churchill Livingstone.

Cui, S. W. (2005). Structural analysis of polysaccharides. In S. W. Cui (Ed.), *Food carbohydrates: chemistry, physical properties, and applications* (pp. 105–157). Boca Raton, Florida: Taylor and Francis.

Cui, S. W., Phillips, G. O., Blackwell, B., & Nikiforuk, J. (2007). Characterization and the properties of Acacia senegal (L.) Willd. Var. senegal with enhanced properties (Acacia (sen) SUPERGUM^{TM}): Part 4. Spectroscopic characterization of Acacia Senegal var. Senegal and Acacia (sen) SUPERGUM^{TM} Arabic. *Food Hydrocolloids*, *21*, 347–352.

Emeje, M., Isimi, C., & Kunle, O. (2008). Effect of grewia gum on the mechanical properties of paracetamol tablet formulations. *African Journal of Pharmacy and Pharmacology*, *2*(1), 001–006.

Figueiro, S. D., Goes, J. C., Moreira, R. A., & Sombra, A. S. B. (2004). On the physicochemical and dielectric properties of glutaraldehyde cross-linked galactomannan-collagen films. *Carbohydrate polymers*, *56*, 313–320.

Fillippove, M. P. (1992). Practical infrared spectroscopy of pectin substances. *Food Hydrocolloids*, *6*, 115–142.

Glicksman, M., & Schachat, R. E. (1959). Some lesser known seaweed extracts. In R. L. Whistler (Ed.), *Industrial gums* (pp. 213–298). New York: Academic Press.

Huber, H. E., & Christenson, G. I. (1996). Utilization of hydrophilic gums for control of drug release from tablet formulation. 1: Disintegration and dissolution behaviour. *Journal of Pharmaceutical Sciences*, *1*, 59–66.

Jimoh, K. O., Olurin, T. O., & Aina, J. O. (2009). Effect of drying method on the rheological characteristics and colour of yam flours. *African Journal of Biotechnology*, *8*(10), 2325–2328.

Kittur, F. S., Harish Prashanth, K. V., Udaya Sankar, K., & Tharanathan, R. N. (2002). Characterization of chitin, chitosan and their carboxymethyl derivatives by differential scanning calorimetry. *Carbohydrate Polymers*, *49*, 185–193.

Middleton, D. L., Leung, S. H. S., & Robinson, J. R. (1990). Ocular bioadhesive delivery systems. In V. Leenaerts, & R. Gurny (Eds.), *Bioadhesive drug delivery systems* (pp. 179–202). Boca Raton, Florida: CRC Press Inc.

Mishra, P., Srivastava, V., Verma, D., Chauhan, O. P., & Rai, G. K. (2009). Physicochemical properties of Chakiya variety of Amla (Emblica officinalis) and effect of different dehydration methods on quality of powder. *African Journal of Food Science*, *3*(10), 303–306.

Muazu, J., Musa, H., & Musa, K. Y. (2009). Compression, mechanical and release properties of paracetamol tablet containing acid treated grewia gum. *Journal of Pharmaceutical Science and Technology*, *1*(2), 74–79.

Nep, E. I., & Conway, B. R. (2010). Characterization of grewia gum, a potential pharmaceutical excipient. *Journal of Excipients and Food Chemicals*, *1*(1), 30–40.

Nep, E. I., & Okafor, I. S. (2006). Evaluation of the bioadhesive property of grewia gum in indomethacin tablet formulation in pig gastric mucus. *Journal of Pharmacy and Bioresources*, *3*(2), 62–69.

Okafor, I. S., Chukwu, A., & Udeala, K. (2001). Some physicochemical properties of grewia gum. *Nigerian Journal of Polymer Science and Technology*, *2*(1), 161–167.

Staniforth, J. N. (2002). Powder flow. In M. E. Aulton (Ed.), *The science of dosage form design* (2nd ed., pp. 205–208). Philadelphia: Churchill Livingstone.

Sujja-areavath, J., Munday, D. L., Cox, P. J., & Khan, K. A. (1996). Release characteristics of diclofenac sodium from encapsulated natural gum mini-matrix formulations. *International Journal of Pharmaceutics*, *139*, 53–62.

Talukdar, M. M., & Vercammen, J. P. (1993). Evalution of xanthan gum as a hydrophilic matrix for controlled-release dosage form preparation. *Drug Development and Industrial Pharmacy*, *19*, 1037–1046.

Tamoda, M., Satoh, N., & Suzuki, Y. (1977). Plant mucilages XV: The main structural features of the backbone chain of paniculatan. *Chemical and Pharmaceutical Bulletin*, *25*, 968–973.

Udeala, O. K., & Chukwu, A. (1985). The binding property of mucuna gum in sulphadimidine and chloroquine phosphate tablets. *Nigerian Journal of Pharmaceutical Sciences*, *1*, 59–66.

US Pharmacopeia. (2007). *US Pharmacopeia 30, NF 25 (2007)*. Rockville: US Pharmacopeial Convention.

Varma, A. J., Kokane, S. P., Pathak, G., & Pradhan, S. D. (1997). Thermal behaviour of galactomannan guar gum and its periodate oxidation products. *Carbohydrate Polymer*, *32*, 111–114.

Varshosaz, J., Tavacoli, N., & Eram, S. A. (2006). Use of natural gums and cellulose derivatives in production of sustained release metoprolol tablets. *Drug Delivery*, *13*(2), 113–119.

Vendruscolo, C. W., Ferrero, C., Pineda, E. A. G., Silveira, J. L. M., Freitas, R. A., Jimenez-Castellanos, M. R., et al. (2009). Physicochemical and mechanical characterization of galactomannan from Mimosa scabrella: Effect of drying method. *Carbohydrate Polymers*, *76*, 86–93.

Wang, Q., & Cui, S. W. (2005). Understanding the physical properties of food polysaccharides. In S. W. Cui (Ed.), *Food carbohydrates: chemistry, physical properties, and applications* (pp. 162–214). Boca Raton, Florida: Taylor and Francis.

Wells, J. I., & Aulton, M. E. (2007). Pharmaceutical preformulation. In M. E. Aulton (Ed.), *Pharmaceutics: The design and manufacture of medicines.* (p. 356). Philadelphia: Churchill Livingstone.

York, P. (1983). Solid-state properties of powders in the formulation and processing of solid dosage forms. *International Journal of Pharmacy*, *14*, 1–28.