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# Relationship between the emulsifying properties of Acacia gums and the retention and diffusion of aroma compounds

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ABSTRACT

Five samples of *Acacia senegal* gum were selected because of their different emulsifying properties. Acacia gum samples were first characterized by various analytical methods including intrinsic viscosity and arabino-galactan protein amount as determined by gel permeation chromatography. In a second step, stability of emulsions containing orange essential oil and Acacia gums was evaluated by measurement of turbidity. In addition, flavour release of two different hydrophobic aroma compounds from Acacia gum aqueous solutions was studied. Retention was measured using the phase ratio variation method under equilibrium whereas diffusion was assessed by DOSY NMR. This study established the relationship between the emulsifying ability of Acacia gum and the behaviour of aroma compounds in the corresponding solution. Better emulsifying ability of Acacia gum sample appears strongly correlated to an increase in flavour retention and a decrease in molecular mobility as the result of mostly hydrophobic interactions.



## 1. Introduction

Acacia gum (GA) is a complex polysaccharide which is obtained as an exudate from Acacia trees. It is a high molecular weight macromolecule that can easily be dissolved and dispersed in water under appropriate conditions. At low concentration (<10%), GA do not modulate significantly rheological properties and is generally used as food stabilizer or emulsifier for various industrial applications. For example, GA is currently used to increase flavour retention in many microencapsulated products and to control release of flavour compounds (Ducel, Richard, Popineau, & Boury, 2005; Tobitsuka, Miura, & Kobayashi, 2006). In beverages flavoured with essential oils also, GA is an effective emulsifier used to stabilize flavour compounds in the aqueous phase (Given, 2009).

At a molecular level, three different fractions can be distinguished from Acacia gum: the Arabino-Galactan fraction (AG) (88% of the total gum and 20% total proteins), the Arabino-Galactan Protein fraction (AGP) (10%–55% total proteins) and the Glyco-Protein fraction (GP) (about 1%–25% total proteins). In emulsions, GA molecules strongly adsorb on the surface of the oil droplet and form thus an interfacial layer that stabilizes the mixtures against droplet aggregation and/or coalescence through steric and electrostatic interactions (Dickinson, 2009). Although GA solution with a concentration higher than 10% is generally required to stabilize emulsion, only a limited gum fraction (1–2%) actually adsorbs at the oil–water interface (Randall, Phillips, & Williams, 1988). Randall et al. (1988) established that it was the high molecular mass, protein-rich AGP fraction which was mainly adsorbed and hence was responsible for the emulsifying capacity of the Acacia gum. Further investigations revealed that two gum characteristics strongly govern the emulsion properties and its stability: the AGP fraction average molecular weight on the one hand and the nature of proteins on the other hand (Al-Assaf, Phillips, & Williams, 2006; Garti & Leser, 2001; Randall, Phillips, & Williams, 1989).

As most natural products, Acacia gum is subject to chemical variability that sharply affects its functional properties. Therefore, it is crucial to find an easy way to evaluate the emulsifying ability of gum samples, with the purpose to reach stability for a substantial period of time, and also reduce the amount of gum required to obtain a consistent and stable emulsion. In this context, a variety of techniques have been developed to study the chemical properties of GA, including hydrophobic interaction chromatography, gel permeation chromatography, intrinsic fluorescence spectroscopy, biochemical analyses… (Al-Assaf, Phillips, & Williams, 2005; Idris, Williams, & Phillips, 1998; Renard, Lavenant-Gourgeon, Ralet, & Sanchez, 2006). Among these techniques, the gel permeation chromatography (GPC) coupled with a triple detection (MALLS, UV and RI) is currently used to characterize Acacia gums, especially

*Abbreviations:* AGP, arabino-galactan protein; DOSY, diffusion ordered spectroscopy; EM, emulsion; GA, Acacia gum; GC, gas chromatography; GPC, gel permeation chromatography; NMR, nuclear magnetic resonance; PRV, phase ratio variation.

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the amount of the most surface-active AGP fraction (Al-Assaf & Phillips, 2006). Nevertheless, GPC remains a quite complex and not widespread technique. Furthermore, only slight differences are usually observed from one GA sample to another in spite of significant differences in their emulsifying ability.

The quality of Acacia gum samples influences the thermodynamic stability of emulsions. As a result, the use of an ineffective gum may result in loss of product quality and a decrease in shelf-life. Among many aspects, flavour is an essential attribute of the quality and acceptability of a food product. A high-quality gum is expected to retain flavour in the product minimizing, thus, the release and loss of the aroma compounds that may lead to a decline in food properties. Aroma release from a food product is generally evaluated through thermodynamic and kinetic parameters (Boland, Delahunty, & van Ruth, 2006; Bylaite, Ilgūnaite, Meyer, & Adler-Nissen, 2004; Nahon, Harrison, & Roozen, 2000; Seuvre, Philippe, Rochard, & Voilley, 2007). On the one hand, measurement of the thermodynamic parameters under equilibrium such as partition coefficients of aroma compounds, makes possible the assessment of flavour retention in a food product. On the other hand, flavour release under dynamic conditions may be evaluated from the measurement of the diffusion coefficient ($D$) of the aroma compounds through the product (Cayot, Dury-Brun, Karbowiak, Savary, & Voilley, 2008). Recent studies focused on aroma retention in GA containing products (Karaiskou, Blekas, & Paraskevopoulou, 2008; Terta, Blekas, & Paraskevopoulou, 2006). However, in these works diffusion was not taken into account and the relation with the emulsifying ability of gums not clearly obtained.

In this study, we propose a method to evaluate the emulsifying potential of several Acacia gums through the study of flavour release. First, different samples of Acacia gums were selected and their physicochemical characteristics were determined. In particular, measurements of the AGP level were carried out using GPC. Then, for each Acacia gum sample, emulsions were prepared with orange essential oil and their stability was evaluated by measurement of turbidity. Additionally, the behaviour of the two aroma compounds in aqueous solutions containing the different GA samples was analysed to determine both their thermodynamic and kinetic parameters. In this way, their gas/liquid partition coefficients were measured using the phase ratio variation (PRV) method to evaluate the retention whereas their diffusion coefficients were determined using nuclear magnetic resonance diffusion ordered spectroscopy (DOSY NMR). The choice of two different compounds was done with respect to detectability in DOSY NMR (solubility limit, prevention of overlapped signals) and in PRV (solubility limit, volatility in aqueous media).

Finally, a comparison of the different methods used made it possible to establish whether flavour retention and diffusion measurements were efficient ways to evaluate the effectiveness of GA and to discriminate samples that presented very similar emulsifying properties.

## 2. Materials and methods

### 2.1. Materials

Ethyl decanoate, α-terpineol, ethanol and sodium chloride (purity $\geq$ 97%) were supplied by Aldrich (Saint-Quentin Fallavier, France) and orange essential oil by Expression Aromatique (Mouans-Sartoux, France). Acacia gums (food grade) were provided by Alland & Robert (Port Mort, France). The water used was ultra pure grade.

### 2.2. Physicochemical characterizations of Acacia gums

Specific optical rotation $[\alpha]_D^{25}$ of the different Acacia gums in water solutions ($1 \times 10^{-3}$ g/dm$^3$) was obtained with a PerkinElmer 241 polarimeter (PerkinElmer, France) in a thermostated (25 °C) cell with a length of 1 dm.

Intrinsic viscosity [$\eta$] was determined at 25 °C by a capillary viscometer (Ubbelohde for dilution sequences, Schott) in a concentration range from 0.5 to 2% (w/w) in NaCl 0.1 mol/L. Intrinsic viscosity was obtained from Huggins extrapolation to zero concentration. Average molecular weight ($M_v$) was determined using Mark-Houwink's equation using coefficients of $K = 1.3 \times 10^{-2}$ and $a = 0.54$ (Anderson & Rahman, 1967).

The AG, GP and AGP percentages were determined using a gel permeation chromatography (GPC) system equipped with a Superose 6 10/300 GL (GE Healthcare). A refractive index (RI) detector (Sopares, France), an ultraviolet (UV) detector (Serie 1100 Helwett Packard, France) at 214 nm and a multiangle laser light scattering (MALLS) detector (Dark V3, Consenxus, Germany) operating at 532 nm were used. The mobile phase was a NaCl solution (0.1 mol/L) and the flow rate was controlled at 0.4 ml/min at ambient temperature. The injection loop volume was 50 μL. The value of the refractive index increment (dn/dc) was 0.142 mL/g as measured in the mobile phase, and mass calibration was carried out using a pullulan standard (Shodex P800). The GA solutions were prepared at 3 g/L in mobile phase 24 h before analysis and filtered (0.45 μm, cellulose ester)1 h prior to injection.

### 2.3. Rheological characterization of GA solutions

5% (w/w) GA solutions in ultra pure water were prepared 24 h before measurement. Apparent viscosities, $\eta$, were then recorded at 25 °C using a Brookfield viscometer model LVT with the spindle no. 1 at 100 rpm.

### 2.4. Emulsion stability

Oil-in-water emulsions were prepared by mixing 3.5 g of orange essential oil with 46.5 g of a 10% (w/w) GA aqueous solution. Both phases were first prepared separately and kept at rest for 1 day. The oil phase was then dispersed in the GA solution under strong shear using a T25 Ultra Turax homogenizer (IKA-Labortechnik, Germany) at 13 500 rpm for 5 min. Five emulsions were prepared and labelled (EM0, EM1, EM2, EM3, and EM4) with the GA corresponding figure (GA0, GA1, GA2, GA3, and GA4). In order to check experience reproducibility, each emulsion was prepared in duplicate. Emulsion samples were stored at 4 °C for 24 h to obtain diffusion of macromolecules and stabilization of the oil–water interface (Erni et al., 2007).

The stability of the emulsions was estimated from measurement of turbidity (Pearce & Kinsella, 1978). A 1 mL aliquot of the emulsion was diluted to 1 L with water and the absorbance ($A$) was measured in a 1 cm path length cell at 650 nm using a UV–vis spectrophotometer (Thermo Spectronic, Genesis 6, France). For each emulsion, dilution was done in duplicate and absorbance of each dilution was measured five times. All measurements were performed on emulsions prior and after centrifugation step (5 min at 1500 rpm) in order to test the emulsion stability. The turbidity parameter ($\tau$) of the different solutions tested can be easily calculated using the relation (1):

$$\tau = \frac{2.303 \cdot A}{l} \quad (1)$$

with $A$, the absorbance at 650 nm and l, the length of the cell.