HOW FLAVOUR RETENTION REFLECTS THE EMULSIFYING PROPERTIES OF ACACIA GUMS

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Abstract

This work focuses on the study of the flavour release of two different hydrophobic aroma compounds from Acacia gum aqueous solutions. 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 hydrophobic interactions.

Introduction

Acacia gum (GA) is a natural polysaccharide associated with a small amount of linked protein (2%, w/w). Three different fractions can be isolated:
- the Arabino-Galactan fraction (AG) (88% of the total gum - 20% total proteins)
- the Arabino-Galactan Protein fraction (AGP) (10% - 55% total proteins)
- the Glyco-Protein fraction (GP) (about 1% - 25% total proteins).

Because of its unique emulsifying and stabilising properties, acacia gum is commonly used in many food applications. In beverage flavoured with essential oil, for instance, the GA efficiently stabilises the flavour compounds in the aqueous phase. For industrial applications it is important to easily evaluate the emulsifying ability of gums. The emulsifying properties seem to be related to two important parameters: the molecular weigh of the AGP fraction and the nature of the proteins (1-4). Gel permeation chromatography (GPC) coupled with a triple detection (MALLS, UV and RI) is currently used to characterise acacia gums, nevertheless most of the time analysis results are only slightly different in spite of significant differences in emulsifying abilities. In this work, we proposed an original way to evaluate the emulsifying potential of several acacia gums selected for their good emulsifying potential. First different samples of Acacia Senegal gums were selected and characterised using GPC. Then the behaviour of two aroma compounds in the solutions containing AG was analysed. Behaviour of these two probes was then compared and put in relation with the stability of corresponding emulsions; such a method made possible to determine whether flavour retention and diffusion measurements were efficient ways or not to evaluate the emulsifying ability of AG.

Experimental
Molecular characterisation. The AG, GP and AGP percentages were determined in a gel permeation chromatography (GPC) system equipped with a Superose 6 10/300 GL (GE Healthcare). A refractive index detector (Sopares, France), an UV detector (Series 1100 Helwett Packard, France) at 214 nm and a Dark V3 detector (Consensus, Germany) operating at 532 nm were used. The mobile phase was 0.1 mol.L⁻¹ sodium chloride at a 0.4 ml min⁻¹ flow at ambient temperature. The injection volume was 50 µL. A value of 0.142 cm³ g⁻¹ was measured for the refractive index increment (dn/dc) in this mobile phase. The GA solution was prepared at 3 g L⁻¹ in mobile phase 24 h before analysis and filtered (0.45 µm) 1 h before injection.

Rheological characterisation of GA solutions. 5% GA solutions in ultra pure water were prepared 24 h before measurement. Apparent viscosities were then recorded at 20 °C using a Brookfield viscometer model LVT with the spindle no. 1 at 100 rpm.

Aroma diffusion measurement. 5% GA aqueous solutions were flavoured with α-terpineol (0.8 g.L⁻¹). DOSY-NMR experiments were performed at 298 K on a Bruker Advanced 300 equipped with a 5 mm gradient inverse probe. A stimulated echo sequence (STE) incorporating bipolar gradients (BP) with longitudinal eddy current delay (LED) of 5 ms was used. Duration of the magnetic field pulse gradient (δ) was 1 ms and a diffusion time (Δ) of 550 ms was applied to observe a complete signal decay with the maximum gradient strength. After Fournier transformation, phase and baseline corrections, the diffusion coefficient (D) was obtained using the xwinnmr 3.5 software.

Aroma retention measurement. The retention of ethyl decanoate in the GA solutions was calculated according to Jouquand et al. (5) using the PRV method. 5% (w/w) solutions of AG were prepared 24 h before analysis. Solutions or water were flavoured with a solution of ethyl decanoate diluted in ethanol at a concentration of 2.76 g L⁻¹ to have a final concentration of 4.6 ppm in the solution. Increasing volumes (1, 2, 3 and 4 mL) of the flavoured solutions were placed into headspace vial (20.7 mL) and hermetically sealed. Once the equilibrium time reached (corresponding to 6 h at 30 °C), a 1 mL sample of headspace was injected into the GC by a gas syringe (30 °C) using a Combipal CTC analytics automatic headspace sampler. A Varian CP-3800 GC system with a flame ionization detector (FID) and a BP-1 column (0.25 mm × 15 m × 0.25 µm, SGE) was used. Oven temperature was programmed at 150 °C for 3 min. Detector and injector temperatures were 250 °C. Helium was used as carrier gas at a flow rate of 1 mL min⁻¹. Injection was performed with a 1/20 split.

Results

Characteristics of the GA samples. In this study, four samples of acacia gums were selected for their good emulsifying potential. The emulsifying property, the AGP and AG + GP fractions percentages and also the apparent viscosity (5% GA solutions) of each sample are given in (Table 1).

Table 1. Characteristics of the acacia gums (* data provided by Alland & Robert).

<table>
<thead>
<tr>
<th></th>
<th>Emulsifying properties</th>
<th>Apparent viscosity (mPa·s)</th>
<th>% AGP</th>
<th>% AG + GP</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA1</td>
<td>+</td>
<td>27</td>
<td>9.3</td>
<td>90.7</td>
</tr>
<tr>
<td>GA2</td>
<td>+</td>
<td>25</td>
<td>11.3</td>
<td>88.7</td>
</tr>
<tr>
<td>GA3</td>
<td>+++</td>
<td>28</td>
<td>14.1</td>
<td>85.9</td>
</tr>
<tr>
<td>GA4</td>
<td>+++</td>
<td>34</td>
<td>14.7</td>
<td>85.3</td>
</tr>
</tbody>
</table>
GA1 and GA2 had a good potential whereas GA3 and GA4 were particularly efficient emulsifier. According to the gums composition reported, the gums GA3 and GA4 were composed of higher fraction of AGP than the two other gums GA1 and GA2. As a consequence, better emulsifying ability corresponds to higher AGP fraction, thus confirming the primary implication of the AGP fraction in the emulsifying properties (1-3). Finally, no significant difference in the apparent viscosity was observed when comparing the different samples of GA. Apparent viscosity of the solutions was notably measured to help understanding the behaviour of the flavour compounds in the GA solutions.

**Flavour retention and diffusion.** Two different aroma compounds were used: α-terpineol and ethyl decanoate (Table 2).

**Table 2. Characteristics of the two aroma compounds.**

<table>
<thead>
<tr>
<th></th>
<th>Solubility in water at 25 °C (g L⁻¹)</th>
<th>log P</th>
<th>Odour characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Terpineol</td>
<td>1.80</td>
<td>3.0</td>
<td>Sweet, floral, lilac</td>
</tr>
<tr>
<td>Ethyl decanoate</td>
<td>0.016</td>
<td>4.7</td>
<td>Sweet, fruit, dry fruits</td>
</tr>
</tbody>
</table>

These compounds, naturally found in several floral or fruity aroma fractions, are soluble in water in the concentration range used in this study and are enough lipophilic (log P) to be representative of compounds present in essential oils currently used to flavour beverages.

The gas/liquid partition coefficients of ethyl decanoate, as measured by the PRV method in water and in the four solutions of GA are reported on (Figure 1).

![Figure 1. Gas/liquid partition coefficients of ethyl decanoate at 30 °C.](image)

The partition coefficient of ethyl decanoate was lower in the GA solutions than in water. This indicates a significant retention of ethyl decanoate whatever the GA samples. Thus, interactions existed between ethyl decanoate and GA. Hydrophobic interaction appear the most probable type as the consequence of the lipophilic nature of this aroma compound. Moreover the decrease in the release of ethyl decanoate in the headspace depended on the GA sample. Two different tendencies were observed: $K_{G/L}$ of ethyl decanoate was similar for GA1 and GA2 solutions, and similar but much lower for GA3 and GA4 solutions. From these results, it is possible to calculate the percentages of retention (R) of ethyl decanoate in the solutions as compared to water. R was 52% and 54% for GA1 and GA2, respectively and 87% and 93% for the better emulsifiers GA3 and GA4, respectively. As a consequence,
the better the emulsifying power of the GA, the higher the retention. The retention of ethyl decanoate indicated the presence of hydrophobic interactions that reflected the quality of the acacia gum. The hydrophobic interactions could be put in relation with the gum’s AGP content. The higher the AGP fraction, the higher the retention of ethyl decanoate. As a consequence, the role of the proteins of the AGP fraction was suggested in the establishment of bindings with lipophilic compounds, even if more experiments should be performed to confirm this result.

In a second step, DOSY NMR measurements were performed to obtain the diffusion coefficients of α-terpineol. (Figure 2) indicates the values obtained in water and in the 5% GA solutions.

Figure 2. Diffusion coefficients of ethyl decanoate at 30 °C.

The diffusion coefficient (D) of α-terpineol decreased in the solution of GA as compared to the diffusion in water. This decrease strongly depended on the GA sample following the order: GA1≥GA2>GA3>GA4. The apparent viscosities of the solutions (Table 1) did not explain this evolution of D. As a result, the D decreasing was rather linked to the emulsifying properties of the gums and these results confirmed the conclusions drawn using the PRV method, a completely different tool based on the utilisation of another volatile probe molecule. The better the emulsifying power, the lower the diffusion coefficient.

Conclusions

This study demonstrated that good GA emulsifying properties induce hydrophobic interactions that sharply reduce the release and the mobility of aroma compounds in the GA solution even at low gum content. Moreover, not only flavour retention but also flavour diffusion correlated well with the emulsifying properties of GA as revealed by the DOSY NMR experiments. These results may be confirmed with samples of GA of wilder origins.

References