



Study of interactions between aroma compounds and acacia gum using headspace measurements



Géraldine Savary*, Nicolas Hucher, Odile Petibon, Michel Grisel

Université du Havre, URCOM, EA 3221, FR CNRS 3038, 25, rue Philippe Lebon CS 80540, 76058 Le Havre cedex, France

ARTICLE INFO

Article history:

Received 19 July 2013

Accepted 28 October 2013

Keywords:

Arabic gum

Flavour release

PRV method

Retention

Hydrophobic interactions

Concentration effect

ABSTRACT

This study deals with retention measurements of aroma compounds in acacia gum aqueous solutions. In that purpose, six volatile molecules differing in their physicochemical properties were analysed: ethyl butyrate, ethyl hexanoate, ethyl octanoate, cumene, 1-octanol and linalool. Their gas/liquid partition coefficients were measured by headspace gas chromatography using the phase ratio variation method from acacia gum solutions. Three acacia gum samples exhibiting different emulsifying properties were studied for concentrations ranging from 0 to 20 wt%. These measurements made possible to evaluate the interactions between aroma compounds and acacia gums through the calculation of retention. A correlation between retention and lipophilicity was observed, thus proving that acacia gum interacts with aroma compounds via hydrophobic bonding. Significant interactions occur for volatile molecules that have a pronounced lipophilic character ($\log P > 3.6$). The effect of gum concentration was also studied. No linear relationship was evidenced with retention and a significant effect was observed for concentration higher than 5 wt%. This work also establishes that the emulsifying properties of acacia gum can be evaluated by retention measurements for lipophilic aroma compounds ($\log P > 3.6$).

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The flavouring process of food, and especially beverage, remains a difficult task due to the complex and reversible association of its two main components, an aqueous matrix and some lipophilic volatile molecules. To improve the stability of such mixtures, specific additives are usually used in order to enhance the stability and to ease the formulation steps (Dickinson, 2009).

Acacia gum (GA) is among the most used additive for beverage flavouring as it is an effective emulsifier used to stabilize aroma compounds in the aqueous phase (Given, 2009). Acacia gum, an exudate from Acacia trees growing in African sub-desert areas, is usually described as a complex heteropolysaccharide containing about 2% of proteins. Three major molecular species have been isolated for the polymer backbone: arabinogalactan (AG), arabinogalactan protein (AGP), and glycoprotein (GP) (Randall, Phillips, & Williams, 1989; Renard, Lavenant-Gourgeon, Ralet, & Sanchez, 2006). This structural complexity makes difficult the comprehension of mechanisms leading to the stabilization of complex food products. In particular, few studies focused on the investigation of the mechanisms of interaction between acacia gum samples and

flavour compounds. Some authors suggested hydrophobic interactions (Savary, Hucher, Bernadi, Grisel, & Malhiac, 2010; Terta, Blekas, & Paraskevopoulou, 2006) but neither the nature of binding nor the conditions of formation were clearly established. Therefore, it is notably important to evaluate the critical hydrophobicity value ($\log P$) for an aroma compound, necessary for the occurrence of interactions with acacia gum.

Moreover, as most natural products, acacia gum is subject to chemical variability that will affect its functional properties and therefore it is crucial to find an easy way to evaluate the emulsifying ability of each gum sample. Gel permeation chromatography is currently used to characterize acacia gums, especially the amount of the most surface-active AGP fraction (Al-Assaf & Phillips, 2006) but remains a quite complex technique sometimes unable to discriminate one GA sample to another in spite of significant differences in their emulsifying ability. In a previous paper we were able to show that, in some cases, these abilities could be predicted on the basis of the association properties of GA solutions and aroma compounds (Savary et al., 2010). Nevertheless these assertions relied on two volatile molecules, α -terpineol and ethyl decanoate, and it seemed important to confirm that only the knowledge of physicochemical properties of the chosen molecules was required to predict the emulsifying ability of random acacia gum samples.

In this study, we evaluate several volatile molecules, chosen among aroma compounds, through the study of their retention in

* Corresponding author. Tel.: +33 232 744399; fax: +33 232 744391.

E-mail address: geraldine.savary@univ-lehavre.fr (G. Savary).

aqueous GA solutions. To this purpose, their gas/liquid partition coefficients were measured using the phase ratio variation (PRV) method to evaluate the retention. GA samples were chosen to exhibit noticeable difference in their emulsifying abilities, and GA concentration in aqueous solution varied from 0 to 20 wt%. Different physicochemical properties of aroma molecule were either measured or estimated. Finally statistical analyses were performed in order to establish whether these physicochemical properties allowed to explain the retention of aroma compounds and to understand the nature of their interactions with GA, or not. The required minimum values of these properties that make possible the discrimination of different samples of GA, based on their effectiveness as emulsifiers, were also evaluated.

2. Materials and methods

2.1. Materials

Ethyl butyrate, ethyl hexanoate, ethyl octanoate, cumene, 1-octanol and linalool (purity $\geq 98\%$) were supplied by Aldrich (Saint-Quentin Fallavier, France). A series of *Acacia senegal* gum samples (food grade) were provided by Alland & Robert (Port Mort, France). Some physicochemical characteristics of gums were indicated in a previous study (Savary et al., 2010) including the percentage of the AGP fraction (14, 9 and 7% for GA0, GA2 and GA4 respectively) and the intrinsic viscosity (0.335, 0.213 and 0.183 dL/g for GA0, GA2 and GA4 respectively). The water used was ultrapure grade.

2.2. Aroma diffusion in water

Water (H₂O/D₂O 50/50 v/v) was flavoured with aroma compound individually to have a final concentration of 0.07 g/L. DOSY NMR experiments were performed at 301.35 K on a Bruker Advanced 300 equipped with a 5 mm inverse probe with z-gradient. A stimulated echo sequence (STE) incorporating bipolar gradients (BP) with water suppression (3–9–19 pulse sequence, delay for binomial water suppression = 219 μ s) was used. Duration of the magnetic field pulse gradient (δ) was 0.5 ms and a diffusion time (Δ) of 600 ms was applied to observe complete signal decay with the maximum gradient strength.

During the NMR diffusion time Δ , the signal intensities of aroma compounds exponentially decrease according to $I/I_0 \propto \exp(-D_w q^2 \Delta)$ where I/I_0 is the signal attenuation and q^2 is the gradient amplitude. The decay rates of the exponential curves are thus proportional to their respective diffusion coefficients.

After Fourier transformation, phase and baseline corrections, the diffusion coefficient (D_w) was obtained through Bayesian DOSY Transform using the MestReNova 6.2.1 software.

2.3. Aroma retention in GA solutions

The retention (R) of aroma compounds in the GA solutions was calculated according to the following relationship:

$$\text{Retention}(\%) = \frac{K_W - K_{GA}}{K_W} \times 100 \quad (1)$$

where K_W and K_{GA} are the gas/solution partition coefficient of aroma compound in water and in the GA solution, respectively. K_W and K_{GA} , defined as the ratio of the concentration of aroma compound in the gas phase to its concentration in the liquid phase at equilibrium, were determined using the PRV method (Jouquand, Aguni, Malhiac, & Grisel, 2008). This method consists in studying the aroma release in the headspace for different phase ratios (β)

inside the vial. β is the ratio between the headspace volume (V_G) and the volume of solution (V_S):

$$\beta = \frac{V_G}{V_S} \quad (2)$$

By plotting the inverse of the chromatographic area ($1/A$) against the phase ratio (β), a linear relationship is obtained:

$$\frac{1}{A} = a\beta + b \quad (3)$$

The partition coefficient K is then defined as the ratio between the slope (a) and the intercept (b).

1, 5, 10 and 20 wt% solutions of GA were prepared 24 h before analysis in ultrapure water using magnetic stirring at ambient temperature for 1 h. GA solutions or water were flavoured with ethyl butyrate, ethyl hexanoate, linalool and 1-octanol to have a final concentration of 0.07 g/L and with ethyl octanoate and cumene to have a final concentration of 0.05 g/L. Aroma compounds were added all together to the solution and concentrations were chosen of same order of magnitude, and remained below their solubility limits.

Increasing volumes (0.5, 1, 2, 3 and 4 mL) of the flavoured solutions were placed into headspace vials (20.7 mL) and hermetically sealed. Thus, each vial represented a gas/liquid phase ratio β of 40.4, 19.70, 9.35, 5.90 and 4.18 respectively.

Preliminary analysis showed that equilibrium time was reached after 6 h at 30 °C without stirring (results not shown). Once the equilibrium achieved, a 1 mL sample of headspace was injected into the GC with 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 (15 m \times 0.25 mm \times 0.25 μ m, SGE) was used. The oven temperature program was set from 40 °C for 10 min to 240 °C at 10 °C/min. Detector and injector temperatures were set at 250 °C. Helium was used as carrier gas at a flow rate of 2 mL/min. Injection was performed with a 1/20 split ratio.

2.4. Data analysis

The statistical analyses were performed using XLSTAT software from Addinsoft (version 2012.1.01). A one-way analysis of variance (ANOVA) was applied to the data. When GA effect was significant compared to water ($P \leq 0.05$), the differences between gums were analyzed using Tukey's method for multiple comparisons of means for each molecule. Principal Component Analysis (PCA) was also performed to study the relationships between physicochemical properties and retention of aroma compounds.

3. Results and discussion

3.1. Effect of the nature of the aroma compound

The six molecules selected for this study and their physicochemical properties are listed in Table 1. Their chemical structures point up the diversity of the compounds that compose the flavour of food products. They are small molecules as illustrated by their molecular weight (M_w) and their volume diameter (D_v) and are volatile species with boiling points (B_p) ranging from 120 to 208 °C and Henry constants (H) ranging from 0.03 to 10.5×10^{-3} atm m³/mol. As we expected hydrophobic interactions between acacia gum and aroma compounds, two parameters were particularly relevant: (i) logP which is the octanol/water partition coefficient and represents the affinity for an oily phase and (ii) the solubility in water (S) which corresponds to the hydrophilic character of the molecule. On

Download English Version:

<https://daneshyari.com/en/article/605146>

Download Persian Version:

<https://daneshyari.com/article/605146>

[Daneshyari.com](https://daneshyari.com)