



Effects of polyols at low concentration on the release of sweet aroma compounds in model soda beverages

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ABSTRACT

This study investigated the effect of polyols erythritol, D-mannitol, and maltitol on the volatility of aroma compounds γ -butyrolactone, 3-methyl-1-butanol, and 2-phenylethanol in aqueous solution. Headspace solid-phase microextraction/gas chromatography and diffusion-ordered nuclear magnetic resonance techniques were used to obtain information on aroma–food matrix interaction. Results demonstrated that adding polyols at final low concentrations of 5% or 10% (w/w) to an aqueous solution of 2-phenylethanol reduced the release of vapor-phase aromas, except in the case of 3-methyl-1-butanol, which was not affected by the presence of polyols in the liquid matrix. Polyols also reduced the diffusion coefficients of all three aroma compounds, probably due to friction between the molecules. At low polyol concentrations, aroma compound volatility and diffusion coefficient values were altered compared to those of aromas released from pure water. This observation is related to the physicochemical properties of the aroma compounds. These insights may help guide the use of the combination of aroma compounds and polyols in the formulation of sugar-free and reduced-sugar beverages.

Chemical compounds: γ -butyrolactone (PubChem CID: 7302), 3-methyl-1-butanol (PubChem CID: 31260), 2-phenylethanol (PubChem CID: 6054), erythritol (PubChem CID: 222285), D-mannitol (PubChem CID: 6251), maltitol (PubChem CID: 493591).

1. Introduction

Changes in dietary habits and the growing sedentarization of the population have led international organizations to issue warning regarding the need to increase physical exercise and consume a healthy diet (World Health Organization, 2015). Sugar in foods and beverages has been linked to diabetes, obesity, and caries (World Health Organization, 2014; World Health Organization, 2017), and, in particular, the sugar in soda beverages (“soft drinks”) has been linked to obesity and other diseases, especially among children (Arenaza et al., 2019; World Health Organization, 2014).

The sugar content in beverages can be reduced by replacing the sugar with new molecules that alter taste perception, by reducing the sugar content while maintaining consumer acceptability, and by using aroma compounds that enhance taste perception (Barba, Beno, Guichard, & Thomas-Danguin, 2018). A common strategy that manufacturers use to reduce the sugar content of soda beverages is to replace the sugar with soluble fiber or carbohydrates such as polyols, which are usually obtained through the chemical reduction of saccharides such as sorbitol,

mannitol, isomalt, maltitol, lactitol, xylitol, and erythritol. Polyols have a sweet flavor and physical properties similar to those of sugar, making them effective as low-calorie sweeteners. Polyols have a lower caloric value than sucrose because they are poorly absorbed in the gut, which can benefit people with diabetes and obesity; further, polyols do not contribute to caries formation because they are not metabolized by the oral microbes associated with dental plaque formation. By contrast, polyols can be metabolized by the gut microbiota, which can lead to gas or laxative effects (Rice, Zannini, Arendt, & Coffey, 2020). Thus, soda beverage manufacturers may combine polyols with high-intensity sweeteners such as aspartame, acesulfame K, or neotame to reduce the polyol concentration while still ensuring sufficient perceived sweetness. However, some high-intensity artificial sweeteners induce glucose intolerance by altering the gut microbiota (Suez et al., 2014); further, this approach goes against a growing trend among food manufacturers toward “clean labeling” with shorter lists of ingredients (Asioli et al., 2017; Cao & Miao, 2022).

Another approach to reducing polyol concentrations is to combine them with volatile compounds whose odors evoke a perception of sweet

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taste (Guichard, Barba, Thomas-Danguin, & Tromelin, 2020; Zhou, Feng, Thomas-Danguin, & Zhao, 2021). For example, adding strawberry aroma to whipped cream led subjects to perceive the cream as sweeter (Frank & Byram, 1988). Adding sweet-smelling ethyl-hexanoate to apple juice enhanced sweetness (Knoop, Bult, & Smit, 2009). By contrast, adding 2-ethyl-3,5-dimethyl pyrazine to a traditional fermented soy bean product increased perceived saltiness (Gao et al., 2022). In this sense, we have demonstrated in previous studies the feasibility of adding ethyl 2-methylbutanoate, furaneol, and γ -decalactone to reduced-sugar fruit juices to enhance perceived sweetness (Barba et al., 2018).

More research is needed into the interactions between aroma compounds and food matrices because their release and therefore effectiveness depend on several factors, including diffusion into the food matrix, mass transfer into the air, and the composition of the food (Guichard, 2015; Taylor, 1996, 2002). The study of the interaction of flavor compounds contributes to understanding flavor release. Among the composition of a food product, main ingredients such as proteins, lipids, and carbohydrates have an impact on aroma release. Proteins are known to bind a trap aroma compounds, being in most cases due to hydrophobic and hydrogen bonding. Lipids are well known to solubilize aroma compounds, trapping aroma compounds. This retention of hydrophobic aroma compounds is higher than for proteins. Carbohydrates often induce retention in the matrix due to the modification of physical properties such as viscosity or intermolecular networks. Interactions of flavor compounds with other food matrix compounds, such as proteins, carbohydrates, and lipids, have been well studied (Guichard, 2015), although there are considerably fewer studies of polyols. It appears likely that polyols affect the volatilization of aroma compounds, but few studies have examined this possibility in food or beverage products. In one study, the type and size of polyols were found to influence the release of volatile flavors from chewing gum (Raitthore & Peterson, 2016, 2018). In another study, polyols influenced the release of aroma compounds from the model solution (Siefarth et al., 2011a, 2011b). Those studies used polyol concentrations of 20% (w/w), which may be higher than what manufacturers are willing, or even legally allowed to, add to food products.

Therefore, to adapt polyol food concentrations to real values, the present study consists of determining how the presence of the polyols at low concentrations (5% or 10% w/w) whose rheological properties are not significantly modified may contribute to the release of aroma compounds. In the present study, levels of the aroma compounds in the vapor phase were measured using straightforward, environmentally friendly headspace solid-phase microextraction (HS-SPME) (Arthur & Pawliszyn, 1990), followed by gas chromatography. HS-SPME has proven to be effective at analyzing the interactions of aroma compounds with food and beverage matrices (Fabre, Aubry, & Guichard, 2002; Jung & Ebeler, 2003).

Nevertheless, HS-SPME only provides indirect information about the interactions of volatile compounds with a food matrix. To directly measure the self-diffusion coefficients of the aroma compounds in the present study, we used diffusion-ordered nuclear magnetic resonance spectroscopy (DOSY NMR) (Gostan, Moreau, Juteau, Guichard, & Delsuc, 2004; Jung, De Ropp, & Ebeler, 2002; Savary, Guichard, Doublier, Cayot, & Moreau, 2006), which, despite its effectiveness, has yet to be applied extensively in food. DOSY NMR is an accurate method to measure the self-diffusion coefficient (Morris, 2009). Self-diffusion measurements are based on the fact that the NMR signal attenuation of a component is directly linked to its diffusion coefficient. The NMR diffusion time scale is defined by a diffusion delay Δ , which generally ranges from milliseconds to seconds. The data-processing approach called DOSY generates a two-dimensional plot with a chemical shift scale in one dimension and diffusion coefficient values in the second dimension. The self-diffusion coefficient is thus directly calculated using the DOSY method (Cornejo et al., 2020; Delsuc & Malliavin, 1998).

Translational movement is the fundamental form of transport and closely linked to the molecular weight. This diffusion process is called

self-diffusion and reflects molecules random movement driven by their kinetic energies. The use of the Stokes–Einstein equation to calculate the self-diffusion coefficient of aroma compounds in a liquid medium has been widely used in the literature (Dél  ris et al., 2010; Gostan et al., 2004; Jung et al., 2002; Rondeau-Mouro, Zykwińska, Durand, Doublier, & Bul  on, 2004; Savary et al., 2006; Young & Cheri, 2006).

Because HS-SPME-GC and DOSY NMR combination techniques to obtain complementary information are not usually addressed in bibliographies, the present study has the following original approach: (i) to evaluate the effect of the polyols erythritol, D-mannitol, and maltitol on the headspace concentration of the aroma compounds γ -butyrolactone, 3-methyl-1-butanol, and 2-phenylethanol using HS-SPME; and (ii) to quantify the self-diffusion coefficients of the three aroma compounds in the presence of the polyols using DOSY NMR. Our aim was to gain insights into how polyols even at low concentrations in a model beverage matrix affect the release of aroma compounds that may enhance perceived sweetness. This study can help guide the development of sugar-free and reduced-sugar drinks containing polyols instead of sucrose.

2. Material and methods

2.1. Reagents

Erythritol (C₄H₁₀O₄, MW 122.12 g/mol), D-mannitol (C₆H₁₄O₆, MW 182.17 g/mol) and maltitol (C₁₂H₂₄O₁₁, MW 344.31 g/mol) were generously donated by Cargill (Minneapolis, MN, USA). The volatile compounds γ -butyrolactone, 3-methyl-1-butanol and 2-phenylethanol (all $\geq 98\%$ pure) were obtained from Merck (Darmstadt, Germany). D₂O (99.9% purity) was purchased from Merck.

Solutions of each volatile compound at a concentration of 100 mg/L were prepared with 5% or 10% (w/w) of each polyol in deionized water by stirring at 200 rpm for 40 min, followed by sonication for 30 min at 19 ± 1 °C. An explanation of why use these polyols, volatile compounds and concentrations is provided in section 3.1.

2.2. Head space – solid phase microextraction (HS-SPME)

After setting up HS-SPME initially as described (Fabre et al., 2002; Jung & Ebeler, 2003), we made slight variations and optimised the procedure while testing absorption of two fibers from the same batch, two different types of fibers (DVB/CAR/PDMS and Carboxen/PDMS) and sample volumes of 1, 3 or 5 mL (data not shown). In the optimised procedure, we used a Supelco holder (Bellefonte, PA, USA) and a SPME Stableflex 2 cm-50/30 DVB/CAR/PDMS fiber (Supelco), whose three-phase coating allows extraction of compounds with diverse volatilities and polarities. The fiber was conditioned for 60 min at 270 °C in the injector port of the gas chromatograph. The fiber was cleaned at 250 °C for 5 min before each analysis, and 3 mL of sample was placed in a 10-mL vial, sealed with Parafilm and equilibrated for 1 h in a 25 °C thermostatic bath (Jung & Ebeler, 2003).

Volatile compounds were extracted at 25 °C in a thermostatic bath at the following times (min): 1, 5, 15, 30, 60, 80, 120, 140 and 180. The compounds were desorbed by inserting the fiber into the injector port at 250 °C for 5 min. HS-SPME was performed on triplicate samples. All analyses were performed with the same SPME-fiber, and the relative standard deviation (RSD) across all measurements was below 5%.

Based on several studies (Jung & Ebeler, 2003; Roberts, Pollien, & Milo, 2000), we inserted the SPME fiber after only 1 min of sampling time in order to determine the “true headspace” concentration at equilibrium between headspace and sample, before reequilibration among the three phases of SPME fiber, head space and liquid.

2.3. Gas chromatography – flame ionization detection (GC-FID)

An Agilent 8860 equipped with split/splitless injector and flame

ionization detector was used. A fused silica capillary column of 30 m with inner diameter of 0.32 mm, coated with a 0.5- μ m layer of polyethylene glycol (DB-Wax, Agilent) was used with a carrier gas of He at 30 cm/s. The oven temperature was 40 °C for 5 min, which was increased to 220 °C at 5 °C/min, then held at 220 °C for 10 min. The injector was held at 250 °C and the detector at 300 °C. Triplicate samples were analysed.

2.4. Diffusion-ordered nuclear magnetic resonance spectroscopy (DOSY NMR)

Diffusion coefficients were measured for erythritol, D-mannitol and maltitol at 5 and 10% (w/w) in D₂O, and for γ -butyrolactone, 3-methyl-1-butanol and 2-phenylethanol at 100 mg/L in D₂O. NMR spectroscopy was performed at 30 °C on a Bruker Ascend III spectrometer equipped with a PABBO 5 probe and operating at 400 MHz for ¹H. All diffusion data were obtained using the *stebgp1s* pulse program in QF acquisition mode, and the diffusion delay (d20) was optimised at 160–170 ms, while the residual H₂O signal keeping gradient pulse length (p30) was kept constant at 1000 μ s. Data were processed using TOPSPIN 3.6.2 software (Bruker), and DOSY spectra were referenced at 4.79 ppm using the residual H₂O signal. Each pseudo-2D experiment consisted of 16 or 32 spectra. The F2 phase was corrected and automatically baseline-corrected using a 5-degree polynomial function. The T1/T2 relaxation module in the software was used to extract free induction decay for the first spectrum (2% gradient) and to select peaks. Intensities obtained from the peaks in the first spectrum were used to fit the Stejskal-Tanner equation. The extracted intensities were exported to the relaxation module, where decay values were fitted to peak intensities using the preinstalled *vargrad* function; the gradient calibration constant was 5.35 G/mm. Spectra were graphically processed using Dynamic Center software (version 2.6.1, Bruker). Self-diffusion coefficients were averaged from several proton peaks on the DOSY spectrum; only peaks showing minimal interference from polyols were selected for analysis.

2.5. Statistical analysis

Pairwise differences in flame ionization detector response areas and self-diffusion coefficients were assessed for significance using analysis of variance (ANOVA) in SPSS 25.0 (IBM, Chicago, IL, USA). Differences among three or more measurements were assessed for significance using Tukey's multiple range test. Differences were considered significant if $P < 0.05$. All analysis were performed on triplicate samples.

Table 1
Physicochemical properties of polyols and aroma compounds in the study.

Compound	Empirical formula	CAS	Molecular weight (g/mol)	log <i>P</i> value ¹	<i>k</i> _H (M atm ⁻¹) ²	Boiling point (°C) ¹	Density (g cm ⁻³) at 20 °C ¹	Topological polar surface area (Å) ⁴	Odour quality ³
Polyols									
Erythritol	C ₄ H ₁₀ O ₄	149-32-6	122.12	- 2.29	1.11·10 ¹²	330.5	1.44	80.9	–
D-mannitol	C ₆ H ₁₄ O ₆	69-65-8	182.17	- 3.10	1.40·10 ⁷	290.0	1.52	121.0	–
Maltitol	C ₁₂ H ₂₄ O ₁₁	585-88-6	344.31	- 4.17	2.30·10 ¹⁵	788.5 ± 60.0	1.70	201.0	–
Aroma compounds									
γ -butyrolactone	C ₄ H ₆ O ₂	96-48-0	86.08	- 0.76	190	204.0	1.12	26.3	Caramel, cheese, fruit, roasted nut, sweet
3-methyl-1-butanol	C ₅ H ₁₂ O	123-51-3	88.15	1.19	0.46	132.5	0.81	20.2	Banana, cocoa, floral, fruit, fusel, malt, must, nail polish
2-phenylethanol	C ₈ H ₁₀ O	60-12-8	122.16	1.36	0.24	218.2	1.02	20.2	Floral, fruit, honey, rose, sweet, sweet apple, wine, yeast

¹ From the SciFinderⁿ database (<https://scifinder-n.cas.org/?referrer=scifinder.cas.org>). ² Compilation of Henry's law constants (version 4.0) (<http://www.henrys-law.org/henry/>). ³ From VCF Volatile Compounds in Food (version 16.9) (<https://www.vcf-online.nl/VcfCompoundSearch.cfm>). ⁴ PubChem (database <https://pubchem.ncbi.nlm.nih.gov>).

3. Results and discussion

3.1. Rationale for the polyols and aroma compounds selected for this study

The physicochemical properties of the polyols and aroma compounds are shown in Table 1. The three polyols were selected because they belong to the same chemical family and are used in food products, although only erythritol is approved for use in flavored beverages (Regulation (EC) No. 1333/2008, 2024). Polyols are continuously evaluated for their safety, food applications, purity criteria, food labeling, nutrition, and health claims by international organizations such as the Food and Agriculture Administration and the European Food Safety Authority. Foods containing >10% added polyols should also bear the following statement: "Excessive consumption may produce laxative effects." The three aroma compounds were selected because their sweetness-enhancing effect has been demonstrated in alcoholic and nonalcoholic beverages (Barba et al., 2018; Tateo & Bononi, 2003).

3.2. Effects of polyols on the release of aroma compounds into the vapor phase

The kinetics of the adsorption of 3-methyl-1-butanol and 2-phenylethanol onto the SPME fiber are shown in Fig. 1. 3-Methyl-1-butanol was released from water into the headspace with linear kinetics during 15 min ($y = 8.44 \cdot 10^2 x + 4.94 \cdot 10^3$, $R^2 = 0.9386$), reflecting its low preference for water. This volatile compound achieved equilibrium in 45 min. In contrast, 2-phenylethanol also showed linear release during 180 min ($y = 8.76 \cdot 10^1 x + 1.25 \cdot 10^2$, $R^2 = 0.9923$), but it was released more slowly, reflecting a stronger preference for water. It did not reach equilibrium even after 180 min. These analyses could not be performed on γ -butyrolactone because its strong hydrophilicity ($\log p = -0.76$) prevented it from entering the headspace.

The addition of any of the three polyols at 5% or 10% (w/w) did not significantly alter the adsorption rate of 3-methyl-1-butanol, including the time to reach equilibrium (Fig. 1a). In contrast, all three polyols slowed the release of 2-phenylethanol, with stronger effects at 10% than at 5% polyol (Fig. 1b).

Siefarth et al. investigated four aroma compounds released from water with high polyol concentrations (43% w/w) using proton-transfer-reaction mass spectrometry (PTR-MS). The authors reported that polyols had a significant effect ($p < 0.05$) on aroma release, finding that the release of all aroma compounds decreased in good correlation when viscosity of solution increased. The same authors used carbohydrates or

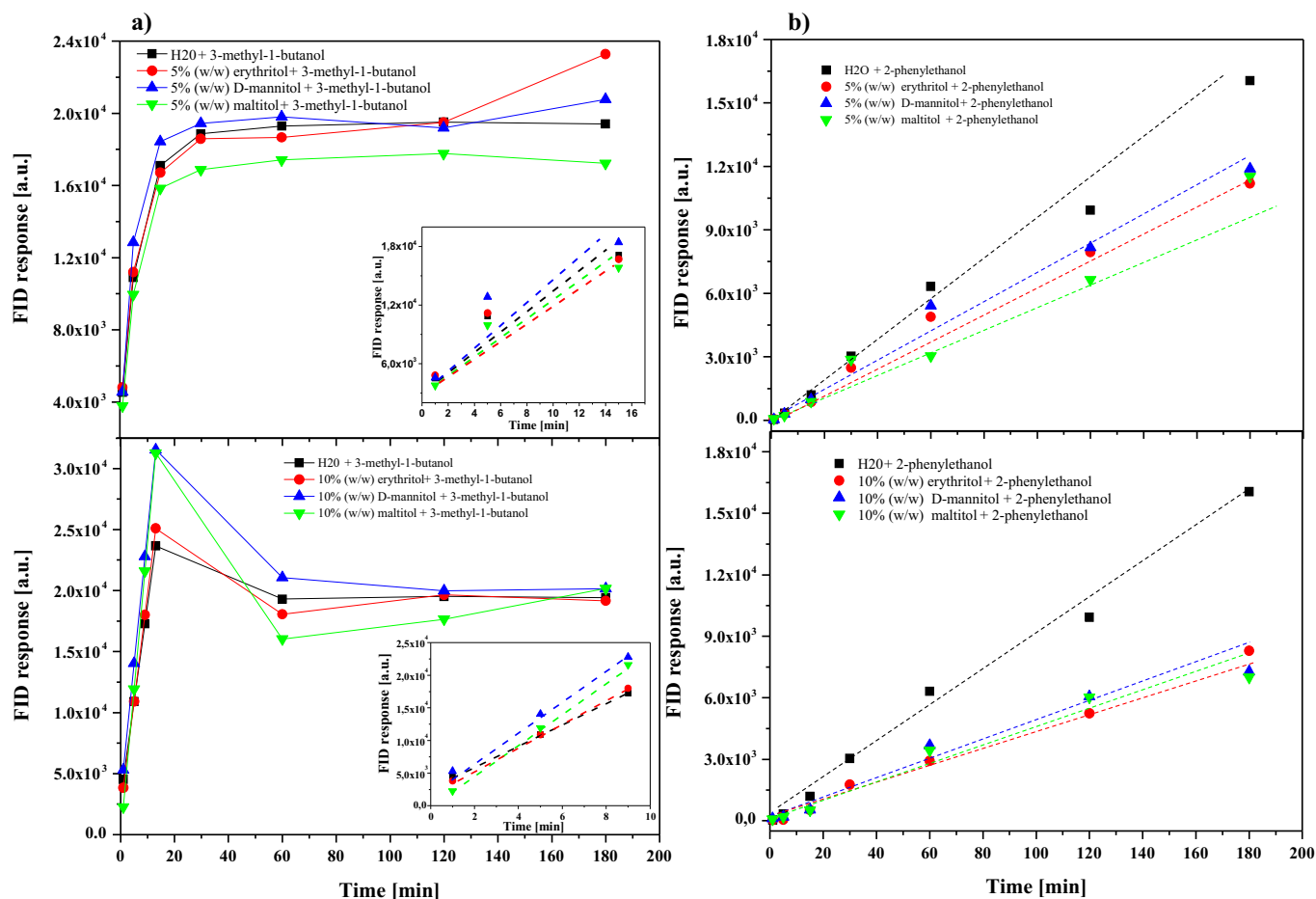


Fig. 1. Kinetics of adsorption of (a) 3-methyl-1-butanol or (b) 2-phenylethanol on the SPME fiber.

polyols with lower concentrations (20% w/w) to demonstrate an inverse relationship between the concentration of polyols and aroma release.

In the present study, the polyol concentration does not affect flavor release for 3-methyl-1-butanol, in agreement with previous investigations. However, the polyol concentration does affect 2-phenylethanol release, showing that at low polyol concentrations, the release highly depends on the characteristic physicochemical properties of the aroma compound.

HS-SPME analysis of flame ionization detection response areas at 1 min of adsorption time showed that adding erythritol or D-mannitol at 10% (w/w), but not at 5% (w/w), significantly altered the release of 3-methyl-1-butanol (Table 2). In contrast, the release of 2-phenylethanol was significantly affected by the presence of erythritol at 5% (w/w), D-mannitol at 10% (w/w), or maltitol at either 5% or 10% (w/w).

Philippe et al., 2003 and Seuvre, Philippe, Rochard, & Voilley, 2007 investigated the release of some aroma compounds from water by gas chromatography flame ionization detection. The authors reported that most hydrophilic compounds (low log P value) exhibited affinity for water molecules and were therefore the compounds with the slowest release rates.

In addition to the log P , another parameter must be taken into account, such as the k_H value. A direct relationship exists between the log P value and the flavor release, and an indirect relationship exists between the k_H value and the flavor release. In the present study, since there are similar values of log P in the two compounds (Table 1), the k_H value has greater relevance. The 2-phenylethanol k_H value is higher, and therefore its volatility is lower, which may explain the decrease in aroma release compared with 3-methyl-1-butanol.

These results confirm that the polyols exerted different effects on the

two aroma compounds, reflecting the importance of the different physicochemical properties of aroma compounds.

3.3. Interactions between polyols and aroma compounds in D_2O

NMR peaks of all aroma compounds showed good signal-to-noise ratios at 100 ppm, although some of their peaks could not be accurately observed in the range of 3–5 ppm because of the presence of peaks from the polyols and broad peaks from residual water at 4.7 ppm. The addition of polyols did not substantially alter the chemical shifts in the 1H NMR spectra of γ -butyrolactone (relative standard deviation $<0.06\%$; Fig. 2). Similar results were observed for 3-methyl-1-butanol and 2-phenylethanol (data not shown).

The results suggest that there were no noticeable chemical interactions between the polyols and the aroma compounds in this study. Similarly, another study reported no detectable interactions of ethyl butyrate with 35% (w/w) solutions of sucrose, starch, or carrageenan in D_2O (Savary et al., 2006). To our knowledge, the present study is the first application of DOSY NMR to the analysis of interactions between volatile compounds and polyols. In the literature, changes in the chemical shift using NMR spectroscopy have been widely reported to verify interactions in binary model solutions of volatiles and wine phenols in the model and wine matrix (Dufour & Bayonove, 1999; Dufour & Sauvatre, 2000; Jung et al., 2002). More recently, an NMR-based approach was developed to directly analyze covalent and non-covalent interactions, such as π - π stacking, hydrogen bonding, dipole-dipole, or van der Waals interactions, between key odorants and polymers in coffee (Gigl et al., 2022; Gigl, Hofmann, & Frank, 2021; Hofmann, Czerny, Calligaris, & Schieberle, 2001) and wine (Gabler,

Table 2Mean flame ionization detector response areas (\pm standard deviation) for water or aqueous solutions of erythritol, D-mannitol or maltitol (5 or 10%, w/w).

(A)	3-methyl-1-butanol							
	Time (min)	H ₂ O	Erythritol		D-mannitol		Maltitol	
			5%	10%	5%	10%	5%	10%
1	4540.7 \pm 227.0 ^{b,D}	4812.4 \pm 140.3 ^{a,b, D}	3840.4 \pm 192.0 ^{c,C}	4563.5 \pm 228.1 ^{b,C}	5304.7 \pm 265.2 ^{a,D}	3786.8 \pm 189.3 ^{c,D}	2254.4 \pm 112.7 ^{d,E}	
5	10,910.4 \pm 545.5 ^{c,d, C}	11,199.3 \pm 326.5 ^{c,d, C}	10,922.4 \pm 546.1 ^{c, d,B}	12,847.4 \pm 642.4 ^{a, b,B}	14,050.8 \pm 702.5 ^{a,C}	9960.8 \pm 498.0 ^{d,C}	11,922.4 \pm 596.1 ^{b, c,D}	
15	17,107.5 \pm 855.4 ^{a,b, B}	16,713.8 \pm 487.3 ^{a,b, B}	15,843.8 \pm 846.8 ^{a, b,A}	18,434.9 \pm 921.7 ^{a, A}	18,511.8 \pm 925.6 ^{a,B}	15,843.8 \pm 792.1 ^{b, A,B}	13,333.2 \pm 666.6 ^{c, D}	
30	18,859.0 \pm 943.0 ^{a,b, A,B}	18,593.5 \pm 542.1 ^{a,b, A, B}	16,877.9 \pm 983.7 ^{a,A}	19,440.1 \pm 972.0 ^{a, A}	20,115.1 \pm 1005.8 ^{a, A}	16,877.9 \pm 792.1 ^{b, B}	19,674.2 \pm 983.7 ^{a, A,B}	
60	19,296.0 \pm 964.8 ^{a,b, A,B}	18,668.5 \pm 544.3 ^{a,b, A,B}	17,417.5 \pm 902.9 ^{b, c, A}	19,808.5 \pm 990.4 ^{a, b,A}	21,058.1 \pm 1052.9 ^{a, A,B}	17,417.5 \pm 843.8 ^{b, c,A}	16,023.6 \pm 801.1 ^{c, C}	
120	19,514.8 \pm 975.5 ^{a,A}	19,495.5 \pm 568.4 ^{a, A}	17,773.5 \pm 982.5 ^{a,A}	19,196.4 \pm 959.8 ^{a, A}	19,981.6 \pm 999.1 ^{a,A}	17,773.5 \pm 888.6 ^{a, A,B}	17,654.2 \pm 882.7 ^{a, B,C}	
180	19,413.9 \pm 970.7 ^{a,b, A,B}	23,285.6 \pm 708.5 ^{a, A, B}	17,224.0 \pm 958.4 ^{a, b, A}	20,766.4 \pm 1038.3 ^{a,A}	20,155.2 \pm 1007.8 ^{a, A,B}	17,224.0 \pm 861.2 ^{b, A,B}	20,168.7 \pm 1008.4 ^{a,A}	

(B) 2-phenylethanol								
Time (min)	H ₂ O	Erythritol		D-mannitol		Maltitol		
		5%	10%	5%	10%	5%	10%	
1	40.8 \pm 2.0 ^{d,F}	59.6 \pm 3.0 ^{c,F}	38.5 \pm 1.9 ^{d,E}	41.1 \pm 2.0 ^{d,E}	109.9 \pm 5.5 ^{a,D}	71.9 \pm 3.6 ^{b,E}	79.8 \pm 4.0 ^{b,D}	
5	335.2 \pm 16.8 ^{a,E,F}	294.8 \pm 14.7 ^{b,E,F}	55.0 \pm 2.7 ^{d,E}	303 \pm 15.1 ^{a,b,D}	192.0 \pm 9.6 ^{c,D}	218 \pm 10.9 ^{c,D,E}	190.0 \pm 9.5 ^{c,D}	
15	1193.2 \pm 59.7 ^{a,E}	863.4 \pm 43.2 ^{b,E}	525.6 \pm 26.3 ^{c,E}	977.6 \pm 48.88 ^{b,D}	542.0 \pm 27.1 ^{c,D}	887.6 \pm 44.3 ^{b,D}	523.1 \pm 26.2 ^{c,D}	
30	3037.6 \pm 151.9 ^{a,D}	2476.8 \pm 123.8 ^{b,D}	1766.0 \pm 88.3 ^{c,D}	–	–	2873.6 \pm 143.7 ^{a,C}	–	
60	6321.6 \pm 316.1 ^{a,C}	4885.9 \pm 244.3 ^{b,C}	2924.8 \pm 146.2 ^{d,C}	5415 \pm 270.7 ^{b,C}	3680.6 \pm 184.0 ^{c,C}	3032.8 \pm 151.6 ^{d,C}	3443.0 \pm 172.2 ^{c,d,C}	
120	9932.7 \pm 493.6 ^{a,B}	7938.4 \pm 396.9 ^{b,B}	5248.9 \pm 262.4 ^{d,B}	8168.4 \pm 408.4 ^{b,B}	6054.8 \pm 302.7 ^{c,d,B}	6639.6 \pm 331.9 ^{c,B}	6023.1 \pm 301.2 ^{c,d,B}	
180	16,053.9 \pm 802.7 ^{a,A}	11,195.9 \pm 559.8 ^{b,A}	8301.6 \pm 415.0 ^{c,A}	11,887 \pm 594.3 ^{b,A}	7277.2 \pm 363.9 ^{c,A}	1152.6 \pm 576.1 ^{b,A}	6999.1 \pm 350.0 ^{c,A}	

Different letters denote significant differences ($p < 0.05$) between polyols (erythritol, D-mannitol and maltitol) at 5 or 10% (w/w). Different capital letters denote significant differences ($p < 0.05$) between adsorption time points (1, 5, 15, 30, 60, 120 or 180 min).

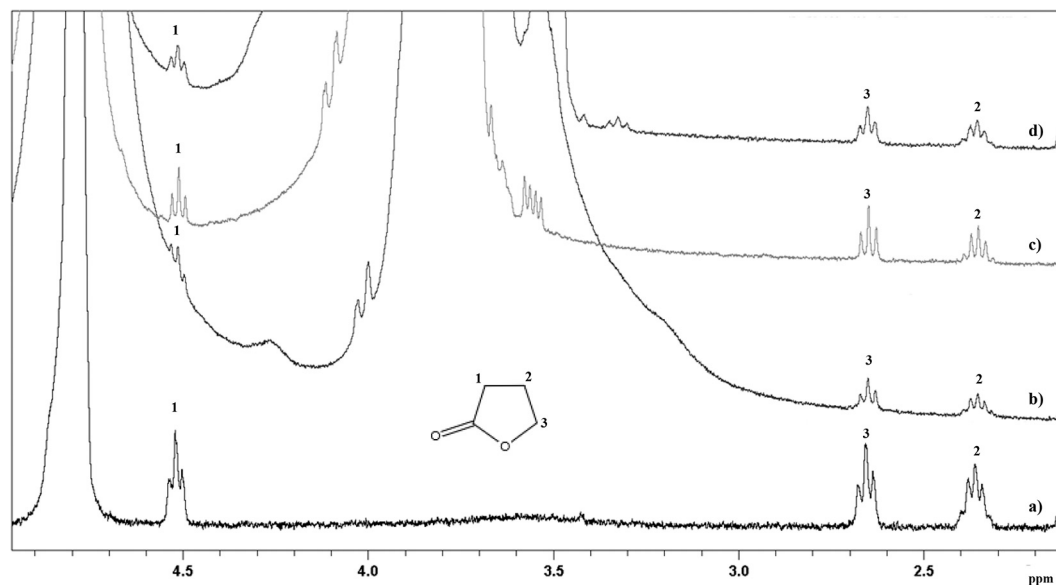


Fig. 2. One-dimensional ¹H NMR spectra of γ -butyrolactone at 100 μ g/L (a) alone or in the presence of (b) erythritol (5%, w/w), (c) D-mannitol (5%, w/w) or (d) maltitol (5%, w/w).

Kreibl, Schweiger, Frank, & Dawid, 2023).

3.4. Effects of polyols on the self-diffusion coefficients of aroma compounds

The DOSY spectrum of 3-methyl-1-butanol in D₂O showed four peaks corresponding to CH₂ (1) at 3.816 ppm, CH₂ (2) at 1.712, CH (3) at 1.465 ppm, and CH₃ (4,4') at 0.907 ppm (Fig. 3). The intensity of each of

the four peak areas was integrated and averaged to give a diffusion coefficient of 0.796×10^{-10} m²/s at 25 °C. In the presence of any of the three polyols, only the peaks corresponding to CH (3) and CH₃ (4,4') were averaged because of the strong signal at approximately 4 ppm due to CH–OH groups in the polyols. As expected, the resulting coefficients ($0.664\text{--}0.790 \times 10^{-10}$ m²/s) were lower than in the absence of polyols (Table 3).

Using a similar approach, we determined self-diffusion coefficients

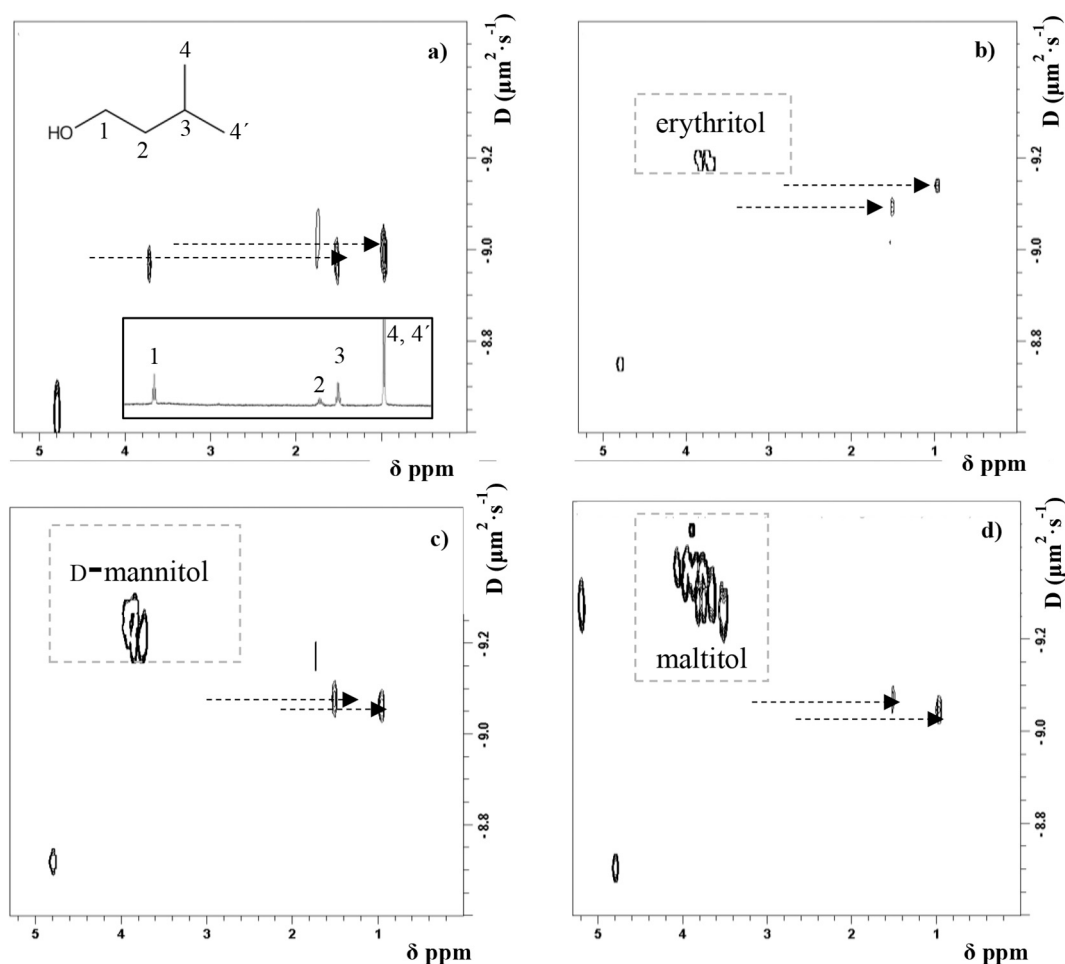


Fig. 3. DOSY NMR spectra of 3-methyl-1-butanol at 100 mg/L in (a) pure D₂O or D₂O containing (b) erythritol, (c) D-mannitol or (d) maltitol at 10% (w/w). The inset shows the one-dimensional ¹H NMR spectrum of 3-methyl-1-butanol in D₂O. The arrow shows peaks corresponding to CH (3) and CH₃ (4,4') of 3-methyl-1-butanol. The square dotted shows peaks corresponding to erythritol, D-mannitol or maltitol.

Table 3

Mean self-diffusion coefficients (10⁻⁹ m²/s) (± standard deviation) of aroma compounds in D₂O in the presence or absence of the indicated concentrations (% (w/w) of erythritol, D-mannitol or maltitol.

Aroma compound	Erythritol			D-mannitol		Maltitol	
	0%	5%	10%	5%	10%	5%	10%
3-methyl-1-butanol	0.792 ^a ± 0.024	0.790 ^a ± 0.024	0.714 ^b ± 0.021	0.733 ^c ± 0.022	0.664 ^d ± 0.020	0.710 ^e ± 0.021	0.673 ^f ± 0.020
2-phenylethanol	0.775 ^a ± 0.023	0.683 ^b ± 0.020	0.503 ^c ± 0.015	0.796 ^a ± 0.024	0.644 ^d ± 0.019	0.596 ^e ± 0.018	0.537 ^f ± 0.016
γ-butyrolactone	1.040 ± 0.031	0.987 ± 0.030	–	0.986 ± 0.038	–	0.715 ± 0.021	–

Different letters denote significant differences ($p < 0.05$) between the samples with or without polyols.

for the other two aroma compounds in the absence or presence of polyols. The diffusion coefficients decreased marginally, but not significantly, in the presence of polyols at 5% (w/w), and they decreased significantly in the presence of polyols at 10% (Table 3).

Some authors have used DOSY NMR to obtain self-diffusion coefficients. Savary et al. measured alpha-terpineol self-diffusion coefficients with different types of Acacia gum, demonstrating that the type of gum strongly governs alpha-terpineol diffusion. The better emulsifying ability of gum provokes a decrease in molecular diffusion and a greater chemical affinity for hydrophobic compounds. Gostan et al. also measured self-diffusion ethyl-butanoate and linalool coefficients with ι-carrageenan gel, observing that self-diffusion coefficients increased with gel strength. Savary et al. found that the diffusion of aroma molecules decreased with increasing sucrose concentration in orange juice. In the current study, it was also observed that the self-diffusion

coefficient of aroma compounds decreased when the viscosity, gel strength, molecular interaction, and concentration of the solute increased. At 10% polyol concentration (w/w), it appears to be the critical concentration that determines aroma molecule self-diffusion. In the case of polyols, if the self-diffusion coefficient of aroma molecules is not related to gel formation or high-viscosity solutions, then aroma properties themselves will be critical to explaining the diffusion process.

3.5. Potential basis for the effects of polyols on the diffusion of aroma compounds

The ability of polyols to slow the volatilization of aroma compounds may cause an increase in viscosity, a decrease in the affinity of 2-phenylethanol for the SPME fiber, and/or interactions between 2-phenylethanol and the polyol. Given that polyols did not substantially alter the

^1H NMR spectra of the aroma compounds, we suggest that interactions between them may be modeled using the Stokes–Einstein equation (Einstein, 1956; Stokes, 1952):

$$D = k_B T / f$$

where k_B is the Boltzmann's constant; T is the temperature; and f is the frictional coefficient, which depends on the viscosity and molecular size. We believe that polyols retard the diffusion of aroma compounds through frictional interactions. This implies that the self-diffusion coefficient of volatile compounds depends on their mass and, to a far smaller extent, their volume. In fact, the slow release of 2-phenylethanol can be explained by the fact that, as it has a higher molecular weight, it is more affected by diffusion. Consistent with our hypothesis, one study found that volatile compounds in water were retained by polyols in direct proportion to their molecular weight using PTR–MS (Siefarth et al., 2011a).

4. Conclusion

The aim of this study was to model how polyols may modify the release of aroma compounds designed to increase the perception of sweetness in beverages. We found that polyols reduced the volatility of 2-phenylethanol but not 3-methyl-1-butanol in a concentration-dependent manner, while they reduced the self-diffusion coefficients of all three aroma compounds. Polyols appear to exert these effects through physical (frictional) effects without extensive chemical interactions, given the minimal effects of polyols on the ^1H NMR spectra of the aroma compounds. With knowledge of the behavior of the aroma compounds at low polyol concentrations obtained by HS-SPME-GC and DOSY NMR, further sensory studies are needed to test this hypothesis and thus better understand, predict, and optimize orthonasal and retronasal aroma perception in sugar-free or reduced-sugar beverages.

CRediT authorship contribution statement

Carmen Barba: Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Ignacio Angós:** Conceptualization. **Juan Ignacio Maté:** Supervision, Conceptualization. **Alfonso Cornejo:** Writing – review & editing, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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