The Hydrostatic and Hydrodynamic Volumes of Polyols in Aqueous Solutions and Their Sweet Taste

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Abstract

The tastes and solution properties of sugar alcohols were studied in an attempt to illuminate the mechanism of sweet taste chemoreception. The SMURF method was used to measure taste time–intensity of aqueous solutions of sugar alcohols and the results were interpreted using the Stevens power function and kinetic parameters. The apparent molar volumes, apparent specific volumes, partial molar volumes, partial specific volumes and intrinsic viscosities of the solutions were studied. Apparent molar volume reflects the size of the molecule in a hydrostatic state whereas intrinsic viscosity gives a measure of the size of the molecules in a hydrodynamic state. Generally the apparent molar volumes of the polyols are 6–13% greater than those of the parent sugars, indicating less interaction with the water structure. Apparent specific volume values can predict taste quality, and the average apparent specific volume for the sugar alcohols studied fits within the central part of the sweet range, i.e. 0.5–0.68 cm^3/g, which accords with their ability to elicit a pure sweet taste response. Intensities and persistences of sweetness in the polyols followed the same trend as intrinsic viscosities. **Chem. Senses 22: 149–161, 1997.**

Introduction

In taste, water is important as not only is it the means of transport to the receptor but it also determines the shape of the solute which accedes to the receptor. When a substance dissolves in water a co-sphere or hydration shell is built; it consists of a primary solvation region in the immediate vicinity of the solute molecule which is being influenced by it, and an interfacial region where the solvent molecules are under the opposing influences of the primary solvation region and the bulk of the solution (Lilley, 1987). The size of the co-sphere depends on how well a solute fits in with the water structure. Hydration effects are extremely sensitive to the stereochemical detail of the solute and are also affected by molecular configuration (Franks, 1985). Conversely, it has been suggested that the water structure determines the conformation of the solute in solution. It is the hydrated molecule which diffuses to the receptor site and therefore the water hydration is important. The path of approach of the solute and ultimately the recognition by the receptor of the hydrated molecule will be affected by the solvation shells surrounding it (Fraga, 1983). The apparent molar volume, Φ_v, may be defined as the apparent change in volume of the solvent when one mole of the solute is dissolved in the solvent, and it varies with concentration. Φ_v may be calculated from density as follows:

$$\Phi_v = \frac{\mathrm{MWt}(1/\rho_s - W_o/\rho_o)}{W_s} \qquad (1)$$

where MWt is the molecular weight of the solute, ρ_0 the density of water (cm^3/g), ρ_s the density of the solution (cm^3/g), W_0 the weight fraction of water and W_s the weight fraction of the solute; Φ_v is in cm^3/mol.

The partial molar volume, $\Phi_v{}^o$, is the apparent molar volume at infinite dilution and can be obtained by linear extrapolation according to the following equation:

$$\Phi_v = \Phi_v^o + mS_v \qquad (2)$$

where m is the molality of the solution and S_v is the slope in cm^3kg/mol^2.

The S_v values are generally thought to be proportional to the volume change of the hydrated molecules with increasing solute concentration. Hence the S_v values can yield information on solute–solute as well as solute–solvent interactions (Wurzburger *et al.*, 1988).

The apparent specific volume, $^{\phi}V$, gives a direct measure of the disturbance or displacement of water by solute and thus reflects the compatibility of solute with water structure. $^{\phi}V$ can be calculated by dividing the apparent molar volume by the molecular weight. A simple linear regression analysis can be used to calculate the partial specific volumes, $^{\phi}V^o$, and the slopes of the lines, S_{ϕ}, according to the following equation:

$$^{\phi}V = {}^{\phi}V^o + mS_{\phi} \qquad (3)$$

where $^{\phi}V^o$ is in cm^3/g and S_{ϕ} is in cm^3/mol.

Intrinsic viscosity is a measure of the hydrodynamic volume of the solute molecules and represents the fractional change in the viscosity of a solution per unit concentration of solute at infinite dilution (Elfak *et al.*, 1977). Intrinsic viscosity, $[\eta]$, is an important solution property that may help to explain the disturbance of the water structure by the sapid molecules, and may reflect the rate at which the taste receptor is reached and acceded by the sapid molecule. The calculation of intrinsic viscosity could be made by the triple extrapolation method (Kemp and Birch 1990). To study the variation of the relative viscosity with concentration the Jones–Dole equation (Jones and Dole, 1929) can be used:

$$\eta_{sp}/C = B + DC \qquad (4)$$

where η_{sp}/C is relative viscosity in l/mol; B is the viscosity coefficient and is a measure of hydrodynamic or size and shape effects, solvation and structural effects; and D is a coefficient that must include all solute–solvent and solute–solute interactions that are not accounted for by the B coefficient.

The B coefficient can be expressed in terms of partial molar volume of the particle, $\Phi_v{}^o$, plus that of the associated or bound solvent M_1V_1 (Herskovits and Kelly, 1973):

$$B = \nu \times 10^{-3}\left(\Phi_v^o + hM_1V_1\right) \qquad (5)$$

where ν is a coefficient accounting for the shape of the solute for spherical particles and can be taken as 2.5, h represents the moles of solvent bound per mole of solute and M_1V_1 is the apparent molar volume of solvent; e.g. for water $M_1V_1 = 18\ cm^3/mol$.

The effective size of the molecule must be important in taste receptor recognition since most tastant compounds follow a taste sprectrum according to their apparent specific volume (Birch and Shamil, 1988) from salty (0–0.33 cm^3/g) to sour (0.33–0.52 cm^3/g) to sweet (0.52–0.71 cm^3/g) to bitter (0.71–0.93 cm^3/g). It is not known, however, whether such solution properties can influence taste potency. The tastes of selected polyols were therefore assessed by the time–intensity method. Time–intensity (T–I) analysis has been defined by Amerine *et al.* (1965) as the measurement of 'the rate, duration and intensity of stimulation by a single stimulus'. It is well known that different sensory stimuli display unique courses of perception, from onset through a maximum to extinction (McBurney, 1972). T–I studies give important sensory information which may be ascribable to molecular properties.

The aim of this research was therefore to study the T–I relationships of the sweet taste of polyols in order to establish any patterns or reasons for any differences that exist between them in terms of their effective size.

Materials and methods

Substances investigated for physico-chemical properties were reagent grade chemicals. Ethylene glycol, 1,2-propanediol, glycerol, meso-erythritol, D-threitol, D-arabitol, L-arabitol, ribitol and galactitol were obtained from Sigma Chemical Co. and Aldrich. Xylitol, D-glucitol, D-mannitol, maltitol and lactitol were kind gifts from Roquette and CCA Biochem b.v. The last five sugar alcohols were used for both solution and taste properties. Sucrose (granulated sugar from Tate & Lyle) was used as a reference in taste studies. Meso-erythritol was recrystallized from ethanol–water solutions and the melting point was checked against reports in the literature. The remaining sugar alcohols were used without further purification. The sugar alcohols were dried in a vacuum oven for at least 24 h at 60°C over P_2O_5 prior to dissolution. Water used for solution studies was of high purity (conductivity 0.05 µS/cm); water used for taste studies was Highland's spring natural mineral water from Blackford, UK.

For Φ_v and $^{\phi}V$ measurements the concentrations used were % w/w whereas for viscosity and taste the concentrations were % w/v. Φ_v values were calculated from density values using equation (1). Density determinations were carried out at 20 ± 0.01°C using an Anton Paar Digital Density Meter; measurements were done at least twice for every solution and the reproducibility of them was better than 3×10^{-6} g/cm^3. $\Phi_v{}^{\circ}$ values were calculated according to equation (2); $^{\phi}V$ values were calculated as mentioned above and $^{\phi}V^{\circ}$ values were calculated from equation (3). The viscosity measurements were carried out at 20 ± 0.2°C using an Ostwald type A viscometer with an efflux time of ~320 s for water. The procedure has been published in detail elsewhere (Kemp and Birch, 1990).

For sensory evaluation, 24 volunteers (15 female and 9 male) from Reading University, between 23 and 65 years of age, were selected on the basis of their ability to discriminate various taste stimuli (ASTM, 1981) and to place in the correct order of sweetness 3, 6, 9 and 12% solutions of sucrose; they were further checked to ensure they could place 1, 3 and 5% sucrose solutions in ascending order. Before the training in the use of the Sensory Measurement Unit for Recording Flux (SMURF), all panellists were given sucrose solutions of 3, 6, 9 and 12% concentration and a 6% sucrose solution as a reference, and asked to estimate the magnitude of the sweetness of the samples in comparison with the reference; the scale used was from 0 to 10, and an arbitrary value of 5 was given to the reference. This procedure was repeated three times to ensure that the results of the panellists were consistent. The panellists who successfully passed the screening requirement were trained in the use of the SMURF generally during three sessions; however, the panellists were permitted as many trials as they wanted until they were confident in its use and their results were consistent. Each sugar alcohol was assessed at four concentrations—3, 6, 9 and 12% w/v—and two replicates were carried out. The samples were presented according to a split plot statistical design: there were six samples of 7 ml, the first and fourth of which were standard 6% sucrose solutions, and the rest, coded with three-digit random numbers, were presented in random order to each panellist. Sucrose and each sugar alcohol were assessed at four concentrations—3, 6, 9 and 12% w/v—and two replicates were carried out.

Results and discussion

The solution properties of polyols give information about the sizes they adopt in the hydrated form and their compatibility with the water structure, i.e. the effects they have on the water structure.

Generally there is an increase in apparent molar volumes and apparent specific volumes of polyols with concentration except for 1,2-propanediol and ethylene glycol. A plot of Φ_v against concentration for ethylene glycol and 1,2-propanediol (see Figure 1) shows that Φ_v decreases with increasing concentration. A minimum in Φ_v is observed when the concentration rises to 7 mol/kg for ethylene glycol and 5.6 mol/kg for 1,2-propanediol. To explain this phenomenon the formation of 'icebergs' around non-polar solute molecules in water has been postulated (Frank and Evans, 1945); the icebergs have an open structure formed near a hydrophobic solute; the solute hence fills interstitial cavities that would normally be formed.

The loss of free space during hydrophobic hydration is larger than the increase in volume accompanying the increase in ice-likeness; as a consequence a net decrease in volume occurs. At higher concentrations (>7 mol/kg for ethylene glycol and >5.6 mol/kg for 1,2-propanediol) the solute–solvent interaction is replaced by a solute–solute interaction; as a result the volume is increased. Although the range of concentration covered in this work is wide, a very good correlation was found between Φ_v and molality (see Table 1).

S_v values are generally thought to be proportional to the volume change of the hydrated molecules with increasing solute concentration (Franks *et al.*, 1973). Monohydric alcohols and diols have negative S_v and S_{ϕ} values which decrease as the size of the hydrocarbon group increases. The S_v and S_{ϕ} values in this study (see Tables 1 and 2) are negative for ethylene glycol and 1,2-propanediol, and become increasingly positive for the higher molecular weight polyols. If the sign of the S_v and S_{ϕ} values reveals the nature of the solute–solvent interaction, as is proposed by Neal and Goring (1970), then we can conclude that ethylene glycol and 1,2-propanediol have structure-making effects on water whereas the rest of the polyols in this study show structure-breaking effects. From the values of Φ_v,

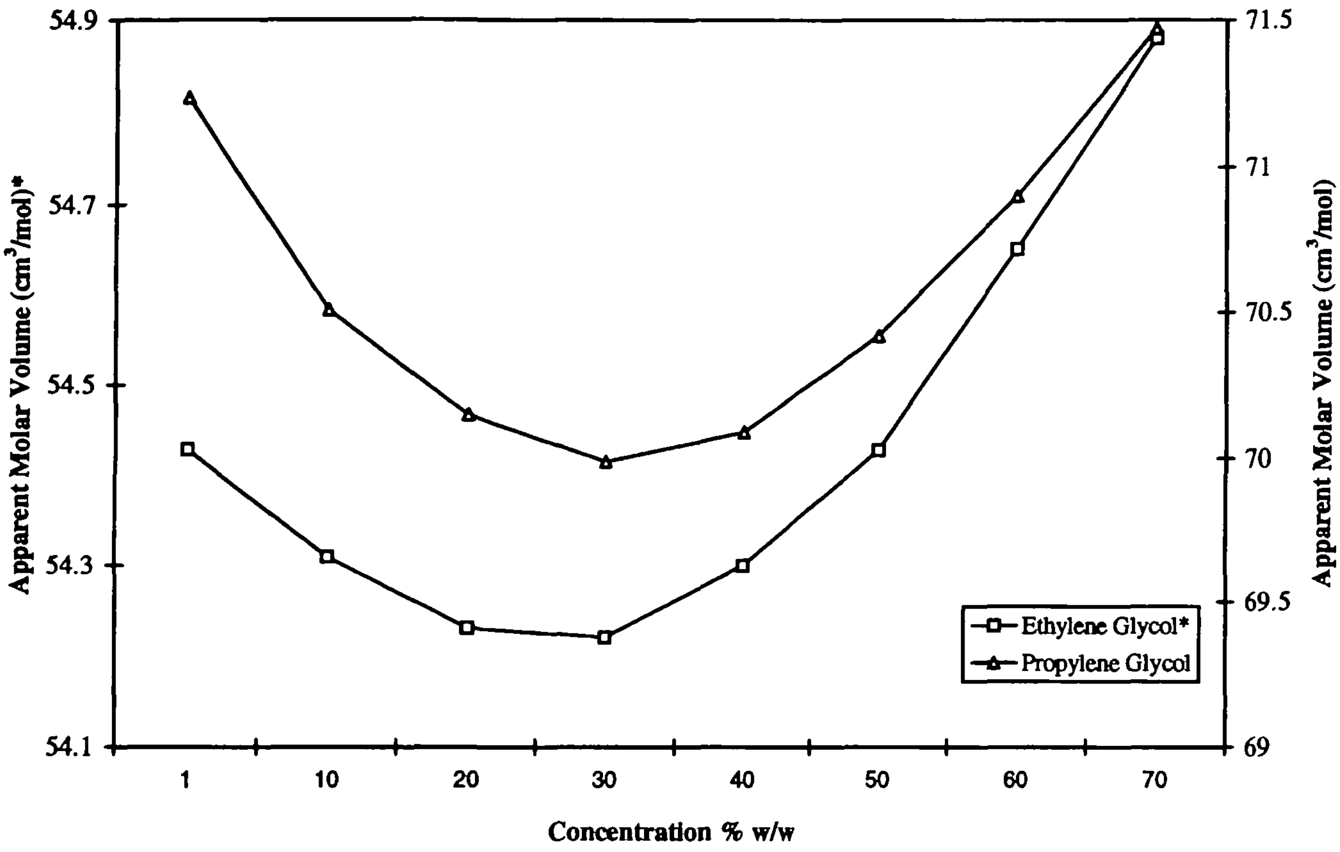


Figure 1 Apparent molar volume against concentration of ethylene glycol and propylene glycol.

Table 1 Partial molal volumes (ϕ_V^0) and slopes (S_V) of polyols in aqueous solutions at 20°C and significance of of the linear functions of apparent molal volumes and concentration (mol/kg)

Polyol	ϕ_V^0 (cm^3/mol)	S_V[a] (cm^{3}kg/mol^2)	Concentration range (mol/kg)	Correlation coefficient	*P*
Ethylene glycol	54.44 (0.02)	−0.06 (0.01)	0.33–4.03	0.97	<0.001
Glycerol	70.78 (0.05)	0.05 (0.00)	0.11–25.3	0.99	<0.001
Propylene glycol	71.03 (0.18)	−0.19 (0.03)	0.13–5.63	0.92	<0.005
D-Threitol	86.13 (0.00)[b]	0.28 (0.01)	0.25–0.91	0.99	–
Meso-erythritol	86.53 (0.07)	0.20 (0.01)	0.08–5.46	0.97	<0.001
Xylitol	101.7 (0.19)	0.31 (0.02)	0.07–9.86	0.97	<0.001
L-Arabitol	102.6 (0.24)	0.29 (0.02)	0.07–9.86	0.98	<0.001
D-Arabitol	102.6 (0.20)	0.28 (0.02)	0.07–9.86	0.98	<0.001
Ribitol	102.7 (0.21)	0.32 (0.03)	0.07–6.57	0.92	<0.001
D-Glucitol	118.0 (0.14)	0.65 (0.12)	0.06–3.66	0.92	<0.001
Galactitol	118.6 (0.02)	1.09 (0.08)	0.06–0.41	0.99	<0.001
D-Mannitol	118.9 (0.03)	0.79 (0.04)	0.06–0.97	0.99	<0.001
Lactitol	200.1 (0.34)	1.80 (0.11)	0.03–2.90	0.97	<0.001
Maltitol	202.2 (0.17)	1.69 (0.06)	0.03–2.90	0.99	<0.005

The standard error is shown in parentheses.

[a] Apparent molal volume concentration dependence constant.

[b] Data are considered unreliable due to the limited number of points investigated (three points).

Table 2 Partial specific volumes (${}^{\phi}V^{o}$) and slopes (S_{ϕ}) of polyols in aqueous solutions at 20°C and significance of the linear function of apparent specific volumes and concentrations (mol/kg)

Polyol	${}^{\phi}V^{o}$ (cm³/g)	$S_{\phi}{}^{a}$ (cm³/mol)	Concentration range (mol/kg)	P
Ethylene glycol	0.877 (0.3)	–0.87 (0.1)	0.33–4.03	<0.001
Glycerol	0.768 (0.6)	0.53 (0.0)	0.11–25.3	<0.001
Propylene glycol	0.933 (2.3)	–2.78 (0.4)	0.13–5.63	<0.001
D-Threitol	0.705 (0.0)[b]	2.33 (0.1)	0.52–0.91	<0.001
Meso-erythritol	0.709 (0.5)	1.62 (0.1)	0.08–5.46	<0.001
Xylitol	0.668 (1.3)	2.04 (0.1)	0.07–9.86	<0.001
L-Arabitol	0.674 (1.6)	1.89 (0.2)	0.07–9.86	<0.001
D-Arabitol	0.674 (0.5)	3.60 (0.1)	0.07–9.86	<0.005
Ribitol	0.675 (1.2)	2.47 (0.3)	0.07–6.57	<0.001
D-Glucitol	0.649 (2.5)	5.80 (0.7)	0.06–3.66	<0.005
Galactitol	0.651 (0.01)	6.28 (0.4)	0.06–0.41	<0.001
D-Mannitol	0.653 (0.3)	4.15 (0.3)	0.06–0.97	<0.001
Lactitol	0.581 (1.0)	5.23 (0.3)	0.03–2.90	<0.001
Maltitol	0.587 (0.5)	4.89 (0.2)	0.03–2.90	<0.005

Standard error values × 10^{-3} are given in parentheses.

[a] Apparent specific volume concentration dependence constant values × 10^{-3}.

[b] Data are considered unreliable due to the limited number of points investigated (three points).

differences between polyols of similar molecular weight were found. Although the differences are small, they are consistent at all concentrations; it seems that the orientations of the -CHOH groups play an important role in these differences. (Tables of Φ_v values of polyols from this study are available from the authors on request.)

A comparison between polyols and their corresponding sugars (see Table 3) shows that the percentage increase in $\Phi_v{}^o$ is greater than the corresponding percentage increase in molecular weight. The difference is due mainly to the linear open structure of polyols and not to the polyhydroxy character of the solutes, as the inositols have Φ_v values that are below those of the sugars (Franks *et al.* 1972). The same could be observed from the $\Phi_v{}^o$ values of alcohols and polyols reported by Høiland (1986). As an example, for 1-butanol $\Phi_v{}^o$ is 86.60 cm³/mol and for 1,4-butanediol it is 88.3 cm³/mol, whereas cyclobutanol has a $\Phi_v{}^o$ of 75.6 cm³/mol.

In general the differences between polyols and sugars could be due to the larger surface exposure of polyols to the solvent through less restricted rotation. Edward *et al.* (1977) suggest that the decrease in volume accompanying ring formation is a consequence of increased overlap of van der Waals surfaces in the molecule.

The range of partial specific volumes found in this work is from 0.581 to 0.933 cm³/g (see Table 2). The ${}^{\phi}V^{o}$ of pentitols, hexitols, lactitol and maltitol fit within the central part of the sweet range, i.e. 0.58–0.66 cm³/g, which accords with their ability to elicit a pure sweet taste response.

Intrinsic viscosity is a measure of the effective size of the hydrated molecule in motion. For all the sugar alcohols analysed the [η] value is about three to four times higher than the partial specific volume. Intrinsic viscosity is likely to be larger as it reflects the tumbling motion of the molecule as it moves through solution. Since the nature of the k' and D coefficients are not well known, it is not easy to explain the differences found for these constants in polyols. According to Huggins (1942), k' is a factor that depends on the sizes, shapes and cohesional properties of both solvent and solute molecules. Mathlouthi and Seuvre (1988) have taken k' to be an interaction factor accounting for the mobility of water around the solute. The maximum values of k' and D were found for galactitol and lactitol; the observed differences in k' (see Table 4) might be due to the differences in compatibility between the hydrated solute and the water structure.

From Table 5 a comparison of the intrinsic viscosity between polyols and their corresponding sugars gives higher values for polyols than sugars; this might be due to the straight chain structures of polyols causing a greater resistance to flow than the parent cyclic structures (Shamil *et al.*, 1988). The exception is galactitol, which showed a lower [η] than D-galactose; this could be because galactitol has two hydrophilic and two hydrophobic domains that are well separated, which could be related to the increased mobility of water around it, as shown by the high k' value for galactitol. The hydration number, h, is a measure of the number of water molecules that have a relatively long residence time with the solute and hence tend to move with it rather than with bulk water. The hydration of the polyols takes place in two ways: by solute–solvent hydrogen bonding and by non-specific hydration of apolar species. The results from Table 4 show a high hydration number for ribitol compared with xylitol and arabitol, and the h value for galactitol is smaller than those for D-glucitol and D-mannitol. This could be because of the higher hydrophilic character of ribitol and hydrophobic character of galactitol molecules compared with their stereoisomers.

Table 3 Relationship between % increase in molecular weight (MWt) and Φ_V^0 of polyols and their corresponding sugars

Compound	Φ_V^0 (cm^3/mol)	% increase in Φ_V^0	% increase in MWt
D-Xylose	93.49		
Xylitol	101.7	8.8	1.3
L-Arabinose	91.38		
L-Arabitol	102.6	12.3	1.3
D-Arabinose	91.12		
D-Arabitol	102.6	12.6	1.3
D-Glucose	110.8		
D-Glucitol	118.0	6.5	1.1
D-Galactose	109.1		
Galactitol	118.6	8.7	1.1
D-Mannose	110.8		
D-Mannitol	118.9	7.3	1.1

Φ_V^0 values were calculated from the results reported by Shamil *et al.* (1988).

The perception of sweetness is a dynamic process that might be characterized by temporal evaluation. Tables 6–11 show the taste characteristics of polyols such as intensity, I, persistence, T, time to onset of maximum intensity, T_o, time to end of maximum intensity, T_i, lingering time, T_l, and overall gustatory response, $(TI)/2$. All the results shown in Tables 6–11 are the mean value and the standard error of 24 assessments and two replicates for each determination. Analyses of variance (ANOVA) to measure significant effects of panellists, replicates, polyol, concentration and polyolconcentration on the time–intensity characteristics of polyols were carried out and the F-values to test for significance are given in Table 12.

The variability between panellists was statistically significant for all the sweetness time–intensity curve characteristics; however, the variability between replicates

Table 4 Viscometric constants, partial molal volumes (ϕ_v^0) and partial specific volumes (${}^{\phi}V^0$) of polyols in aqueous solution

Polyol	[η]^a (cm^3/g)	k'	B (dm^3/mol)	D (l^2/mol^2)	h (H_2O mol/mol)	ϕ_v^0 (cm^3/mol)	${}^{\phi}V^0$ (cm^3/g)
Ethylene glycol	2.59	0.13	0.161	0.003	0.6	54.45	0.877
Glycerol	2.36	1.01	0.216	0.047	0.9	70.78	0.768
Propylene glycol	3.17	0.62	0.241	0.036	1.4	71.03	0.933
Meso-erythritol	2.85	0.30	0.349	0.037	2.9	86.53	0.709
Xylitol	2.62	1.10	0.397	0.173	3.2	101.7	0.668
L-Arabitol	2.68	1.27	0.405	0.208	3.3	102.6	0.674
D-Arabitol	2.73	0.91	0.414	0.157	3.5	102.6	0.674
Ribitol	2.95	0.38	0.450	0.078	4.3	102.7	0.675
D-Glucitol	2.55	1.88	0.461	0.299	3.7	118.0	0.648
Galactitol	2.28	2.94	0.410	0.495	2.5	118.6	0.651
D-Mannitol	2.56	1.14	0.464	0.245	3.7	118.9	0.653
Lactitol	2.69	2.86	0.918	2.410	6.5	200.1	0.581
Maltitol	3.06	0.85	1.053	0.939	9.0	202.2	0.587

[a] Viscosity results were obtained at 20°C and concentrations from 2 to 5%.

was not significant, i.e. the panellists were consistent in their responses. It is important to point out that, in this study, all the polyols and also sucrose were prepared at the same concentrations on a weight basis. From the results shown in Table 6 the sugar alcohols could be ranked from least sweet to most sweet as follows: lactitol < D-glucitol = D-mannitol < maltitol = xylitol. However, when the concentrations are expressed on a molar basis, the ranking changes due to differences in the molecular weights of the different polyols. This is illustrated for intensity and persistence in Figures 2 and 3.

The greater the molecular weight of sugar alcohol, the smaller the number of molecules and consequently the lower the molar concentration. As can be seen from the graphs, the ranking of sugar alcohols for sweet intensity and persistence taking concentration on a molar basis is as follows:

Table 5 Hydration number (*h*) of polyols and corresponding sugars

Compound	*h* (H_2O mol/mol)	H_2O mol/OH radical
D-Xylose[a]	2.3	0.58
Xylitol	3.2	0.64
D-Arabinose[a]	3.5	0.89
D-Arabitol	3.5	0.70
D-Glucose[a]	3.5	0.70
D-Glucitol	3.7	0.62
D-Galactose[b]	4.3	0.86
Galactitol	2.5	0.42
D-Mannose[b]	3.3	0.66
D-Mannitol	3.7	0.62
Lactose[b]	6.28	0.79
Lactitol	6.50	0.72
Maltose[a]	4.2	0.53
Maltitol	9.0	1.00

[a] From Shiito (1957).

[b] From Kawaizumi *et al.* (1981).

Table 6 Intensity (in SMURF units) of sweetness of sugar alcohols and sucrose

Sugar	Concentration (% w/v)			
	3	6	9	12
D-Glucitol[a]	1.3 (0.13)[b]	2.9 (0.19)	4.9 (0.27)	6.6(0.30)
Lactitol	1.2 (0.17)[b]	2.5 (0.21)	4.3 (0.31)	5.7 (0.34)
Maltitol	2.2 (0.16)[c]	4.2 (0.21)	7.0 (0.24)[c]	8.4 (0.2 1)[c]
D-Mannitol[a]	1.2 (0.14)[b]	3.1 (0.21)	4.5 (0.23)	6.5 (0.21)
Sucrose	2.4 (0.25)	5.0 (0.26)	7.7 (0.23)	9.0 (0.20)
Xylitol	2.1 (0.19)[c]	5.0 (0.32)	7.0 (0.30)[c]	8.3 (0.27)[c]

The standard error is given in parentheses.

[a] No significant difference between D-glucitol and D-mannitol at all concentrations.

[b] No significant difference between D-glucitol, D-mannitol and lactitol.

[c] No significant difference between maltitol and xylitol.

Table 7 Persistence (in s) of sweetness of sugar alcohols and sucrose

Sugar	Concentration (% w/v)			
	3	6	9	12
D-Glucitol[a]	13.4 (1.1)	22.5 (1.6)	31.3 (2.1)	39.4 (2.9)
Lactitol[a]	12.6 (1.3)	20.7 (1.7)	31.4 (3.4)	38.1 (3.2)
Maltitol	22.1 (2. 1)[b]	33.8 (2.9)[b]	48.2 (4.0)	56.8 (4.1)
D-Mannitol[a]	11.8 (1.1)	23.8 (2.0)	33.3 (2.3)	41.4 (2.6)
Sucrose	35.2 (3.9)	45.0 (4.4)	65.1 (4.4)	66.2 (5.5)
Xylitol	20.3 (2.3)[b]	34.9 (3.3)[b]	44.2 (3.7)	50.0 (3.8)

The standard error is given in parentheses.

[a] No significant differences between D-glucitol, D-mannitol and lactitol at all concentrations.

[b] No significant difference between maltitol and xylitol.

Table 8 Time (in s) to onset of maximum intensity (T_0) of sugar alcohols and sucrose

Sugar	Concentration (% w/v)			
	3[a]	6	9	12
D-Glucitol[b]	2.6 (0.4)	3.2 (0.4)	4.3 (0.5)	4.1 (0.5)
Lactitol[b]	2.6 (0.3)	3.7 (0.4)	4.8 (0.3)	5.3 (0.5)
Maltitol[b]	3.0 (0.3)	4.3 (0.5)	5.7 (0.7)	5.0 (0.6)
D-Mannitol[b]	2.4 (0.3)	3.5 (0.4)	3.9 (0.4)	4.7 (0.6)
Sucrose[b]	6.0 (0.5)	6.0 (0.6)	8.0 (0.5)	9.0 (0.6)
Xylitol[b]	2.4 (0.2)	3.6 (0.5)	4.4 (0.6)	4.6 (0.8)

The standard error is given in parentheses.

[a] No significant difference between T_0 values of sugar alcohols at 3%.

[b] No significant difference between 9 and 12% concentrations in this sugar.

Table 9 Lingering time (in s) of sweetness of sugar alcohols and sucrose

Sugar	Concentration (% w/v)			
	3	6	9	12
D-Glucitol[a]	6.8 (1.0)	14.6 (1.4)	21.9 (2.0)	30.0 (2.6)
Lactitol[a]	6.4 (1.1)	12.7 (1.5)	22.3 (3.2)	27.9 (2.9)
Maltitol[b]	14.1 (2.0)	24.2 (2.6)	36.4 (3.7)	45.2 (4.0)
D-Mannitol[a]	6.7 (1.0)	16.3 (1.7)	25.0 (2.1)	31.9 (2.5)
Sucrose	22.6 (2.9)	27.7 (2.9)	49.9 (3.9)	49.4 (5.3)
Xylitol[b]	13.2 (2.1)	26.2 (3.1)	35.1 (3.6)	39.9 (3.6)

The standard error is given in parentheses.

[a] No significant differences between D-glucitol, D-mannitol and lactitol at all concentrations.

[b] No significant differences between maltitol and xylitol at 3, 6 or 9% concentration.

Table 10 Time (in s) to end of maximum intensity of sugar alcohols and sugar

Sugar	Concentration (% w/v)			
	3	6	9	12
D-Glucitol[a]	4.1 (0.5)	4.7 (0.8)	5.1 (0.8)	5.3 (0.8)
Lactitol[a]	3.6 (0.3)	4.4 (0.4)	4.2 (0.5)	4.9 (0.7)
Maltitol[a]	5.1 (0.7)	5.2 (0.5)	6.1 (0.9)	6.6 (0.8)
D-Mannitol[a]	2.9 (0.3)	4.1 (0.5)	4.4 (0.5)	4.8 (0.7)
Sucrose[b]	6.7 (1.0)	6.8 (0.8)	6.7 (0.8)	5.9 (0.6)
Xylitol[b]	5.2 (0.7)	5.5 (1.1)	4.9 (0.8)	5.6 (1.0)

The standard error is given in parentheses.

[a] No significant difference at 6, 9 or 12% concentration in this sugar alcohol.

[b] No significant difference at all concentrations in this sugar.

Table 11 Total gustatory response, as the product of intensity and persistence divided by two [(IT)/2], in SU/s

Sugar	Concentration (% w/v)			
	3	6	9	12
D-Glucitol	11.0 (1.9)	36.5 (3.8)	79.8 (6.7)	135.5 (12.1)
Lactitol	9.8 (2.1)	30.4 (4.3)	75.9 (10.6)	117.3 (12.8)
Maltitol	27.5 (3.4)	73.7 (7.6)	172.6 (15.4)	239.4 (17.8)
D-Mannitol	9.4 (2.0)	41.3 (4.7)	77.3 (7.0)	135.0 (9.6)
Sucrose	77.6 (13.4)	105.6 (12.9)	252.5 (19.5)	297.6 (34.5)
Xylitol	27.1 (5.1)	92.3 (9.7)	159.9 (15.0)	215.9 (17.8)

The standard error is given in parentheses.

D-glucitol = D-mannitol < xylitol < lactitol < maltitol.

DuBois and Lee (1983) reported a taste onset time of 5.1 s for 5% w/v sucrose solution. In this study a T_0 value of 6 s was observed for 6% w/v sucrose solutions; the observed T_0 value for sugar alcohols at a range of concentrations of 3–12% w/v was 2.4–5.3 s. The rate of onset, I/T_0, is a taste temporal factor that may be related to the mechanism whereby the stimulus molecules arrive at the receptor. In 1960 Stevens showed that sweetness intensity could be related to molar or percentage concentration of the tasting stimulus by the simple power function

$$I = K_i C_i^n \qquad (6)$$

where I is the sweetness intensity, C is the concentration and K and n are constants. In log–log coordinates, the power function becomes a straight line:

$$\log I = n_i \log C + \log K_i \qquad (7)$$

The slope of the line provides the exponent η_i, and the intercept provides the value for log K_i. The intercept is the scale factor and may change from experiment to experiment without affecting the exponent. The exponent η_i gives the rate at which sweetness increases with concentration. Munton (1982) and Shamil (1987) found that the intensity and persistence of sweet substances measured with the SMURF can be related to concentration using the Stevens power function; for persistence they used the following power function relationship:

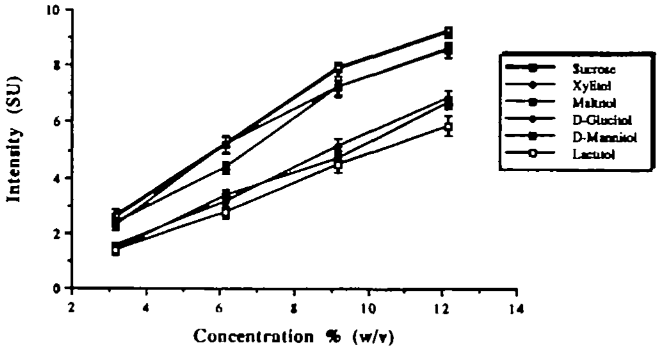
$$T = K_t C_t^n \qquad (8)$$

where T is the time of total persistence, K_t is a constant and n_t is the exponent of persistence. The mean values of 24 assessments of I and T were used for the calculations and concentration was used in both percentage and molarity. Analysis of variance on the regression was also performed to check that straight lines for the relationships were statistically valid. The resulting values of K_i, n_i, K_t and n_t, and the correlation coefficients and significance of the relationship are shown in Table 13. The value of n_i for sucrose in this study was 0.98, which is in good agreement with Meiselman (1972) and Halpern (1992), who reported the same value. The variability in published exponents for

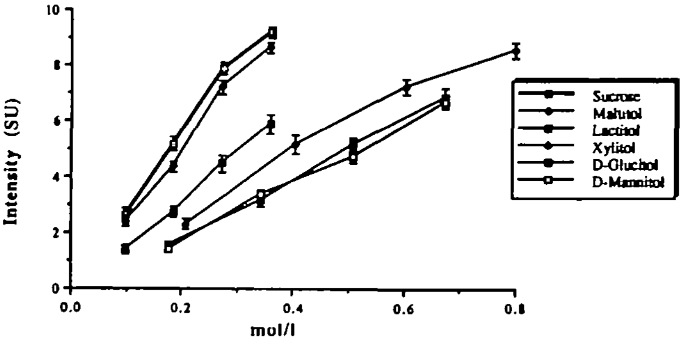
Table 12 Sugar alcohol sweetness time–intensity analysis of variance *F*-values to test for significance

Sources of variance	DF	Dependent variable				
		I	T	T_o	T_i	T_l
Panellists	23	17.26	46.06	43.07	42.91	35.63
Replicate	1	0.96^a	0.14^a	4.22	0.10^a	0.34^a
Sugar	5	211.68	73.51	7.12	6.24	67.07
Panellists•sugar•replicate	258	3.91	3.72	1.39	1.60	4.19
Concentration	3	1255.34	323.64	50.50	7.77	279.14
Sugar•concentration	15	10.89	1.55	0.70^a	0.66^a	1.72

^{a}No significant difference.

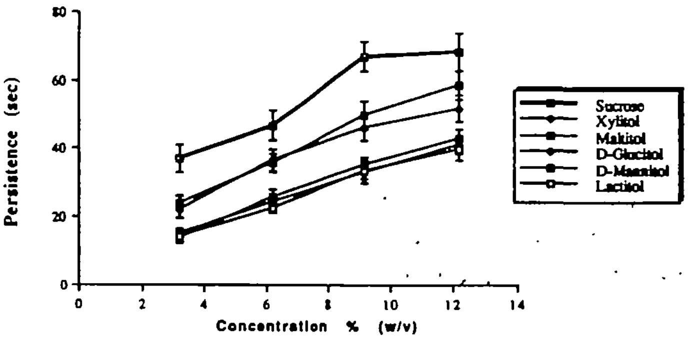


Intensity Vs. Concentration on Weight Basis

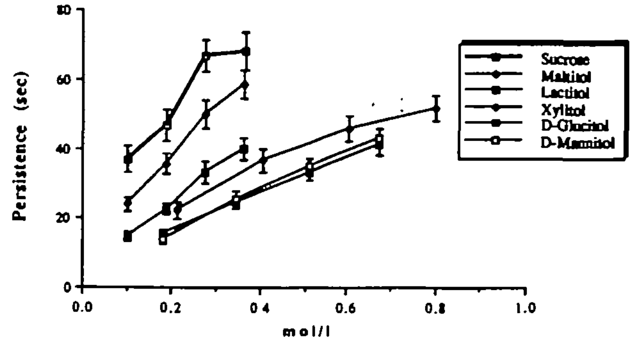


Intensity vs. Concentration on Molar Basis.

Figure 2 Intensity of polyols and sucrose at different concentrations.



Persistence vs. Concentration on Weight Basis



Persistence vs. Concentration on Molar Basis.

Figure 3 Persistence of polyols and sucrose at different concentrations.

sucrose is very large; a table with the different values and references for n_i has been reported by Meiselman (1971, 1972); Yamaguchi *et al.* (1970) reported an n_i value of 1.16 for D-glucitol and Moskowitz (1970) gave an n_i of 1.22: the n_i value obtained in this study was 1.18; for D-mannitol Yamaguchi *et al.* (1970) reported n_i = 1.16 and Moskowitz (1970) reported n_i = 1.24; in this study the n_i for D-mannitol was 1.21; Yamaguchi *et al.* (1970) reported an n_i value of 1.06 for xylitol, and Harrison and Bernhard (1984) reported an n_i of 0.98; in this study the exponent value obtained was 1.02; for lactitol and maltitol no exponents values have been reported.

Table 13 Constants (K_i and K_t), slopes (n_i and n_t), coefficients of determination (r_i^2 and r_t^2) and significance (P_i and P_t) of the relationships derived from intensity and persistence power functions for sweetness ($I = K_iC_i^n$ and $T = K_tC_t^n$)

Sugar	K_i	n_i	r_i^2	P_i	K_t	n_t	r_t^2	P_t
D-Glucitol	10.96 0.36[a]	1.18 (0.02)	0.999	<0.001	53.9 5.7[a]	0.78 (0.01)	0.999	<0.001
Lactitol	13.31 0.32[a]	0.98 (0.13)	0.963	<0.025	90.3 5.0[a]	0.81 (0.04)	0.994	<0.005
Maltitol	25.36 0.71[a]	1.01 (0.06)	0.993	<0.005	118.2 10.2[a]	0.69 (0.08)	0.994	<0.005
D-Mannitol	10.85 0.33[a]	1.21 (0.07)	0.992	<0.005	62.4 4.4[a]	0.91 (0.04)	0.995	<0.005
Sucrose	26.84 0.84[a]	0.98 (0.04)	0.995	<0.005	115.2 19.2[a]	0.51 (0.1)	0.972	<0.05
Xylitol	11.50 0.72[a]	1.02 (0.10)	0.979	<0.025	61.1 10.1[a]	0.66 (0.05)	0.987	<0.01

The standard error is given in parentheses.

[a] Constant using concentration % w/v.

Table 14 Affinity (K_m; mol/l) of the sweet receptors for sugar alcohols and sucrose

Sugar	K_m
Sucrose	0.063
Maltitol	0.190
Lactitol	0.281
Xylitol	0.429
D-Mannitol	1.049
D-Glucitol	1.355

Values of K_m were calculated from equation (10).

The time–intensity profiles can be used to measure the rate at which the maximum intensity is reached, or the magnitude estimation rate, MER. MER may be calculated as:

$$\mathrm{MER} = I/T_0 \tag{9}$$

MER and concentration can be related using a Lineweaver–Burk plot (Ray, 1980; Munton, 1982; Shamil 1987; Kemp, 1989):

$$1/\mathrm{MER} = 1/\mathrm{MER}_{\max} + K_m/(\mathrm{MER}_{\max} \cdot C) \tag{10}$$

According to Ray (1980), the K_m values are a measure of the affinity of the receptor site for the sapid molecule in the same way that, in enzyme kinetics, they are a measure of the affinity of the enzyme for the substrate. The greater the K_m value, the lower the degree of affinity for the substrate, or in this case the sapid molecule. The affinity of the receptor for the sapid molecule is a measure of its ability to form a complex with the sapid molecule. The K_m values are summarized in Table 14, and the sugar alcohols and sucrose are ordered according to decreasing affinity for the receptor.

Moskowitz (1970) suggested that relative sweetness could be calculated as I_a/I_b, where I_a is the sweet intensity of compound *a* and I_b is the intensity of compound *b*; the relative sweetness values of sugar alcohols calculated at 6% concentrations on a weight basis are compared with the relative sweetness values at 0.3 mol/l of concentration in Table 15.

In the literature the relative sweetness is usually expressed on a weight basis and the results in this study are in agreement with those reported (Hough, 1979; Sicard, 1982; Sicard and Leroy, 1983; Bar, 1986; Dwivedi, 1986; Anon., 1991) except for lactitol, for which the value reported by Tunaley *et al.* (1987), 0.23–0.35, is just under 50% of the value found by the panel in this study.

The relative sweetness expressed on a weight basis has been used for practical reasons in the food industry but for scientific purposes the comparison between compounds should be done on a molar basis, especially to study how the sweetness perception takes place. The interaction efficiency of the stimulus molecule with the receptor, which is the main

Table 15 Relative sweetness of sugar alcohols

Sugar	Molality[a]	Percentage[b]
Sucrose	1.0	1.0
Maltitol	0.9	0.8
Lactitol	0.6	0.6
Xylitol	0.4	0.9
D-Mannitol	0.3	0.6
D-Glucitol	0.3	0.6

[a] Values calculated at 0.3 mol/l.

[b] Values calculated at 6% w/v.

Table 16 Values of intensity (SU), *I*, persistence (s), *T*, intrinsic viscosity (cm^3/g), $[\eta]$, and total gustatory response (SU/s), $(IT)/2$, for sugar alcohols

Sugar alcohol[a]	*I*	*T*	$(IT)/2$	$[\eta]$
Maltitol	8.4	56.8	239.4	
Lactitol	5.7	38.1	117.3	2.69
Xylitol	3.9[b]	29.2[b]	61.9[b]	2.62
D-Mannitol	3.1	23.8	41.3	2.56
D-Glucitol	2.9	22.5	36.5	2.55

[a] Concentrations of 0.3 mol/l were taken for *I*, *T* and $(IT)/2$.

[b] This value was taken by extrapolation from the relationship between concentration (0.19–0.79 mol/l) and *I* and *T* respectively.

factor in taste perception, depends on the space-filling properties of the molecule (size and shape) and on the nature, availability and orientation of the active group involved in the interaction.

No clear relationship between apparent molar volume and intensity was found for sugar alcohols; however, as can be seen in Table 16, there is a trend between intensity and intrinsic viscosity: the higher the intrinsic viscosity the greater the sweet taste intensity of the sugar alcohol.

Conclusion

Since all sapid molecules mediate their effects through water, their effective size depends on their state of hydration. In this study the effective sizes were measured as partial molar volumes and as intrinsic viscosities.

Variation in water compatibility affects molecular hydration, which in turn affects accession and interaction with receptors; therefore molecules having better packing characteristics in the water structure can be anticipated to exchange hydration water for receptors the quickest. Studies of the solution properties can result in particular deductions about the efficiency of the sapid molecule–receptor interaction. Measurements of perceived intensity and stimulus duration are useful supplements to the unidimensional relative sweetness measurements.

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