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The chemical basis of sweetness perception in beverages

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For the chemist, sweet taste perception must begin with the simple principles of chemoreception. Molecules endowed with an appropriate 'Glucophore' are able to interact with, and elicit a response in, a putative receptor. The challenge is thus to explore the structures of sweet molecules, their modification in the environments in which they are presented and their access to, and activation of receptors. A recent approach to structure–activity relationships in sweeteners has centred on the role of water. This has led to a clearer picture of the real hydrated state of sweet molecules and differences between them based on their solution properties. The role of water is of particular relevance in beverages and offers the tantalising prospect of sensory control of formulations based on objective solution measurements. Parameters such as ^{1}H NMR pulse relaxation times, intrinsic viscosities and apparent specific volumes can be compared to evaluate the solution behaviour of sweet molecules. Apparent specific volumes offer direct experimental verification of computed volumes and, more importantly, are measures of the effective volumes of sweet solutes in the vicinity of receptor sites. They have already been shown to be broad determinants of taste quality. Sweet molecules belong to vastly different chemical classes and they elicit different qualities, intensities and persistences of response. Future progress in the optimisation of sweet taste perception may lie in enhancement or inhibition of the response and control of solution interactions

INTRODUCTION

It is generally agreed that sweet taste chemoreception originates in a loose and temporary binding of a sweet molecule with a putative taste receptor (Birch, 1991; Mathlouthi *et al.*, 1993). This initial chemoreceptive event is then 'transduced' within the taste cell and converted to action potentials in adjoining neurones. The loose attachment must involve weak forces such as hydrogen bonds and is probably still best conceptualised as in the original Shallenberger and Acree (1967) bipartite AH,B system. However, the accession to and orientation at receptor sites are also important aspects of chemoreception which involve solution thermodynamics and multi-point interactions of sweet molecules with receptors and such mechanisms have been invoked to explain the very high intensities of some newly discovered sweeteners (Nofre & Tinti, 1993). The entire theory of taste chemistry has recently been exhaustively summarised (Shallenberger, 1993).

The sweet taste of beverages can thus be chemically interpretable by understanding the nature of the sweet molecules which they contain and their structures and properties in the aqueous medium of their presentation. Sweetener molecules and water molecules interact before receptor stimulation occurs and it is interesting to explore this interaction in relation to the sweet perception itself.

THE ROLE OF WATER

The role of water in beverages is obviously important in terms of safety, quality, appearance, preservation and flavour dispersion. In terms of sweetness quality, intensity and interactions of these with the above attributes, it is critically important and we are only now beginning to understand how water affects the perception of sweetness.

First, all substances must be water-soluble in order to have any taste and second, once dissolved, some degree of molecular solute–solvent interaction occurs. This interaction then governs accession of sapid molecules to receptors and their orientation and activity in the receptor microenvironment.

Many different classes of chemical have now contributed to our understanding of taste in relation to water interaction (Birch & Kemp, 1989; Kemp & Birch, 1992; Shamil, 1991) but the sugars have a special place of importance in regard to structure–activity relationships

(Birch,1976). This is because of their well-understood stereochemistry (pyranose and furanose rings are stabilised by water) and it is often forgotten that the father of carbohydrate chemistry, Emil Fischer, originated the lock and key hypothesis of enzyme specificity: '*To use a picture, I would say that the enzyme and glucoside must fit each other like a lock and key to effect a chemical reaction on each other*' (Fischer, 1894).

Sugars and water remain the major components of soft drinks despite the range of 13 types of sweetener currently permitted in the UK. This is not simply because of product image but rather product quality, resulting from the unique interaction of sugars with water which confers a pure taste response. It is interesting that this particular quality characteristic can now be attributed to defined solution properties.

When water molecules interact with sweet molecules they cause some degree of solute hydration. In the sugars this is quite extensive (Birch & Shamil, 1987) because of the multiplicity of their hydroxyl groups and depends on the axial and equatorial dispositions of these in pyranose molecules.

MOLECULAR SIZE AND SWEETNESS

Although most known sweeteners are small molecules (< 500 Daltons) some, such as thaumatin and monellin, are not (> 20,000 Daltons). This means that the optimum size of a sweet molecule with regard to fit with the sweet receptor remains unclear. The degree of hydration of the sweet solute molecule will clearly affect its effective size at the receptor and this has prompted an extensive study (Shamil *et al.*, 1987; Shamil & Birch, 1990) of apparent molar volumes and apparent specific volumes of sapid molecules usually at normal tasting concentrations. The significance of the latter parameter is that it allows molecules of different molecular weight to be compared in terms of their hydrostatic compatibility with water structure (packing efficiency). Table 1 lists the ranges of apparent specific volumes of sapid molecules across the basic taste spectrum (Shamil *et al.*, 1987) and indicates how this parameter may be a broad determinant of taste quality. The remarkable finding portrayed in Table 1 is not due to a size exclusion effect. Rather it is due to degree of compatibility with water structure. The interpretation put upon the results of Table 1 is thus that those solutes with the greatest compatibility with water structure, e.g. salts (low apparent specific volumes, i.e. high packing efficiency), are conveyed by the water to the deepest layers of the taste epithelium, where, presumably, the appropriate receptors are located. This is of particular relevance to beverage formulation when the nature and concentration of a sweetener is altered. Such alterations may affect the ability of salt solutes to recruit receptors and thus alter sensory balance. A further point about Table 1 is that all sugars have apparent specific volumes in the centre of the sweet range (*c.* 0·60–0·62 $cm^3\ g^{-1}$) which accounts for the purity of their sweet taste. Departure from this range by substitution of sugars by intense sweeteners is liable to contaminate the sweetness with salty, sour or bitter notes (e.g. see Birch & Kemp, 1989).

Table 1. Approximate apparent specific volume ranges and taste qualities ($cm^3\ g^{-1}$; Shamol *et al.*, 1987)

Range	Quality
0·1–0·3	Salty
0·3–0·5	Sour
0·5–0·7	Sweet
0·7–0·9	Bitter
> 1·0	Tasteless (odorous)

When a sweetener is dissolved it disturbs water structure but a more highly ordered state of hydration is imposed within the system. Many different solution properties have therefore been explored to quantify the effect in detail. Intrinsic viscosities, for example, which measure hydrodynamic volumes allow direct comparisons with apparent specific volumes (Table 2) though the latter are understandably smaller by a factor of 2–4. A disadvantage of viscometry is that it is less useful for comparing the molecular architectures of different size molecules (Mathlouthi *et al.*, 1993) because larger molecules suffer greater drag effects. Apparent specific volumes therefore remain the best predictors of taste quality and they are also obtained by the most precise measurements. They are therefore useful for deriving structure–activity relationships and more especially for fragmental effects within a single molecule (Lopez-Chavez, 1993; Birch *et al.*, 1994). Table 3 lists some exemplar volumes of molecular fragments achieved in this way. The measurement of fragmental contributions allows those parts of a molecule which are interacting most strongly with surrounding water

Table 2. Apparent specific volumes (ASV) and intrinsic viscosities $[\eta]$ of sugars (Kemp *et al.*, 1990)

	$[\eta]$ ($cm^3\ g^{-1}$)	ASV ($cm^3\ g^{-1}$)	$[\eta]$/ASV
D-Glucose	2·38	0·626	3·80
D-Galactose	2·36	0·607	3·89
D-Mannose	2·30	0·601	3·83
D-Fructose	2·27	0·616	3·69
D-Xylose	2·30	0·625	3·68
(D-Glucitol	1·97	0·638	3·09)

Table 3. Apparent specific volumes of molecular fragments (Shamil *et al.*, 1989; Lopez-Chavez, 1993)

Fragment	App. Sp. Vol. ($cm^3\ mol^{-1}$)
$-CH_2OH$	28
-CHOH	16
-CHO	3·1
$-CO_2H$	4·5
H+	Negative

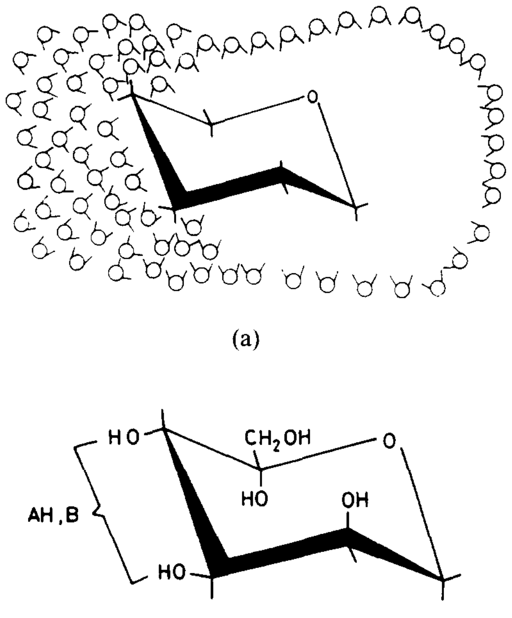

Fig. 1. (a) Postulated clustering of water molecules around the sugar molecule. (b) β-D-Fructopyranose.

molecules to be identified, namely the 3,4 α-glycol group of glucopyranoside structures (Shamil *et al.*, 1989). In contrast, the anomeric centre does not seem to interact at all strongly with water. On the other hand, those sugars which exist mainly in the alternative chair conformation, e.g. fructopyranose, probably do undergo hydration effects in the anomeric region, a conclusion which follows from the structural analogy of the two pyranose forms. It is of interest that the 3,4 α-glycol group of hexpyranoses has also been identified as the glucophore, i.e. the region of the molecule responsible for hydrogen bonding with the sweet receptor and eliciting the sweet taste response (i.e. the Shallenberger and Acree AH,B system) (Fig. 1). (Table 4). It follows that water 'polarises' analogous molecules in an analogous manner and hence orientates them analogously at the receptor site. Sugar molecules all have apparent specific volumes between 0·60 cm^3 g^{-1} and 0·62 cm^3 g^{-1}. Most offer a similar quality of pure sweetness and all are of similarly low intensity.

Table 4. Significance of the 3,4 α-glycol group of hexopyranoses

Role	References
1. Sweet glucophore	Birch & Lee, 1974
2. Tasteless 'galacto' analogue	Mathlouthi *et al.*, 1993
3. Compatibility with water structure	Galema *et al.*, 1992
4. Interaction with water	Shamil *et al.*, 1989
5. Hydrophilicity region in ring	Lichtenthaler & Immel, 1993
6. Specificity of blood group substances	Lemieux *et al.*, 1991

HIGH-POTENCY SWEETENERS

It is now well accepted that all high potency sweeteners are more lipophilic than sugar molecules. This makes them less water-soluble than sugars yet still of great economic importance in beverages owing to their sweetening power (mostly 200–1000 times higher than sugar). Lipophilicity probably provides an additional mode of attachment (stronger binding) to the taste receptor but it alters the solution properties so that the sweet taste becomes contaminated, principally with bitter notes. The greatest success of high-potency sweeteners in beverages has been with aspartame but even this sweetener is sensorially distinguishable from sugars. It is also unstable under low pH conditions in storage, and gradually breaks down to tasteless or unpleasant products. Possibly, the best new sweetener yet designed is sucralose (4,1^1, 6^{1}trichloro 4, 1^1, 6^{1}trideoxy galacto sucrose) which is 650 times sweeter than sucrose and has solution properties sufficiently close to those of sucrose to confer a similarly pleasant taste (Shamil & Birch, 1992). This molecule is both more hydrophobic and more polar than sucrose and its sweetening power is as much attributable to its orientational hydration as to its lipophilic attachment at the receptor. Sucralose has already been permitted for food use in Canada.

SWEET TASTE PERCEPTION IN BEVERAGES

Sweet taste perception in beverages is of course dictated by the formulation. Certain mixtures of high potency sweeteners evidently exhibit synergy. However, the presence of other tastants (e.g. bitter substances) may seriously modify these effects. (It is well known that sweet and bitter stimuli mutually suppress one another whereas certain sweetener pairs, e.g. saccharin–aspartame, exhibit enhancement). Most soft drinks contain sweet and sour components and much 'in-house' information exists about their interaction. The acceptability of comminuted drinks, for example, is critically dependent on the acidity at the low solids concentrations at which they are normally drunk and the so-called 'Brix–acid ratio' is an important control parameter in the citrus industry. McBride & Finlay (1990) have demonstrated that the psychophysically dominant characteristic in sugar–citric acid model systems is the acidity, which makes the greatest contribution to the overall taste intensity. This raises the interesting question of whether such an effect is entirely perceptual or whether it can be attributed to defined chemical changes. Solution parameters such as apparent specific volumes, intrinsic viscosities and ^{1}H-NMR pulse relaxation times ^{1}H-NMR pulse relaxation times which are measured as either T_1 (spin–lattice) or T_2 (spin–spin) relaxation times (the times needed for the protons to dissipate their spin energy by interacting with their environment or with one another, respectively) all reflect degree of order in a given solution conferred by hydration and hydrogen bonding. It is

Table 5. Spin–spin relaxation times (T_2-values) of single sugars with and without 1% citric acid

Solution (weak)	T_2 (s)	
	With citric acid	Without citric acid
5% Fructose	4.25	3.33
5% Glucose	4.18	3.39
5% Sucrose	4.23	3.28
10% Fructose	4.04	2.83
10% Glucose	4.13	2.41
10% Sucrose	3.80	2.34
1% Citric acid (alone)	4.75	

thus of interest to note (Table 5) that the spin–spin relaxation times (T_2 values) of sugar–citric acid solutions are most affected by their acidities, a trend which, is in agreement with the sensorial results of McBride & Finlay (1990). It is of course well known that T_2 values are dependent on pH but the results of Table 4 show that the low T_2 values of the sugar solutions (higher degree of order of protons) are brought close to the T_2 value of pure water (lower degree of order of protons) by the presence of the citric acid, and this may be responsible for the taste effect. It has already been observed that the taste detection thresholds of amino acids are related to T_2 values, an effect which might be attributable to disturbance of water structure (Kemp *et al.*, 1992). These results show that NMR is a sensitive tool for monitoring sensorially important solution effects. Taken together with experimental volume measurements it may offer a theoretical explanation of solution interactions which affect sweetness perceptions in beverage formulations.

The role of temperature in sweet taste perception has previously been studied by Hyvonen *et al.* (1978) and, obviously, temperature may be expected to affect sweet taste perception by altering the overall extent of hydrogen-bonding. However, it is not at all clear how the temperature of the receptor microenvironment differs from the temperature of the oral cavity, although it is known (Frankmann & Green, 1987) that salty and sour solutions are less affected by temperature changes than sweet or bitter solutions, a result which might be directly related to the results of Table 1. Temperature effects must therefore be considered alongside kinetic models of sweet taste (Ennis, 1992).

Likewise, alcoholic beverages must be interpreted by the changed solvent polarity of alcohol–water solvents (Serghat *et al.*, 1992; Hoopman *et al.*, 1993) which lowers sweetness perception. However, such effects need to be cautiously interpreted in view of the critical importance of salivary flow rate (Fischer & Nobel, 1994).

GLUCOSE SYRUPS AND THEIR EFFECTS IN BEVERAGES

Glucose syrups constitute one of the most extensively used group of sweet substances used in soft drink formulation. However, in the UK, only hydrogenated glucose syrups are classified as sweeteners. Both ordinary and hydrogenated glucose syrups have enabled advances to be made in our understanding of the mechanism of sweet taste chemoreception, principally because each type can be defined in terms of average molecular size and each is available in sufficient quantities for meaningful taste tests to be carried out.

An early significant finding (Kearsley *et al.*, 1978) was that the sweetness threshold value of ordinary glucose syrup increased with degree of polymerisation (DP) or, in other words, as the average molecular size becomes greater, the sweetness potency on a weight basis decreases. This, of course, is logical in view of the identification of the 3,4-α glycol group of the non-reducing ends of the chains as the 'glucophore'. It has also been axiomatic in the food industry that maximum sweetening power accords with the lowest DP (i.e. highest DE or dextrose equivalent) in a beverage formulation. Moreover, the Kearsley *et al.* (1980) results showed that exactly the same trend occurs for hydrogenated glucose syrups as for unhydrogenated and more importantly, that the thresholds for the hydrogenated and corresponding unhydrogenated glucose syrups were similar and there is indeed no significant difference between them. This proves that the anomeric centre of malto-oligosaccharides is not involved in the sweetness response.

If the Kearsley *et al.* (1980) results are carefully re-examined (Table 6), it emerges that the authors missed an important conclusion. This was that the taste thresholds of the higher DP syrups were not as high as anticipated from their average molecular weights, or, in other words, the larger molecules were sweeter than the smaller ones. This result has therefore been re-explored in terms of solution properties and time–intensity taste analysis. The former have established that, as DP increases, malto-oligosaccharides pack more efficiently between water molecules (lower apparent specific volumes) and exhibit lower spin-spin relaxation times. (T_2 values), indicating fewer mobile protons (Fig. 2) (Birch & Karim, 1992). The latter show that both the sweet taste intensity and sweet taste persistence of glucose syrup solutions are greater for larger molecules (Birch *et al.*, 1994), an effect which may be ascribable to their more orderly interaction with water structure. An example of this for 30% glucose syrup solutions is shown

Table 6. Threshold sweetness values (% w/v) of ordinary and hydrogenated glucose syrups (Kearsley *et al.*, 1978)

DE	Ordinary glucose syrup	Hydrogenated[a] glucose syrup
21	2·00	1·98
31	1·95	1·82
43	1·45	1·37
50	1·22	1·12
65	1·07	1·02
100	0·75	0·73

[a] Now legally classified as bulk sweeteners in the UK.

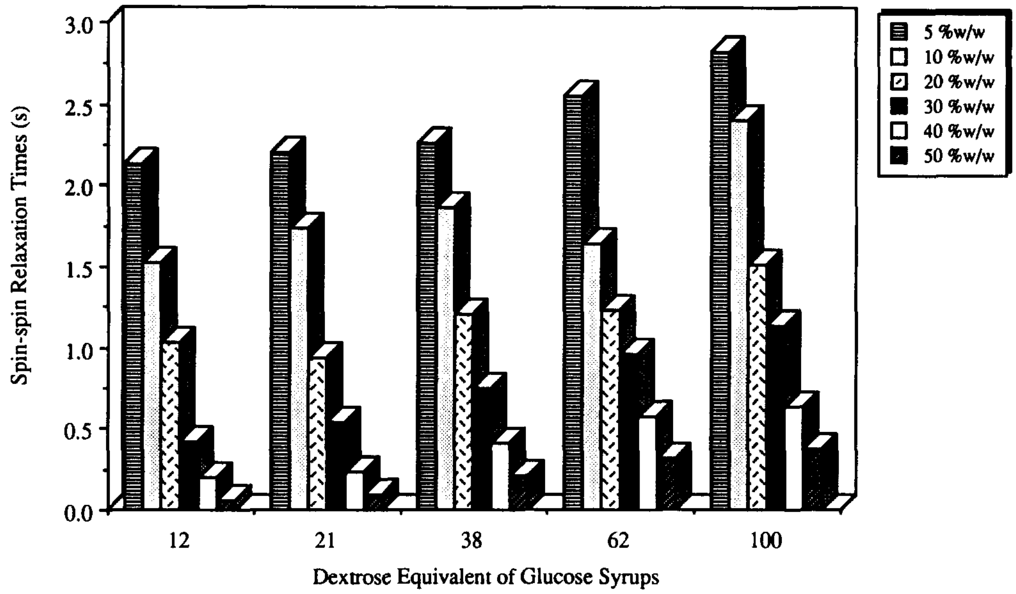

Fig. 2. Spin–spin relaxation times (T_2 values) of glucose syrups at different concentrations.

Table 7. Sweetness intensity and sweetness persistence values 30% w/v glucose syrups solutions

Dextrose equivalent (DE)	Degree of polymerisation (DP)	Concentration (molar)	Intensity of sweetness (smurf units)	Persistence of sweetness (s)
12	8·3	0·219	15·8	32·8
21	4·8	0·380	22·7	35·6
38	2·6	0·675	41·5	45·7
62	1·6	1·073	52·0	53·7
100	1·0	1·665	63·2	66·2

in Table 7. These results again demonstrate the importance of apparent specific volume in predicting and determining taste response. It also seems possible that taste is only one of several biological responses governed by this parameter (McGowan & Mellors, 1986), which generally accords well with theoretical computations (Spillane *et al.*, 1992 *a,b*).

CONCLUSIONS

Although the explanation of sweet taste perception must be multidisciplinary, its chemical interpretation is of primary concern. Recent structure–activity approaches to the understanding of sweetness have underlined the importance of water interaction with sweet molecules. In particular, the apparent specific volume of a taste molecule may be indicative of its taste quality and, within gluco-oligomers, may govern sweet potency. These results have helped in the theoretical interpretation of sweet taste mechanisms, and may eventually aid day-to-day control of beverage quality.

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