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Structural Basis of and Interaction Between Sweetness and Bitterness in Sugars

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The relationships between concentration and subjective intensity of (a) sweetness and (b) bitterness have been separately determined and the effect of each on the subjective intensity of the other has been evaluated. The depression of sweetness by bitter additives, or bitterness by sweet additives obeys a simple mathematical relationship which may be used to calculate the "true" sweetness of a bitter-sweet sugar. This facilitates the structural explanation of sweetness in model sugars.

1. Introduction

In a previous publication[1] we substantiated the Shallenberger[2] sweetness hypothesis by taste-panel measurement of the sweetness of the stable monosaccharide, methyl α-D-glucopyranoside, and its disaccharide analogue α,α-trehalose. These two substances were isosweet in molar solutions thus indicating that only one half of the trehalose molecule binds to the taste bud protein. It is only by comparing the relative sweetness of stable analogues in this way that the structural basis of sweetness may be explained. However, one difficulty we have encountered in our investigation is that many of the model sugars under examination are reported by taste-panellists to possess a contaminating taste[3] ranging from trace-bitter to distinctly bitter. This effect may either enhance or depress the sweetness which is being measured and thus lead to erroneous conclusions.

Many of the free-reducing model sugars exhibit the phenomenon of bitter-sweetness and this is often associated with the presence of β-anomers. Furthermore, methoxyl groups are often observed to confer bitterness. Thus, the analogues α- and β-glucose and α- and β-xylose are all sweet, but of the four corresponding glycosides all are distinctly bitter-sweet except methyl α-D-glucopyranoside (Figure 1). It is known[4–6] that the subjective intensity of sweetness increases linearly with the logarithm of the concentration of the sweet substance in the normal test range. It is not known whether bitterness follows a similar pattern and therefore, assuming sweetness and bitterness do interfere with one another, at what level interference might begin. With these problems in mind we have investigated the sweetness of sucrose and the bitterness of quinine sulphate, and the effect of one on the subjective intensity of the other. Subsequently we measured the sweetness and the bitterness of the model substance methyl β-D-glucopyranoside.

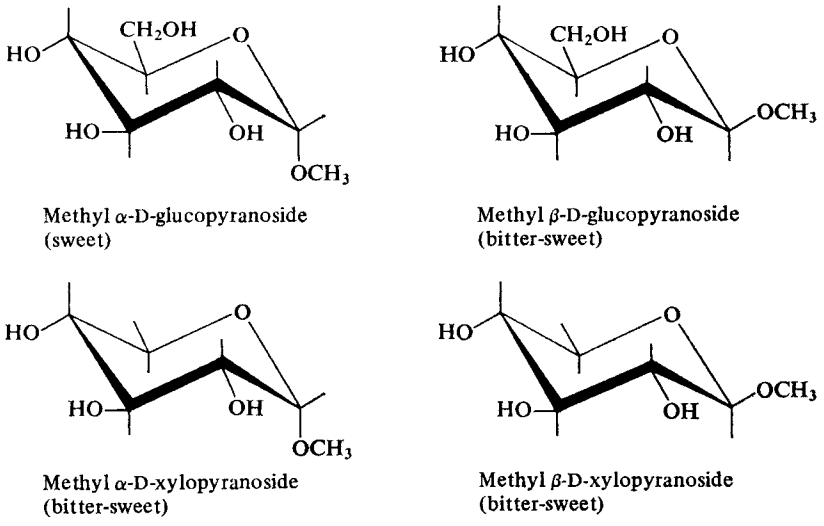

Figure 1. Structure and taste of analogous glycosides.

2. Experimental

Separate taste panels, each of six members, were selected from random groups for the assessment of sweetness and bitterness. The criterion of selection for sweetness assessment was the ability of the individual panellists to place in correct order of sweetness three or four sucrose solutions of concentrations differing by 0.3 units on the Shutz and Pilgrim scale (i.e. concentration differences of about 1% at the 10% level). For the purpose of bitterness measurement, a scale was derived (Figure 3) using the single-stimulus technique described by Shutz and Pilgrim,[4] quinine sulphate being selected as a standard bitter compound. The ability of panellists to detect differences of 0.8 units on the bitterness scale, corresponding to quinine sulphate concentrations of 0.00038, 0.00055 and 0.00073 %, was considered a suitable criterion of selection. The panellists were asked to rinse their mouths with tap water and pause (for about 1 min) between tastings.

The taste interactions and the intensity of sweetness and bitterness of methyl β-D-glucoside were investigated using a ranking technique. Four solutions for measurement, comprising three of known taste intensity and one unknown, were presented to panellists in random order and they were asked to place them in the correct order of intensity. The process was repeated six times and the results converted to scores and submitted to an analysis of variance. There was no evidence that order of presentation of the solutions to panellists affected results.

3. Results and discussion

Figures 2 and 3 show that for bitterness as well as sweetness subjective intensity increases linearly with log of concentration. Mixing of quinine sulphate with sucrose solutions causes a depression of the subjective intensity of sweetness which again

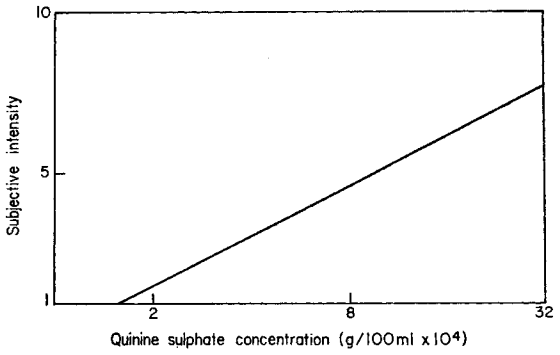

Figure 2. Subjective intensity of sweetness (after Shutz and Pilgrim). Semi-log plot.

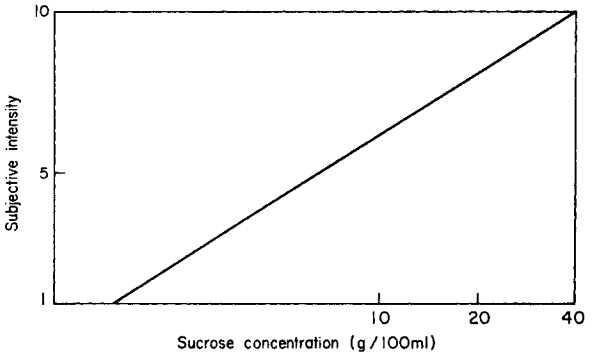

Figure 3. Subjective intensity of bitterness. Semi-log plot.

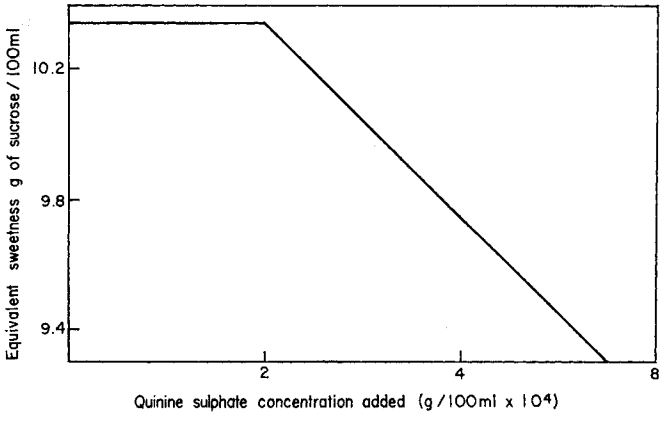

Figure 4. Effect of quinine sulphate on the sweetness of 10.34 g of sucrose/100 ml. Semi-log plot.

results in a linear relationship with log of quinine sulphate concentration (Figure 4). Similarly, addition of sucrose to quinine sulphate solutions causes a depression of the bitter subjective intensity in linear relationship to the log of the sucrose concentration (Figure 5).

A notable difference between Figures 4 and 5 is that quinine sulphate only begins to depress the sweetness of sucrose at a concentration of 0.0002% (w/v), i.e. at the threshold level of quinine sulphate (Figure 4). Sucrose on the other hand (Figure 5) begins to depress the bitterness of quinine at 0.15% (w/v), i.e. *below* the threshold level of sucrose solution. From Figures 4 and 5 it is clear that sweetness and bitterness interact according to the equation:-

$$\Delta T = K \log C/C_M. \quad (1)$$

Where ΔT = depression in taste—i.e. sweetness or bitterness;
C = concentration of additive (quinine sulphate or sucrose solution) producing the depression;
C_M = maximum concentration of additive having no effect on the taste;
K = constant.

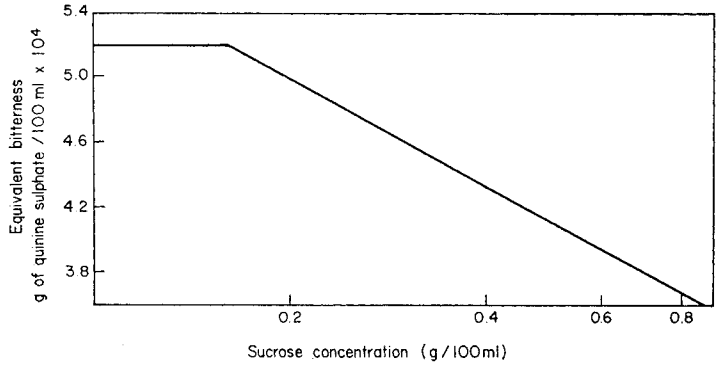

Figure 5. Effect of sucrose on the bitterness of 0.00053 g of quinine sulphate/100 ml. Semi-log plot.

Assuming that K remains constant for a family of related sweet compounds (e.g. carbohydrates) it may be possible to calculate the effect of bitterness on the sweetness of a bitter-sweet substance such as methyl β-D-glucopyranoside. We have measured the sweetness of methyl β-D-glucopyranoside relative to sucrose and compared this value (5.95 × less sweet than sucrose on a molar basis) with that of methyl α-D-glucopyranoside (4.35 × less sweet than sucrose on a molar basis). Using these values (Table 1) 10.35% methyl α-D-glucopyranoside is isosweet with 14.20% methyl β-D-glucopyranoside. Assuming that the difference between these two (i.e. 14.20 − 10.35 = 3.85%) is ΔT in equation (1) the concentration (C) of methyl β-D-glucopyranoside required to produce this ΔT can be calculated. The "true" concentration of methyl β-D-glucopyranoside equivalent in sweetness to 10.35% methyl α-D-glucopyranoside is thus calculated to be 11.62% (Table 1).

Many sweet substances are now known to possess bitter or astringent off-flavours. These include β-glucosides such as gentiobiose and laevoglucosan, sodium cyclamate and saccharin. The synthetic product β-D-glucosyl saccharin is intensely bitter and devoid of sweetness.[7] More recently some isomeric carboxylic acids from pine-rosin have been reported[8] with intense sweetness and a high degree of bitterness.

TABLE 1. Relative sweetness of methyl α- and β-D-glucoside

Glycoside	Mol isosweet with 1 M-sucrose	Mol isobitter with 1 M-quinine sulphate	"True" mol isosweet with 1 M-sucrose (correcting for intrinsic bitterness)
Methyl α-D-glucopyranoside	4.35	—	4.35
Methyl β-D-glucopyranoside	5.95	5000	4.89

Previously we have shown that the fourth hydroxyl group of glucopyranoside structures appears to be of unique importance in eliciting the sweet response,[3] possibly acting as the AH group of Shallenberger's AH, B system. If this postulate is correct the anomeric centre in these structures is too far removed from the AH, B system to exert any influence on the binding of the AH, B system to the taste-bud protein. It is thus difficult to see why there should be any difference in sweetness between α- and β-glucose. Literature reports of the sweetness of these two substances conflict. Thus, Cameron[9] states that α-D-glucose is sweeter than β-D-glucose in solution whereas Shallenberger[10] states that β-D-glucose is slightly sweeter in the solid state. It is clearly advantageous to examine the effect of the anomeric centre in stable glycoside structures in which structural isomerisation cannot interfere with the measurement, and this is why we have selected the glycosides-methyl α- and β-D-glucopyranoside. Our results show that methyl β-D-glucopyranoside has a "true sweetness" (i.e. allowing for the depression of its sweetness by its own bitterness) lower than that of methyl α-D-glucopyranoside (Table 1). However, the difference in "true sweetness" between these anomeric glycosides is so small as to possibly result from experimental error. These findings and the distinct sweetness[11] of the 1-deoxy sugars support the idea that change of configuration or indeed absence of hydroxyl groups at the anomeric centre has little or no effect on the sweetness of glucopyranoside structures.

4. Conclusion

A logarithmic increase in the concentration of an added bitter substance depressed linearly the subjective intensity of sweetness and a similar relationship applies to the depression of subjective intensity of bitterness by added sweetness. In the case of a bitter-sweet substance such as methyl β-D-glucopyranoside the depression of sweetness in the molecule, due to its intrinsic bitterness, may be calculated. The result of this calculation largely accounts for the difference in sweetness between methyl α- and β-D-glucopyranoside. These results support the idea that the anomeric centre of glycosides has no significance in determining their degree of sweetness.

Acknowledgement

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