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Application of the U and Γ' Models in Binary Sweet Taste Mixtures

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Abstract

The U and Γ' models of sensory interactions, successfully applied in olfaction for several years, are tested here using data from published studies on sweetness. The models are subsequently tested on new data obtained in studies of binary mixtures of four sodium sulfamates. The U model allows for the estimation of a global interaction, whereas the Γ' model allows for the distinction between that which is due to an intrinsic interaction in the mixture itself and that which may be due to the power function exponents in the mixture. The models give satisfactory predictions for observed phenomena of sweet taste suppression, synergism or pure additivity. Additionally, they appear to be more suitable than other models recently applied in taste, particularly the equiratio model. Application of the models to the sulfamate mixtures, reveals additivity for sodium cyclohexylsulfamate (cyclamate)/potassium cyclohexylsulfamate and sodium cyclohexylsulfamate/sodium exo-2-norbornylsulfamate, respectively; whereas for sodium cyclohexylsulfamate/sodium 3-bromophenylsulfamate, the models revealed a slight hypo addition which is simply due to the dissimilarity values of the power function exponents of the components.

Introduction

Based on analysis of several sets of data, the U model (Patte and Laffort, 1979) appears to be a satisfactory predictive tool for olfactory binary mixtures. While being very similar to the vector model of Berglund *et al*. (Berglund *et al*., 1973), the U model can be considered as an improvement on the latter. In both models, each pair of odorants is characterized by a parameter of interaction, called cos α, which is almost constant irrespective of the respective concentrations of the components of the mixture. Without entering into the mathematical details, it appears that both the experimental basis and theoretical considerations support the fact that the scattering of cos α values is less widespread using the U model rather than the vector model (Laffort and Dravnieks, 1982).

The family of Γ models (Laffort *et al*., 1989) is based on the U model, but it allows one to consider separately (from the observed synergies and suppressions) what is due to an intrinsic interaction within a given pair of odorants and what is due to the odorants themselves taken separately (their power function exponents). Among all the tested members of the Γ family, the model called Γ' appears to be the most suitable for studies on olfactory, gustatory and pharmacological mixtures (Sérée and Laffort, 1997; Thomas-Danguin and Laffort, 1998).

It has also been shown that other models applied in taste are particular cases of the Γ' model (Laffort *et al*., 1989; Laffort, 1994), for example the substitution model (Hyman and Franck, 1980) or the equiratio model (Frijters *et al*., 1984; De Graaf and Frijters, 1986). Their validity is therefore less general (see Appendix A).

The models U and Γ' are applied here to published studies on sweet mixtures, i.e. glucose/fructose, sucrose/aspartame and sucrose/sodium cyclamate. The models are also tested on unpublished data on sulfamate mixtures, including sodium cyclohexylsulfamate (cyclamate) mixtures, which are also sweet.

The U and Γ' models

The U model is very simply defined by the following:

$$R_{AB} = R_A + R_B + 2\cos\alpha_U \sqrt{R_A R_B} \qquad (1)$$

in which R_A, R_B and R_{AB} are, respectively, the perceived intensities of the components A and B and the mixture AB; cos α_U is the parameter of interaction (not related with a real angle α, as in the vector model, but named by analogy in this manner).

The Γ' model is given by:

$$\Gamma' = 1 + \cos\alpha_U - \cos\alpha_{UPL2} \qquad (2)$$

in which Γ' is an index of intrinsic interaction. $\Gamma' = 1$ corresponds to an absence of intrinsic interaction; $\Gamma' > 1$ corresponds to an intrinsic synergy; $\Gamma' < 1$ corresponds to an intrinsic suppression; and cos α_U is directly derived from equation (1):

$$\cos\alpha_{\mathrm{U}} = \frac{R_{\mathrm{AB}} - R_{\mathrm{A}} - R_{\mathrm{B}}}{2\sqrt{R_{\mathrm{A}} R_{\mathrm{B}}}}$$

cos α_{UPL2} is the parameter of interaction due to the power function exponents of components (UPL2 stands for the second version of the model, in which the power law was applied to the U model). The definition of cos α_{UPL2} requires the prior definitions of P (as proportion) and cos α_{A} and cos α_{B}:

$$P = \frac{R_{\mathrm{B}}^{1/n_{\mathrm{B}}}}{R_{\mathrm{A}}^{1/n_{\mathrm{A}}} + R_{\mathrm{B}}^{1/n_{\mathrm{B}}}}$$

$$\cos\alpha_{\mathrm{A}} = \frac{1 - P^{n_{\mathrm{A}}} - (1-P)^{n_{\mathrm{A}}}}{2\mathrm{P}^{n_{\mathrm{A}}/2}(1-P)^{n_{\mathrm{A}}/2}}$$

$$\cos\alpha_{\mathrm{B}} = \frac{1 - P^{n_{\mathrm{B}}} - (1-P)^{n_{\mathrm{B}}}}{2\mathrm{P}^{n_{\mathrm{B}}/2}(1-P)^{n_{\mathrm{B}}/2}}$$

$$\cos\alpha_{\mathrm{UPL2}} = \frac{R_{\mathrm{A}}\cos\alpha_{\mathrm{A}} + R_{\mathrm{B}}\cos\alpha_{\mathrm{B}}}{R_{\mathrm{A}} + R_{\mathrm{B}}} \qquad (3)$$

The mathematical proof of relation (3) is reported in Appendix B. When the above equations are applied to a given set of data, predicted values of perceived intensities are easy to obtain for chosen concentrations. However, the reverse is not true: if one attempts to obtain concentrations corresponding to given perceived intensities, the Γ′ model lead to analytically intractable equations. To solve this difficulty, Laffort and coworkers use an iterative computer program called MIG (mixtures intensities generation) [first application in 1989 (Laffort *et al.*, 1989)]. The program allows, for example, the construction of iso-intensity curves. Several examples are provided below.

Application to several published data sets on sweet taste mixtures

Three data sets were selected from published studies on sweet taste mixtures in order to underline the various equisweet types of curves which can be observed.

Glucose/fructose

These experimental data (De Graaf and Frijters, 1986) involve five levels of sweetness, respectively equivalent to molar concentrations of glucose of 0.125, 0.250, 0.500, 1.000 and 2.000. Each of these levels of intensities includes five points: two pure sugars and three mixtures. The exponent of glucose being fixed at 1, the exponent for fructose was found equal to 0.82 and the Γ′ value equal to 1.08 ± 0.04 (mean ± SD), which corresponds to a slight intrinsic synergy. Figure 1 reproduces the 25 experimental points, as well as the five superimposed equisweet curves obtained by using the MIG computer program.

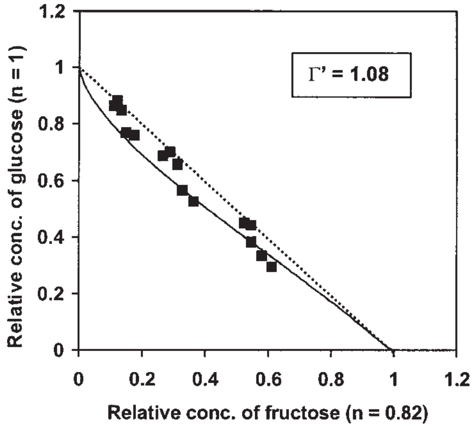

Figure 1 Five superimposed equisweet curves of mixtures of fructose and glucose. Experimental points are from previously published work (De Graaf and Frijters, 1986). The five levels of perceived intensity correspond to the sweetness of molar concentrations of glucose of 0.125, 0.250, 0.500, 1.000 and 2.000. The solid line was obtained using the MIG computer program, with Γ′ = 1.08 and the power function exponents of fructose and glucose equal to 0.82 and 1.00, respectively. The dotted line corresponds to the Beidler's mixture equation and the equiratio model.

It is clear that, in this particular case, the Γ′ value is close to 1 and the exponent values are also close to 1; the equisweet curves are very close to the diagonal dotted line and therefore the equiratio model is approximately applicable. That is true only in this particular case.

Sucrose/aspartame

The data for the mixture sucrose/aspartame (Schifferstein, 1995) also include 25 experimental points. The mixture of molar concentrations—0.0016 of aspartame and 0.1376 of sucrose—is fixed at a sweetness intensity of 10. The subjects' responses correspond to multiples of this reference. The power function exponents found by the author were, under these conditions, 0.915 for aspartame and 1.275 for sucrose. The Γ′ value then obtained is 1.03 ± 0.34), i.e. not significantly different from 1. The five equisweet curves obtained for perceived intensities from 1 to 50 by using the MIG computer program are superimposed. They are shown in Figure 2, as well as the experimental points of Schifferstein.

The interesting result displayed by the theoretical curve according to the Γ′ model is that an observed global synergy appears at the top of the figure and a global partial suppression at the bottom, in spite of the absence of an intrinsic interaction (Γ′ # 1). Both results are due only to the difference in the power function exponents of the components. The treatment cannot, however, be applied to the present experimental points, due to the widespread scattering in relation to the curve, as is indicated by a rather high value of the standard deviation for the Γ′ index for these data. Probably the only method by which the shape of

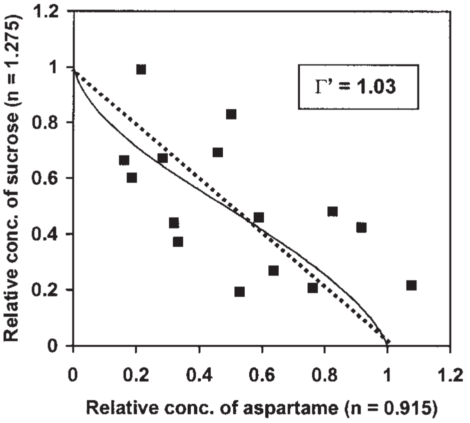

Figure 2 Five superimposed equisweet curves of mixtures of sucrose and aspartame corresponding to magnitude estimations equal to 1, 5, 15, 30 and 50. The solid line was obtained using the MIG computer model with the $\Gamma' = 1.03$ and power function exponents equal to 0.915 for aspartame and 1.275 for sucrose. The dotted line corresponds to Beidler's equation and the equiratio model (as in Figure 1). The experimental points were obtained from previously published work (Schifferstein, 1995) and personal communication with H.N.J. Schifferstein (1996).

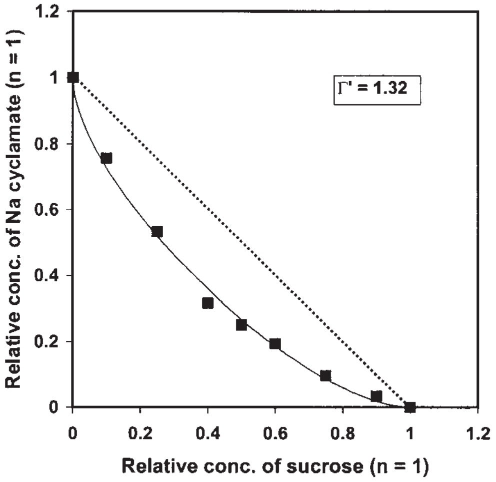

Figure 3 Equisweet experimental points (10 % SEV) for the mixture sucrose/Na cyclamate, according to previously published data (Nahon *et al.*, 1998). These data are in agreement with a curve generated using the MIG computer model, with both exponents values taken equal to 1 and $\Gamma' = 1.32$. The dotted line is derived as in Figures 1 and 2.

this figure could be verified would be using equisweet experimentation and not magnitude estimation as used by Schifferstein, after fixing the power function exponent of sucrose to 1.

Sucrose/Na cyclamate

A mixture sucrose/Na cyclamate was studied previously (Nahon *et al.*, 1998) at only one level of sweetness: 10 w/v% sucrose solution, denoted as 10 % SEV (sucrose equivalent value). Exponents of the power function cannot therefore be obtained. The curve reported in Figure 3 is, however, consistent with equal exponent values for the two components, taken as equal to 1, and to a Γ' value equal to 1.32, i.e. strongly synergistic (indicating good agreement between the theoretical curve and the experimental points).

This third type of curve observed in taste is, of course, not at all in agreement with Beidler's mixture equation and the equiratio model, since the dotted straight line corresponding to that model does not fit the experimental points, whereas the curve derived from the Γ' model fits them well.

New experimental data on sulfamate mixtures

Studies were carried out on three sets of binary mixtures: sodium 3-bromophenylsulfamate/sodium cyclohexylsulfamate (cyclamate); potassium cyclohexylsulfamate/sodium cyclohexylsulfamate; and sodium exo-2-norbornylsulfamate/sodium cyclohexylsulfamate.

These mixtures were chosen because they gave a wide range of relative sweetness (RS) values against 3% sucrose as standard and it was hoped the study of their mixtures would yield interesting results (see Drew *et al.*, 1998). The relative sweetness is defined, according to Paul (1921), as the ratio of concentrations, in mg/l, of sucrose solution and a compound equisweet with the sucrose solution. The RS values for the selected sulfamates are: sodium 3-bromophenylsulfamate, 11.2; sodium cyclohexylsulfamate, 39.8; potassium cyclohexylsulfamate, 40.2; and sodium exo-norbornylsulfamate, 70.5.

Methods

The previously published procedure (Frank *et al.*, 1989) was followed using a panel of eight tasters. All stimuli were made by combining solutes, not solutions. Stimuli for the binary mixtures and component solutions were chosen so as to approximately match the taste intensity of the sodium cyclohexylsulfamate at millimolar concentrations of 2.5, 4.5 and 7.5, respectively. This matching was accomplished during preliminary testing with each component. In addition, distilled water was also used as stimulus.

Panelists were asked to judge the sweetness of a number of stimuli on a 21 point category scale which was labeled as follows: 0, no taste; 5, weak; 10, medium; 15, strong; and 20, very strong. Prior to tasting, the panelists were presented with either three (binary mixtures) or four (self-mixtures) stimuli and were told that these stimuli encompassed the range of sweetness levels they would encounter. The test volume was set at 5 ml and tasters were required to sample the entire volume. Panelists were told to ignore all other sensations and just concentrate on the sweetness of the compounds.

Results

The experimental results and the calculations are summarized in Tables 1 and 2, respectively. A category scale can be considered as a logarithmic scale of the perceived intensity

Table 1 Self-mixtures of the four studied sulfamates in the three binary mixtures procedures (present study)

C_a	$\log C_a$	R_a	$\log R'_a$	C_a	$\log C_a$	R_a	$\log R'_a$	C_a	$\log C_a$	R_a	$\log R'_a$
3-Bromophenyl-				Potassium cyclohexyl-				Exo-2-norbornyl-			
11.00	1.04	10.00	0.40	5.20	0.72	5.00	0.20	2.50	0.40	6.00	0.24
18.00	1.26	11.00	0.44	7.20	0.86	11.00	0.44	3.10	0.49	12.00	0.48
25.50	1.41	13.00	0.52	10.25	1.01	15.00	0.60	4.85	0.69	16.00	0.64
25.00	1.40	12.00	0.48	9.20	0.96	13.00	0.52	3.70	0.57	12.00	0.48
32.50	1.51	15.00	0.60	12.25	1.09	16.00	0.64	5.45	0.74	16.00	0.64
40.00	1.60	16.00	0.64	15.30	1.18	17.00	0.68	7.20	0.86	19.00	0.76
$n = 0.44$				$n = 1.02$				$n = 1.04$			
$R^2 = 0.89$				$R^2 = 0.94$				$R^2 = 0.93$			
Sodium cyclohexyl-				Sodium cyclohexyl-				Sodium cyclohexyl-			
5.00	0.70	9.00	0.36	5.00	0.70	7.00	0.28	5.00	0.70	6.00	0.24
7.00	0.85	12.00	0.48	7.00	0.85	9.00	0.36	7.00	0.85	10.00	0.40
10.00	1.00	15.00	0.60	10.00	1.00	14.00	0.56	10.00	1.00	14.00	0.56
9.00	0.95	13.00	0.52	9.00	0.95	13.00	0.52	9.00	0.95	11.00	0.44
12.00	1.08	17.00	0.68	12.00	1.08	15.00	0.60	12.00	1.08	15.00	0.60
15.00	1.18	17.00	0.68	15.00	1.18	18.00	0.72	15.00	1.18	18.00	0.72
$n = 0.72$				$n = 0.94$				$n = 0.98$			
$R^2 = 0.95$				$R^2 = 0.98$				$R^2 = 0.97$			

C_a stands for millimolar concentrations, R_a for responses in a 21-point category scale and R'_a for transformed responses according to equation (4). Note that the first exponent (slope) n for sodium cyclohexyl- differs from the two others.

(Patte *et al.*, 1975). Therefore, the experimental responses for pure components and mixtures (termed, respectively, R_a, R_b and R_{ab}) were transformed into R' values, according to the equation:

$$\log R' = 0.04R \tag{4}$$

The regression equations applied to $\log R'$ values versus $\log C_a$ values provide power function exponents (slopes) n with satisfactory R^2 values, as can be seen in Table 1.

The main comment concerning the data in Table 2 is that, using the U model, the correlation coefficients between predicted and perceived sweetness of mixtures (R_{ab}) are rather satisfactory; furthermore, the averages of the ratios of predicted/experimental sweetness are also very close to 1. This rather good prediction is shown in Figure 4.

The second comment concerning Table 2 is that Γ' values are almost equal to 1 in each case (absence of intrinsic interaction). A slight negative value of $\cos \alpha_U$ for the first mixture and an almost zero value for the two other mixtures is also observed. This means that when data are considered in terms of perceived intensities, a slight hypoaddition occurs in the first case only—due to differences of power function exponents—and additivity is observed for the two other mixtures.

A possible further use of the data in Table 2 would be to draw equisweet curves, similar to those of Figures 1, 2 and 3 for data already published. However, it can be seen in Table 2, that the values of the standard deviations for Γ' are intermediate between those obtained by magnitude estimation and the equisweet procedure respectively. Thus, in this case there was poor agreement between the experimental points and the theoretical curves and therefore these are not shown.

General discussion

Classically, in studies of taste and olfactory mixtures, there are normally two theoretical references of additivity which can be considered in the analysis of experimental data: (i) additivity of relative concentrations (Beidler, 1971) in taste and generalized with the equiratio model; and (ii) additivity of perceived intensities (Berglund *et al.*, 1973) in olfaction.

In the first case, when additivity is not observed, the divergences will change with the proportions of the two components; i.e. the mutual interaction (synergism or suppression) cannot be characterized by a single index, preventing any generalization from a limited number of experiments. This difficulty is overcome by using the second method, which in turn allows us to come back to the first one with the use of the Γ' index.

In several studies (Frank *et al.*, 1989) a third way has been tried: additivity of responses using a category scale. This is not an appropriate method, since the responses obtained can be considered to be proportional to logarithmic values for the perceived intensities (Patte *et al.*, 1975). Here, therefore, a change of variable must to be made before applying tests for additivity. This procedure is applied in the present study to the new experimental data on sulfamate mixtures.

Regarding the present study, it can be concluded that U and Γ' models, previously applied in olfaction, can be satisfactorily applied in sweet taste also. The U model, from

Table 2 Results obtained for the three studied mixtures

C_a	C_b	R_a	R_b	R_{ab} ex.	R'_a	R'_b	R'_{ab} ex.	cos α_U	Γ'	R'_{ab} pred.	R_{ab} pred.
3-Bromophenyl-/sodium cyclohexyl- ($n_A = 0.44$; $n_B = 0.72$)											
5.50	2.50	3.00	3.00	9.00	1.32	1.32	2.29	−0.13	1.12	2.26	8.86
5.50	4.50	3.00	6.00	11.00	1.32	1.74	2.75	−0.10	1.14	2.63	10.48
5.50	7.50	3.00	11.00	13.00	1.32	2.75	3.31	−0.20	1.02	3.53	13.70
12.50	2.50	5.00	3.00	11.00	1.58	1.32	2.75	−0.05	1.20	2.49	9.92
12.50	4.50	5.00	6.00	12.00	1.58	1.74	3.02	−0.09	1.15	2.85	11.38
12.50	7.50	5.00	11.00	13.00	1.58	2.75	3.31	−0.25	0.98	3.75	14.34
20.00	2.50	10.00	3.00	12.00	2.51	1.32	3.02	−0.22	1.02	3.31	13.01
20.00	4.50	10.00	6.00	15.00	2.51	1.74	3.98	−0.06	1.18	3.66	14.08
20.00	7.50	10.00	11.00	16.00	2.51	2.75	4.37	−0.17	1.07	4.52	16.38
							Mean =	−0.14	1.10	Correl. =	0.94
							SD =	0.07	0.08	Mean pred/ex	1.00
Potassium cyclohexyl-/sodium cyclohexyl- ($n_A = 1.02$; $n_B = 0.94$)											
2.60	2.50	2.00	2.00	8.00	1.20	1.20	2.09	−0.13	0.88	2.47	9.81
4.60	2.50	5.00	2.00	10.00	1.58	1.20	2.51	−0.10	0.91	2.86	11.41
7.65	2.50	10.00	2.00	14.00	2.51	1.20	3.63	−0.02	0.98	3.81	14.51
2.60	4.50	2.00	5.00	10.00	1.20	1.58	2.51	−0.10	0.92	2.86	11.41
4.60	4.50	5.00	5.00	14.00	1.58	1.58	3.63	0.15	1.16	3.25	12.81
7.65	4.50	10.00	5.00	17.00	2.51	1.58	4.79	0.17	1.18	4.20	15.59
2.60	7.50	2.00	9.00	13.00	1.20	2.29	3.31	−0.05	0.97	3.58	13.85
4.60	7.50	5.00	9.00	17.00	1.58	2.29	4.79	0.24	1.26	3.98	14.99
7.65	7.50	10.00	9.00	18.00	2.51	2.29	5.25	0.09	1.10	4.93	17.32
							Mean =	0.03	1.04	Correl. =	0.96
							SD =	0.14	0.14	Mean pred/ex	1.03
Exo-2-norbornyl-/sodium cyclohexyl- ($n_A = 1.04$; $n_B = 0.98$)											
1.25	2.50	2.00	2.00	7.00	1.20	1.20	1.91	−0.21	0.79	2.43	9.63
1.25	4.50	2.00	4.00	10.00	1.20	1.45	2.51	−0.05	0.94	2.67	10.68
1.25	7.50	2.00	10.00	15.00	1.20	2.51	3.98	0.08	1.08	3.75	14.35
1.85	2.50	5.00	2.00	11.00	1.58	1.20	2.75	−0.01	0.98	2.81	11.24
1.85	4.50	5.00	4.00	13.00	1.58	1.45	3.31	0.09	1.08	3.06	12.15
1.85	7.50	5.00	10.00	16.00	1.58	2.51	4.37	0.07	1.06	4.14	15.42
3.60	2.50	10.00	2.00	14.00	2.51	1.20	3.63	−0.02	0.96	3.75	14.35
3.60	4.50	10.00	4.00	16.00	2.51	1.45	4.37	0.11	1.09	4.00	15.04
3.60	7.50	10.00	10.00	18.00	2.51	2.51	5.25	0.04	1.04	5.07	17.63
							Mean =	0.01	1.00	Correl. =	0.97
							SD =	0.10	0.10	Mean pred/ex	1.03

Γ' values are observed as almost equal to 1 (absence of intrinsic interaction). The predicted responses values R'_{ab} were calculated using the U model and then transformed into R_{ab} values using equation (4).

a limited number of experiments for a given binary sweet taste mixture, allows for the generalization of predicted perceived intensity values, irrespective of the experimental method (magnitude estimation, category scaling or equisweet procedure).

The principal usefulness of the Γ' model is that it can be used to draw equisweet theoretical curves from a limited number of experiments. In sweet taste, the curves produced for several levels of perceived intensity often appear to be superimposed (this superimposition is not observed in olfaction). Equisweet curves allow observation of interactions in terms of concentrations, instead of perceived intensities. Equisweet curves adopt shapes according to the phenomenon which is occurring: additivity, synergy, or synergy and partial suppression at the same time, according to the relative concentrations. Only the equisweet experimental procedure appears to be precise enough to verify the theoretical curves obtained. Neither the magnitude estimation nor category scaling procedures seem sufficiently accurate, even if the latter is the slightly better of the two.

Many published experimental studies cannot be tested comparatively with the U and Γ' models as presented here, usually due to an absence of tables reproducing the experimental data in full. That is the case, for example, with all the

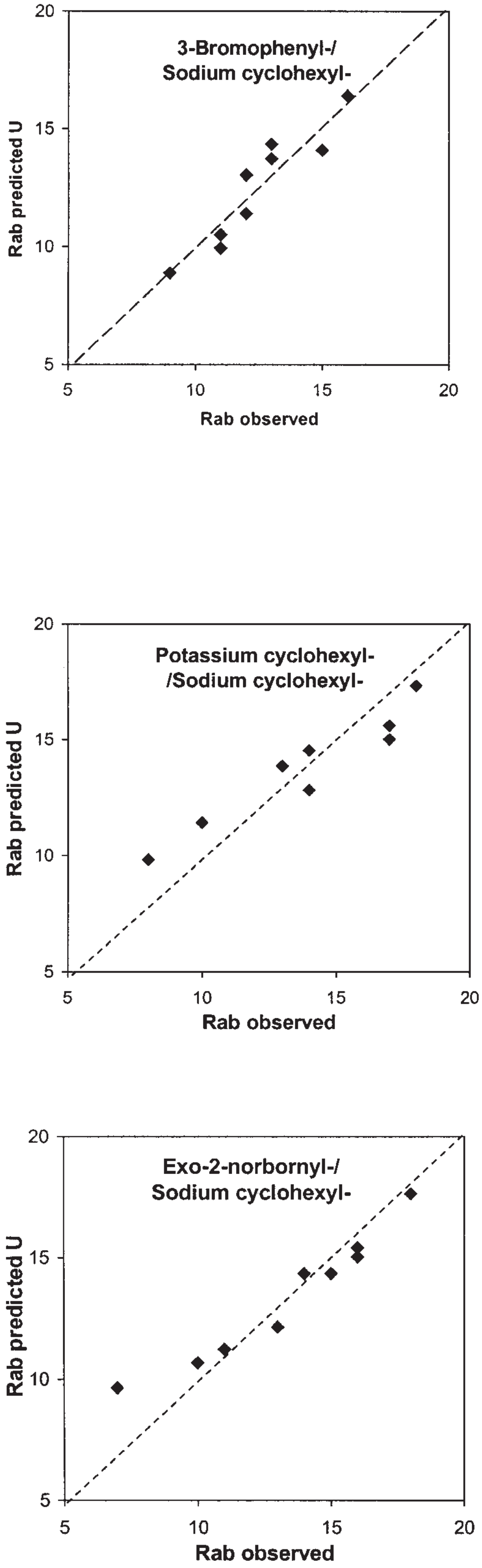

Figure 4 Correlograms between predicted and experimental sweetness (R_{ab}) for several mixtures of sulfamates, according to the data shown in Table 2.

binary mixtures of nine sweet taste compounds (Frank *et al.*, 1989) already quoted. Be that as it may, in Appendix C several examples are given in which the Γ' model is applied to published data on taste mixtures.

The sulfamate studies presented show that, in terms of perceived intensities, the mixtures of potassium cyclohexylsulfamate/sodium cyclohexylsulfamate and sodium exo-2-norbornylsulfamate/sodium cyclohexylsulfamate are almost additive, whatever the levels of perceived intensities and the relative concentrations. By contrast, the mixture of sodium 3-bromophenylsulfamate/sodium cyclohexylsulfamate presents a slight hypoaddition (slightly negative value of $\cos\alpha_U$).

Expressed in terms of concentration *S*, the experimental results on sulfamates give satisfactory equisweet curves for the potassium cyclohexyl/sodium cyclohexyl and sodium exo-2-norbornyl/sodium cyclohexyl mixtures (all the power function exponents being close to 1), but not for the sodium 3-bromophenyl/sodium cyclohexyl mixture.

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References

Beidler, L.M. (1971) *Taste-receptor stimulation with salts and acids*. In Beidler, L.M. (ed.), Handbook of Sensory Physiology IV/2, Taste. Springer, New York, pp. 200–220.

Berglund, B., **Berglund, U.**, **Engen, T.** and **Ekman, G.** (1973) *Multidimensional analysis of twenty-one odors*. Scand. J. Psychol., 14, 131–137.

Blanchard, J. (1976) *Relations between the odour of a gas and its mercaptan content*. Gas (Rome), 26, 287–309.

Borelli, F. and **Angleraud, O.** (1965) *Some practical investigations about odorizing. Smell intenseness of the various gases*. Gas (Rome), Suppl. 7–8.

Callegari, P. (1998) *Aspects conceptuels, expérimentaux et calculatoires de la qualité olfactive*. Thesis, University of Bourgogne, Dijon.

De Graaf, C. and **Frijters, J.E.R.** (1986) *A psychophysical investigation of Beidler's mixture equation*. Chem. Senses, 11, 295–314.

Drew, M.G.B, **Wilden, G.R.H.**, **Spillane, W.J.**, **Walsh, R.M.**, **Ryder, C.A.** and **Simmie, J.M.** (1998) *Quantitative structure–activity relationship studies of sulfamates $RNHSO_3Na$: distinction between sweet, sweet–bitter, and bitter molecules*. J. Agric. Food Chem., 46, 3016–3026.

Frank, R.A., **Mize, S.J.S.** and **Carter, R.** (1989) *An assessment of binary mixture interactions for nine sweeteners*. Chem. Senses, 14, 621–632.

Frijters, J.E.R. and **De Graaf., C.** (1987) *The equiratio taste mixture model successfully predicts the sensory response to the sweetness intensity of complex mixtures of sugars and sugar alcohols*. Perception, 5, 615–628.

Frijters, J.E.R. and **Oude Ophuis, P.A.M.** (1983) *The construction and prediction of psychophysical power functions for the sweetness of equiratio sugar mixtures*. Perception, 12, 753–767.

Frijters, J.E.R., De Graaf, C. and **Koolen, H.C.M.** (1984) *The validity of the equiratio taste mixture model investigated with sorbital–sucrose mixtures*. Chem. Senses, 9, 241–248.

Hyman, A.M. and **Frank, M.E.** (1980) *Effects of binary taste stimuli on the neural activity of the hamster chorda tympani*. J. Gen. Physiol., 76, 125–142.

Hyvönen, L., Kurkela, R., Koivistoinen, P. and **Ratilainen, A.** (1978) *Fructose–saccharin and xylitol–saccharin synergysm*. J. Food Sci., 43, 251–254.

Laffort, P. (1994) *The application of synergy and inhibition phenomena to odor reduction*. In Vigneron, S., Hermia, J. and Chaouki, J. (eds), Characterization and Control of Odors and VOC in the Process Industries. Elsevier, Amsterdam, pp. 105–117.

Laffort, P. and **Dravnieks, A.** (1982) *Several models of supra-threshold quantitative olfactory interaction in humans applied to binary, ternary and quaternary mixtures*. Chem. Senses, 7, 153–174.

Laffort, P., Etcheto, M., Patte, F. and **Marfaing, P.** (1989) *Implications of power law exponent in synergy and inhibition of olfactory mixtures*. Chem. Senses, 14, 11–23.

McBride, R.L. (1989) *Three models for taste mixtures.* In Laing, D.G., Cain, W.S., McBride, R.L. and Ache, B.W. (eds), Perception of Complex Smells and Tastes. Academic Press, Sydney, pp. 265–282.

Nahon, D.F., Roozen, J.P. and **De Graaf, C.** (1998) *Sensory evaluation of mixtures of sodium cyclamate, sucrose and an orange aroma*. J. Agric. Food Chem., 46, 3426–3430.

Patte, F. and **Laffort, P.** (1979) *An alternative model of olfactory quantitative interaction in binary mixtures*. Chem. Senses Flavor, 4, 267–274.

Patte, F., Etcheto, M. and **Laffort, P.** (1975) *Selected and standardized values of suprathreshold odor intensities for 110 substances*. Chem. Senses Flavor, 1, 283–305.

Paul, T. (1921) *Physikalische Chemie der Lebensmittel: V. Der Sussungrade der Susstoffe*. Z. Elektrochem., 27, 539–546.

Sales, M. (1958) *Odour and odorization of gases.* In Seventh International Conference on Gases, Rome. 36.

Schiet, F.T. and **Frijters, J.E.R.** (1988) *An investigation of the equiratio-mixture model in olfactory psychophysics: a case study*. Percept. Psychophys., 44, 643–653.

Schifferstein, H.N.J. (1995) *Prediction of sweetness intensity for equiratio aspartame/sucrose mixtures*. Chem. Senses, 20, 211–219.

Schifferstein, H.N.J. (1996) *An equiratio mixture model for non-additive components: a case study for aspartame/acesulfame-K mixtures.* Chem. Senses, 21, 1–11.

Schifferstein, H.N.J. (1997) *Perceptual and imaginary mixtures in chemosensation*. J. Exp. Psychol., 23, 278–288.

Schifferstein, H.N.J. and **Frijters, J.E.R.** (1990) *Sensory integration in citric acid/sucrose mixtures*. Chem. Senses, 15, 87–109.

Schifferstein, H.N.J. and **Kleykers, R.W.G.** (1996) *An empirical test of Olsson's interaction model using mixtures of tastants.* Chem. Senses, 21, 283–291.

Seree, N. and **Laffort, P.** (1997) *Fitting comparison of the Γ (gamma) and Γ-vector models applied to experimental data in olfactory, gustatory and pharmacological mixtures*. Chem. Senses, 22, 221–222.

Täufel, K. and **Klemm, B.** (1925) *Untersuchungen über natürliche und künstliche Süßstoffe. I. Studien über den Süßungsgrad von Saccharin und Dulcin*. Z. Untersuchung Nahr. Genussmittel., 50, 264–273.

Thomas-Danguin, T. and **Laffort, P.** (1998) *The Γ′ model applied to sweet and other taste mixtures*. TOSTQ Workshop, Wageningen, 11 December.

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Appendix A

Relations between the substitution, equiratio and Γ′ models

This clarification is drawn from previous work (Laffort *et al.*, 1989; Laffort, 1994).

The substitution model

The mixture discrimination index (MDI), also called the substitution model, is defined according to Hyman and Frank (Hyman and Frank, 1980), as follows:

$$\mathrm{MDI} = \frac{R_{\mathrm{AB}}}{R'}$$

in which R' is 'the response to either component at a concentration equal to the sum of two concentrations of one chemical, equivalent in effect to the components of the mixture'.

Applying the power function, $R = (C/C_0)^n$, to the above definition, two equations result: the first expression of R'

$$R' = \left(R_{\mathrm{A}}^{1/n_{\mathrm{A}}} + R_{\mathrm{A}}^{1/n_{\mathrm{A}}} \right)^{n_{\mathrm{A}}}$$

and the second expression of R'

$$R' = \left(R_{\mathrm{B}}^{1/n_{\mathrm{B}}} + R_{\mathrm{B}}^{1/n_{\mathrm{B}}} \right)^{n_{\mathrm{B}}}$$

These two equations are only equivalent when the exponents for the two components are the same. That is a restrictive view of the reality (even in taste, but perhaps less dramatically than in olfaction). No rule is suggested when the exponents differ, but one could make an arithmetic mean of the two values of R'. In the particular case where the two exponents are the same, it can be easily demonstrated that MDI is equivalent to the first expression in the Γ family indices (called Γ, not Γ′) for equally strong components. By contrast, no equivalence is found between MDI and the Γ′ index currently used and judged more suitable.

Therefore, from the initial definitions, we have:

$$\mathrm{MDI} = \frac{R_{\mathrm{AB}}}{R'} = \frac{R_{\mathrm{A}} + R_{\mathrm{B}} + 2\cos\alpha_{\mathrm{U}}\sqrt{R_{\mathrm{A}}R_{\mathrm{B}}}}{\left(R_{\mathrm{A}}^{1/n} + R_{\mathrm{B}}^{1/n} \right)^{n}}$$

If $R_{\mathrm{A}} = R_{\mathrm{B}}$, the relation becomes:

$$\mathrm{MDI} = \frac{2R_{\mathrm{A}} + 2\cos\alpha_{\mathrm{U}}\sqrt{R_{\mathrm{A}}^{2}}}{\left(2R_{\mathrm{A}}^{1/n} \right)^{n}} = \frac{2 + 2\cos\alpha_{\mathrm{U}}}{2^{n}} = 2^{1-n}\left(1 + \cos\alpha_{\mathrm{U}}\right)$$

Similarly, from the first definition of the Γ index, in the particular case where $n_A = n_B$ and where $R_A = R_B$, i.e. they are equally strong components in the mixture, we have:

$$\Gamma = \frac{1+\cos\alpha_U}{1+\cos\alpha_{UPL2}} = \frac{1+\cos\alpha_U}{\left[1+\dfrac{1-\left(\frac{1}{2}\right)^n-\left(\frac{1}{2}\right)^n}{2\left(\frac{1}{2}\right)^{n/2}\left(\frac{1}{2}\right)^{n/2}}\right]} = \frac{1+\cos\alpha_U}{\left[1+\dfrac{1-\frac{2}{2^n}}{\frac{2}{2^n}}\right]}$$

$$= 2^{1-n}(1+\cos\alpha_U)$$

This relation is equivalent to that found for MDI, but once again, only under the two stated conditions: $n_A = n_B$ and $R_A = R_B$.

The equiratio model

This model (Frijters and Ooude Ophuis, 1983) was proposed for the study of taste mixtures. Even if the name was new, the method had been proposed previously (Sales, 1958) for odorous mixtures and used in the gas industry over a period of many years (Borelli and Angleraud, 1965; Blanchard, 1976).

The principle of the equiratio model is quite simple: the concentration–response straight line in log–log coordinates for a series of dilutions of a mixture is expected to lie between the straight lines corresponding to the components of the mixture, based on the ratio of the mixture's components. Angleraud (personal communication, 1968) and later Blanchard (Blanchard, 1976) demonstrated that this assumption was not experimentally verifiable. The non-applicability of this model to olfaction has been confirmed (Schiet and Frijters, 1988).

By contrast, the model has been successfully applied in studies of sweet taste mixtures (Frijters *et al.*, 1984; De Graaf and Frijters, 1986; Frijters and De Graaf, 1987).

In the particular case where the values of the exponents are very similar and near to 1, the equiratio model for iso-intensity mixtures (equisweet for sweet taste) is simplified as follows:

$$1 = \frac{C_A}{C^\circ_A} + \frac{C_B}{C^\circ_B}$$

which is equation (9) in De Graaf and Frijters (De Graaf and Frijters, 1986). The graphic expression of the equation is shown by the dotted line in Figures 1, 2 and 3.

Similarly, in that particular case the Γ′ model is also very simplified:

$$\cos\alpha_A = \cos\alpha_B = \frac{1-P-(1-P)}{2P(1-P)} = 0$$

which is derived from equations (3).

Therefore, cos α_{UPL2} also equals zero and the Γ′ index becomes:

$$\Gamma' = 1 + \cos\alpha_U$$

from equation (2).

On the other hand, we have:

$$\cos\alpha_U = \frac{R_{AB} - \dfrac{C_A}{C^\circ_A} - \dfrac{C_B}{C^\circ_B}}{2\sqrt{\dfrac{C_A}{C^\circ_A}\times\dfrac{C_B}{C^\circ_B}}}$$

from equation (1).

For iso-intensity mixtures, this becomes:

$$\cos\alpha_U = \frac{1 - \dfrac{C_A}{C^\circ_A} - \dfrac{C_B}{C^\circ_B}}{2\sqrt{\dfrac{C_A}{C^\circ_A}\times\dfrac{C_B}{C^\circ_B}}}$$

and

$$\Gamma' = 1 + \cos\alpha_U = 1 + \frac{1 - \dfrac{C_A}{C^\circ_A} - \dfrac{C_B}{C^\circ_B}}{2\sqrt{\dfrac{C_A}{C^\circ_A}\times\dfrac{C_B}{C^\circ_B}}}$$

When equation (9) of De Graaf and Frijters (De Graaf and Frijters, 1986) is verified, Γ′ = 1 (numerator equal to zero in the above equation) and it becomes possible for the equiratio model to be successfully applied. In all other cases, the Γ′ index value may provide an estimation of the divergence between the equiratio model and the experimental results (the case shown in Figure 3). Once again, the comparisons are only possible when $n_A = n_B = 1$.

Appendix B

Mathematical proof of relation (3)

This demonstration is from Callegari (Callegari, 1998).

The aim of the Γ family models is to separate what is due to the interaction itself and what is due to characteristics of the components. For this purpose, the power function is considered to be effective in the range of studied concentrations, i.e. a straight line in log–log coordinates. [When that fact is not experimentally verified, it is just necessary to make a change of variables until one obtains a straight line in log–log coordinates. Once the calculations with the U and Γ′ models are done, a reverse change of variables allows one to obtain calculated data to be compared with the original data. Such a procedure was followed in the present work for the reported calculations on sulfamates.] The challenge is to transform exponential expressions into multiplicative coefficients.

We start with the definition of the power function for a given compound A, at two concentrations A and A′. We have:

$$R_A = \left(\frac{C_A}{C^\circ_A}\right)^{n_A}$$

and

$$R'_A = \left(\frac{C'_A}{C^\circ_A}\right)^{n_A}$$

There is necessarily a multiplicative factor linking R_A and R'_A. We define:

$$R'_A = \beta^{n_A} R_A$$

Expressed in concentrations, this expression becomes:

$$R'_{\mathrm{A}} = \left(\frac{C'_{\mathrm{A}}}{C^{\circ}_{\mathrm{A}}}\right)^{n_{\mathrm{A}}} = \beta^{n_{\mathrm{A}}}\left(\frac{C'_{\mathrm{A}}}{C^{\circ}_{\mathrm{A}}}\right)^{n_{\mathrm{A}}} = \left(\beta\frac{C_{\mathrm{A}}}{C^{\circ}_{\mathrm{A}}}\right)^{n_{\mathrm{A}}}$$

The perceived intensity $R_{\mathrm{AA'}}$ can be expressed as a function of the concentrations:

$$R_{\mathrm{AA'}} = \left(\frac{C_{\mathrm{A}}}{C^{\circ}_{\mathrm{A}}}+\frac{C'_{\mathrm{A}}}{C^{\circ}_{\mathrm{A}}}\right)^{n_{\mathrm{A}}} = \left(\frac{C_{\mathrm{A}}}{C^{\circ}_{\mathrm{A}}}+\beta\frac{C_{\mathrm{A}}}{C^{\circ}_{\mathrm{A}}}\right)^{n_{\mathrm{A}}} = \left[\left(\frac{C_{\mathrm{A}}}{C^{\circ}_{\mathrm{A}}}\right)(1+\beta)\right]^{n_{\mathrm{A}}}$$

$$= R_{\mathrm{A}}(1+\beta)^{n_{\mathrm{A}}}$$

From the U model [equation (1)], we have:

$$R_{\mathrm{AA'}} = R_{\mathrm{A}} + R_{\mathrm{A'}} + 2\cos\alpha_{\mathrm{A}}\sqrt{R_{\mathrm{A}}R_{\mathrm{A'}}}$$

$$= R_{\mathrm{A}} + \beta^{n_{\mathrm{A}}}R_{\mathrm{A}} + 2\cos\alpha_{\mathrm{A}}\sqrt{R_{\mathrm{A}}R_{\mathrm{A'}}}$$

By identification of the two above equations, it becomes:

$$(1+\beta)^{n_{\mathrm{A}}} = 1+\beta^{n_{\mathrm{A}}} + 2\cos\alpha_{\mathrm{A}}\sqrt{\beta^{n_{\mathrm{A}}}}$$

and therefore:

$$\cos\alpha_{\mathrm{A}} = \frac{(1+\beta)^{n_{\mathrm{A}}} - 1 - \beta^{n_{\mathrm{A}}}}{2\beta^{n_{\mathrm{A}}/2}}$$

In other respects, for an addition of an odorant to itself, we have from the definition of P:

$$P = \frac{R'^{1/n_{\mathrm{A}}}_{\mathrm{A}}}{R_{\mathrm{A}}^{1/n_{\mathrm{A}}} + R'^{1/n_{\mathrm{A}}}_{\mathrm{A}}} = \frac{\beta R_{\mathrm{A}}^{1/n_{\mathrm{A}}}}{R_{\mathrm{A}}^{1/n_{\mathrm{A}}} + \beta R_{\mathrm{A}}^{1/n_{\mathrm{A}}}} = \frac{\beta}{1+\beta}$$

or

$$\beta = \frac{P}{1-P}$$

Therefore we have:

$$\cos\alpha_{\mathrm{A}} = \frac{\left(1+\dfrac{P}{1-P}\right)^{n_{\mathrm{A}}} - 1 - \left(\dfrac{P}{1-P}\right)^{n_{\mathrm{A}}}}{2\left(\dfrac{P}{1-P}\right)^{n_{\mathrm{A}}/2}} = \frac{1-P^{n_{\mathrm{A}}}-(1-P)^{n_{\mathrm{A}}}}{2P^{n_{\mathrm{A}}/2}(1-P)^{n_{\mathrm{A}}/2}}$$

This expression is the first step in the chain of equations (3). The second step is the analogous one for the component B and the third step is a simple rule of proportionality.

Appendix C

Applications of the Γ′ model to additional published data on binary sweet taste mixtures

The aim of global models such as the U and the vector models is to characterize binary olfactory or taste mixtures with a single index, in order to extend (predict) the perceived intensity of mixtures at any concentrations from a limited number of experimental data. To be valid, the models must present indices of interaction as constant as possible (low value of standard deviation). In previous work we have demonstrated that the scattering of cos α is smaller by using the U model in place of the vector model (Laffort and Dravnieks, 1982) and also smaller than that obtained when using an alternative model called the V model (Patte and Laffort, 1979). We have pursued the same goal with the so-called Γ family models. Here, the respective contributions of the intrinsic interaction of the mixture on the one hand and of the power function exponents of the components on the other are separated. As shown previously (Seree and Laffort, 1996; Thomas-Danguin and Laffort, 1998), the so-called Γ'-vector model is not at all suitable. Note that equation (2) for the Γ′-vector model is similar to that for the Γ′ model, with $\cos\alpha_{\mathrm{VECT}}$ instead of $\cos\alpha_{\mathrm{U}}$ and $\cos\alpha_{\mathrm{VCPL}}$ instead of $\cos\alpha_{\mathrm{UPL2}}$. The chain of equations (3) for $\cos\alpha_{\mathrm{VCPL}}$ is similar to that for $\cos\alpha_{\mathrm{UPL2}}$, with the definition of $\cos\alpha_{\mathrm{A}}$ and $\cos\alpha_{\mathrm{B}}$ being:

$$\cos\alpha_{\mathrm{A}} = \frac{1-P^{2n_{\mathrm{A}}}(1-P)^{2n_{\mathrm{A}}}}{2P^{2n_{\mathrm{A}}/2}(1-P)^{2n_{\mathrm{A}}/2}}$$

$$\cos\alpha_{\mathrm{B}} = \frac{1-P^{2n_{\mathrm{B}}}(1-P)^{2n_{\mathrm{B}}}}{2P^{2n_{\mathrm{B}}/2}(1-P)^{2n_{\mathrm{B}}/2}}$$

By contrast, the Γ′ model is suitable and also it is slightly better than the original Γ model.

Once the more appropriate model is developed, its suitability can be tested and assessed on the basis of the standard deviation of its index of interaction, in this case the Γ′ index.

The sweet mixture aspartame–acesulfame-K has been studied (Schifferstein, 1996) by applying magnitude estimation. The results show exponent values equal to 0.994 for aspartame and 1.095 for acesulfame-K, with a strong synergistic Γ′ value: 1.72 ($\Gamma' > 1$, corresponding to a synergy and $\Gamma' < 1$ to a suppression). Unfortunately, the value for the standard deviation of Γ′ is high (0.78). This standard deviation value, greater than that found for the sucrose/aspartame mixture reported in Figure 2 (Schifferstein, 1995) does not allow reasonable predictions. Furthermore, it seems to confirm that magnitude estimation may not be a suitable tool for the study of sweet taste mixtures. This is surprising since, for example, for overall intensity estimations of sucrose/citric acid mixtures, also using magnitude estimation, a relatively constant suppression Γ′ index value has been observed by several authors, with low standard deviations and not too great a difference from that obtained with other techniques (difference estimation procedure or 150 mm line scale): by magnitude estimation, $\Gamma' = 0.82 \pm 0.11$ (McBride, 1989) and 0.73 ± 0.05 (Schifferstein and Kleykers, 1996); by a difference estimation procedure, $\Gamma' = 0.81 \pm 0.03$ (Schifferstein and Frijters, 1990); and by a 150 mm line scale, $\Gamma' = 0.83 \pm 0.11$ (Schifferstein, 1997).

The sweet taste mixtures fructose/saccharin and xylitol/saccharin have been studied (Hyvönen *et al.*, 1978) by successively applied magnitude estimation, paired comparison and the triangle test. According to the authors, the power function exponents are supposed to be equal to 1 for these three compounds. Under these conditions the Γ′ indices obtained are 1.53 ± 0.08 for fructose/saccharin and 1.53 ± 0.14 for xylitol/saccharin.

The scattering for Γ′ is comparable to that obtained with the data reported in Figure 1 and Table 2. The equisweet diagram would be analogous to that shown in Figure 3 and in that case it is clear that the equiratio model would not be suitable either. It should be noted that the authors studied these mixtures at three different temperatures (5, 23 and 50°C) and that they found that temperature had a slight influence on the observed synergy. By separating the three temperatures, slightly different Γ' values are observed, with reduced values of the standard deviations (the mean Γ' value is almost equal to that at 23°C).

The sweet taste mixture saccharin/dulcin has been studied (Täufel and Klemm, 1925) by using an equisweet procedure with sucrose. According to the experimental data of the authors, the power function exponents are 0.578 for saccharin and 0.464 for dulcin. On the basis of these exponents, the saccharin/dulcin Γ' value is $\Gamma' = 1.16 \pm 0.04$.

These results for the saccharin/dulcin mixture also generates an equisweet diagram comparable to that of Figure 3, but with experimental points only in the zone of relative concentrations: 10% of dulcin and 50–70% of saccharin.