Ratio scales of acid sourness

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Experiments were conducted to assess the relation between concentration, or pH, and the perceived sourness of 24 acids. The psychophysical functions for sourness conform to the power relation $S = kC^n$ which relates sensory intensity, S, to physical concentration. C. Averaged across the 24 acids, the exponent for sourness was 0.85 for both molar and percentage concentrations, and about -1.70 for pH concentration. The intercept, k, which is a measure of relative sourness, differed across acids. The particular measure used to designate the concentration of an acid markedly influenced its magnitude and rank order of sourness.

The measurement of sourness is an attractive problem in taste psychophysics because sourness is the only primary taste quality for which a necessary chemical stimulus has been established, namely the H + ion. The number of such ions in solution is not sufficient, however, to predict sourness (Harvey, 1920).

A number of studies have appeared that attempted to evaluate how factors other than the H+ion affect the perceived intensity of the sour taste. For example, Becker and Herzog (1907) showed that the normality of acids, the number of functional H + ions per molecule, did not predict sourness since acids were not equally sour at equal normalities. For equal normalities, their rank ordering of sourness, from high to low, was HCl, HNO3, lactic, acetic, and butyric acids. Paul (1922) reported that acids matched for sourness differed both in molar concentration and in the number of free H + ions. In a review of the early work on sourness, Taylor (1928) suggested that the ability of an acid to penetrate living tissue was also an important variable that contributed to the degree of acid sourness. Beatty and Cragg (1935) argued that sourness could be measured by the "objective" technique of determining the amount of buffer required to bring the pH of selected acids to a preset pH value. They chose acids that matched the sourness of a reference level of HCl, performed the titrations, and reported estimates of relative sourness.

Psychophysical scales of sourness have been reported by Corin (1888), Paul (1922), and Pangborn (1963). Corin used category scales to determine whether acids initially matched for sourness were equally sour after equivalent dilutions were made. His results suggest that the equivalent dilutions did not produce equal decreases in apparent sourness, Paul and Pangborn described equal-sourness contours across several organic acids, analogous to the

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equal-loudness contours measured in audition. A replot of their sourness

matches in log-log coordinates reveals that the relative growth functions of the different acids may be power functions. Similar direct matches between the sweetness of sugars (Cameron, 1947) also produced equal-sweetness functions that appear as straight lines in log-log coordinates (see Fig. 6).

The direct psychophysical scaling of sourness was undertaken by Beebe-Center and his students, and a standard scale of sourness was proposed (Beebe-Center, 1949; Beebe-Center & Waddell, 1948). Using a "fractionation" procedure, they determined concentrations of tartaric acid that were judged half as sour as a set of standard concentrations. In presenting

Table 1 Stimulus Concentrations

		Sti	mulus Co	ncentratio	ns				
	Acid Molar and pH Concentrations								
	(Molecular Weight)		1	2	3	4	5	6	
Gr	oup A: Saturated Acids								
1.	Lactic (90)	M = pH =	.003 3.6	.006 3.4	.01 25 3. 2	.025 3.0	.05 2.9	.1 2.7	
2.	Tartronic (120)	M = pH =	.003 2.9	.006 2.8	.01 25 2.6	.025 2.5	.05 2.3	.1 2.1	
3.	DL Malic (134)	M = pH =	.003 3.3	.006 3.1	.01 25 3.0	.025 2.8	.05 2.7	.1 2.6	
4.	L Malic (134)	M = pH =	.003 3.4	.006 3.2	.0125 3.0	.025 2.9	.05 2.8	.1 2.6	
5.	Tartaric (150)	M = pH =	.003 3.2	.006 3.0	.01 25 2.7	.025 2.5	.05 2.4	2.4	
6.	Dihydroxy Tartaric (182)	M = pH =	.003 3.1	.006 2.8	.0125 2.6	.025 2.4	.05 2.2	.1 2.1	
7.	Citric (192)	M = pH =	.003 3.3	.006 3.1	.01 25 3.0	.025 2.9	.05 2.7	.1 2.5	
8.	Succinic (118)	M = pH =	.003 3.7	.006 3.6	.0125 3.4	.025 3.3	.05 3.1	.1 2.9	
9.	L Glutamic (147)	M = pH =	.003 3.6	.006 3.5	.0125 3.4	.025 3.4			
10.	N Acetyl L Glutamic (189)	M = pH =	.003 3.3	.006 3.1	.01 2 5 2.9	.025 2.8	.05 2.7	.1 2.5	
11.	Glutaric (132)	M = pH =	.0015 3.9	.003 3.7					
12.	3,3 Dimethyl Glutaric (160)	M = pH =	.003 3.2	.006 3.1	.01 25 3.0	.025 2.9	.05 2.8	.1 2.7	
Gı	roup B: Sugar Derived Acid	8							
13.	Ribonolactone (148)	M = pH =	.05 3.7	.1 3.6	.2 3.4	.4 3.3	.8 3.1		
14.	Glucono Δ Lactone (178)	M = pH =	.025 3.0	.05 2.8	2.7	.2 2.6	.4 2.4	.8 2.3	
15.	Galactono Δ Lactone (178)	M = pH =	.025 3.4	.05 3.4	.1 3.3	.2 3.2	.4 3.0	.8 2.8	
16.	Galactouronic (194)	M = pH =	.025 2.9	.05 2.7	.1 2.6	.2 2.5	.4 2.3	.8 2.2	
17.	Phytic (660)	M = pH =	.003 2.5	.006 2.3	.0125 2.0	.025 1.8	.05 1.7	.1 1.5	
Gı	roup C: Ascorbic								
18.	D Ascorbic (176)	M = pH =	.00625 3.4	.01 25 3.3	.025 3.2	.05 3.0	.1 2.9		
19.	L Ascorbic (176)	M = pH =	.00625 3.5	.0125 3.3	.025 3.2	.05 3.0	.1 2.8		
Gı	roup D: Unsaturated Acids								
20.	Sorbic (112)	M = pH =	.003125 3.9	.006 25 3.7	.0125 3.5				
21.	Fumaric (116)	M = pH =	.00625 3.0	.01 25 2.8	.025 2.7				
22 .	Levulinic (116)	M = pH =	.003125 3.8	.006 2 5 3.7	.0125 3.6	.025 3.4	.05 3.3	.1 3.1	
23.	Itaconic (130)	M = pH =	.003 3.4	.006 3.3	.01 25 3.1	.025 3.0	.05 2.9	.1 2.7	
24.	Trimellitic (210)	M = pH =	.0015 3.2	.002 3.0	.006 2.8	.0125 2.6	.025 2.5	.05 2.3	

Table 2
Parameters of the Power Relation (S = KCN) Between Sourness and (a) Molarity,
(b) Percentage Concentration, and (c) pH

	Least	Squares (a	Least Squares (c)		
Acid	Exponent N	Molar Intercept K	Percentage Intercept K	pH Exponent N	pH Intercept K
1. Lactic	0.84	165.2	26.1	-1.46	5.31
2. Tartronic	0.85	360.4	43.6	-1.56	5.01
3. DL Malic	0.77	263.4	35.7	-1.62	5.81
4. L Malic	0.72	204.1	31.5	-1.40	5.24
5. Tartaric	0.82	274.0	29.7	-1.32	4.58
6. Dihydroxy Tartaric	0.81	370.2	35.3	-1.18	4.16
7. Citric	0.72	201.0	23.9	-1.39	5.09
8. Succinic	0.76	199.4	30.5	-1.39	5.62
9. Glutamic	0.71	51.5	7.6	-2.87	10.43
10. N Acetyl L Glutami	c 0.55	24.1	4.8	-1.10	3.65
11. Glutaric	1.59	114.0	.19	-2.53	9.51
12. 3,3 Dimethyl Glutar	ric 0.94	536 O	39.6	-2.84	9.45
13. Ribonolactone	1.21	53.0	2.0	-2.38	9.01
14. Glucono Lactone	0.64	86.1	13.6	-1.40	5.08
15. Galactono Lactone	0.82	30.2	2.8	-1.90	6.81
16. Galactouronic	0.69	128.2	16.6	-1.52	5.36
17. Phytic	0.78	134.7	51.3	-1.23	4.13
18. D Ascorbic	0.91	171.8	12.6	-1.55	5.69
19. L Ascorbic	0.94	262.9	17.7	-2.16	7.73
20. Sorbic	0.84	179.6	23.6	-1.27	5.08
21. Fumaric	0.86	400.9	48.7	-1.64	5.60
22. Levulinic	0.73	114.4	19.1	-1.60	6.20
23. Itaconic	1.03	706.0	50.3	-2.25	7.94
24. Trimellitic	0.93	538.1	31.7	-1.59	5.17

evidence for his power law, Stevens (1957) noted that the functions generated by the fractionation procedure approximated power functions. In particular, when plotted in log-log coordinates, the relation between scale value and molar concentration of tartaric acid was a straight line with slope (exponent) of approximately 1.0. Other studies using direct magnitude estimation of sensory magnitude, in which the O adjusts numbers to match taste intensity, have produced different exponents, from low values around 0.5 (Feallock, 1965, with HCl: Kocher & Fisher, 1969, with citric acid) to higher values around 0.9 (Meiselman, 1968, with HCl) and 1.0 (Moskowitz, 1968, with tartaric acid).

The present study was undertaken to assess the relationship between perceived sourness and concentration, or pH for 24 different acids. Most of the acids were carbohydrate derivatives, although several other organic acids were evaluated as well.

PROCEDURE

All of the acids used were reagent-grade (Fisher Chemical Corp., Nutritional Biochemicals Corp., Sigma Chemical Corp., or Eastman Organic Chemicals), and solutions were prepared from distilled and deionized water of pH 6.9-7.1. Each series of stimuli for an acid conformed to a geometric sequence of molar concentrations, with a ratio of 2:1 between successive concentrations. Table 1 presents the acids tested, with concentration expressed in molarity and pH (pH measured with a Photovolt digital pH meter).

In each of four experiments, 12 Os were given a series of 40-48 acid concentrations, comprising several series of different acids. The acids were presented in irregular order, and the O was instructed to taste the sample, write down his magnitude estimate of sourness, expectorate, and rinse with water. Each O participated in two sessions each day, once in the morning and once in the afternoon. No initial numerical modulus was assigned by the E, and the standard was whatever solution in the series was first chosen by the O. Other than the interstimulus rinse, the O was not constrained to follow any time pattern in sampling the stimuli. The Os were enlisted men at the U.S. Army Natick Laboratories, who were test volunteers.

The detailed instructions and the method of analysis have been presented previously (Moskowitz, 1970a, b). In brief,

the Os were instructed to assign numbers in proportion to apparent sourness. The number matches across all sessions were normalized through the inclusion of six standard solutions of citric acid in each session. The procedure of modulus normalization (Moskowitz, 1970a) was used to bring the absolute magnitudes of the judgments of each O into agreement with a preset level, without, however, altering the ratios of his magnitude estimates.

RESULTS

The numerical matches to sourness were analyzed with the concentration expressed as molarity, percentage-by-weight, and pH. Molarity and percentage assess the overall amount of acid in solution, whereas pH is a logarithmic function of the number of H+ions in solution. For the same set of concentrations of a single acid, molarity and percentage may be related by a multiplicative constant, whereas pH must be independently measured.

Table 2 presents the relations obtained between sourness and three measures of concentration. The power function $S = kC^n$ relating sourness S to concentration C was assumed adequate to represent the sourness function. Both exponent (slope) n and intercept k were calculated by a least-squares procedure after the judgments had been converted to logarithms. The corresponding sourness functions, plotted relative to molarity, are presented in Figs. 1-4. The coordinates are log-log and the straight lines represent power functions whose exponents are given by the slopes of the lines. The mean exponent for sourness as a function of molarity and percentage is approximately 0.85, suggesting that sourness grows as a negatively accelerating function of concentration.

The relation between pH and log sourness is also linear, but the mean slope

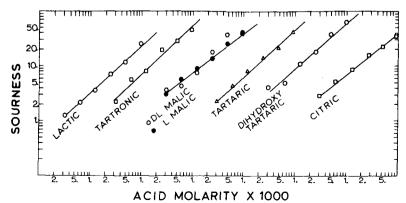


Fig. 1. The relation between sourness and molarity for seven saturated acids. The coordinates are log-log, so that straight lines represent power functions.

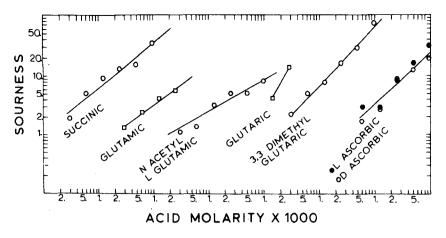


Fig. 2. Sourness functions for seven additional saturated acids. The coordinates are log-log. The ordinate values for glutaric acid have been shifted upward by one log unit.

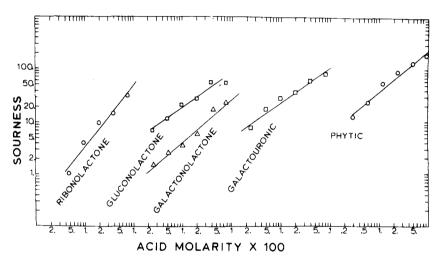


Fig. 3. Sourness functions for acids derived from sugars. The coordinates are log-log.

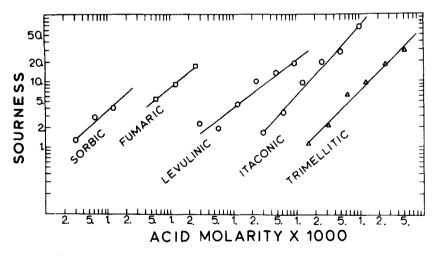


Fig. 4. Sourness functions for unsaturated acids. The coordinates are log-log.

is about -1.70, suggesting that apparent sourness grows as an accelerating function of the concentration of the H + ion (high pH indicates low concentrations of H + ion, and vice versa). The mathematical transformation from overall concentration

to that of the H+ion decreases the effective range of concentration (abscissa). Therefore, the psychological range of sourness, which remains unchanged through the transformation, must fit a smaller range of concentrations. Hence the exponent for sourness must increase. Accelerating functions for taste intensity have already been reported for sweetness relative to the molarity of sugar, and saltiness relative to the molarity of NaCl (Moskowitz, 1968, 1970a, b; Stevens, 1969). In each case, the exponent was between 1.3 and 1.6.

RELATIVE SOURNESS OF ACIDS

The intercept k of the power function relating sourness to concentration may be used as a measure of relative sourness across acids. Table 2 lists the numerical values of the intercepts of the 24 sourness functions when concentration is expressed as molarity, percentage, or pH. These values relative to a standard acid (here citric acid) represent relative magnitudes of sourness at 1 molar, 1%, or pH of 0. Because the various sourness functions are diverging lines in log-log coordinates, their logarithmic distances, which represent ratios of sourness, change continuously across concentration, and therefore the values in Table 2 pertain only to the concentrations given by the intercept.

In a previous study (Moskowitz, 1970a), the exponent for sugar sweetness was fixed at a representative value for 15 sugars, and therefore the sweetness functions of the various sugars became parallel lines in log-log coordinates. As a result, the distance separating the functions was constant, and therefore across the entire continuum of concentration only one number was needed to characterize relative sweetness. In this study a similar analysis was made; the sourness exponent was fixed at 0.7 (for molarity and percentage), or -1.4 for pH. These two exponents are rounded averages for the exponents of the citric acid standard used in all the sourness tests. Figure 5 shows the logarithms of the relative values (citric acid = 0.0) of the intercepts for the 24 acid functions obtained with the three measures of concentration. The single number for each measure suffices to characterize relative sourness across different concentrations.

A number of relations between molecular structure and relative sourness may be obtained from Fig. 5:

(1) When pH is used as the measure of concentration, acids having lower molecular weight appear to be the more sour. There is no consistent relation, however, between molecular weight and relative sourness when the measure of

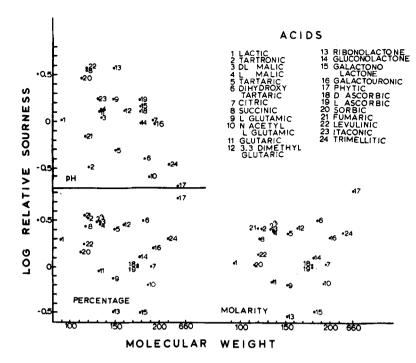


Fig. 5. The relation between sourness and molecular weight, when the measure of concentration is molarity, percentage-by-weight, and pH.

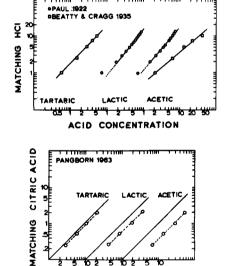


Fig. 6. Equal-sourness matches between acids obtained in previously reported studies.

ACID CONCENTRATION

concentration is either molarity percentage by weight.

(2) The measure of concentration affects the order and magnitude of relative sourness. When molarity is the measure, the introduction of additional groups to a simple acid molecule makes the acid relatively more sour (e.g., tartaric vs dihydroxy tartaric acid, L glutamic vs Nacetyl L glutamic, and glutaric vs 3,3 dimethyl glutaric acids). When percentage is the measure, the increase in sourness with additional groups is not so obvious, and when pH is the measure, the order of sourness is almost reversed, so that the lighter molecules are more sour than the heavier ones.

(3) The D, DL, and L forms of optically active acids (e.g., malic and ascorbic) appear to be equally sour, except that when pH is the concentration measure, the L form is more sour.

(4) The presence of the COOH group at different carbon positions of the sugar molecule (i.e., galactono Δ lactone vs galactouronic) produces a sixfold difference in the degree of sourness of the molecule. On the other hand, when pH is the measure of concentration the sourness of the two acids is more nearly equal.

SOURNESS FUNCTIONS FROM OTHER STUDIES

The form of the sourness function obtained in the present experiments by direct number matches may be related to results previously reported on the basis of direct sourness matches. Figure 6 presents the equal-sourness functions obtained by Paul (1922), Beatty and Cragg (1935), and Pangborn (1963). Although there is disagreement about the relative sourness of acids, the functions are virtually all linear across concentrations. Therefore, if the

sourness of one of the acids conforms to a power function, sourness of the rest do also. In other words, the two different types of matches, acid-acid, and acid-number, give results that are generally consistent. As a first approximation, therefore, the power law that describes the growth of sensory magnitude with physical intensity on more than two dozen continua (Stevens, 1957, 1969) appears to describe the growth function of apparent sourness.

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