Estimated carboxylic acid ester hydrolysis rate constants for food and beverage aroma compounds

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Abstract

Aroma compounds in the Flavornet database were screened for potentially hydrolyzable carboxylic acid ester functionalities. Of the 738 aroma compounds listed in this database, 140 molecules contain carboxylic acid ester groups that may be amenable to hydrolysis in various food and beverage products. Acid- (k_A) and base- (k_B) catalyzed and neutral (k_N) hydrolysis rate constants in pure water at 25°C were estimated for these aroma compounds. Where available, good agreement between theoretical and experimental hydrolytic half-lives was obtained at various pH values. Wide ranges and broad frequency distributions for k_A, k_B, and k_N are expected among the various hydrolyzable aroma compounds, with estimated k_A ranging from 3.7×10^{-8} to 4.7×10^{-4} M^{-1} s^{-1}, estimated k_B ranging from 4.3×10^{-4} to 43 M^{-1} s^{-1}, and estimated k_N ranging from 4.2×10^{-17} to 7.6×10^{-9} M^{-1} s^{-1}. The resulting hydrolytic half-lives also range widely, from 10 days to 370 years at pH 2.8, 18 days to 4,900 years at pH 4.0, 1.8 days to 470 years at pH 7.0, and 26 minutes to 5.1 years at pH 9.0. The findings presented herein attest to the importance of considering abiotic hydrolysis and matrix pH when modeling the evolution of sensory characteristics for foods and beverages with carboxylic acid ester based aroma compounds.

Keywords: aroma compounds, hydrolysis, acid catalysis, base catalysis, odor threshold

Aroma compounds are often present in plant and animal derived foods and beverages as non-volatile and odorless conjugates (e.g., glyco- and sulfate conjugates) [1]. Subsequent hydrolysis of the conjugate linkage releases the volatile aroma compound (aglycone). Although substantial effort has been invested towards better understanding the rates, mechanisms, and products involved in the hydrolysis of these types of aroma precursors [2-7], comparatively little work has been conducted on the hydrolysis reactions of aroma compounds with hydrolyzable functional groups. In particular, a significant number of aroma compounds contain carboxylic acid ester moieties, which can participate in various acid- and base-catalyzed and neutral hydrolysis mechanisms [8-10]. For example, of the 738 aroma compounds listed in the online Flavornet database (http://www.flavornet.org/), 140 (19%) contain carboxylic acid ester groups amenable to hydrolysis.

In the current study, we obtained the identities, Chemical Abstracts Service (CAS) registry numbers, and characteristic aromas of these 140 hydrolyzable aroma compounds from the Flavornet database and estimated the acid- (k_A) and base- (k_B) catalyzed and neutral (k_N) hydrolysis rate constants in pure water at 25°C (Table 1) using the hydrolysis module in the SPARC software program (http://archemcalc.com/sparc/; September 2009 release w4.5.1522-s4.5.1522). Previous work has benchmarked the accuracy of this software program for estimating k_A, k_B, and k_N for carboxylic acid ester hydrolysis rates across a broad range of organic compounds [11-13]. Based on the estimated k_A, k_B, and k_N values for each compound, hydrolytic half-lives ($t_{1/2}$) in pure water were calculated at pH 2.8, 4.0, 7.0, and 9.0 and 25°C using the following equation,

$$t_{1/2}=\ln 2/(k_A[H_3O^+]+k_N[H_2O]+k_B[OH^-])$$

where $[H_3O^+]$ is the pH dependent concentration of hydronium ions ($pH=-\log[H_3O^+]$), $[H_2O]$ is the concentration of undissociated water in pure aqueous solution (assumed constant at 55 M), and $[OH^-]$ is the pH dependent concentration of hydroxide ions ($pOH=-\log[OH^-]$; $pH+pOH=14$).

For six representative volatile esters (ethyl butanoate, ethyl hexanoate, ethyl octanoate, isobutyl acetate, isoamyl acetate, and hexyl acetate) whose hydrolytic half-lives were experimentally determined in pure water pH adjusted to three representative model wine solution pH values (2.95, 3.58, and 4.10) at an unspecified temperature (assumed to be sufficiently close to 25°C for comparison with the computational data) [14], we find excellent agreement (within a factor of two [i.e., the expected accuracy of the theoretical approach]) between the SPARC and experimental data with the exception of the hydrolytic half-lives at pH 3.58 and 4.10 for ethyl octanoate (where deviations of 4.4 and 18-fold, respectively, are observed) (Table 2).

The authors of the experimental data [14] noted progressively greater uncertainty and problems in the experimental values with increasing molecular weight (potentially due to confounding solubility/sorption/aggregation issues), ultimately resulting in low confidence for their ethyl decanoate data. It appears likely that similar problems existed with the ethyl octanoate data at the higher pH values measured in ref. [14], suggesting the SPARC estimates reported herein may be more accurate than the experimental data. Support for this hypothesis exists in the experimental data from ref. [14] that suggests no significant change in the hydrolytic half-life for ethyl octanoate between pH 3.58 and 4.10 (180±35 and 164±35 days, respectively), despite large increases (in agreement with expectations due to the lower hydronium ion concentrations at pH 4.10) in the experimental hydrolytic half-lives between these two pH values reported in ref. [14] for ethyl butanoate (441±27 and 843±67 days, respectively), ethyl hexanoate (311±31 and 1,935±2,240 days, respectively), and the other compounds

under consideration.

Wide ranges and broad frequency distributions for k_A, k_B, and k_N are expected among the various hydrolyzable aroma compounds, with estimated k_A ranging from 3.7×10^{-8} to 4.7×10^{-4} M^{-1} s^{-1} (>4 orders of magnitude), estimated k_B ranging from 4.3×10^{-4} to 43 M^{-1} s^{-1} (>5 orders of magnitude), and estimated k_N ranging from 4.2×10^{-17} to 7.6×10^{-9} M^{-1} s^{-1} (>8 orders of magnitude; Figure 1). The resulting hydrolytic half-lives also range widely, from 10 days to 370 years at pH 2.8, 18 days to 4,900 years at pH 4.0, 1.8 days to 470 years at pH 7.0, and 26 minutes to 5.1 years at pH 9.0. As an illustration, the pH dependence for the hydrolytic half-lives of (3H)-ethylfuranone, linalyl formate, and sotolon (3-hydroxy-4,5-dimethyl-2(5H)-furanone) (Figure 2) between pH 0 and 14 are shown in Figure 3. Although (3H)-ethylfuranone and linalyl formate have effectively equivalent hydrolytic half-lives between pH 4 and 5, their hydrolytic half-lives diverge rapidly under more acidic/basic conditions to values between one and two orders of magnitude difference, and all three compounds display large hydrolysis half-life variation over the possible pH range.

Between pH 2.8 and 4.0, the typical ranges for wines in which a number of these aroma compounds are present, estimated hydrolytic half-lives are always predicted to be longer at pH 4.0 (slower hydrolysis) than at pH 2.8 by factors ranging from 1.4 to 16 (with the majority [>70%] of compounds having a pH 4.0:pH 2.8 hydrolytic half-life ratio >15, and ~90% having a ratio >10; Figure 4). Thus, even relatively minor variations in wine pH can strongly influence the rate at which hydrolyzable aroma compounds are degraded. To the best of our knowledge, the temporal profiles of hydrolyzable aroma compounds in aging wines are poorly constrained, but the results presented herein demonstrate the importance of accounting for abiotic loss of such compounds via hydrolysis when estimating how the sensory properties of the wine will evolve during long-term storage.

The presence of ethanol in alcoholic beverages, and other matrix components in various foods, may also influence the hydrolysis rate constants. Insufficient broadly applicable experimental data is available to make unambiguous predictions in this respect. The SPARC software program predicts only minor changes in the k_A, k_B, and k_N for 25 representative aroma compounds at volumetric ethanol concentrations between 0% and 40% at 25°C in pure water (Table 3), with k_A declining by between 0.13 and 0.48 log units, a variable response in k_B with changes between -0.19 and +0.37 log units depending on the compound, and k_N declining by between 0.27 and 0.55 log units, over the range from 0% to 40% ethanol v/v.

This lack of a clear and significant trend in carboxylic acid ester hydrolysis rate response with varying ethanol concentrations (most changes are within the expected error of the computational method) is consistent with the experimental findings of Ramey and Ough [14], who found no significant effect on the hydrolytic half-lives of ethyl butanoate, ethyl hexanoate, ethyl octanoate, isobutyl acetate, isoamyl acetate, hexyl acetate, and 2-phenylethyl acetate at typical wine ethanol concentrations of 10-14% v/v. Similarly, these authors found no substantial matrix effects on the hydrolysis rates of these esters when comparing model wine solutions with real wines (Pinot Noir and Chardonnay), suggesting theoretical and experimental data for pure water and water/ethanol mixtures may reasonably be extrapolated to actual alcoholic beverages. However, the effects (or lack thereof) by other types of matrix components on the hydrolysis rates of aroma compounds cannot readily be predicted, in light of substantial evidence showing that various organic cosolvents can exert significant influences on the rates of ester hydrolysis, and that the matrix effects are often substrate specific owing to the differing influences on the micro-solvated structures of individual reactants, products, and transition state(s), as well as the

125 effects of aggregation and pK_a shifts for various leaving groups (see, e.g., ref. [15-26]).
126
127 Overall, the findings presented herein attest to the importance of considering abiotic hydrolysis and
128 matrix pH when modeling the evolution of sensory characteristics for foods and beverages with
129 carboxylic acid ester based aroma compounds. The database of hydrolytic rate constants presented
130 herein are expected to be near chemical accuracy, and will thus facilitate the pH dependent modeling of
131 aroma compound hydrolysis in sensory modeling studies.
132

Figure Captions

Figure 1. Relative frequency histograms showing the distribution of estimated (a) acid- (k_A) and (b) base- (k_B) catalyzed and (c) neutral (k_N) hydrolysis rate constants in pure water at 25°C for the 140 carboxylic acid ester hydrolyzable aroma compounds from the Flavornet database.

Figure 2. Structures of (3H)-ethylfuranone (**1**), linalyl formate (**2**), and sotolon (3-hydroxy-4,5-dimethyl-2(5H)-furanone; **3**).

Figure 3. Estimated pH dependent hydrolytic half-lives ($t_{1/2}$) in pure water at 25°C for (3H)-ethylfuranone (**1**; solid line), linalyl formate (**2**; dash-dot-dot line), and sotolon (3-hydroxy-4,5-dimethyl-2(5H)-furanone; **3**; dashed line).

Figure 4. Relative frequency histogram for the estimated ratio of hydrolytic half-lives at pH 4.0 and pH 2.8 in pure water at 25°C for the 140 carboxylic acid ester hydrolyzable aroma compounds from the Flavornet database.

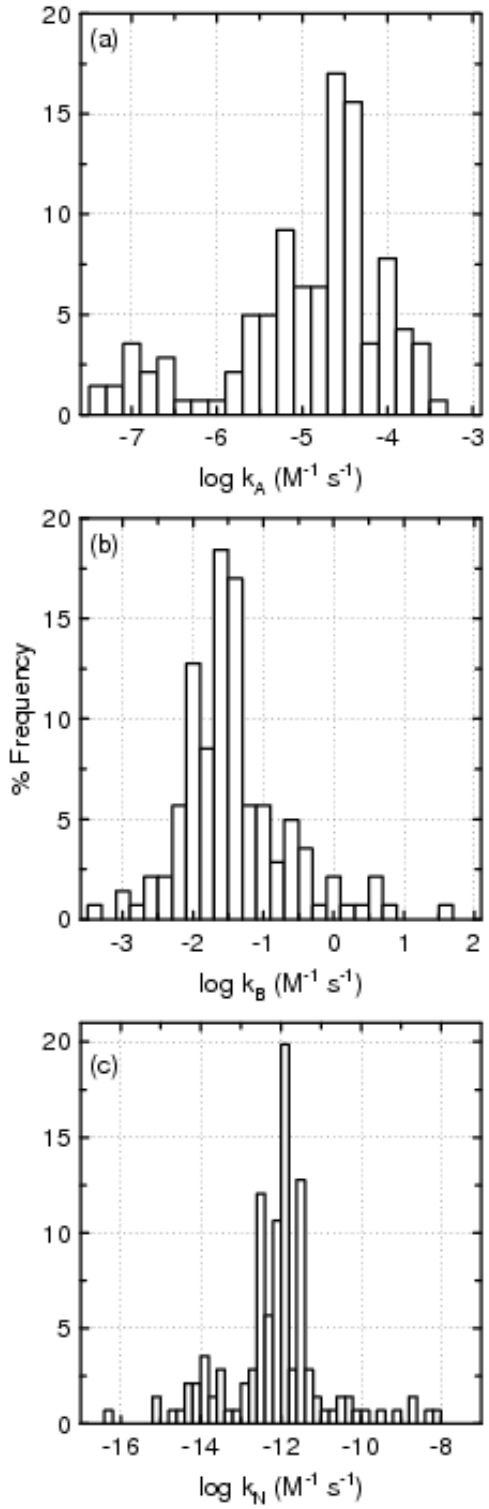
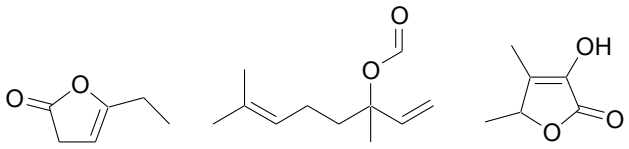


Figure 1.



1 **2** **3**

Figure 2.

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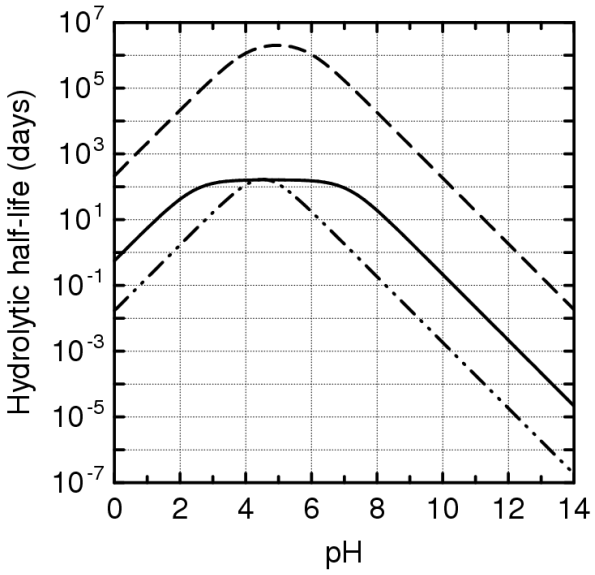

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163 Figure 3.

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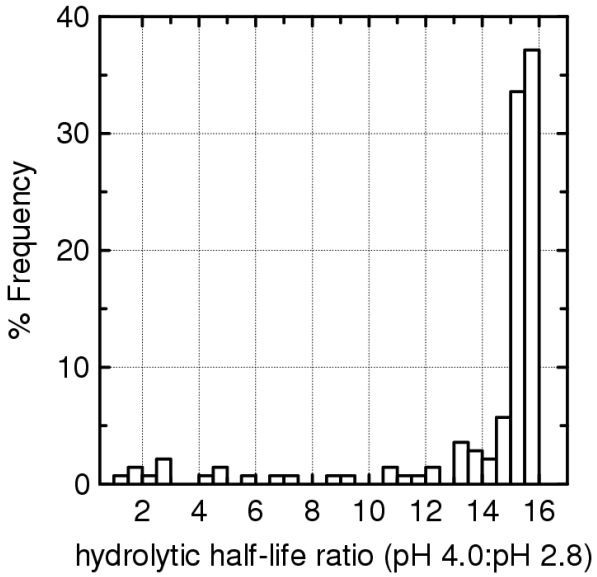

Figure 4.

170 **Table 1.** Identities, Chemical Abstracts Service (CAS) registration numbers, characteristic odors, estimated acid- (k_A) and base- (k_B) catalyzed and neutral (k_N) hydrolysis rate constants in pure water at 25°C, and corresponding
171 hydrolysis half-lives ($t_{1/2}$) at pH 2.8, 4.0, 7.0, and 9.0 for 140 hydrolyzable aroma compounds in the Flavornet database.
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compound	CAS	odor	log k_A (M^{-1} s^{-1})	log k_B (M^{-1} s^{-1})	log k_N (M^{-1} s^{-1})	$t_{1/2}$ (pH 2.8, days)	$t_{1/2}$ (pH 4.0, days)	$t_{1/2}$ (pH 7, days)	$t_{1/2}$ (pH 9, days)
(3H)-ethylfuranone	2313011	spice	-4.85	-0.43	-9.05	110	160	93	2.2
(5H)-ethylfuranone	2407434	spice	-6.94	-2.70	-14.08	44,000 (120 y)	660,000 (1,800 y)	40,000 (110 y)	400
(E,E)-farnesyl acetate	4128170	oil, wax	-3.56	-0.06	-12.33	18	290	91	0.91 (22 h)
(E)-oak lactone	3963867	coconut, flower	-5.33	-2.08	-12.42	1,100	16,000 (44 y)	9,500	97
(E)-whiskey lactone	80041016	flower, lactone	-5.27	-1.99	-11.85	940	13,000 (36 y)	7,300	79
(Z)-3-hexenyl hexanoate	31501118	fruit, prune	-3.95	-1.02	-11.63	45	700	820	8.3
(Z)-6-dodecene-γ-lactone	18679180	peach, sweet	-5.05	-2.01	-12.42	560	8,700	8,100	83
(Z)-whiskey lactone	80041005	coconut	-5.27	-1.99	-11.85	940	13,000 (36 y)	7,300	79
2-methylbutyl acetate	624419	fruit	-4.40	-1.50	-12.30	130	2,000	2,500	26
3-mercaptohexyl acetate	136954206	box tree	-4.29	-1.21	-12.08	99	1,500	1,300	13
4-carbethoxybutyrolactone (chain[a])	1126518	roast, smoke	-4.74	-0.41	-10.52	260	2,300	200	2.1
4-carbethoxybutyrolactone (ring[b])	1126518	roast, smoke	-5.04	-1.53	-12.15	550	8,400	2,700	27
4-hexanolide	695067	coumarin, sweet	-5.29	-2.05	-12.40	980	15,000 (41 y)	8,800	90
5-octanolide	698760	peach	-5.51	-2.25	-12.49	1,600	24,000 (66 y)	14,000 (38 y)	140
7-methoxycoumarin	531599	balsamic, sweet	-6.95	-1.15	-12.89	43,000 (120 y)	310,000 (850 y)	1,100	11
benzyl acetate	140114	fresh, boiled vegetable	-3.92	-0.29	-12.70	42	660	160	1.6
benzyl benzoate	120514	balsamic, oil, herb	-6.54	-0.98	-14.45	17,000 (47 y)	200,000 (550 y)	770	7.7
benzyl butanoate	103377	plum	-4.42	-0.71	-12.41	130	2,100	400	4.1
bornyl benzoate	26927902	pine, balsamic	-7.42	-2.33	-14.39	130,000 (360 y)	1,800,000 (4,900 y)	17,000 (47 y)	170
bornyl butyrate	13109701	herb, wood	-5.31	-2.07	-12.41	1,000	16,000 (44 y)	9,200	94
bornyl formate	7492413	green	-3.83	0.64	-8.64	22	56	14	0.18 (4.3 h)
bornyl isovalerate	76506	herb, earth, green	-5.49	-2.23	-12.48	1,500	23,000 (63 y)	13,000 (36 y)	140
butyl acetate	123864	pear	-3.99	-1.13	-12.13	49	780	1,100	11
butyl benzoate	136607	balsamic	-6.61	-1.83	-13.99	21,000 (58 y)	300,000 (820 y)	5,400	54
butyl decanoate	30673360	whiskey	-4.58	-1.62	-11.86	190	3,000	3,300	34
butyl hexanoate	626824	fruit	-4.57	-1.61	-11.86	190	2,900	3,200	33
butyl laurate	106183	oil	-4.58	-1.62	-11.86	190	3,000	3,300	34
butyl methylbutyrate	15706737	fruit, cocoa	-5.16	-2.10	-11.57	720	9,500	8,600	100
butyl octanoate	589753	fruit	-4.58	-1.62	-11.86	190	2,900	3,200	34
carvyl acetate	97427	green, spearmint	-4.12	-0.58	-13.04	67	1,100	300	3.1
citronellyl acetate	150845	rose, dust	-4.30	-1.41	-12.26	100	1,600	2,000	20
citronellyl butyrate	141162	fruit, sweet, rose	-4.80	-1.82	-11.96	320	4,900	5,100	53
citronellyl isobutyrate	97892	fruit, rose	-5.01	-1.96	-11.50	500	6,900	6,400	74
citronellyl valerate	7540536	warm, honey, herb, rose	-4.86	-1.87	-11.98	360	5,500	5,700	60
coumarin	91645	green, sweet	-6.75	-0.60	-12.79	28,000 (77 y)	150,000 (410 y)	300	3.2
diethyl 2-hydroxyglutarate	69134538	cotton candy	-5.32	-0.86	-10.50	860	3,600	520	5.8
diethyl malate	7554123	brown sugar, sweet	-4.56	-0.87	-11.38	180	2,700	580	5.9
diethyl malonate	105533	apple	-3.78	0.48	-11.32	30	470	26	0.27 (6.5 h)
diethyl succinate	123251	wine, fruit	-3.86	-0.51	-11.39	36	570	260	2.6
diethyl tartrate	87912	earth, must	-5.70	-0.66	-10.21	1,200	2,200	320	3.7
dihydrocarvyl acetate	20777495	mint, camphor, medicine	-4.61	-1.43	-12.66	200	3,200	2,200	22
ethyl (E)-cinnamate	4192772	flower, honey	-5.67	-1.09	-15.06	2,400	36,000 (99 y)	1,000	10
ethyl 3-hydroxybutanoate	5405414	marshmallow	-4.57	-1.34	-11.56	190	2,800	1,700	18

ethyl 3-methylbutanoate	108645	fruit	-4.60	-1.64	-11.87	200	3,100	3,40	35
ethyl acetate	141786	pineapple	-3.92	-1.07	-12.10	42	660	930	9.4
ethyl benzoate	93890	camomile, flower, celery, fruit	-6.55	-1.78	-14.03	18,000 (49 y)	260,000 (700 y)	4,800	48
ethyl butanoate	105544	apple	-4.43	-1.49	-11.80	140	2,100	2,400	25
ethyl cinnamate	103366	honey, cinnamon	-5.67	-1.09	-15.06	2,400	36,000 (99 y)	1,000	10
ethyl cyclohexanoate	3289289	fruit	-5.19	-1.78	-11.42	770	9,300	4,300	48
ethyl decanoate	110383	grape	-4.51	-1.56	-11.83	160	2,500	2,800	29
ethyl dihydrocinnamate	2021285	flower	-4.57	-1.41	-12.02	190	2,900	2,000	21
ethyl formate	109944	pungent	-3.57	0.67	-8.29	11	26	11	0.17 (4.1 h)
ethyl heptylate	106309	fruit	-4.51	-1.56	-11.83	160	2,500	2,800	29
ethyl hexadecanoate	628977	wax	-4.51	-1.56	-11.83	160	2,500	2,800	29
ethyl hexanoate	123660	apple peel, fruit	-4.50	-1.55	-11.83	160	2,500	2,800	29
ethyl hydroxybutanoate	999100	caramel	-4.50	-1.44	-11.70	160	2,400	2,200	22
ethyl hydroxyhexanoate	2305251	fresh	-5.18	-1.89	-11.81	760	11,000 (30 y)	5,900	62
ethyl isobutyrate	97621	sweet, rubber	-4.63	-1.62	-11.34	220	3,100	3,100	34
ethyl isohexanoate	25415672	fruit	-4.44	-1.50	-11.81	140	2,200	2,500	25
ethyl lactate	97643	fruit	-4.71	-0.50	-10.27	240	1,600	230	2.5
ethyl laurate	106332	leaf	-4.51	-1.56	-11.83	160	2,500	2,800	29
ethyl mercaptopropionate	19788499	sulfur	-4.82	-0.36	-10.11	280	1,400	170	1.9
ethyl methylbutyrate	7452791	apple	-5.09	-2.04	-11.54	620	8,300	7,500	88
ethyl octanoate	106321	must, oil, fruit, pungent	-4.51	-1.56	-11.83	160	2,500	2,800	29
ethyl phenylacetate	101973	fruit, sweet	-4.56	-0.88	-12.42	180	2,800	610	6.1
ethyl propionate	105373	fruit	-4.28	-1.35	-11.74	96	1,500	1,800	18
ethyl salicylate	118616	wintergreen, mint	-7.11	-2.12	-13.86	65,000 (180 y)	870,000 (2,400 y)	10,000 (27 y)	100
ethyl tetradecanoate	124061	ether	-4.51	-1.56	-11.83	160	2,500	2,800	29
ethyl undecanoate	627907	cognac, coconut	-4.51	-1.56	-11.83	160	2,500	2,800	29
ethyl valerate	539822	yeast, fruit	-4.48	-1.53	-11.82	150	2,400	2,700	27
ethyl vanillate	617050	flower, fruit, sweet, vanilla	-6.91	-2.56	-14.11	41,000 (110 y)	620,000 (1,700 y)	29,000 (79 y)	290
geranyl acetate	105873	rose	-3.56	-0.06	-12.33	18	290	91	0.91 (22 h)
geranyl butyrate	106296	fruit, rose, apple	-3.93	-0.47	-12.03	43	670	240	2.4
geranyl isovalerate	109206	fruit, rose, apple	-4.10	-0.63	-12.11	64	1,000	340	3.4
geranyl valerate	10402478	rose, fruit	-3.98	-0.52	-12.05	48	760	270	2.7
hexenyl acetate	3681718	green, banana	-3.77	-0.53	-11.89	30	470	270	2.7
hexyl acetate	142927	fruit, herb	-4.00	-1.14	-12.13	50	800	1,100	11
hexyl butanoate	2639636	apple peel	-4.51	-1.56	-11.83	160	2,500	2,800	29
hexyl hexanoate	6378650	apple peel, peach	-4.58	-1.62	-11.86	190	2,900	3,200	34
hexyl methylbutyrate	10032152	strawberry	-5.17	-2.11	-11.57	740	9,700	8,700	100
hexyl octanoate	1117551	herb, green, oil	-4.59	-1.63	-11.87	200	3,000	3,300	34
isoamyl acetate	123922	banana	-3.84	-0.99	-12.06	35	550	780	7.9
isobornyl formate	1200675	green, earth, camphor	-3.83	0.64	-8.64	22	56	14	0.18 (4.3 h)
isobornyl propionate	2756561	fruit, turpentine	-5.16	-1.93	-12.35	730	11,000 (30 y)	6,700	69
isobutyl acetate	110190	fruit, apple, banana	-4.02	-1.16	-12.14	53	830	1,100	11
isopropyl benzoate	939480	sweet, fruit	-6.83	-2.02	-14.37	34,000 (93 y)	510,000 (1,400 y)	8,400	84
isopropyl hexanoate	2311468	fresh	-4.79	-1.81	-12.29	310	4,900	5,100	52
isopropyl palmitate	142916	fat	-4.80	-1.82	-12.29	320	5,000	5,200	53
isopulegyl acetate	89496	mint, leaf	-4.61	-1.43	-12.66	210	3,300	2,200	22
linalyl acetate	115957	sweet, fruit	-4.92	-1.22	-13.80	420	6,600	1,300	13

linalyl butyrate	78364	pear, sweet	-5.43	-1.63	-13.50	1,400	21,000 (58 y)	3,500	35
linalyl formate	115991	citrus, coriander	-3.33	1.64	-9.47	11	120	1.8	0.018 (26 min)
linalyl isovalerate	1118270	sweet, apple, citrus	-5.60	-1.79	-13.58	2,000	32,000 (88 y)	5,000	50
linalyl valerate	10471962	citrus, lavender	-5.48	-1.68	-13.53	1,500	24,000 (66 y)	3,900	39
mercaptomethylbutyl formate	50746106	cat, roast	-3.59	0.84	-8.12	9.7	18	7.2	0.11 (2.6 h)
methyl 2-(methylthio)acetate	16630663	cooked potato, roasted nut	-4.49	0.30	-9.80	130	660	38	0.40 (9.6 h)
methyl 2-methylbutanoate	868575	apple	-4.92	-1.89	-11.15	410	5,000	4,800	62
methyl 2-methylpropanoate	547637	flower	-4.46	-1.47	-10.95	140	2,000	2,000	24
methyl 3-methylbutanoate	556241	apple	-4.43	-1.49	-11.48	140	2,000	2,400	25
methyl anthranilate	134203	honey, flower	-7.10	-2.67	-16.38	63,000 (170 y)	970,000 (2,700 y)	37,000 (100 y)	370
methyl benzoate	93583	prune, lettuce, herb, sweet	-6.38	-1.63	-13.75	12,000 (33 y)	180,000 (490 y)	3,500	35
methyl butanoate	623427	ether, fruit, sweet	-4.25	-1.33	-11.41	90	1,400	1,600	17
methyl cinnamate	103264	strawberry	-5.49	-0.94	-14.67	1,600	24,000 (66 y)	700	7.0
methyl cyclohexanecarboxylate	4630824	fruit, ester	-5.02	-1.63	-11.03	510	5,400	2,800	34
methyl decanoate	110429	wine	-4.34	-1.41	-11.45	110	1,700	1,900	20
methyl dihydroepijasmonate	39647115	jasmine	-4.51	-1.40	-11.50	160	2,400	1,900	20
methyl epijasmonate	95722422	jasmine	-4.48	-1.35	-11.50	150	2,300	1,700	18
methyl geranate	11890909	flower, green, fruit	-6.27	-2.97	-12.92	9,200	130,000 (360 y)	71,000 (190 y)	750
methyl hexanoate	106707	fruit, fresh, sweet	-4.33	-1.40	-11.44	110	1,600	1,900	20
methyl jasmonate	1211296	jasmine	-4.48	-1.35	-11.50	150	2,300	1,700	18
methyl laurate	111820	fat, coconut	-4.34	-1.41	-11.45	110	1,700	1,900	20
methyl nonanoate	1731846	coconut	-4.34	-1.41	-11.45	110	1,700	1,900	20
methyl octadecenoate	112618	fat	-4.34	-1.41	-11.45	110	1,700	1,900	20
methyl octanoate	111115	orange	-4.33	-1.41	-11.45	110	1,700	1,900	20
methyl salicylate	119368	peppermint	-6.95	-1.98	-13.65	44,000 (120 y)	590,000 (1,600 y)	7,700	77
methyl tetradecanoate	124107	orris	-4.34	-1.41	-11.45	110	1,700	1,900	20
methyl vanillate	3943746	caramel, butterscotch, vanilla	-6.74	-2.42	-13.85	28,000 (77 y)	410,000 (1,100 y)	21,000 (58 y)	210
neryl acetate	141128	fruit	-3.56	-0.06	-12.33	18	290	91	0.91 (22 h)
nonyl acetate	143135	sweet, fruit	-4.00	-1.14	-12.13	50	800	1,100	11
octyl acetate	2051505	fruit	-4.92	-1.96	-12.85	420	6,500	7,300	74
p-menth-1-en-9-yl acetate	28839136	fruit, herb	-4.77	-1.84	-12.45	300	4,700	5,500	56
pantolactone	599042	cotton candy	-5.84	-1.18	-10.69	2,300	6,300	1,000	12
pentyl butanoate	540181	banana	-4.50	-1.55	-11.83	160	2,500	2,800	29
phenylethyl benzoate	97473	flower, honey	-6.59	-1.71	-14.00	20,000 (55 y)	290,000 (790 y)	4,100	41
propyl butyrate	105668	pineapple, solvent	-4.48	-1.53	-11.82	150	2,400	2,700	27
propyl hexanoate	626777	fruit	-4.55	-1.60	-11.85	180	2,800	3,100	32
propyl propanoate	106365	pineapple	-4.33	-1.40	-11.76	110	1,700	1,900	20
R-δ-decenolactone	54814641	peach	-7.20	-3.05	-14.23	80,000 (220 y)	1,200,000 (3,300 y)	89,000 (240 y)	890
sotolon	28664359	cotton candy, spice, maple	-7.43	-3.36	-13.24	130,000 (360 y)	1,200,000 (3,300 y)	170,000 (470 y)	1,900
terpinyl acetate	80262	wax	-5.86	-2.62	-13.50	3,700	58,000 (160 y)	33,000 (90 y)	330
wine lactone	182699770	coconut, spice	-6.02	-2.49	-12.13	5,100	58,000 (160 y)	22,000 (60 y)	250
β-phenethyl acetate	103457	rose, honey, tobacco	-3.97	-1.01	-12.20	47	750	820	8.3
γ-butyrolactone	96480	caramel, sweet	-5.03	-2.03	-12.05	540	8,100	8,100	85
γ-decalactone	706149	peach, fat	-5.29	-2.05	-12.40	980	15,000 (41 y)	8,800	90
γ-dodecalactone	2305057	sweet, fruit, flower	-5.29	-2.05	-12.40	980	15,000 (41 y)	8,800	90
γ-nonalactone	104610	coconut, peach	-5.29	-2.05	-12.40	980	15,000 (41 y)	8,800	90
γ-octalactone	104507	coconut	-5.29	-2.05	-12.40	980	15,000 (41 y)	8,800	90

γ-undecalactone	104676	apricot	-5.29	-2.05	-12.40	980	15,000 (41 y)	8,800	90
δ-decalactone	705862	coconut	-5.51	-2.25	-12.49	1,600	24,000 (66 y)	14,000 (38 y)	140
δ-dodecalactone	713951	fruit, sweet	-5.51	-2.25	-12.49	1,600	24,000 (66 y)	14,000 (38 y)	140
δ-undecalactone	710043	peach	-5.51	-2.25	-12.49	1,600	24,000 (66 y)	14,000 (38 y)	140

[a] hydrolysis of the chain carboxylic acid ester moiety. [b] hydrolysis of the ring carboxylic acid ester moiety.

Table 2. Comparison between SPARC estimated (at 25°C) and experimental hydrolytic half-lives (in days) for six volatile esters at three representative wine pH values in pure water. The temperature at which the experimental data was obtained was not specified in the source publication [14], and is assumed to be sufficiently close to 25°C for a meaningful comparison with the computational data.

	pH 2.95		pH 3.58		pH 4.10	
	SPARC	expt. [14]	SPARC	expt. [14]	SPARC	expt. [14]
ethyl butanoate	190 (+52%)[a]	125±4[b]	810 (+84%)	441±27	2,600 (+208%)	843±67
ethyl hexanoate	230 (+135%)	98±7	950 (+205%)	311±31	3,100 (+60%)	1,935±2,240
ethyl octanoate	230 (+113%)	108±10	970 (+439%)	180±35	3,200 (+1,851%)	164±35
isobutyl acetate	75 (+27%)	59±3	320 (+59%)	201±9	1,000 (+146%)	407±48
isoamyl acetate	49 (-21%)	62±2	210 (-15%)	246±9	690 (+21%)	569±109
hexyl acetate	71 (+37%)	52±2	300 (+47%)	204±17	1,000 (+129%)	437±95

[a] values in parentheses are percent deviations from the experimental data. [b] error bars are standard deviations.

Table 3. Estimated acid- (k_A) and base- (k_B) catalyzed and neutral (k_N) hydrolysis rate constants of 25 representative aroma compounds at 25°C in pure water with varying volumetric ethanol concentrations.

	log k_A (M^{-1} s^{-1})									log k_B (M^{-1} s^{-1})									log k_N (M^{-1} s^{-1})								
compound	0%	5%	10%	15%	20%	25%	30%	35%	40%	0%	5%	10%	15%	20%	25%	30%	35%	40%	0%	5%	10%	15%	20%	25%	30%	35%	40%
(E)-whiskey lactone	-5.274	-5.324	-5.375	-5.426	-5.479	-5.532	-5.585	-5.638	-5.690	-1.992	-1.996	-2.002	-2.011	-2.023	-2.040	-2.061	-2.088	-2.123	-11.853	-11.907	-11.964	-12.024	-12.087	-12.154	-12.224	-12.299	-12.378
7-methoxycoumarin	-6.945	-7.000	-7.056	-7.114	-7.173	-7.233	-7.293	-7.353	-7.414	-1.149	-1.157	-1.169	-1.183	-1.201	-1.224	-1.252	-1.286	-1.328	-12.890	-12.947	-13.006	-13.069	-13.134	-13.204	-13.277	-13.355	-13.437
bornyl formate	-3.834	-3.852	-3.870	-3.887	-3.903	-3.917	-3.930	-3.939	-3.946	0.642	0.691	0.739	0.788	0.836	0.884	0.930	0.975	1.016	-8.635	-8.663	-8.692	-8.723	-8.756	-8.790	-8.826	-8.864	-8.905
carvyl acetate	-4.122	-4.155	-4.188	-4.221	-4.254	-4.286	-4.317	-4.347	-4.374	-0.580	-0.568	-0.558	-0.550	-0.545	-0.542	-0.544	-0.550	-0.562	-13.043	-13.090	-13.140	-13.192	-13.247	-13.305	-13.366	-13.431	-13.499
diethyl malate	-4.556	-4.590	-4.632	-4.671	-4.709	-4.748	-4.785	-4.822	-4.857	-0.869	-0.862	-0.857	-0.854	-0.853	-0.856	-0.864	-0.876	-0.895	-11.378	-11.427	-11.479	-11.533	-11.591	-11.651	-11.715	-11.783	-11.854
diethyl succinate	-3.858	-3.879	-3.900	-3.920	-3.940	-3.958	-3.974	-3.988	-3.999	-0.512	-0.490	-0.469	-0.450	-0.432	-0.417	-0.405	-0.397	-0.394	-11.389	-11.431	-11.476	-11.523	-11.572	-11.624	-11.679	-11.737	-11.798
ethyl dihydrocinnamate	-4.573	-4.614	-4.655	-4.696	-4.738	-4.779	-4.821	-4.861	-4.900	-1.411	-1.406	-1.403	-1.403	-1.406	-1.412	-1.423	-1.438	-1.461	-12.024	-12.075	-12.128	-12.183	-12.242	-12.304	-12.369	-12.438	-12.512
ethyl formate	-3.566	-3.585	-3.602	-3.619	-3.635	-3.650	-3.662	-3.672	-3.678	0.666	0.714	0.763	0.812	0.860	0.908	0.954	0.999	1.040	-8.286	-8.314	-8.343	-8.374	-8.406	-8.441	-8.477	-8.515	-8.555
ethyl isobutyrate	-4.631	-4.671	-4.712	-4.753	-4.794	-4.836	-4.876	-4.916	-4.955	-1.624	-1.619	-1.616	-1.616	-1.618	-1.624	-1.634	-1.650	-1.672	-11.344	-11.394	-11.447	-11.502	-11.561	-11.623	-11.688	-11.757	-11.830
ethyl isohexanoate	-4.444	-4.479	-4.515	-4.550	-4.586	-4.621	-4.655	-4.688	-4.719	-1.500	-1.490	-1.482	-1.477	-1.474	-1.474	-1.478	-1.487	-1.503	-11.807	-11.855	-11.905	-11.959	-12.015	-12.070	-12.136	-12.202	-12.272
ethyl salicylate	-7.114	-7.170	-7.228	-7.287	-7.347	-7.408	-7.469	-7.532	-7.594	-2.116	-2.125	-2.137	-2.153	-2.196	-2.196	-2.225	-2.261	-2.304	-13.858	-13.915	-13.975	-14.038	-14.104	-14.170	-14.248	-14.327	-14.409
hexyl methylbutyrate	-5.168	-5.222	-5.277	-5.333	-5.390	-5.448	-5.506	-5.565	-5.623	-2.112	-2.119	-2.129	-2.141	-2.158	-2.179	-2.205	-2.237	-2.277	-11.570	-11.626	-11.684	-11.746	-11.811	-11.880	-11.953	-12.029	-12.111
hexyl octanoate	-4.586	-4.625	-4.664	-4.704	-4.743	-4.783	-4.821	-4.859	-4.896	-1.629	-1.622	-1.618	-1.616	-1.617	-1.621	-1.629	-1.643	-1.663	-11.866	-11.916	-11.968	-12.023	-12.081	-12.142	-12.206	-12.274	-12.346
linalyl formate	-3.328	-3.346	-3.364	-3.381	-3.397	-3.411	-3.423	-3.433	-3.440	1.638	1.687	1.730	1.784	1.832	1.880	1.926	1.971	2.012	-9.468	-9.496	-9.525	-9.556	-9.589	-9.623	-9.659	-9.697	-9.738
methyl 2-(methylthio)acetate	-4.492	-4.523	-4.555	-4.586	-4.616	-4.646	-4.675	-4.703	-4.728	0.303	0.316	0.328	0.337	0.344	0.349	0.349	0.345	0.335	-9.795	-9.841	-9.890	-9.942	-9.996	-10.053	-10.113	-10.177	-10.244
methyl 2-methylpropanoate	-4.456	-4.493	-4.530	-4.567	-4.604	-4.641	-4.677	-4.712	-4.746	-1.472	-1.463	-1.457	-1.453	-1.451	-1.453	-1.459	-1.470	-1.488	-10.954	-11.003	-11.054	-11.108	-11.165	-11.225	-11.288	-11.355	-11.426
methyl anthranilate	-7.095	-7.149	-7.203	-7.259	-7.316	-7.373	-7.431	-7.489	-7.547	-2.667	-2.674	-2.683	-2.696	-2.712	-2.732	-2.758	-2.790	-2.829	-16.381	-16.437	-16.496	-16.558	-16.623	-16.691	-16.764	-16.840	-16.921
methyl cyclohexanecarboxylate	-5.015	-5.056	-5.098	-5.140	-5.182	-5.224	-5.266	-5.307	-5.346	-1.629	-1.624	-1.622	-1.622	-1.625	-1.632	-1.643	-1.660	-1.683	-11.027	-11.078	-11.131	-11.187	-11.246	-11.308	-11.374	-11.443	-11.516
methyl octanoate	-4.334	-4.367	-4.401	-4.434	-4.467	-4.500	-4.532	-4.562	-4.590	-1.406	-1.394	-1.385	-1.377	-1.372	-1.370	-1.372	-1.379	-1.391	-11.445	-11.492	-11.542	-11.594	-11.649	-11.707	-11.769	-11.833	-11.902
methyl salicylate	-6.945	-6.998	-7.052	-7.107	-7.162	-7.219	-7.276	-7.333	-7.390	-1.984	-1.991	-1.999	-2.011	-2.027	-2.047	-2.072	-2.103	-2.141	-13.651	-13.706	-13.765	-13.826	-13.891	-13.959	-14.031	-14.107	-14.188
methyl vanillate	-6.740	-6.783	-6.827	-6.871	-6.916	-6.961	-7.005	-7.049	-7.092	-2.423	-2.421	-2.421	-2.423	-2.428	-2.437	-2.451	-2.470	-2.496	-13.845	-13.896	-13.950	-14.007	-14.067	-14.130	-14.197	-14.268	-14.343
p-menth-1-en-9-yl acetate	-4.773	-4.816	-4.860	-4.904	-4.948	-4.993	-5.037	-5.081	-5.124	-1.843	-1.840	-1.840	-1.842	-1.847	-1.856	-1.870	-1.889	-1.915	-12.452	-12.503	-12.558	-12.614	-12.674	-12.737	-12.804	-12.875	-12.949
phenylethyl benzoate	-6.593	-6.642	-6.692	-6.743	-6.795	-6.847	-6.899	-6.951	-7.002	-1.709	-1.712	-1.717	-1.725	-1.737	-1.753	-1.773	-1.799	-1.833	-14.004	-14.058	-14.115	-14.175	-14.237	-14.304	-14.374	-14.448	-14.526
sotolon	-7.430	-7.480	-7.531	-7.583	-7.636	-7.690	-7.744	-7.797	-7.850	-3.364	-3.368	-3.374	-3.384	-3.397	-3.414	-3.436	-3.464	-3.499	-13.239	-13.293	-13.350	-13.411	-13.474	-13.541	-13.612	-13.686	-13.765
γ-octalactone	-5.290	-5.340	-5.391	-5.442	-5.495	-5.548	-5.601	-5.654	-5.706	-2.051	-2.055	-2.061	-2.070	-2.082	-2.099	-2.120	-2.148	-2.182	-12.401	-12.455	-12.512	-12.572	-12.635	-12.702	-12.772	-12.847	-12.926

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