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Descriptors for terpene esters from chromatographic and partition measurements; estimation of human odor detection thresholds.

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ABSTRACT

We have used gas chromatographic retention data together with other data to obtain Abraham descriptors for 30 terpene esters. These include the air-water partition coefficient, as log *Kw*, for which no experimental values are available for any terpene ester. The other descriptors are the ester dipolarity, *S*, the hydrogen bond basicity, *B*, (the ester hydrogen bond acidity is zero for the esters studied), and *L* the logarithm of the air-hexadecane partition coefficient. Both *S* and *B* are larger than those for simple aliphatic esters, as expected from the terpene ester structures that include ring systems and ethylenic double bonds. These descriptors can then be used to obtain a large number of physicochemical and environmental properties of terpene esters. We have analyzed experimental results on human odor detection thresholds and have constructed another equation for the calculation of these thresholds, to go with a previous equation that we have reported. Then the descriptors for terpene esters can be used to estimate the important odor detection thresholds.

Keywords:

Terpene esters

Gas liquid chromatography

Partition coefficient

Air-water partition coefficient

Descriptors
Linear free energy relationships
Simultaneous equations
Odor detection thresholds

1. Introduction

Terpene esters are important compounds in the fragrance industry. Linalyl acetate, isobornyl acetate and α-terpinyl acetate are manufactured to around 2000 tons per annum [1]. Gas-liquid chromatographic (GLC) retention indices are known for a substantial number of terpene esters [2-24], partition coefficients in hexane-nitromethane [3] and hexane-acetonitrile [25, 26] have been determined for some terpene acetates, and normal-phase chromatographic data are available for terpene acetates on a number of system phases [27, 28]. Leo [29] has compiled literature data on water-octanol partition coefficients that include values for a few terpene esters. Several terpene esters are naturally occurring, and so their environmental properties are of particular importance. One such property is the air-water partition coefficient, *Kw*, equivalent to the inverse of Henry's law constant. Sander [30] lists values for 4632 compounds, but no experimental values were given for any terpene ester.

We have obtained descriptors for a large number of terpene hydrocarbons [31], and Karunasekara and Poole [32] have obtained descriptors for a number of varied terpenes, but the only reported descriptors for terpene esters are those for five terpene acetates listed by Ahmed and Poole [26]. Our aim was therefore to use the available literature data on the physicochemical properties of terpene esters to derive descriptors, including the important descriptor, *Kw*. Note that the descriptors listed by Ahmed and Poole [26] did not include *Kw*.

2. Methods

Our method [33-35] is based on the two linear free energy relationships, LFERs, Eq. (1) and Eq. (2).

$$SP = c + eE + sS + aA + bB + vV \quad (1)$$

$$SP = c + eE + sS + aA + bB + lL \quad (2)$$

The dependent variable, *SP*, is some property of a series of solutes in a given system. In Eq (1) *SP* may be a set of partition coefficients as, log P_s, for a series of solutes in a given water-solvent, or in a solvent-solvent system, or can be a set of liquid chromatographic retention data. In Eq. (2), *SP* is usually a set of gas-chromatographic retention data. The number of dependent variables, and hence the number of equations, can be extended through Eq. (3) where *Ks* is the solute air to solvent partition coefficient. If log *Kw* is taken as another descriptor to be obtained, then values of log *Ps* can be converted into values of log *Ks,* and the latter used as the dependent variable in Eq. (2).

$$P_s = K_s / K_w \quad \log Ps = \log Ks - \log Kw \qquad (3)$$

We then have a series of equations, Eq. (1) and Eq. (2), with known dependent variables, and we either have already, or can calculate from known data, the corresponding coefficients *c*, *e*, *s*, *a*, *b* and *l* in the equations. Then the entire set of simultaneous equations can be solved to obtain values of the (unknown) solute descriptors in Eq. (1) and Eq. (2), and also the additional descriptor log *Kw*. We invariably have more equations than unknown solute descriptors and so the set of simultaneous equations is solved by trial-and-error. We have described the method previously [33-35], and there have been several reviews that detail the procedure [36-38].

The independent variables, or Abraham descriptors, in Eq. (1) and Eq. (2) are properties of solutes as follows [33-38]: *E* is an excess molar refraction in $cm^3\ mol^{-1}/10$, *S* is a combined dipolarity/polarizability descriptor, *A* is the overall solute hydrogen bond acidity, *B* is the overall solute hydrogen bond basicity, *V* is McGowan's [39] characteristic molecular volume in $cm^3\ mol^{-1}/100$ and *L* is logarithm of the gas to hexadecane partition coefficient at 25^oC. At first sight it appears that we have seven solute descriptors to obtain, *E*, *S*, *A*, *B*, *V*, *L* and log *Kw*. However *V* can always be calculated from the solute molecular formula [33, 39], and there are a number of ways of obtaining *E*. If the liquid solute refractive index at 20^oC is available then *E* can easily be determined, or *E* can be obtained from a calculated refractive index [40]. There are two software programs available [41, 42] that calculate the descriptor *E*, *S, A*, *B, V* and *L* just from structure, so that it is invariably possible to obtain *E* as described in several reviews [36-38]. In addition, the terpene esters that we shall study all have *A* = 0, so that from the set of simultaneous equations we need to derive *S*, *B*, *L* and log *Kw*, that is only four unknown descriptors.

3. Results and Discussion

Gas chromatographic stationary phases, even the more polar phases, invariable have no hydrogen bond acidity and hence the *b*-coefficient in Eq. (2) will be zero. It is therefore very useful to be able to include the water-octanol partition system in the set of simultaneous equations, because the *b*-coefficient in Eq. (1) for this system is numerically large (-3.460). If log *Ps* in this system is converted to log *Ks*, through Eq. (3), the corresponding Eq. (2) for log *Ks* also has a numerically quite large value of the b-coefficient (1.429). Geranyl acetate is an example of an ester for which there are a considerable number of reports on GLC retention indices, and for which there is an available value for log *Ps* in the water-octanol system. We therefore use geranyl acetate as an example of the construction and solution of the set of simultaneous equations. Details are in Table 1, where the observed and calculated dependent variables are given, the latter from the deduced descriptors listed in Table 2. We give retention indices as I/1000 in order to have comparable weights to the partition measurements.

Table 1

Systems for the determination of descriptors for geranyl acetate through solution of simultaneous equations.

System	Ref	Dependent variable	Calc	Obs
Water-octanol	27	log *Ps*	4.076	4.040
Air-water	A	log *Kw* Eq. (1)	2.613	2.659
Air-octanol	B	log *Ks* Eq. (2)	6.663	6.699
Air-water	A	log *Kw* Eq (2)	2.741	2.659
GLC DMS-Oil	21	Ret Index	1.390	1.361
GLC DIMS	21	Ret Index	1.389	1.361
GLC DIMS5P	21	Ret Index	1.404	1.379
GLC PEG	21	Ret Index	1.744	1.751
GLC PhMeSiloxane	3	Ret Index	1.391	1.383
GLC OV101	19	Ret Index	1.380	1.363
GLC PEG	19	Ret Index	1.731	1.755
GLC OV101	22	Ret Index	1.384	1.360
GLC SE54	22	Ret Index	1.406	1.384
GLC PEG	22	Ret Index	1.141	1.147
GLC SE-30	20	Ret Index	1.386	1.360

System	Ref	Dependent variable	Calc	Obs
GLC BPX5	10	Ret Index	1.262	1.275
GLC DB-Wax	11	Ret Index	1.730	1.746
GLC DB-1	11	Ret Index	1.379	1.363
GLC DB-1	12	Ret Index	1.385	1.358
GLC CP-Sil-5CB	14	Ret Index	1.382	1.359
GLC AT-Wax	14	Ret Index	1.716	1.735
GLC BPX5	15	Ret Index	1.414	1.387
GLC HP-5MS	23	log tR	1.395	1.361
GLC Supelcowax 10	24	Ret Index	1.731	1.752
GLC SE-30	24	Ret Index	1.367	1.368

[a] Log *Kw* is an additional (unknown) descriptor. [b] Through Eq. (3).

For the 25 systems in Table 1, the descriptors listed in Table 2 for geranyl acetate yielded calculated values of the dependent variable with an absolute error of 0.009 log units and a standard deviation, SD, of 0.030 log units. Descriptors for the other terpene esters listed in Table 2 were obtained in exactly the same way as for geranyl acetate. The corresponding number of simultaneous equations, Ne, and the SD values are also given in Table 2. Note that in all cases, the value of the *A*-descriptor is zero.

Table 2.

Descriptors for terpene esters, the number of simultaneous equations used in the calculations, and the standard deviation between observed and calculated dependent variables.

Terpene ester	*E*	*S*	*B*	*L*	*V*	Log *Kw*	N	SD
Linalyl formate	0.341	0.67	0.68	5.699	1.6469	2.64	13	0.098
Linalyl acetate	0.331	0.65	0.65	5.848	1.7878	2.47	26	0.088
Linalyl propanoate	0.300	0.66	0.66	6.332	1.9287	2.39	27	0.110
Linalyl butanoate	0.285	0.69	0.69	6.987	2.0696	2.48	12	0.155
Geranyl formate	0.381	0.66	0.68	5.933	1.6469	2.81	15	0.030
Geranyl acetate	0.368	0.65	0.68	6.326	1.7878	2.66	25	0.030
Geranyl propranoate	0.350	0.64	0.68	6.776	1.9287	2.51	15	0.041
Geranyl butanoate	0.333	0.62	0.68	7.205	2.0696	2.34	17	0.048
Neryl formate	0.345	0.65	0.67	5.784	1.6469	2.70	14	0.059
Neryl acetate	0.330	0.65	0.67	6.011	1.7878	2.52	28	0.096

Terpene ester	***E***	***S***	***B***	***L***	***V***	**Log *Kw***	N	SD
Neryl propranoate	0.320	0.63	0.67	6.665	1.9287	2.39	15	0.085
Neryl butanoate	0.315	0.63	0.67	7.057	2.0696	2.26	12	0.133
β-Cittronellyl formate	0.200	0.59	0.63	5.836	1.6899	2.26	11	0.033
β-Cittronellyl acetate	0.198	0.59	0.64	6.192	1.8308	2.19	14	0.040
β-Cittronellyl propranoate	0.190	0.58	0.63	6.609	1.9717	2.00	15	0.050
β-Cittronellyl butanoate	0.185	0.56	0.63	7.057	2.1126	1.84	14	0.061
Carvyl formate	0.516	0.61	0.67	5.705	1.5373	2.80	5	0.027
Carvyl acetate	0.508	0.69	0.68	6.224	1.6792	2.93	15	0.027
Carvyl propranoate	0.495	0.68	0.69	6.666	1.8201	2.84	10	0.035
Carvyl butanoate	0.493	0.69	0.71	7.168	1.9610	2.86	5	0.061
Bornyl acetate	0.400	0.52	0.59	5.899	1.6566	2.03	32	0.025
Isobornyl acetate	0.400	0.52	0.59	5.889	1.6566	2.03	17	0.018
Fenchyl acetate	0.333	0.56	0.57	5.712	1.6566	1.97	17	0.062
Menthyl acetate	0.243	0.65	0.54	5.985	1.7652	1.90	16	0.073
Lavendulyl acetate	0.330	0.63	0.64	5.783	1.7878	2.46	15	0.048
Farnesyl acetate	0.450	0.75	0.78	8.779	2.4493	2.90	10	0.086
Myrtenyl acetate	0.527	0.55	0.68	5.915	1.6136	2.64	13	0.046
cis-Chrisanthenyl acetate	0.530	0.54	0.68	5.889	1.6360	2.62	9	0.031
α-Terpinyl acetate	0.401	0.63	0.64	6.156	1.7222	2.50	29	0.043
Terpin-4-yl acetate	0.390	0.62	0.62	5.997	1.7222	2.38	10	0.072
Decyl acetate	0.041	0.60	0.45	6.240	1.8738			

The only comparison that can be made of our descriptors and any obtained previously is with the five terpene esters listed by Ahmed and Poole [26], see Table 3. There is reasonable agreement between the two sets of descriptors, except for *V* for α-terpinyl acetate where the value of 1.7726 [26] is incorrect. We calculate *V* as 1.7222, the same as calculated by the ADME software [41] and by the UFZ-LSER software [42]. There is nothing exceptional about the descriptors for the terpene esters in Table 2. By comparison to a simple aliphatic ester such as decyl acetate, values of *E, S* and *B* are enhanced due to the ethylenic double bonds and the various ring systems present in terpenes.

Table 3

Comparison of descriptors for five terpene esters.

Terpene ester	E	S	B	V	L	log Kw
Linalyl acetate [26]	0.311	0.60	0.55	1.7878		
This work	0.331	0.65	0.65	1.7878	5.848	2.47
Geranyl acetate [26]	0.368	0.72	0.65	1.7878		
This work	0.368	0.65	0.68	1.7878	6.326	2.66
Neryl acetate [26]	0.350	0.70	0.65	1.7878		
This work	0.330	0.65	0.67	1.7878	6.011	2.52
Bornyl acetate [26]	0.397	0.54	0.58	1.6566		
This work	0.400	0.52	0.59	1.6566	5.899	2.03
α-Terpinyl acetate [26]	0.447	0.62	0.64	1.7726		
This work	0.401	0.63	0.64	1.7222	6.156	2.50

We are limited to studies of the terpene esters listed in Table 2 because of lack of experimental data, especially with regard to systems that yield equations on the lines of Eq. (1) with substantial values of the *b*-coefficient. We have therefore attempted to construct simple fragmentation schemes that could be used to estimate descriptors for other terpene esters. For terpene acetates that have a six-membered ring we find Eqs. (4-8), where the independent variables are ‘4R’ the number of 4-membered rings, ‘5R’ the number of five-membered rings, and ‘ND’ the number of ethylenic double bonds. In these equations, N is the number of data points, SD is the standard deviation, R is the correlation coefficient and F is the F-statistic.

$$E = 0.253 + 0.143*4\mathrm{R} + 0.125*5\mathrm{R} + 0.133*\mathrm{ND} \tag{4}$$

N = 9, SD = 0.026, R^2 = 0.952, F =33.04

$$S = 0.628 - 0.104*4\mathrm{R} -0.094*5\mathrm{R} + 0.020*\mathrm{ND} \tag{5}$$

N = 9, SD = 0.025, R^2 = 0.896, F =14.42

$$B = 0.550 + 0.060*4\mathrm{R} + 0.033*5\mathrm{R} + 0.070*\mathrm{ND} \tag{6}$$

N = 9, SD = 0.013, R^2 = 0.960, F =40.43

$$L = 5.971 - 0.189*4\mathrm{R} - 0.138*5\mathrm{R} + 0.120*\mathrm{ND} \tag{7}$$

$N = 9, SD = 0.085, R^2 = 0.808, F = 7.03$

$$\text{Log } Kw = 1.912 + 0.204*4R + 0.093 *5R + 0.514*ND \quad (8)$$

$N = 9, SD = 0.044, R^2 = 0.991, F = 176.41$

Although the number of data points is very small, these equations may still be useful in estimating the descriptors for terpene acetates. Even the worst equation out of Eq. (4) to Eq. (8), that is the equation for the *L*-descriptor, Eq. (7), yields estimates that are somewhat better than those obtained through the ADME Suite [41] or the UFZ-LSER software [42], as shown in Table 4. For the acetates in Table 4, the SD values between the estimated values and the experimental values of log *L* from Table 2 are 0.0687 Eq. (7), 0.1855 [41] and 0.1070 [42]. On this basis, estimates from Eq. (7) and from the UFZ-LSER software [42] are those recommended.

Table 4.

Estimates of the *L*-descriptor for terpene acetates.

Terpene acetate	**Table 2**	**Eq. (7)**	**[41]**	**[42]**
Carvyl acetate	6.22	6.21	6.03	6.12
Bornyl acetate	5.90	5.83	5.99	5.79
Isobornyl acetate	5.90	5.83	5.99	5.79
Fenchyl acetate	5.71	5.83	5.99	5.68
Menthyl acetate	5.98	5.97	6.14	5.82
Myrtenyl acetate	5.92	5.90	6.18	5.95
cis-Chrisanthenyl acetate	5.90	5.90	6.07	5.80
α-Terpinyl acetate	6.16	6.09	6.01	6.02
Terpin-4-yl acetate	6.00	6.09	6.01	6.02

The descriptors in Table 2 can now be used to calculate water-solvent and air-solvent partition coefficients into a wide range of solvents, both wet (that is water-saturated) and dry, for which we have [34, 35] the required coefficients in Eq. (1) and Eq. (2). Endo and Goss [43] have detailed corresponding equations for numerous environmental processes, and so the present descriptors for terpene esters can be used to calculate environmental data in a similar way. Many terpene esters occur naturally in essential oils, and are also found in wines [44], so that a particularly important environmental property is their human odor detection thresholds, ODTs. We have previously set out an equation, Eq. (9), for a standardized set of ODTs for 353 compounds [45], based on the ODTs determined by Nagata [46]. The set of 353 compounds does not include any terpene esters, but we can use the equation to predict values of ODT on the Nagata scale, as shown in Table 5. In Eq. (9) M is an indicator variable for mercaptans, AL for aldehydes, AC for carboxylic acids and UE for unsaturated esters. The additional statistics in Eq. (9) are the leave-one-out PRESS and Q, and the predicted standard deviation PSD. Q is defined through Q^2 = 1- (PRESS/SSTO) where SSTO is the total sum of squares for the regression.

$$\text{Log (1/ODT, ppm)} = -1.560 + 0.398\,E + 0.571\,S + 1.103\,A + 1.355\,B + 0.580\,L + 3.817\,\text{M} + 1.935\,\text{AL} + 1.462\,\text{AC} + 1.310\,\text{UE} \quad (9)$$

$N = 353$ $SD = 0.818$ $R^2 = 0.759$ $F = 70.70$

$PRESS = 254.810$ $Q^2 = 0.728$ $PSD = 0.869$

Devos *et al.* [47] have also listed a standardized set of ODTs that includes values for a number of terpenes. We have fitted the values of log (1/ODT) to our descriptors as shown in Eq. (10) and Eq. (11), where DB is an indicator variable for the number of ethylenic double bonds, and RG is an indicator variable for the number of rings present. We used only aliphatic acyclic and cyclic hydrocarbons, halides, ethers, ketones, aldehydes and alcohols because these are the functional groups commonly encountered in terpene chemistry. We give equations using the descriptors *V* and *L*, but there is very little difference in the statistics, and we use Eq. (11) to predict the ODT values listed in Table 5 only because Eq. (11) is of the same form as eq. (9).

$$\text{Log (1/ODT, ppm)} = 2.866 + 0.097\,E + 1.690\,S + 0.340\,A + 0.686\,B + 2.319\,V + 1.247\,\text{AL} + 0.366\,\text{DB} - 0.240\,\text{RG} \quad (10)$$

$N = 242$ $SD = 0.864$ $R2 = 0.702$ $F = 68.52$

$PRESS = 189.080$ $Q2 = 0.676$ $PSD = 0.901$

$$\text{Log 1/ODT, ppm)} = 3.406 - 0.838\,E + 1.211\,S + 0.011\,A + 0.859\,B + 0.643\,L + 1.195\,\text{AL} + 0.435\,\text{DB} - 0.258\,\text{RG} \quad (11)$$

$N = 242$ $SD = 0.869$ $R2 = 0.699$ $F = 67.56$

$PRESS = 191\text{-}209$ $Q2 = 0.673$ $PSD = 0.906$

Table 5. Calculation of odor detection thresholds for terpene esters, as log (1/ODT), with values on the Devos and Nagata scales

Terpene ester	**Log (1/ODT, p.ol), Devos**		**Log (1/ODT, ppm), Nagata**
	Calc	Obs [47]	Calc
Linalyl formate	9.05		3.19
Linalyl acetate	9.10	8.05	3.22
Linalyl propanoate	9.46		3.50
Linalyl butanoate	9.95		3.93
Geranyl acetate	9.40		3.55
Neryl acetate	9.22		3.34
β-Cittronellyl acetate	8.92		3.31
Carvyl acetate	9.01		3.57
Bornyl acetate	7.48	7.86	3.12
Isobornyl acetate	7.48		3.11
Fenchyl acetate	7.45		3.98
Menthyl acetate	8.04		3.11
Lavendulyl acetate	9.03		3.15
Farnesyl acetate	11.55		5.20
Myrtenyl acetate	7.94		3.32
cis-Chrisanthenyl acetate	8.60		3.30
α-Terpinyl acetate	8.52		3.40
Terpin-4-yl acetate	8.39		3.27
Propyl acetate	6.24	6.24	1.06
Butyl acetate	6.61	6.71	1.37
Pentyl acetate	7.51	6.93	1.65

We give in Table 5 some values for simple esters as a comparison. The Nagata values of ODT are expressed in units of ppm but the Devos values [47] are in a volume unit denoted as ‘p.ol’. The relationship between log (1/ ODT) with ODT in units of p.ol and ppm is [47],

$$\mathrm{Log}\ (1/\ \mathrm{ODT,\ ppm}) = \log\ (1/\ \mathrm{ODT,\ p.ol}) - 6 \qquad [12]$$

Even when expressed in the same units, there is no reason why the standardized ODT values of Nagata [46] and of Devos *et al*. [47] should be the same. The constant term in Eq. (9) of -1.560 and in Eq. (11) of 3.406 indicates that the difference between the Nagata log (1/ ODT/ppm) and the Devos log (1/ ODT/p.ol) sets is 4.966, so that all the Devos values in Table 5 can be converted into values on the Nagata scale in ppm by subtraction of 4.97

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