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Determination of descriptors for fragrance compounds by gas chromatography and liquid–liquid partition

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ABSTRACT

Retention factors on a minimum of eight stationary phases at various temperatures by gas–liquid chromatography and liquid–liquid partition coefficients for five totally organic biphasic systems were combined to estimate descriptors for 28 fragrance compounds with an emphasis on compounds that are known or potential allergens. The descriptors facilitated the estimation of several properties of biological and environmental interest (sensory irritation threshold, odor detection threshold, nasal pungency threshold, skin permeability from water, skin–water partition coefficients, octanol–water partition coefficients, absorption by air particles, adsorption by diesel soot particles, air–water partition coefficients, and adsorption by film water). The descriptors are suitable for use in the solvation parameter model and facilitate the estimation of a wide range of physicochemical, chromatographic, biological, and environmental properties using existing models.

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1. Introduction

Essential oils are liquids containing volatile aroma compounds obtained mainly from plant materials by steam distillation, infusion, extraction or cold-pressing [1]. They are widely used in the cosmetics, perfumery, pharmaceuticals, beverage, personal care, and food industries where their attractive odor and/or flavor is exploited to enhance the value of consumer products. Fragrances may also contain synthetic aroma compounds as well as compounds of natural origin. Several natural fragrances are terpene hydrocarbons and their oxygenated derivatives with high structural diversity. Some fragrance compounds are known or suspect allergens and subject to regulatory control [2]. These are the compounds emphasized in this report and are indicated in Table 1 together with their systematic chemical names. For perspective, when used as cosmetic products in the European Union it is required to inform consumers of the presence of potential allergenic compounds in cosmetic products if present at a concentration that exceeds 0.001% in leave-on products or 0.01% in rinse-off products [2] with similar regulations in force in other countries and trading blocks around the globe. Effective analytical methods employing headspace and/or extraction methods for isolation and gas chromatography for separation with mass spectrometric detection have been developed for cosmetics to support compliance with regulatory requirements [3–6].

The use of properties that are easy to measure in order to estimate properties that are inaccessible, expensive or difficult to measure is a well established approach in chemistry and biology. This approach requires that some sort of empirical or theoretical model is established beforehand that provides a connection between the two sets of properties. Since a large number of transport-related processes can be described by equilibrium or rate approaches it is not surprising that free-energy related models are the most successful for these applications. Whether or not these studies involve the prediction of retention in separation systems, the distribution of compounds across biological membranes (e.g., skin permeation, nasal pungency, odor thresholds, etc.), environmental fate assessment (e.g., air–particulate, air–water distribution, octanol–water distribution, etc.) and so on: the ultimate goal is to establish a suitable quantitative structure–property relationship (QSPR) to facilitate the prediction of further system properties for compounds lacking experimental values [7–13].

Two general strategies are commonly employed in QSPR studies. The first approach starts with the generation of a large number of molecular descriptors using structure-based computational methods such as DRAGON, SYBYL, CODESSA (e.g., more than 800 descriptors can be calculated using CODESSA) [14]. Statistical tools are then used to reduce the number of descriptors to a manageable number while maximizing the experimental variance explained. The final output is usually a linear or non-linear model suitable for the prediction of properties for other compounds. The main weakness of this approach is that the selected descriptors may be

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Table 1
Plant-derived and synthetic fragrance compounds with those indicated as known or suspect allergens according to European Union regulations [2].

Common name	Systematic chemical name		Source[a]
(i) Allegens			
Amyl cinnamal	(Phenylmethylene)heptanal		TCI
Anise alcohol	4-Methoxybenzyl alcohol		CS
Benzyl alcohol			SA
Benzyl benzoate			ACROS
Benzyl cinnamate	Benzyl 3-phenylpropenoate		TCI
Benzyl salicylate	Benzyl 2-hydroxybenzoate		TCI
Cinnamyl alcohol	3-phenyl-2-propen-1-ol		ACROS
Citral (geranial)	3,7-Dimethylocta-2,6-dienal	(E-isomer)	CS
Citral (neral)		(Z-isomer)	CS
Coumarin	2H-1-Benzopyran-2-one		SA
Eugenol	2-Methoxy-4-prop-2-enylphenol		ACROS
Farnesol	3,7,11-trimethyldodeca-2,6,10-trien-1-ol		SA
Geraniol	3,7-Dimethylocta-2,6-dien-1-ol		TCI
Hydroxycitronellal	3,7-dimethyl-7-hydroxyoctanal		SA
α-Isomethyl ionone	3-Methyl-4(2,6,6-trimethyl-1-cyclohex-2-enyl)but-3-en-2-one		
Lilial	3-(4-*tert*-butylphenyl)butanal		TCI
Limonene	1-Methyl-4-(1-methethenyle)cyclohexene		CS
Linalool	3,7-Dimethyl-1,6-dien-3-ol		ACROS
Methyleugenol	1,2-Dimethoxy-4-prop-2-enylbenzene		TCI
(ii) Not known to be allegens			
Borneol	1,7,7-Trimethyl-bicyclo[2.2.1]heptan-2-ol		ACROS
Camphor	1,7,7-Trimethylbicyclo[2.2.1]heptan-2-one		CS
Carvone	2-Methyl-5-(1-methylethenyl)-2-cyclohexanone		ACROS
Citronellal	3,7-Dimethylocta-2,6-dienal		CS
2-Methoxycinnamaldehyde			SA
α-Pinene/β-pinene	4,7,7-Trimethylcyclo[3.1.1]hept-3-ene		CS
Terpinen-4-ol	4-Isopropyl-1-methyl-1-cyclohexen-4-ol		ACROS
Vanillin	4-Hydroxy-3-methoxybenzaldehyde		SA

[a] ACROS = ACROS Organics, Morris Plains, NJ, USA; CS = Chem Services Inc., West Chester, PA, USA; SA = Sigma–Aldrich, Milwaukee, WI, USA; and TCI = TCI America, Portland, OR, USA

difficult to understand and the models may lack obvious chemical significance. The best set of reduced descriptors for the correlation of any given property is unlikely to be the same as the best set for the correlation of any other (often similar) property.

The above problems are circumvented by less flexible models that define a small number of descriptors in advance, and use just these descriptors to characterize all processes. The descriptors may be derived from theory [15], such as the five COSMOments (COSMO-RS is a model combining quantum theory, dielectric continuum models, surface interactions and statistical thermodynamics) or experimentally derived parameters, such as the six descriptors used in Abraham's solvation parameter model [16–18]. Theoretical models allow the calculation of descriptors for compounds that are unavailable or yet to be synthesized, but for accessible compounds, computational techniques can be slow and no faster than experimental methods for estimating descriptor values. The purpose of this report is the experimental determination of descriptor values for fragrance compounds to facilitate the estimation of a range of physicochemical and biological properties available through use of the solvation parameter model. These descriptors also provide chemical insight into how different compounds behave in transfer systems.

Many of the compounds in Table 1 have low water solubility and their descriptor values are difficult to determine by conventional methods based on aqueous liquid–liquid partitioning [17]. We encountered a similar problem in calculating descriptors for organosilicon compounds and developed an alternative procedure that uses a combination of gas chromatography and partitioning in totally organic solvent systems for this purpose [19,20]. In recent years the number of possible totally organic biphasic systems available for descriptor measurements has increased significantly [21] and advantage is taken of these developments to facilitate the determination of descriptors for fragrance compounds in this report. Abraham and co-workers have determined descriptor values for a several terpenes [13,22,23] based on a combination of experimental and estimated property values with little overlap with the compounds in Table 1. By minimizing the use of estimated properties in the calculations it is hoped to provide improved values for all compounds including those in Table 1 previously estimated by Abraham and co-workers.

The solvation parameter model as generally used in studies of transfer properties takes two forms. For transfer from a gas phase to a condensed phase (for example, gas–liquid chromatography)

$$\log\ k = c + eE + sS + aA + bB + lL \quad (1)$$

and for transfer between condensed phases (for example, as in liquid–liquid partition)

$$\log\ K_p = c + eE + sS + aA + bB + vV \quad (2)$$

where the dependent variable is an experimental property such as a chromatographic retention factor, k, or a partition coefficient, K_p [16–18,24,25]. The capital letters in Eqs. (1) and (2) are descriptors that define the capability of a solute for electron lone pair interactions, E, dipole-type interactions, S, hydrogen-bonding interactions with the solute acting as a hydrogen bond acid, A, or base, B, the gas–liquid partition coefficient on n-hexadecane at 298.2 K, L, and McGowan's characteristic volume, V. The lower case letters are the complementary system properties to the solute descriptors with e determined by interactions with electron lone pairs, s dipole-type and induced dipole-type interactions, a hydrogen-bond basicity (because a hydrogen-bond acid solute will interact preferentially with a hydrogen-bond base solvent), b hydrogen-bond acidity, and l and v are determined by the difference in the work require to form a cavity in the receiving and donating phases and contributions from dispersion interactions that are not self-cancelling in the two phases. To determine the solute descriptors it is necessary to set up a series of equations similar to Eqs. (1) and (2) with known system constants that allow the convenient measurement of the partition or retention property for the solute. The descriptors are calculated by finding the unique values for each descriptor that

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