

CHAPTER 1

Definitions

This chapter aims to introduce the family of compounds, how they are referred to, the likely structures that will be found and their chemistry from an environmental point of view.

1.1 Names and Structures

Fatty alcohol is a generic term for a range of aliphatic hydrocarbons containing a hydroxyl group, usually in the terminal or *n*-position. The accepted definition of fatty alcohols states that they are naturally derived from plant or animal oils and fats and used in the pharmaceutical, detergent or plastics industries (*e.g.* Dorland's Illustrated Medical Dictionary). However, it is possible to find the hydroxyl (–OH) group in other positions within the aliphatic chain, but these secondary or tertiary alcohols are not discussed to any great extent in this book.

The generic structure of fatty alcohols or *n*-alkanols can be seen in Figure 1.1 and specific examples in Figure 1.2. The value of the *n*-component is variable and is discussed below.

The range of chain lengths for these *n*-alkanols can be from 8 to values in excess of 32 carbons. With such a wide range of chain lengths, the chemical properties and consequently the environmental behaviour vary considerably. As well as these straight chain moieties, a range of branched chain compounds are also naturally produced by micro-organisms in the environment. The major positions for the methyl branches are on the carbons at the opposite end of the molecule to the terminal –OH. If the methyl branch is one position in from the end of the molecule (ω -1), it is termed an *iso* fatty alcohol; if it is two in from the end (ω -2), it is called an *anteiso* fatty alcohol. Examples of these branches can be seen in Figure 1.2.

Most fatty alcohols are saturated in that they have no double bonds present in their structure. However, there are a limited number of mono-unsaturated compounds that can be found in nature. The two most common compounds are phytol (3,7,11,15-tetramethyl-2-hexadecen-1-ol), an isoprene¹ derived from

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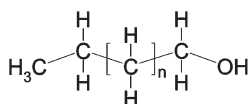


Figure 1.1 Generic structure of a fatty alcohol. The total number of carbons needs to be greater than 8–10 to be a “fatty” alcohol; shorter chain compounds have an appreciable water solubility and are generally just called alcohols.

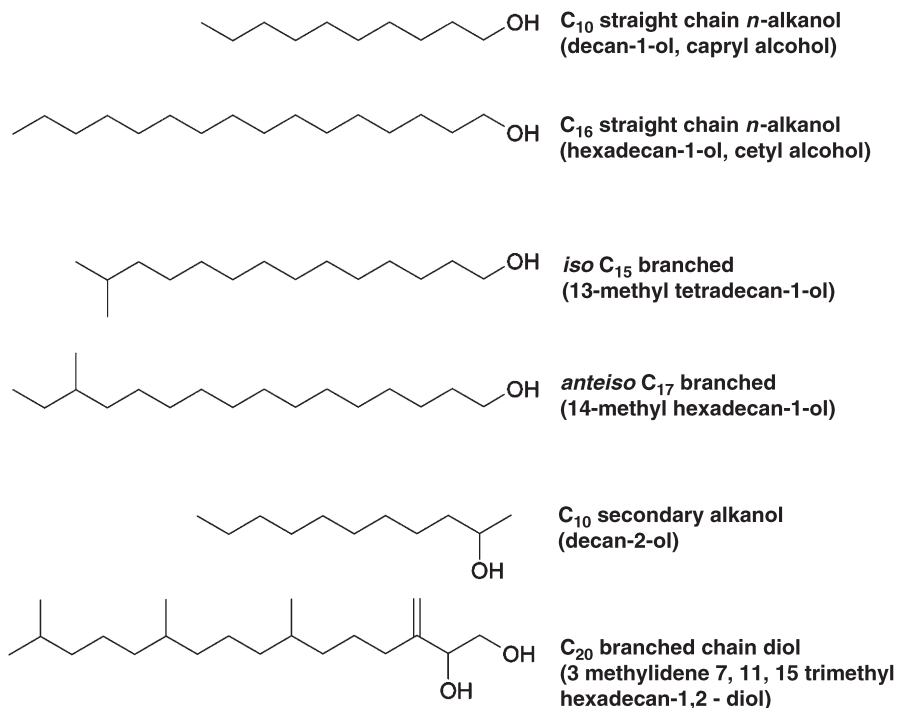


Figure 1.2 Example fatty alcohol structures. The majority found in nature are of the straight chain type with smaller amounts of the branched chain compounds also being present. Secondary alcohols and diols are relatively uncommon.

the side chain of chlorophyll (Figure 1.3), and a straight chain C₂₀ alcohol with a double bond in the ω₉ position counted from the terminal carbon (eicos-11-en-1-ol; Figure 1.3).²

There have been occasional reports of polyunsaturated fatty alcohols, but these are relatively rare³ and are confined to di-unsaturates such as octadecadienol, 18:2. There is a group of isoprenoid lipids which may be found in bacteria and are essentially repeating isoprene subunits strung together and terminated by a hydroxyl group.⁴ These compounds are also uncommon in environmental analyses and are not reported to any great extent.

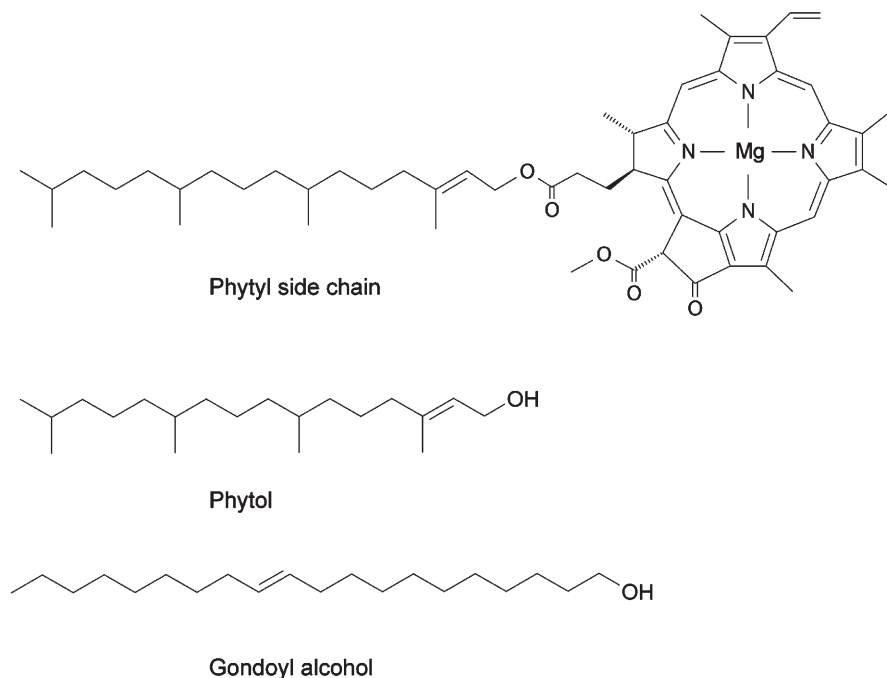


Figure 1.3 Chlorophyll-a molecule with the phytyl side chain labelled. Cleavage of this chain at the COO^- group produces free phytol in the environment. Eicos-11-en-1-ol or 20:1 fatty alcohol is one of the most frequently observed straight chain mono-unsaturated alcohols in the environment.

Fatty alcohols together with many other groups of compounds have both systematic and trivial or common names. The common name is based on the length of the alkyl chain and the root is common between aliphatic hydrocarbons and fatty acids. These common names together with the systematic name and carbon number are shown in Table 1.1.

1.2 Physicochemical Properties

1.2.1 Solubility *Versus* Chain Length

One of the key factors in determining the environmental behaviour of any compound is its water solubility; this will determine the partitioning between solid and solution phases. Compounds with low water solubility will be preferentially adsorbed to particulate matter, either settled or suspended in water. These compounds will also partition into the lipid phase of organisms and would have higher bioconcentration factors if not offset by metabolism. The available physicochemical properties for the fatty alcohol series from C_4 to C_{30}

Table 1.1 Names and key properties of fatty alcohols from C₄ to C₃₀. The horizontal line indicates the arbitrary division between alcohols and fatty alcohols.

Systematic name	Common name (excluding “alcohol” part)	Carbon number	CAS registry number	d^{20} (g cm ⁻³)	Melting point (°C)	Boiling point ^a (°C)	Water solubility ^b (at 25 °C)	Predicted water solubility ^c (mg l ⁻¹)
Butanol	Butyl	4	71-36-3	0.810	-90	117	91 ml l ⁻¹	
Pentanol	Amyl	5	71-41-0	0.815	-79	137.5	27 g l ⁻¹	
Hexanol	Caproyl	6	111-27-3	0.815 at 25 °C	-51.6	157	5.9 g l ⁻¹	7671.3
Heptanol	Oenanyl	7	111-70-6	0.819 at 25 °C	-34.6	175.8	1.6 g l ⁻¹	1743.6
Octanol	Caprylic	8	111-87-5	0.827	-16	194	0.5 g l ⁻¹	400.7
Nonanol	Pelorgonyl	9	143-08-8	0.828	-5	215	0.1 g l ⁻¹	94.2
Decanol	Capryl	10	112-30-1	0.830	6.4	232.9	0.04 g l ⁻¹	22.9
Undecanol		11	112-42-5	0.832	15	244	0.008 g l ^{-1d}	5.8
Dodecanol	Lauryl	12	112-53-8	0.831 at 24 °C	24	259	BML	1.6
Tridecanol		13	112-70-9	0.915	30	278	BML	0.451
Tetradecanol	Myristyl	14	112-72-1	0.824	38	289	BML	0.141
Pentadecanol		15	629-76-5	0.893	42		BML	0.0490

Hexadecanol	Cetyl	16	36653-82-4	0.811	49	344	BML	0.0190
Heptadecanol	Margaryl	17	1454-85-9	0.885	53		BML	0.00842
Octadecanol	Stearyl	18	112-92-5	0.811	59	360	BML	0.00433
Nonadecanol		19	1454-84-8	0.882	62		BML	
Eicosanol	Arachidyl	20	629-96-9	0.88	65		BML	
Henticosanol		21	15594-90-8		68.5		BML	
Docosanol	Behenyl	22	661-19-8	0.8	70		BML	
Tricosanol		23	3133-01-5		72		BML	
Tetracosanol	Lignoceryl	24	506-51-4		72		BML	
Pentacosanol		25	26040-98-2		75		BML	
Hexacosanol	Ceretyl	26	506-52-5		73		BML	
Heptacosanol	Carboceryl	27	2004-39-9		80		BML	
Octacosanol	Montanyl	28	557-61-9		81		BML	
Nonacosanol		29	6624-76-6		83.5		BML	
Tricontanol	Melissyl	30	593-50-0		87		BML	

^aThe boiling point values quoted are at atmospheric pressure.

^bBML, below measurement limits.

^cAs the water solubility becomes harder to measure, the predicted water solubility is frequently used instead. The values presented here are taken from Fisk *et al.*⁵ and use the ECOSAR model.

^dAt 20 °C.

are summarised in Table 1.1. These data are drawn from many sources, but principally from the online Beilstein Chemical Database (Elsevier MDL). The density and melting points in the summary data (Table 1.1) have a degree of uncertainty about them as some compounds, especially the longer chain and odd carbon number moieties, are less well studied. Density data are not available for all compounds.

The short chain compounds (up to C₉) have appreciable water solubility (Table 1.1) and would not be classified as “fatty” alcohols as the free compounds are more likely to have a substantial amount in solution rather than in the solid phase (abiotic or biotic). Compounds with a chain length greater than 10 carbons are essentially insoluble in water and will partition on to the solid phase in the environment.

1.2.2 Partitioning (K_{ow}) and Sediment Associations

It is usual to measure the water solubility and related factors such as bio-concentration factors (BCFs) through the octanol–water partition coefficient (K_{ow}) or its logarithm ($\log K_{ow}$). There is relatively little information published for *measured* K_{ow} values for fatty alcohols, although there are some data estimated from HPLC retention times.⁶ Difficulties arise in the measurement of these coefficients due to the hydrophobic–hydrophilic nature of the different parts of the molecule (Figure 1.4). The hydroxyl group gives that end of the molecule a degree of water solubility while the alkyl carbon chain is hydrophobic. Therefore, these compounds sit at the interface of octanol and water in the experimental situation.

The $\log K_{ow}$ values for compounds (Table 1.2; shown graphically in Figure 1.5) with a chain length greater than C₉ are above 4, which is indicative of materials that will be preferentially absorbed to particulate matter. In most environmental situations, this means the compounds will be associated mainly with particles such as settled and suspended sediments. The nature of these particulate materials is that they will settle out to the benthos at some stage and will be transferred

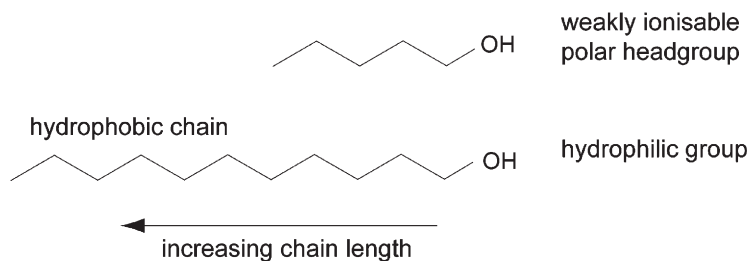
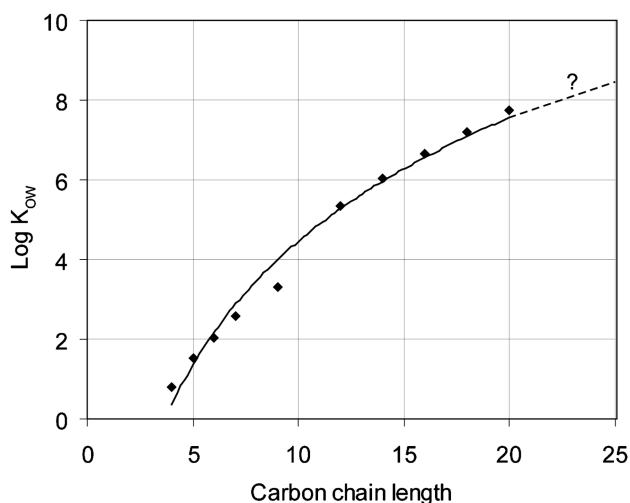


Figure 1.4 The –OH group is weakly ionisable to form O^- and H^+ and as such will “dissolve” in water. However, with increasing alkyl chain length, the effect of this is diminished and the compound has lower water solubility. This property allows the molecule to be used as a detergent, one of the principal anthropogenic functions of fatty alcohols.

Table 1.2 Octanol–water partition coefficients.

<i>Fatty alcohol</i>	<i>Carbon number</i>	<i>Log K_{ow}</i>
Butanol	4	0.785 ^a 0.84 ^c
Pentanol	5	1.53 ^a
Hexanol	6	2.03 ^a 1.84 ^c
Heptanol	7	2.57 ^a 2.34 ^c
Nonanol	9	3.31 ^b 3.77 ^a
Dodecanol	12	5.36 ^b
Tetradecanol	14	6.03 ^b
Hexadecanol	16	6.65 ^b
Octadecanol	18	7.19 ^b
Eicosanol	20	7.75 ^b

^aFrom Tewari *et al.*⁷^bFrom Burkhard *et al.*⁶^cFrom Hansch *et al.*⁸**Figure 1.5** Effect of carbon chain length in fatty alcohols on log K_{ow} .

to the geosphere. This partitioning between the solution phase for short chain compounds and solid phase for long chain compounds may lead to the separation of mixtures such that short chain moieties will remain in solution while longer chain moieties may settle out. There will also be different degradation steps possible as materials in the solid phase may enter anaerobic environments in sediments; this may lead to preservation of some materials and differential products of degradation.

The association of fatty alcohols with suspended matter will be of importance in sewage treatment plants as incoming materials may be removed from the system by partitioning into the solid phase which subsequently settles out. Experiments using radiolabelled alcohols with activated sewage sludge⁹ measured the time dependent partition coefficients (K_d) for a range of alcohols typically used in detergent formulations (Table 1.3). The mean K_d values can be seen in Figure 1.6; the data are presented on a logarithmic axis and a linear relationship can be seen in this figure. These values are relatively high implying that, in such a system, free fatty alcohols will be actively scavenged by the particulate phase and may be removed with the sludge or associated with suspended solids in wastewater. Thus, alcohols may leave sewage treatment plants either bound or unbound (free). Fisk *et al.*⁵ using the wastewater treatment model SIMPLETREAT (a module in the European environmental distribution model EUSES) demonstrated that as carbon number increases, the fraction of fatty alcohol that is degraded by microbes in wastewater declines as the amount sorbed increases. Federle and Itrich¹⁰ postulated that eventually at chain lengths of 16 and greater, the equilibrium desorption controls the biodegradation rate.

Table 1.3 The average (± 1 standard deviation) partition coefficients (K_d) for fatty alcohols with activated sewage sludge suspended in river water.

Time (h)	C_{12}	C_{14}	C_{15}	C_{16}	C_{18}
1	4100 \pm 267	14700 \pm 645	4070 \pm 387	34100 \pm 1700	107000 \pm 6330
5	3410 \pm 119	12700 \pm 675	3820 \pm 183	33300 \pm 1600	90300 \pm 3070
16	3320 \pm 276	10500 \pm 167	3590 \pm 104	28600 \pm 1720	89900 \pm 1980
30	3100 \pm 143	10200 \pm 670	3480 \pm 77	27600 \pm 1930	82400 \pm 2970
72	3000 \pm 78	8490 \pm 916	3080 \pm 271	23800 \pm 3160	78700 \pm 5350

Data from van Compernelle *et al.*⁹

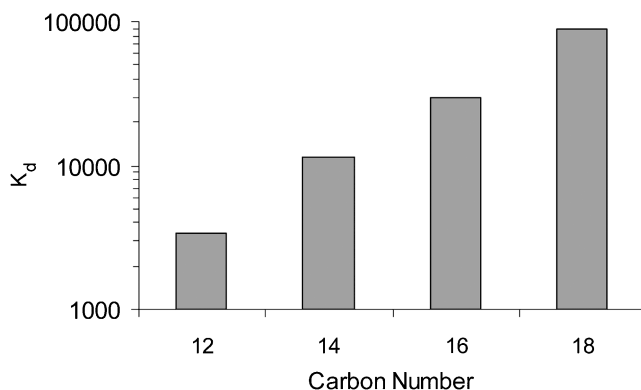


Figure 1.6 Mean K_d for the even carbon numbered fatty alcohols (data from Table 1.3). Note that the y -axis has a logarithmic scale.

Summary

- Fatty alcohols found in the environment are principally linear with a terminal hydroxyl group.
- As the alkyl chain becomes longer, the water solubility decreases leading to a wide range of octanol–water partition coefficients.
- Compounds with a chain length greater than C₁₀ are more likely to be associated with the solid phase in the aquatic environment and become coupled with sediments and soils in the environment.
- These lower water solubility compounds will tend to bioaccumulate more than their short chain moieties, although all may be metabolised by bacteria.