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Chiral Recognition by Molecular Monolayers: Inclusion of Terpenes in tert-Butyldimethylsilyl-O6-β-Cyclodextrin

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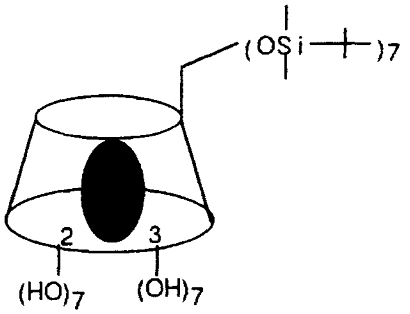
Chiral discrimination has been shown at the air-water interface for the binding of terpenes to heptakis-6-O-(tert-butyldimethylsilyl)-β-CD.

The cyclodextrins are a class of cyclic-oligosaccharides possessing a relatively nonpolar molecular cavity which is capable of complexing a wide variety of organic molecules.[1] Their natural chirality has led to them being widely used in enantiomeric separations,[2] and in particular their interactions with terpenes has been extensively studied.[3] A number of amphiphilic cyclodextrin derivatives have been synthesised,[4] and their ability to form inclusion complexes at the air-water interface has been shown.[5] Heptakis-tert-butyldimethylsilyl-β-cyclodextrin (**1**) forms stable molecular monolayers at the air-water interface in which the wider secondary hydroxyl face is open to the aqueous phase, Ca^{2+} adsorption and inclusion in the layer has been demonstrated,[6] and **1** forms a 1:1 complex with pyrene strong component arising from included and bound water molecules,[7] which makes this molecule a good choice for the study of chiral recognition of guest molecules.



Here we present the complexation study of **1** with borneol, a strongly bound terpene,[3] and two pairs of enantiomers (R)-(−)-Carvone and (S)-(+)-Carvone; and (1R,2S,5R,)-(−)-Menthol and (1S,2R,5S)-(+)-Menthol.

the surface potential arise from the different orientation of the enantiomers within the chiral cavity leading to different orthogonal dipole moments.

The surface potential values of the monolayers were measured under static conditions,[8] with the terpenes injected into the subphase, under the experimental conditions used the surface potential is related to the orthogonal dipole moment of the molecule and its bound water by Equation 1.

$$\Delta V = 12\Pi\, n\, \mu_{\perp}$$

As the molecular areas occupied by the host alone and its complexes are identical, as given in Table I, and hence no guest molecules are adsorped between molecules of **1**, we will only be concerned with the contribution arising from the dipoles of the included water molecules or the guest molecules replacing them.

In Figure 1 are given the variations in ΔV as a function of the surface concentration of **1** when the subphase is composed of a) pure water, b) a 10^{-4} M solution of Borneol, c) a 10^{-4} M solution of (+) Carvone and d) a 10^{-4}M solution of (−) Menthol.

The curves show that there is a clear variation in ΔV as the guest molecules changes, thus the method is sufficiently sensitive to detect differences in the orthogonal dipole moment arising effectively from the different orientation of the guest in the cavity and any effects this may have on the hydration of the monolayer. The values for ΔV and the apparent dipole moments are given in Table I.

In Figure 2a are shown the variations in ΔV for the two Menthol enantiomers and in Figure 2b the corresponding curves for the Carvone enantiomers. The apparent discrimination is much smaller for the Menthol enantiomers than for the Carvone enantiomers.

Previous studies on the Menthol isomers have shown that there is only 5% chiral discrimination in crystallisation experiments, and ^{1}H NMR studies on the complexes with O2,O6-dimethyl-β-cyclodextrin showed a small difference in the spectrum of methyl region for the two enantiomers.[9] In a molecular modelling study we assumed that possible hydrogen bonds between the terpenes and the CD macrocycle would dominate in positioning the guest in the cavity, this leads to a probable hydrogen bond between the Menthol OH and an O4 glycosidic oxygen and a second between the Carvone CO and an OH2 hydroxyl. The two Menthol enantiomers will position essentially along the molecular axis with almost no difference in the orientation of the guest dipole, however for the two Carvone isomers there exists a large difference in the orientation of the olefin, in the case of the (−) isomer it is almost parallel to the molecular axis and for the (+) isomer it is probably at about 45° to the axis. As shown in Figure 3. These large differences in guest orientation are expected to be the major factor in the much larger difference

TABLE I Molecular Areas, Surface Potential Values and Orthogonal Dipoles Moments for the Interfacial Complexes of **1** with Various Terpenes.

	MOLECULAR AREA (Å^2)	SURFACE POTENTIAL (mV)	DIPOLE MOMENT (mD)
PURE WATER	417	298	3296
BORNEOL	417	345	3816
(+) MENTHOL	417	304	3362
(−) MENTHOL	417	312	3451
(+) CARVONE	417	270	2986
(−) CARVONE	417	318	3517

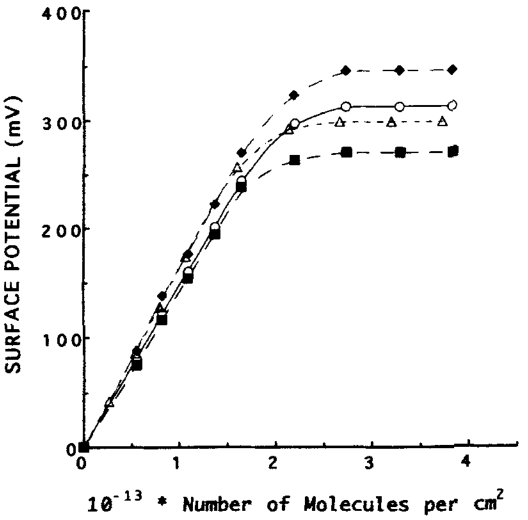


FIGURE 1 Surface potential as a function of number of molecules of **1** present on subphases of a) (Δ) pure water; b) (◆) Borneol; c) (■) (+) Carvone; d) (○) (−) Menthol.

in ΔV observed for Carvone a molecule having only one chiral centre as compared to Menthol a molecule having three chiral centres.

In conclusion we have shown that monolayers composed of amphiphilic cyclodextrin molecules give rise to a chiral discrimination between included terpene molecules and that this discrimination is related to the molecular orientation of the guest in the CD cavity.

The surface potential of spread cyclodextrin monolayers was measured as previously described.[10] The Keithley Instruments Electrometer (model 610C) was connected to two identical ^{241}Am air ionising a emitting electrodes suspended at about 2–3 mm above the reference (left cell) and the measuring cell (right cell) as previously described. The two cells are connected by a liquid bridge for electrical continuity. The measured difference in surface potential (ΔV) is that between the surface potential of the measuring cell (V_M) and the monolayer free reference cell (V_R). In the presence of a cyclodextrin monolayer, the surface potential of the system is given by the following equation:

$$\Delta V = V(M) - V(R)$$

The potential jump at the water-air interface, ΔV, induced by formation of a monolayer, is defined by the Helmholz equation as:

$$\Delta V = (\varepsilon_0)^{-1}\, n\mu_{\perp}$$

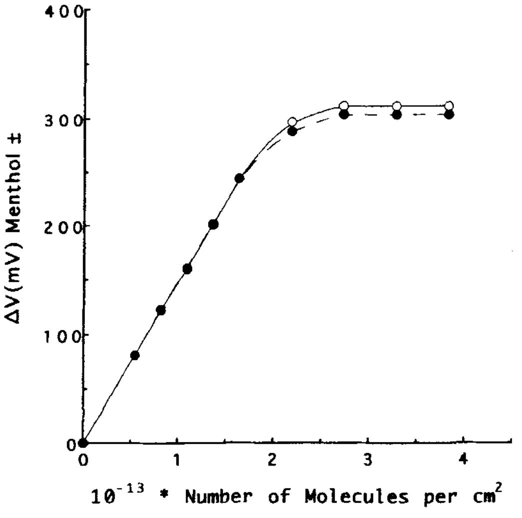


FIGURE 2A Variation in the surface potential of **1** in the presence of (○) (−) Menthol; (•) (+) Menthol.

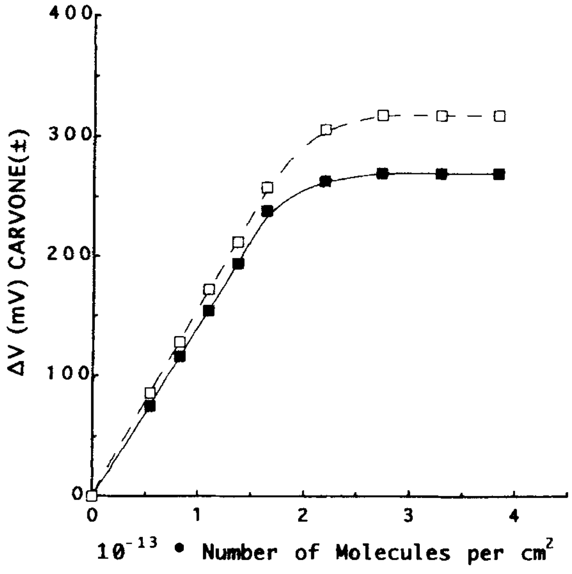


FIGURE 2B Variation in the surface potential of **1** in the presence of (□) (-Carvone); (■) (+) Carvone).

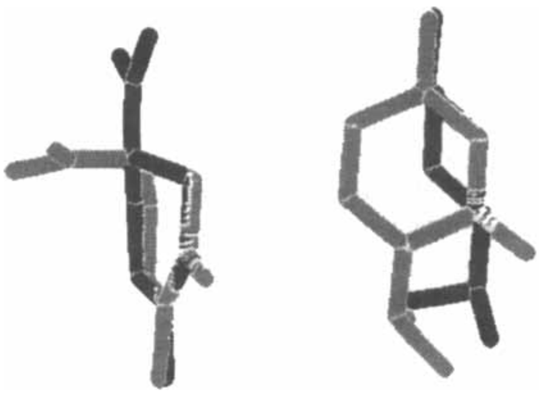


FIGURE 3 Models of the Carvone (a) and Menthol (b) enantiomers where the hydrogen bonding groups have been aligned.[11] (See color plate I).

where n = 1/A is the number of molecules, A the mean area per molecule and ϵ_0 the permittivity in the vacuum. The quantity $\mu_{\perp}$ is the effective dipole moment in direction perpendicular to the surface.

The formation of monolayer brings about a change in surface potential which is proportional to the change of the vertical component of the dipole density of the spread molecule with respect to the pure water surface. In the case of cyclodextrin monolayer the local contributions of the hydrophobic and hydrophilic parts of the CDs will both influence onto the total surface potential. Hence, surface potential measurements can be used to predict the magnitude and the direction of potential changes which occur as a consequence of changes in the packing density of the cyclodextrins.

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The sensitivities of measurements were 1 mV in the 0–100 mV range and 10mV in the 100–400 mV range. It was considered that equilibrium was established when the value of ΔV did not change after 30 mn. All reported surface potential values are mean values of at least three measurements. The standard deviation of the mean never exceeded ± 5 mV.

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