

Crown Ethers Derived from Cyclodextrin: Interaction with Triphenylmethane Derivatives

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Abstract. Periodate oxidation followed by borohydride reduction of beta cyclodextrin results in crown ether type derivatives. The polyaldehyde obtained by periodate oxidation has been reduced to polyalcohol and converted to a permethylated derivative. These macrorings are much more flexible than beta cyclodextrin itself.

The interaction of beta cyclodextrin (β -CD), methylated beta cyclodextrin (DIMEB), polyalcohol and permethylated crown ethers derived from beta cyclodextrin with two triphenylmethane derivatives and their triphenyltin analogues has been studied. On the basis of the changes in the UV spectra and the solubility enhancement it can be concluded that cyclodextrins (β -CD and DIMEB) form complexes only with the triphenylmethane derivatives. On the other hand the crown ethers prepared from β -CD give complexes only with the triphenyltin derivatives.

Key words: Cyclodextrin, crown ether, triphenylmethane, herbicides.

1. Introduction

The polyaldehyde prepared from beta cyclodextrin by periodate oxidation of the C₂—C₃ bonds of all glucopyranose units, can easily be reduced to a polyalcohol [1]. The rigid ring of cyclodextrin is converted into a highly hydrophilic, flexible macroring of the crown ether type. By permethylation of this polyalcohol a crown ether macroring is obtained which is soluble in water as well as in organic solvents. The preparation of similar derivatives has been reported in a previous work [2].

To ascertain the complex forming properties of these crown ether type compounds their effect on the UV spectra and the solubility of two triphenylmethane and two triphenyltin derivatives were studied. For comparison beta cyclodextrin (β -CD) and heptakis(2,6-di-*O*-methyl)beta cyclodextrin (DIMEB) were similarly studied.

The triphenylmethane derivatives and their tin analogues (Nuarimol, Triarimol, Torque and Bristan) are herbicides of poor solubility in water. In the molecules of the analogues the carbon atom of methane is substituted by a tin atom (Figure 1).

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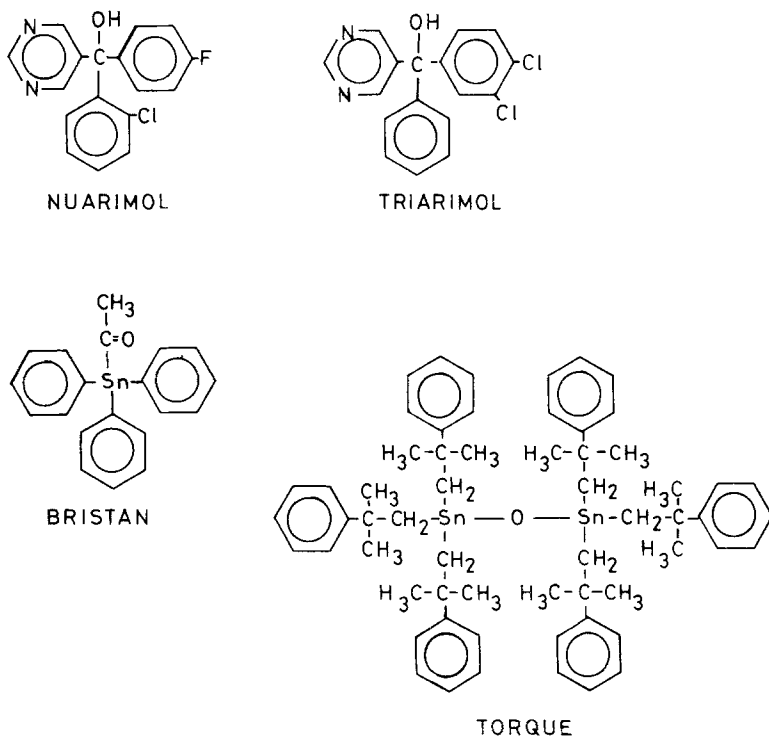


Fig. 1. Structure of the triphenylmethane derivatives and analogues studied.

2. Experimental

100 mg β -CD (or a derivative) was dissolved in 5 ml phosphate buffer (0.1 N, pH = 5.0) and 0.3, 0.6, 0.9, 1.2 and 1.5 ml of this solution was diluted to 3 ml. The molecular weights of the β -CD, DIMEB, polyalcohol crown ether and methylated crown ether are 1134, 1330, 1148 and 1442 D, respectively. Consequently the concentration of the solutions was in the range of 2.5–15.86 mM. 20 mg triphenylmethane derivative or an analogue was added to the 3 ml solutions and shaken at room temperatures for 48 hr. After that the undissolved parts were removed by filtration and the UV spectra were recorded over the whole UV range. The blank was prepared by shaking 20 mg of a triphenyl methane or an analogue in 3 ml buffer solution.

3. Results

β -CD and DIMEB reacted only with the triphenylmethane derivatives (Nuarimol, Triarimol), while the crown ethers interacted only with the tin-centered Bristan and Torque. The intensity of UV absorption of both Nuarimol and Triarimol increased in the presence of β -CD. Simultaneously a shift of the absorption maximum from 220 nm to approximately 230 nm was observed, and an isosbestic point appeared at 210 nm. The value of the UV absorption at 240 nm is a linear function of the β -CD concentration.

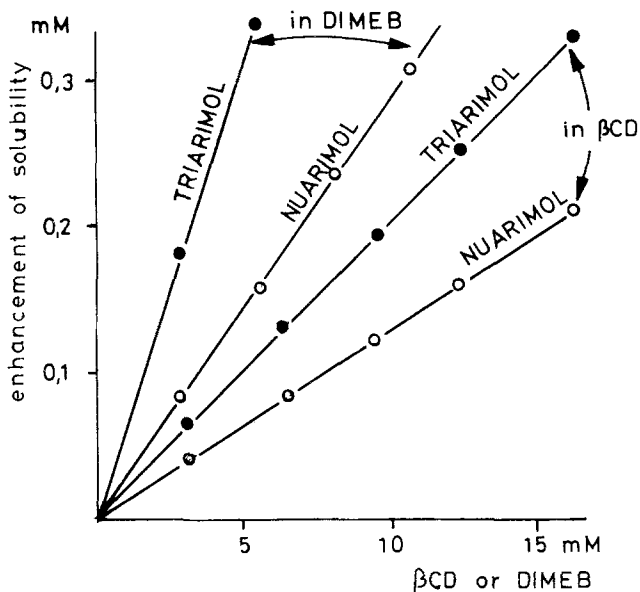


Fig. 2. Solubility enhancement of triphenylmethane derivatives (solubility in host solution – solubility in water) as a function of host concentration.

Similar phenomena were observed in the case of DIMEB solutions. The absorption maxima of both triphenylmethanes were shifted from 220 to 230 nm in the presence of DIMEB. The isosbestic point also occurred at 210 nm, and the value of the absorption at 240 nm proved to be in a linear relationship with the concentration of the cyclodextrin derivative. The effect of β -CD and DIMEB on the solubility of Nuarimol and Triarimol is illustrated in Fig. 2.

β -CD does not interact with the tin-centered triphenylmethane analogues. A negligible increase in the extinction was found in the range of 240–280 nm, and less remarkable isosbestic points occurred at 210 and 230 nm. The intensity and the wavelength of the absorption maximum remained practically unchanged. The same phenomena were also observed in the case of DIMEB solutions.

The solubility of triphenylmethane derivatives was not considerably enhanced by the CD crown ethers, and this enhancement was independent of their concentration. No change in spectra was observed.

The solubility of the tin-centered Bristan and Torque is, however, increased by the effect of the crown ether type derivatives. The absorption maxima were not shifted, but an isosbestic point appeared at 210 nm. The values of UV absorption at every wavelength increased linearly as the concentration of the crown ether derivative increased. The solubility enhancement of the tin-centered triphenylmethane analogues in the solutions of the cyclodextrin crown ethers is illustrated in Fig. 3. The effect of the methylated crown ether is considerably higher than that of the polyalcohol. The methylated derivative increases especially the solubility of Torque, while the polyalcohol shows the same influence in the case of the two compounds studied.

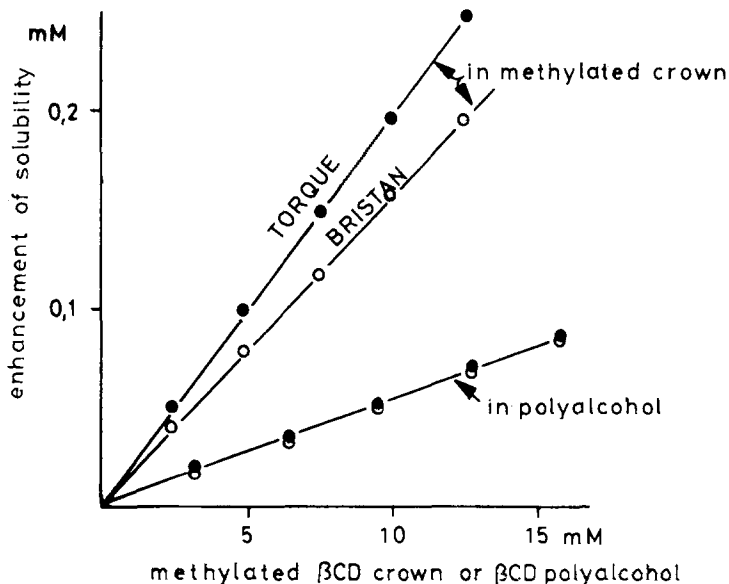


Fig. 3. Solubility enhancement of triphenyltin derivatives (solubility in host solution – solubility in water) as a function of host concentration.

4. Conclusion

The absorption maxima of the triphenylmethane derivatives are shifted by 10 nm toward higher wavelengths in the presence of cyclodextrins. The isosbestic points at 210 and 230 nm suggest a highly complicated equilibrium: complexes of different stoichiometry are likely to be present in the solution at the same time, and their ratio is determined by the concentration of the cyclodextrin derivatives. The shift of absorption maxima was not observed in the case of the crown ether derivatives. Only the crown ether type derivatives are able to enhance the solubility of the tin-centered triphenylmethane analogues.

The stability constants of complexes calculated from the solubility isotherms are illustrated in Table I. The complexes of the highest stability are formed by DIMEB, the stabilities of complexes with β -CD and methylated crown ether are approximately equal, and complexes of the lowest stability are formed by the polyalcohol.

Table I. Stability constants calculated from solubility isotherms at room temperature (M^{-1})

Guest	Host			
	DIMEB	β -CD	Methylated crown	Polyalcohol
<i>Triphenylmethane</i>				
Nuarimol	31	13	–	–
Triarimol	62	21.5	–	–
<i>Triphenyltin</i>				
Torque	–	–	20	5,5
Bristan	–	–	15	5,5

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