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β-Ionone cyclodextrins inclusion complexes ^{1}H NMR study and photolysis

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Abstract

Complexes of β-ionone (BI) with β-cyclodextrin (β-CD), 2-hydroxypropyl-β-cyclodextrin (HP-β-CD) and 2-hydroxypropyl-γ-cyclodextrin (HP-γ-CD) were studied by ^{1}H NMR spectroscopy in aqueous and methanolic solutions. From the dependence of chemical shifts of the BI protons on CD concentration (Job's plot), it was concluded that BI forms 2:1 inclusion complexes (CD:BI) with β-CD and HP-β-CD, but a 1:1 complex with HP-γ-CD. The stability constants in water are K_{21} (BI/β-CD) $\geq 2 \times 10^6\ M^{-2}$; K_{21} (BI/HP-β-CD) $= 5 \times 10^6\ M^{-2}$; K_{11} (BI/HP-γ-CD) $= 1 \times 10^4\ M^{-1}$. In 1:1 water/methanol solution the stability constants decrease by about two orders of magnitude compared to those in water. For example, for BI/HP-β-CD complex, $K_{21} = 8 \times 10^4\ M^{-2}$ in this case. Photolysis of *trans*-β-ionone in water and aqueous CD solutions leads to only one final product, retro-γ-ionone. Other isomers, *cis*-β-ionone and racemic α-pyran, are formed at earlier stages of the photolysis. The role of cyclodextrin in this process is discussed.

Keywords: Cyclodextrin; Hydroxypropyl-cyclodextrin; Inclusion complex; β-ionone; Photoisomerization; Retro-γ-ionone; α-pyran; Chiral isomers

1. Introduction

Cyclodextrins (CDs) are macrocyclic oligosaccharides, which are torus-shaped structures with rigid lipophilic cavities and can form host–guest inclusion complexes with suitably sized hydrophobic molecules. The most common α-, β-, and γ-CDs consist of six to eight D-glucopyranosyl units and have internal cavity diameters of 4.7–5.3 Å, 6.0–6.5 Å and 7.5–8.3 Å, respectively. The guest molecules encapsulated by CDs usually exhibit some changes in their physical, chemical, and biological properties [1–3]. Biotechnological advances have resulted in dramatic improvements in the efficient manufacture and application of cyclodextrins during the last decade. In the pharmaceutical, cosmetics, and food industry, cyclodextrins have been used as complexing agents to increase the water solubility of various compounds, such as drugs, vitamins, food colorants, and others [4–6]. In addition, complexation can considerably increase stability and bioavailability of these substances. For instance, cyclodextrins have been used to reduce gastrointestinal and ocular irritation, eliminate unpleasant odors or taste, and prevent drug-additive interactions. Investigation of the ability of CDs for molecular recognition and separation of enantiomers is of fundamental importance for developing artificial enzymes [7,8].

β-Ionone is a natural short-chain analog of the polyene retinoids and carotenoids. Phototransformation of β-ionone in homogeneous solutions has been investigated in detail ([9,10] and references therein), in particular, in the presence of electron donors and acceptors [11,12]. Also, it is known that complexation of β-ionone and similar compounds with β-CD results in the significant changes in product distribution [13–15]. This paper focuses on two aspects: (1) Elucidation of the role of complexation in the photochemical behavior of β-ionone. (2) Characterization of β-ionone/CD inclusion complexes as simple models for carotenoid complexes. Carotenoids are highly hydrophobic, air-, light-, and temperature-sensitive compounds, so that increasing their stability towards irradiation and reactive oxygen species is important. In spite of wide application of carotenoid/CD complexes in the food, cosmetics, and pharmaceutical industries [16–18], there is no direct evidence for inclusion complex formation, only a few attempts of structural studies of such complexes have been reported [19,20]. β-Ionone has the same terminal substituted cyclohexene ring as β-carotenes. Thus, if the cyclohexene end, rather than the other terminus, becomes embedded in CD,

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then the length of the conjugated chain would not be a variable and similar structure of inclusion complexes would occur for these compounds.

In the present work, the inclusion complexes of β-ionone were investigated by ^{1}H NMR spectroscopy.

2. Experimental

2.1. Chemicals

β-Cyclodextrin, 2-hydroxypropyl-β-cyclodextrin (DS 4.6) and 2-hydroxypropyl-γ-cyclodextrin (MS) were supplied by CarboMed Inc. (*E*)-β-Ionone was supplied by Sigma and the deuterated solvents CD_3OD and D_2O were from Aldrich. All compounds were used as supplied.

2.2. Preparation and analysis of inclusion complexes

For aqueous solutions, a mixture of β-ionone and an appropriate CD dissolved in D_2O was magnetically stirred for 4–6 h at ambient temperatures when solutions were obtained. For experiments in D_2O/CD_3OD mixture, a methanolic solution of BI was added to an aqueous solution of the requisite amount of a CD prior to stirring for 4–6 h. Final concentrations were 1–10 mM of BI and CD. ^{1}H NMR spectra of CDs and their BI complexes were obtained with Bruker AM-360 or AM-500 instruments. The characteristic changes of ^{1}H NMR chemical shifts due to complexation are about 50 Hz (0.1 ppm) for both molecules, BI and CD. This is two orders higher than the accuracy of NMR measurements (about 0.5 Hz).

2.3. Photolysis

For the photochemical study the D_2O solutions of BI (1 mM) and CDs (3 mM) purged with N_2 were irradiated with a xenon lamp (250 W) through a thermal water filter in the Pyrex NMR tube. Phototransformation of β-ionone was monitored by ^{1}H NMR (500 MHz) spectroscopy. Complete transformation of β-ionone to the final product was detected after 12 min irradiation. The photolysis of 10% CD_3OD/D_2O solution of β-ionone in the absence of CD was carried out under the same conditions. Since β-ionone is not soluble in pure water, the solution was prepared by addition of a CD_3OD solution of BI to D_2O. The extent of conversion of BI to the final product, retro-γ-ionone, in this CD_3OD/D_2O solution of BI and aqueous BI/HP-β-CD solution was obtained from the areas of the corresponding NMR signals.

2.4. Calculation of stoichiometry of inclusion complexes and association constants

The change in chemical shift of CD protons upon complexation is widely used for calculation of the stoichiometry of inclusion complexes and their association constants [21]. The equilibrium formation of the n:m complex (C_{nm}) between cyclodextrin (CD) and guest (G) molecules is represented by Eq. (1):

$$mG + n\mathrm{CD} \leftrightarrows C_{nm} \tag{1}$$

The association constant of this complex is described as

$$K_{nm} = \frac{[C_{nm}]}{[G]^m[\mathrm{CD}]^n} \tag{2}$$

Since the association–dissociation process is rapid relative to the NMR time scale (in the microsecond to millisecond range [22]), the chemical shift of CD protons can be determined as follows:

$$\delta_{\mathrm{obs}} = f_{\mathrm{CD}}\delta_{\mathrm{CD}} + f_{C_{nm}}\delta_{C_{nm}} \tag{3}$$

where δ_{CD} and $\delta_{C_{nm}}$ are the chemical shifts of the free and complexed CD, and f_{CD} and $f_{C_{nm}}$ are their molar fractions. Substituting $\Delta\delta_{\mathrm{obs}} = \delta_{\mathrm{obs}} - \delta_{\mathrm{CD}}$ and $\Delta\delta_{C_{nm}} = \delta_{C_{nm}} - \delta_{\mathrm{CD}}$ we obtain

$$\Delta\delta_{\mathrm{obs}} = n\,\Delta\delta_{C_{nm}}\frac{[C_{nm}]}{[\mathrm{CD}]_o} \tag{4}$$

From the mass balance, the initial concentrations of β-ionone $[G]_0 = [G] + m[C_{nm}]$ and cyclodextrin $[\mathrm{CD}]_0 = [\mathrm{CD}] + n[C_{nm}]$. If $m = n = 1$, from Eq. (2) the following equation for concentration of a 1:1 complex can be obtained

$$[C_{11}]^2 - \left([G]_0 + [\mathrm{CD}]_0 + \frac{1}{K_{11}}\right)[C_{11}] + ([G]_0[\mathrm{CD}]_0) = 0 \tag{5}$$

Combination of Eqs. (4) and (5) results in the Eq. (6) from which the value K_{11} can be obtained from the G_0 concentration dependence of $\Delta\delta_{\mathrm{obs}}$ (CD).

$$\Delta\delta_{\mathrm{obs}} = \frac{n\,\Delta\delta_{C_{nm}}}{2[\mathrm{CD}]}\left\{[G]_0 + [\mathrm{CD}]_0 + \frac{1}{K_{11}} - \left(\left([G]_0 + [\mathrm{CD}]_0 + \frac{1}{K_{11}}\right)^2 - 4[G]_0[\mathrm{CD}]_0\right)^{1/2}\right\} \tag{6}$$

For a 2:1 complex, a more complicated equation was solved numerically. A similar equation was obtained for variation of BI proton chemical shifts with the CD concentration. In the case of substituted CDs, the measurement of $\Delta\delta_{\mathrm{obs}}$ (BI) is the only possible way of calculating of the association constants due to complicated NMR spectrum of CD. Experimentally, $\Delta\delta_{\mathrm{obs}}$ (BI) was measured at different CD but constant concentrations of BI. Small amount of CH_3OH (~1 mM) was used as reference. It has been shown [23] that methanol can be used as an internal standard due to its low association constant with cyclodextrins [24].

The stoichiometry of the BI/CD inclusion complexes was determined by using the continuous variation technique (Job's plot). For this purpose, solutions with different

BI/CD molar ratios but constant total molar concentration (BI + CD) were prepared.

3. Results and discussion

3.1. Measurement of association constants and stoichiometry of inclusion complexes

At present, ^{1}H NMR spectroscopy is the most convenient and informative method for studying CD complexes with various organic substrates [2]. This technique can provide direct evidence for inclusion complex formation. The reasoning is based on the expectation that if the guest molecule is imbedded in the CD cavity, the screening environment should be sensed by magnetic nuclei inside the cavity (H_3 and H_5) but not by outside protons H_1, H_2, and H_4 (see Scheme 1). This should result in a variation of chemical shifts of the inside protons (H_3 and H_5). In addition, interactions in the CD cavity could cause variation of chemical shifts of the guest molecule incorporated inside CD. NMR experiments can provide information about stoichiometry, dynamics, and structure of CD complexes [25]. In particular, Job's plot [26], which depicts the dependence of chemical shift on substrate/CD ratio, has been widely used to determine complex stoichiometry [27,28].

Table 1 shows the chemical shifts of β-CD and BI protons in the free and complexed states. Since β-ionone is not soluble in pure water, the solution of uncomplexed BI was prepared by addition of a CD_3OD solution of BI to D_2O (∼10%).

The displacements of chemical shifts of internal β-CD protons detected in the present work are typical for inclusion complexes of most of organic compounds ([2] and references therein). At the same time, the most significant changes of BI chemical shifts were observed for the CH_3 and CH_2 protons of the cyclohexene ring. This fact points to insertion of the BI cyclohexene ring into the β-CD cavity.

Different results were observed for BI complexes with substituted CDs, HP-β-CD and HP-γ-CD (Table 2).

Significant changes of BI chemical shifts were observed for ring protons as well as for 7-H, 8-H, and 9-CH_3 in both β- and γ-hydroxypropyl-CD solutions. Two explanations could be offered for this result. The first is encapsulation of the entire BI molecule by CD. This is reasonable for HP-γ-CD which has a larger cavity than β-CD. Another reason could be the formation of a 2:1 complex. To elucidate the structures of BI complexes with different CDs, the stoichiometry of these complexes was deduced from the NMR data.

Fig. 1 presents Job's plots for two different cyclodextrins, 2-hydroxypropyl-β-cyclodextrin and 2-hydroxypropyl-γ-cyclodextrin. The position of the maximum in Job's plot, at $R = [BI]/([BI]+[CD]) = 0.5$ corresponds to a 1:1 complex. This stoichiometry was detected for the HP-γ-CD complex.

Table 1
^{1}H NMR chemical shifts (ppm) of β-CD and β-ionone in free and complexed states (D_2O)

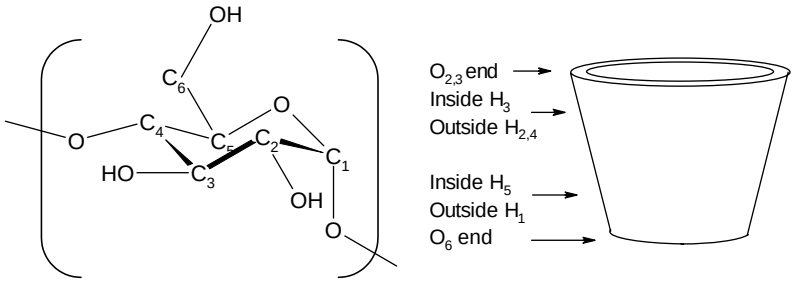
H	δ (free)	δ (complexed)	Δδ
CD-H1	5.090	5.080	−0.010
CD-H2	3.668	3.645	−0.023
CD-H3	3.987	3.922	−0.065
CD-H4	3.605	3.609	+0.004
CD-H5	3.875	3.817	−0.058
CD-H6	3.899	3.922	+0.023
BI 1-CH_3	1.085	1.212	+0.127
BI 2-CH_3	1.507	1.609	+0.102
BI 3-CH_3	1.630	1.741	+0.111
BI 4-CH_3	2.130	2.224	+0.094
BI 5-CH_3	1.803	1.910	+0.107
BI 7-CH_3	7.514	7.522	+0.008
BI 8-CH_3	6.234	6.222	−0.012
BI 9-CH_3	2.363	2.379	+0.016

Concentration of both reagents is 10 mM.

Table 2
Variation of ^{1}H NMR chemical shifts (ppm) of β-ionone in the presence of HP-β-CD and HP-γ-CD in D_2O

H	Δδ (HP-β-CD)	Δδ (HP-γ-CD)
BI 1-CH_3	+0.164	+0.165
BI 2-CH_3	+0.083	+0.066
BI 4-CH_3	+0.145	+0.060
BI 5-CH_3	+0.134	+0.135
BI 7-CH_3	+0.030	+0.046
BI 8-CH_3	+0.056	+0.070
BI 9-CH_3	+0.054	+0.069

Concentration CD > [BI].



Scheme 1.

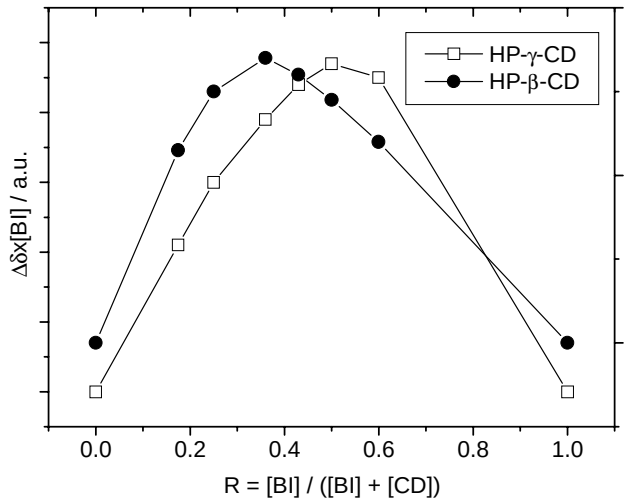


Fig. 1. Job's plots corresponding to the chemical shift displacement of 5-CH_3 protons of BI for BI/HP-β-CD and BI/HP-γ-CD complexes in aqueous solution.

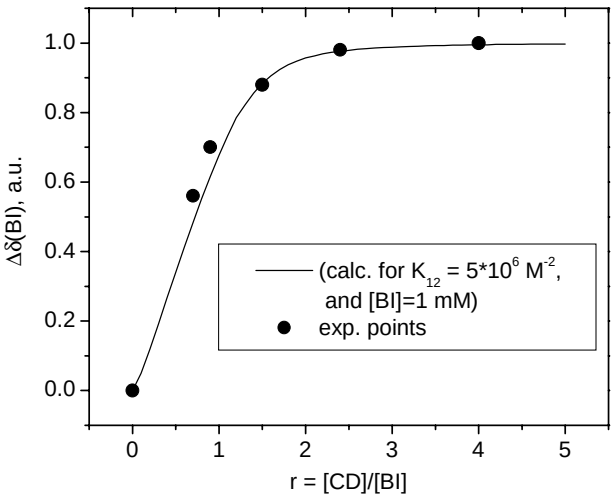


Fig. 3. Variation of BI proton chemical shifts in BI/HP-β-CD complex with cyclodextrin concentration in D_2O: experimental points and calculated curve for association constant $K_{21} = 5 \times 10^6\,M^{-2}$. [BI] = 1 mM.

However, the maximum at $R = 0.33$ observed for HP-β-CD indicates formation of a 2:1 complex. Examples of 2:1 complexes for similar systems, HP-β-CD/all-*trans*-retinal and all-*trans*-retinoic acid, were recently described by Munoz-Botella et al. [29]. In other words both the cyclohexene ring and the other terminal group can be incorporated into two CD cavities. However, one can suggest that interaction with the cavity interior is stronger for the cyclohexene ring, due to similar sizes of the cavity and the ring, than for the smaller carbonyl group.

The stability constants for all systems under study were calculated by using the theoretical background described in Section 2. As an example, Fig. 2 shows calculated curves for 1:1 complexes with different association constants, as well as experimental points for the BI/HP-γ-CD system. The value $K_{11} = 10^4\,M^{-1}$ was extracted from the fitting procedure for BI/HP-γ-CD complex. According to Fig. 2, the chemical shift dependence on the concentration of CD is very sensitive to the value of association constants when $K_{11} \times [CD] < 1$. For the opposite situation, the curves saturate at $[CD]/[G] = 1$ for the 1:1 complex and at $[CD]/[G] = 2$ for the 2:1 complex, and the shape of the curves is almost insensitive to any further increase of the association constants. Figs. 3 and 4 show the experimental points and calculated curves for the BI/HP-β-CD system in D_2O and D_2O/CD_3OD. The values of $K_{21} = 5 \times 10^6\,M^{-2}$ and $8 \times 10^4\,M^{-2}$ were calculated for the BI/HP-β-CD inclusion complex for these solvents. The results show that the presence of methanol (50% in this experiment) leads to a decrease of complex stability by almost two orders of magnitude. The effect of organic

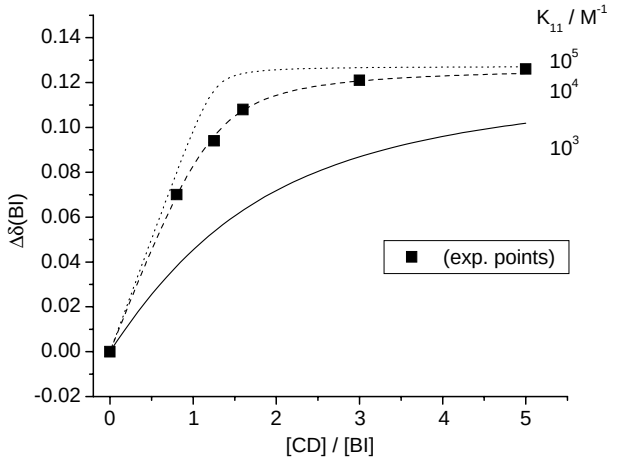


Fig. 2. Variation of BI proton chemical shifts in BI/HP-γ-CD complex with cyclodextrin concentration in D_2O: experimental points and calculated curves for different association constants K_{11}[BI] = 1 mM.

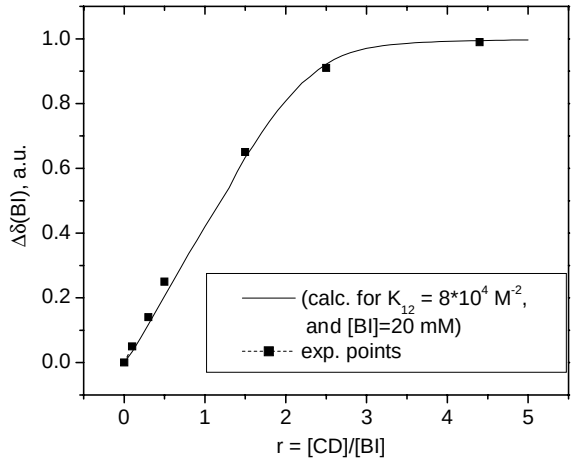
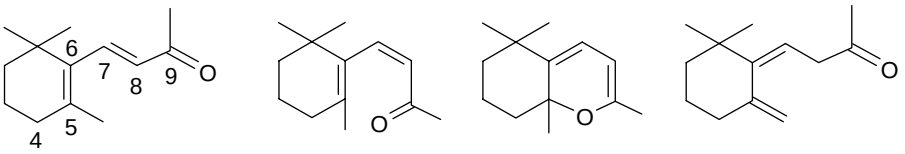


Fig. 4. Variation of BI proton chemical shifts in BI/HP-β-CD complex with cyclodextrin concentration in D_2O/CD_3OD (1:1): experimental points and calculated curve for association constant $K_{21} = 8 \times 10^4\,M^{-2}$. [BI] = 20 mM.



Scheme 2.

solvents on the inclusion complex behavior has been widely investigated [3] because of its importance to both fundamental and application aspects. Since solvent molecules can also form inclusion complexes with CDs, they can displace guest molecules from the cavity. And, although association constant for methanol/β-CD complex is very low (K_a = 0.3 M^{-1} [24]), at high concentration of methanol this effect can be significant. Another reason for the decrease of the complex stability in the presence of methanol might be the good solubility of BI in methanol.

3.2. Photochemical study

Brief irradiation of *trans*-BI (**I**, see Scheme 2) in 10% CD_3OD/D_2O or BI/CDs complexes in D_2O gives rise to the same products shown below.

The same set of isomers was earlier detected during photolysis of **I** in several organic solvents: acetonitrile, methanol, benzene, etc. [9,11,13]. However, after prolonged irradiation of both water and aqueous CDs solutions of **I** with a xenon lamp (see Section 2), the final exclusive product was retro-γ-ionone. All CDs under study showed the same results (see Fig. 5 as an example). Note that in the organic solvents retro-γ-ionone is present in only minor amounts.

A similar result was described earlier by Arjunan and Ramamurthy [13] for the photolysis of BI in aqueous β-CD solution. The authors suggested two hypotheses about the role of the medium on the product distribution. One possible reason for a change in isomer distribution might be steric factors. There are several examples in the literature (see, for example, [14,15]) which describe the photolysis of α,β-unsaturated ketones, where steric hindrance leads to the formation of completely different products. Another possible reason is the switching of the lowest excited singlet states, nπ and ππ* of BI in the presence of H-donors. Such a mechanism was earlier suggested [30] for photoisomerization of all-*trans*-retinal in different media. The variation of isomer ratio was explained by a change in the relative position of energy levels: nπ is the lowest excited state in non-polar solvents, and ππ* state in polar media [31]. It has been established [9], that retro-γ-ionone is formed from singlet excited states of **I** and **III**, and other isomers are formed from the triplet state of **I**. Since retro-γ-ionone is the only final product of the photolysis of **I** in aqueous CD solution, it is reasonable to suggest that the observed difference in the photochemical behavior of BI in other media is the result of the switching of the lowest reactive states, nπ and ππ*. Arjunan and Ramamurthy [13] concluded that the CD cavity itself can provide a polar environment for BI and play the role of H-donor for BI. The authors also reported that retro-γ-ionone is the only phototransformation product. Our results show that at the intermediate stages of the photolysis

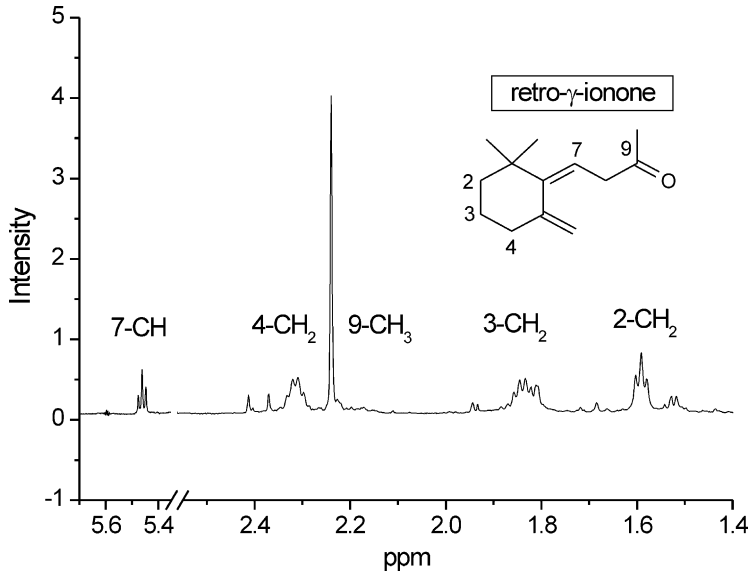


Fig. 5. ^{1}H NMR (500 MHz) spectrum observed after irradiation of 1 mM BI solutions by a xenon lamp (12 min) in HP-γ-CD complex, [CD] = 3 mM.

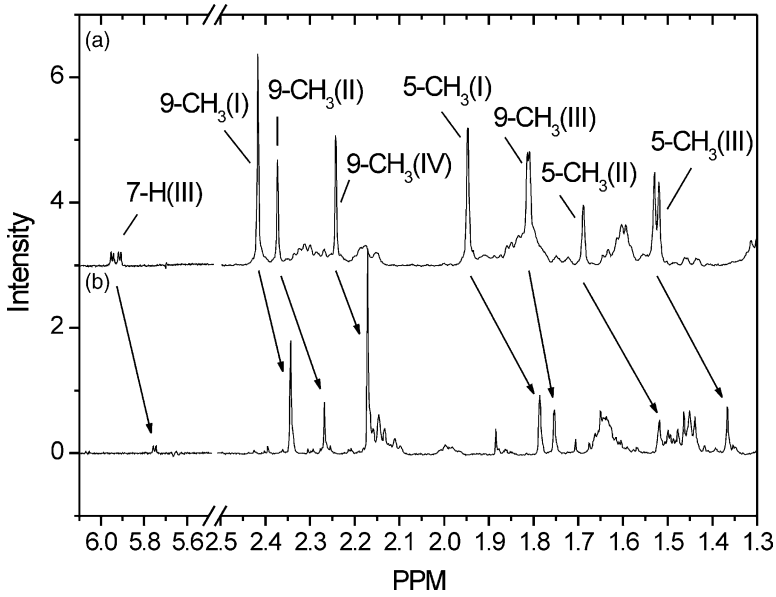


Fig. 6. ^{1}H NMR (500 MHz) spectra observed after irradiation of 1 mM BI solutions by a xenon lamp (3 min.). (a) in 10% CD_3OD/D_2O, and (b) in HP-β-CD complex, [CD] = 3 mM. Unmarked signals are CH_2 groups of BI isomers.

all major isomers (*cis*-isomer, α-pyran and retro-γ-ionone) are formed (Fig. 6).

Analysis of reference data on the polarity of CD interior [3,32] and our results allowed us to draw other conclusions about the role of cyclodextrins in the phototransformation of BI. First, since the CD cavity is hydrophobic with polarity close to that of an alcohol solution, incorporation into the CD cavity cannot be the reason for the proposed mechanism. Our conclusion is that the aqueous environment is the key feature for the change of photochemical behavior of β-ionone. This conclusion follows from the similar photochemical behavior of β-ionone observed in 10% CD_3OD/D_2O and aqueous CDs solutions. Since free and complexed molecules are in equilibrium, we suggest that photochemical transformation occurs primarily in uncomplexed portion of β-ionone in this medium.

To elucidate the role of CD in this process, the products formed during the early stages of the photolysis of BI in aqueous CD and 10% CD_3OD/D_2O solutions were compared. As stated above, only one final product, retro-γ-ionone was formed in both cases after 12 min irradiation (see Section 2). However, after shorter irradiation times all isomers, **I**–**IV**, are present. The conversion degrees of BI to the final product retro-γ-ionone were compared for 10% CD_3OD/D_2O solution and aqueous HP-β-CD solution of BI as an integral ratio of corresponding NMR signals. Compared to the behavior in water solution, the ratio **IV**/**I** in the presence of CD decreased more than three fold (from 2 to 0.6, see Fig. 6). It is suggested that complexation of BI with CD increases only the photostability of BI but does not change the reaction mechanism.

As evident from Fig. 6, the chemical shifts of different groups of protons of all isomers of BI are changed in the presence of HP-β-CD. Similar effects were observed for other CDs. Also, comparison of spectra (a) and (b) shows that two sets of NMR signals occur for **III** in the presence of HP-β-CD. Since HP-β-CD is a chiral compound (that has been used for separation of enantiomers [7,33]), and **III** has a chiral center, it was expected that, if present, the enantiomers of **III** would give rise to two sets of signals. The equal intensity of the NMR signals of corresponding protons of enantiomers (see for example, 7-H (**III**)) indicates that the racemate was most probably formed in an achiral environment, i.e. in solution, not the CD cavity, in accord with the conclusion reached above.

4. Conclusion

It was shown that *trans*-β-ionone forms 2:1 inclusion complexes (CD:BI) with β-CD and HP-β-CD, and a 1:1 complex with HP-γ-CD. The values of association constants for all systems under study point to high stability of these complexes. It was demonstrated that the presence of methanol in water significantly decreases the complex stability.

A change in product distribution during the photolysis of *trans*-β-ionone in aqueous cyclodextrin solution compared to that in organic solvents was observed. The aqueous environment plays the key role in the change of photochemical behavior of β-ionone. The major, if not the only, role of CD in this case is only to decrease the rate of phototransformation of β-ionone. No substantive difference was observed in the results of photolysis of the complexes with different CDs, β-CD, HP-β-CD, and HP-γ-CD. In addition, formation of equal amounts of the enantiomers of the α-pyran as

detected when CDs were present by ^{1}H NMR spectroscopy, implies that the phototransformation occurred in the achiral solvent, not the CD cavity.

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