In the present treatment of the cluster orbitals, the major drawback is the limitation on the shape of a cluster. A cluster must be rectangular parallelepiped and have the surface characterized as (1, 0, 0)-plane.

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Comparison of Photophysical and Photochemical Properties of Khellin and 8-Methoxypsoralen

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The photophysical and photochemical properties of khellin were compared with those of 8-methoxypsoralen (8-MOP). Quantum yields of fluorescence and triplet formation decreases as solvent polarity increases, which is opposite to 8-MOP, and photocycloadditivity of khellin to olefins is much lower than that of 8-MOP. Electron ejection from khellin by laser flash was not observed, but observed from 8-MOP. As models of 4',5'-monoadducts of khellin or 8-MOP with thymine base, khellin<>dimethylfumarate 4',5'-monoadduct (KDF) was also compared with 8-MOP<>thymidine 4',5'-monoadduct (F-2) in those properties to give some insight on the second-step biadduct formation resulting in cross-links of DNA duplex. KDF ad F-2 were very similar to khellin and 8-MOP in photophysical properties, respectively. However, KDF did not form adducts with various olefins, and thus it is thought that 2,3-double bond of chromone moiety in khellin is hardly reactive in contrast with 3, 4-double bond of coumarin moiety in 8-MOP. These results indicate that khellin is fairly photostable compound, a poor type I photodynamic sensitizer and producer of O_2^- which is some cause of phototoxic erythemal reactions and undesirable side effects. Therefore khellin is safer to use than 8-MOP in photochemotherapy of some skin diseases. Although khellin is much less reactive than 8-MOP, khellin must be also a monofunctional drug. Since khellin is, however, as effective as 8-MOP in photochemotherapy of some skin diseases, it is suggested that khellin may be different from 8-MOP in the action mechanism.

Introduction

Furocoumarins are well-known skin photosensitizing agent and have been used in the treatment of various skin diseases such as *vitiligo*[1] and *psoriasis*[2] and as molecular probes for

studying nucleic acid structure[3] and also more recently in the treatment of AIDS.[4] The biological effects of furocoumarins plus UV treatment appear to the mediated primarily by the formation of [2+2]-cyclobutane adducts which arise from [2+2]-photocycloaddition of the 3,4- and/or 4',5'-double bonds of furocomarin intercalated into duplex nucleic acid with the 5, 6-double bond of pyrimidine bases.[5] However,

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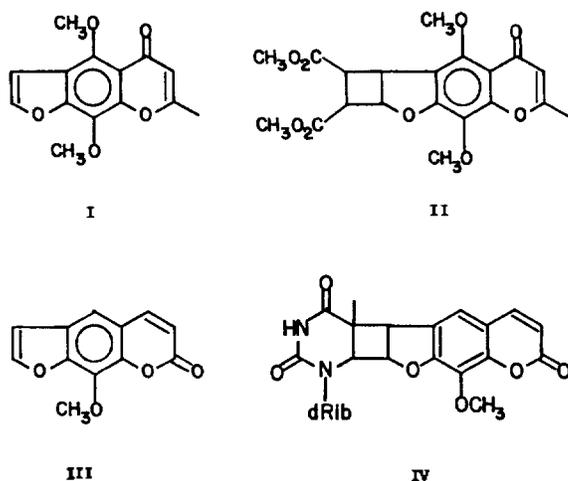*Bull. Korean Chem. Soc., Vol. 12, No. 5, 1991* 555

Figure 1. Structure of khellin(I), khellin<>dimethylfumarate 4', 5'-monoadduct(II), 8-methoxypsoralen(III), and 8-MOP<>thymidine 4', 5'-monoadduct(IV).

possible deleterious effects such as carcinoma development in hairless mice as well as possible liver injury from the use of 8-methoxypsoralen (8-MOP), which has been used most widely in photochemotherapy (PUVA), have been reported[8] and furocoumarins are also the cause of some forms of dermatitis such as erythema resulting from skin contact with certain plants or vegetable materials such as fig leaves and celery.

The two photobiological active furochromones, khellin and visnagin (see Figure 1), which closely resemble furocoumarin in structure, can be isolated from the plant *Ammi visnaga.*[9] Khellin has been used to sensitize λ-phages with 360 nm UV light[10] and the furochromones are phototoxic to several organisms.[11-13] Although the photochemotherapy of some skin diseases such as psoriasis and vitiligo is almost restricted to the use of furocoumarins,[2,4] recent observations indicate that oral administration of khellin and subsequent exposure to sunlight or long-wavelength UV (UVA) light induces repigmentation in vitiligo.[15-17] Compared with the usual furocoumarin photochemotherapy of vitiligo, khellin plus UVA treatment appears to be equally effective and has the major advantage that khellin neither produces significant side effects nor phototoxic erythemal reactions.

The excited singlet and triplet state properties and photochemistry of furocoumarins have been extensively investigated in order to understand their photobiologica activities.[18-20] Although photophysical properties of furochromones have not been studied extensively, we reported previously some excited properties and photochemistry of a furochromone khellin.[21,22] In continuation of studies on the photoreaction of khellin, comparison between khellin and 8-MOP in some photophysical and photochemical properties was carried out to give some insight into development of new photochemotherapeutic agents.

Experimental

Materials. Khellin and 8-methoxypsoralen (8-MOP) were purchased from Sigma Chemical Company and recrystallized from methanol. Quinine sulfate, 9, 10-diphenylanthracen, and

Table 1. Fluorescence Quantum Yield (Φ_f) and Triplet Formation Quantum Yield (Φ_T) of 8-Methoxypsoralen and Khellin in Various Solvents at 25°C

Solvent	Φ_f		Φ_T	
	8-MOP[a]	Khellin[b]	8-MOP[c]	Khellin
H_2O	0.0028	0.0006	0.06	—
CH_3OH	0.0022	0.0018	—	—
EtOH	0.0020	0.0036	0.04	0.15
i-PrOH	0.0012	—	—	—
CH_3CN	(2.6×10^{-4})	0.013	$(0.012)^d$	—
CH_2Cl_2	—	0.021	—	0.4
Benzene	—	—	0.011[e]	—
CF_3CH_2OH	(0.011)	—	(0.10)	—

[a] From ref. 29. [b] From ref. 21. [c] From ref. 28. [d] Data in parentheses were cited from ref. 27. [e] From ref. 20a.

dimethylfumarate were purchased from Aldrich Chemical Company and purified by recrystallization from water, ethanol, and methanol, respectively. C_4-monoadduct (F-2) of 8-MOP and thymidine was prepared according to the procedure reported previously in dry film state of 8-MOP and thymidine.[23] Khellin-dimethylfumarate C_4-cycloadduct was prepared by photoreaction of khellin and dimethylfumarate in dichloromethane using a Rayonet photochemical reactor (RPR-208) equipped with four RUL-350 nm fluorescent lamps. 2-Methylpentane, tetramethylethylene (Aldrich), and other solvents of extra pure grade were purified according to the literature procedures.[24] Doubly distilled and deionized water was also used for spectroscopic studies. The other solvents (Merck) used in measurement of emission spectra were of spectroquality.

Laser Flash Photolysis. The nanosecond laser flash photolysis experiments were carried out using pulses from a XeF excimer laser (351 nm) or a KrF excimer laser (248 nm) (a Lambda Physik EMG 500 excimer laser, pulse width of about 15 ns) for excitaion and pulsed Xe flash lamp (EG & G Xenon flash lamp) for monitoring of transient species. The monitoring light was divided into two beams after passing through the sample cell, and one beam was entered into a Nikon P250 monochromator, the other into a Jobin Yvon H20UVL monochromator. The detectors were Hamamatsu R758 photomultipliers and signals were displayed on a Tektronix R7104 oscilloscopes with 7A26 and 7B80 plug-in units. The concentration of samples was adjusted such that suitable amount of the laser light was absorbed in the laser system.

Results and Discussion

Solvent Effect on Some Photophysical Properties. The photobiological activity of furocoumarins results from a two-step process of the complex formation between furocoumarin and DNA by intercalation of furocoumarin into DNA duplex in the dark followed by formation of covalent bonds upon irradiation with long-wave UV light. Intercalation of furocoumarin into DNA is prerequisite for the photoreaction with DNA. The interior of the DNA helix is less polar than water[25] and thus the solvent effect on the excited states

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Table 2. Fluorescence Maximum (λ'_{max}), Phosphorescence-to-Fluorescence Quantum Yield Ratio (Φ_p/Φ_f), and Phosphorescence Lifetime (τ_p) of 8-Methoxypsoralen and Khellin in Various Solvents at 77 K

Solvent	8-MOP[a]			Khellin[b]		
	λ'_{max}·nm	Φ_p/Φ_f	τ_p·s	λ'_{max}·nm	Φ_p/Φ_f	τ_p·s
EtOH	440	5.6	0.76	430	0.015	1.4
Et₂O	440	8.5	0.80	-	-	-
2-MeP[d]	-	-	-	455	0.014	1.3
Isopentane	475	-	-	467	-	-
EEM[c]	440	23.5	0.31	433	0.025	-
				475 (sh)		

[a] From ref. 29. [b] From ref. 21. [c] Ethanol: ethyl iodide: methanol, 16 : 5 : 4, by volume. [d] 2-Methylpentane.

Table 3. Fluorescence Quantum Yield (Φ_f) and Phosphorescence-to-fluorescence Quantum Yield Ratio (Φ_p/Φ_f) of KDF and F-2 at 25℃ and 77 K in Various Solvents

Solvent	Φ_f		Φ_p/Φ_f	
	KDF[a]	F-2[b]	KDF[a]	F-2[b]
H₂O	0.002	0.044		
CH₃OH	0.004	0.007		
EtOH	0.007	0.005	0.07	0.68
i-PrOH	-	0.003		
Isopentane	5.5×10⁻⁴		0.04	
EtOH-Et₂O	-		-	0.26
2-MeP[c]	-	-	0.03	
EtOH-EtI[d]				4.1
EEM[e]		0.1		

[a] Cited from ref 31. [b] Cited from ref 29. [c] 2-Methylpentane. [d] 2 : 1 by volume. [e] Ethyl iodine : ethanol : methanol, 5 : 16 : 4 by volume.

should give some information on photoreactivity and photobiological activity of 8-MOP and khellin.

Table 1 shows the fluorescence and triplet formation quantum yields of 8-MOP and khellin in various solvents at 25℃. The fluorescence quantum yield of 8-MOP decreases as solvent polarity decreases, while the reverse is the case of khellin. Solvent dependence of the triplet formation quantum yields of the two compounds shows similar fashion to that of the fluorescence quantum yield, respectively. It was also observed that the triplet quantum yield of khellin in acetonitrile decreases to about one-fifth by addition of small amount of water (9% by volume) and the fluorescence lifetime in water is much shorter than about 500 ps in ethanol. This implies that the triplet excited state of 8-MOP is generated moderately even if not intercalated in DNA, while the triplet excited state of khellin should not be nearly formed in outside environment of DNA helix. Thus the results confirm that khellin is a poor photodynamic sensitizer which is some cause of phototoxic erythemal reactions. This is well consistent with the fact that the phototoxic erythemal reactions in the treatment of vitiligo with khellin is very low in comparison to 8-MOP.[17]
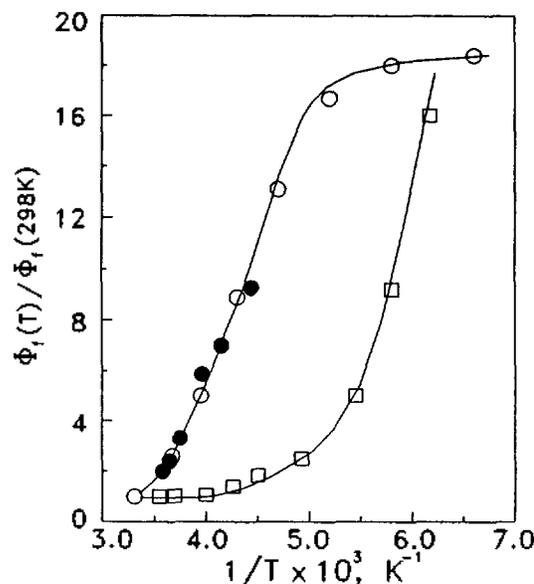
As shown in Table 2, the phosphorescence to fluorescence quantum yield ratio of khellin at 77 K is remarkably small in comparison to 8-MOP and remain essentially independent of solvent. However, the fluorescence quantum yield of khellin at 77 K increases remarkably with increasing the solvent polarity (0.61 in ethanol, 0.19 in ethyl ether, and 0.07 in isopentane). If intersystem crossing is the main nonradiative decay process, the phosphorescence to fluorescence quantum yield ratio at 77 K should be relatively high and influenced by solvent polarity. Therefore, it is likely that the dominant nonradiative decay process, which is sensitive to solvent properties at 77 K, is not the excited singlet-to-triplet intersystem crossing, but the excited singlet-to-ground internal conversion. This is supported by the fact that both fluorescence quantum yield and triplet formation quantum yield decrease as the solvent polarity increases at 25℃ (Table 1).

Some photophysical properties of KDF and F-2, as the models of monoadducts of khellin or 8-MOP with thymine, were also investigated to give some insights on the second-step photoreaction of khellin and 8-MOP intercalated in DNA, resulting in interstrand cross-linkage of DNA duplex.

Figure 2. Temperature dependence of fluorescence quantum yields of khellin(□) and 8-methoxypsoralen(●) in ethanol. The open circles were redrawn from data of 8-methoxypsoralen in ref. 26.

As shown in Table 3, it is noticeable that fluorescence quantum yield of KDF at 25℃ increase, while that of F-2 decreases, as the solvent polarity decreases. The phosphorescence to fluorescence quantum yield ratio of KDF at 77 K is much lower than that of F-2 and decreases with decreasing the solvent polarity. The ratio of KDF is also affected much less than that of F-2 by external heavy atom in solvent containing ethyl iodide. The very low ratio for KDF is consistent with the fact that fluorescence quantum yield at 77 K is very high in ethanol (0.73), ehylether (0.60), and isopentane (0.54), respectively.

Temperature Dependence. Figures 2 and 3 show the temperature dependences of fluorescence of 8-MOP and khellin in ethanol and 2-methylpentane, respectively. Since the two compounds possess the excited $^1(n, \pi^*)$ state which

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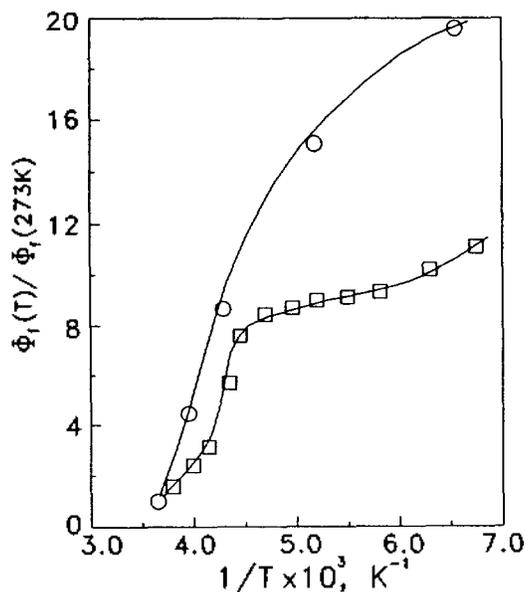*Bull. Korean Chem. Soc., Vol. 12, No. 5, 1991* 557

Figure 3. Temperature dependence of fluorescence quantum yields of khellin(□) and 8-methoxypsoralen(O) in 2-methylpentane. Data for 8-methoxypsoralen were redrawn using the fluorescence intensity in ref. 26.
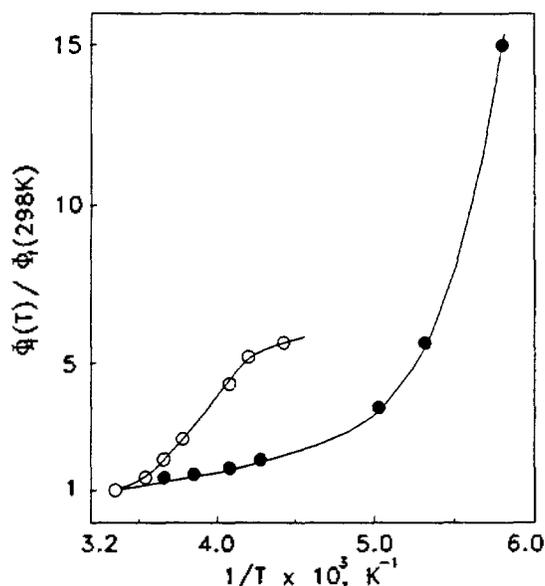

Figure 5. Triplet-triplet absorption spectra of 8-methoxypsoralen in water (upper) and ethanol (lower) at $20°C$ on irradiation with 351 nm XeF excimer laser.

Figure 4. Temperature dependence of fluorescence quantum yields of khellin<>dimethylfumarate 4',5'-monoadduct(●) and 8-MOP<>thymidine 4',5'-monoadduct(O) in ethanol.

lies close in energy to the lowest excited $^1(\pi, \pi^*)$ state, the temperature and solvent dependences of fluorescence have been examined. The closeness of the two states may play an important role in electronic relaxation of excited states, and thus in the photochemistry and photobiology. In ethanol the fluorescence quantum yield of khellin increases slowly first and then rapidly with decreasing the temperature, while that of 8-MOP shows opposite trends. In 2-methylpentane, those of both 8-MOP and khellin, however, increase greatly as the temperature decreases initially.

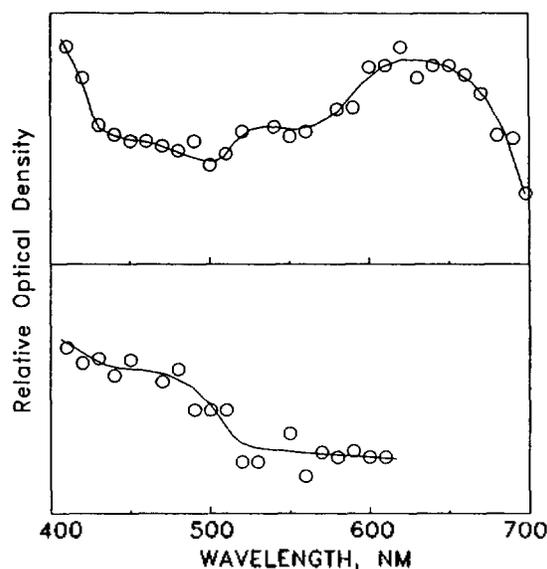As expected from the proximity effect in the lowest excited

singlet state,[26] the process mainly affecting the temperature dependence of fluorescence is internal conversion at relatively high temperature, while it is intersystem crossing at low temperature. If the slow increase of fluorescence of khellin at relatively high temperature is attributed to the decrease of S_1-S_0 internal conversion as expected from larger $^1(n, \pi^*)$-$^1(\pi, \pi^*)$ energy gap in ethanol than that in 2-methylpentane, its rapid increase at low temperature may be due to decrease of intersystem crossing to triplet excited state, which is supported by the facts that the phosphorescence to fluorescence quantum yield ratio of khellin in ethanol at 77 K is very low (0.015) and the fluorescence quantum yield is remarkably high (0.61) in comparison to 0.0036 at $25°C$. The temperature dependence of fluorescence for KDF and F-2 in ethanol are shown in Figure 4, which are very similar to those of khellin and 8-MOP, respectively, in Figure 2. These results can be also explained as in the case of khellin and 8-MOP.

Triplet-Triplet Absorption Spectra. The triplet-triplet absorption spectra of 8-MOP in water and ethanol were obtained to estimate the behavior of its triplet excited states and shown in Figure 5. The spectrum of 8-MOP in water reveals a small contribution from solvated electron and the presence of radical ions of 8-MOP such as 8-MOP⁻ and 8-MOP⁺ as well as the triplet,[20b,c] except for a band of 600-650 nm. The transient spectrum of 8-MOP in ethanol is consistent with its triplet-triplet absorption spectrum[20d] and no sign of photoionization was observable in ethanol. Since the triplet-triplet absorption spectrum of 8-MOP, eliminating the contribution by other species than 8-MOP triplet, in water is essentially identical to that in ethanol, it is thought that the solvent effect on the triplet excited states of 8-MOP is negligible.

Triplet-triplet absorption spectra of khellin (Figure 6) show, however, significantly different shapes according to the change of solvents, but photoionization of khellin by laser flash was not detected in all solvent used. The results con-
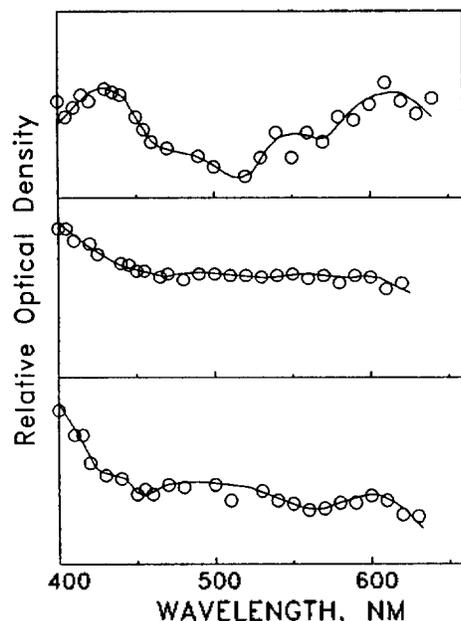
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Figure 6. Triplet-triplet absorption spectra of khellin in ethanol (upper), acetonitrile (middle), and n-hexane (lower) at 20°C on irradiation with 351 nm XeF excimer laser.
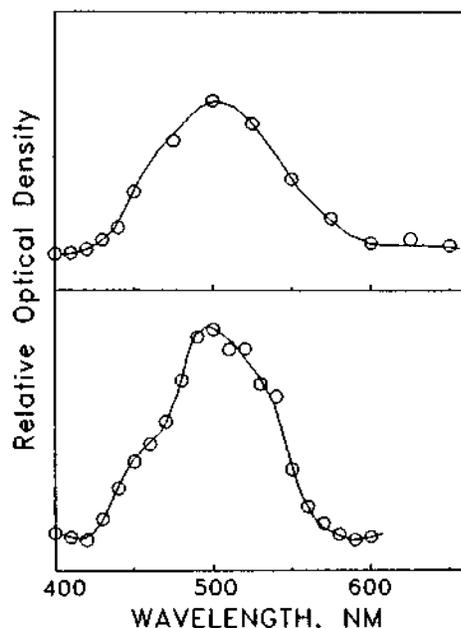

Figure 7. Triplet-triplet absorption spectra of 8-MOP<>thymidine 4',5'-monoadduct in water (upper) and ethanol (lower) at 20°C on irradiation with 351 nm XeF excimer laser.

Figure 8. Triplet-triplet absorption spectra of khellin<>dimethyl fumarate in ethanol (upper), acetonitrile (middle), and n-hexane (lower) at 20°C on irradiation with 248 nm KrF excimer laser.

Table 4. Quantum Yield (Φ_{2+2}) of [2+2]-Photocycloaddition Reaction of Khellin, 8-MOP, and F-2 with Dimethylfumarate or Tetramethylethylene at 25°C

Solvent	$\Phi_{2+2}{}^a$		
	Khellin[b]	8-MOP[c]	F-2[d]
EtOH	10^{-3}	—	0.025
CH_3CN	0.022	0.004	
$CHCl_3$		0.011	
CH_2Cl_2	0.045	0.009	
Et_2O		0.002	

[a] Irradiated with 366 nm light and measured within 10% conversion of reactant. [b] Concentrations of khellin and dimethylfumarate are 0.016 M and 0.1 M, respectively (cited from ref 22a). [c] Concentrations of 8-MOP and tetramethylethylene (TME) are 0.01 M and 0.25 M, respectively. [d] Concentrations of F-2 and TME are 0.011 M and 0.22 M, respectively (cited from ref. 30).

firm that in comparison to 8-MOP, khellin is fairly photostable compound and a poor producer of $O_2{}^-$ radicals responsible for the photobiological side effects.

As shown in Figure 7, triplet-triplet absorption spectrum of F-2 in water shows a broad absorption band with a peak maximum of 500 nm, and in ethanol a similar band with two shoulders at about 460 and 540 nm. Thus, this broad absorption band must be composed of three $T_n \leftarrow T_1$ absorptions at least. Triplet-triplet absorption spectrum of KDF (Fi-
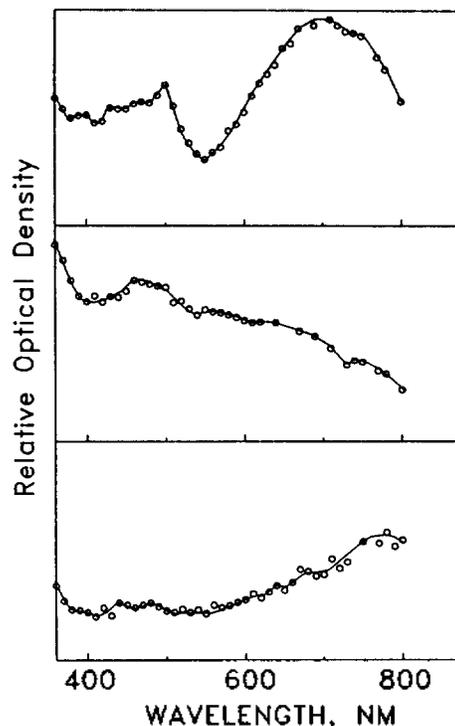
gure 8) shows a strong solvent dependence and in hexane shows an absorption peak at longer wavelength (790 nm) than in ethanol (700 nm). The $T_n \leftarrow T_1$ absorption spectrum in ethanol is very similar to $S_n \leftarrow S_0$ absorption spectrum. Since the shape of spectra obtained at different delay times after laser flash remain unchanged, there must be no sign on electron ejection by laser flash and thus the absorption peak at 700 nm in ethanol is not due to the solvated electron. It is likely that the low-lying triplet excited states are very close in energy, strongly mixed, and its order in energy is inversed by changing solvents.

Photocycloadduct Formation. Photoreaction of khellin and 8-MOP with olefin, as model of thymine, was carried out to estimate the photoreactivity and reactive excited states and the results are shown in Table 4. In the case of [2+2]-photocycloaddition reaction of 8-MOP with tetramethylethylene (TME), the reaction quantum yield increases as solvent polarity increases. However, khellin formed quantitatively the [2+2]-cycloadduct with dimethylfumarate (DF), while not with TME. The quantum yield of the[2+2]-cycloadduct formation of khellin with DF in hydroxy solvent, ethanol, is very low. The reaction quantum yield ratio (Φ_1/Φ_3) through singlet and triplet excited states on direct irradiation was also estimated from curve fitting of triplet quenching data by azulene. Φ_1/Φ_3 is 0.5 for 8-MOP in dichloromethane and 0.2 for F-2[30] in ethanol. In the case of khellin, the cycloadduct was formed at 4',5'-double bond with site-selectivity, only through the triplet excited state of khellin.[22] However, the cycloadduct formation from the singlet excited states of khellin can not be ruled out, since deviation from the pure triplet mechanism increased with high olefin concentrations. Another important result is that while F-2 formed the [2+2]-cycloadduct with TME, KDF never produce the cycloadduct at 2, 3-double bond of chromone moiety with TME or other olefins. These results confirm that 8-MOP is very reactive bifunctional and crosslinkable drug in DNA duplex, but khellin is low reactive monofunctional and non-crosslinkable drug. Thus, khellin may be safer to use than the known bifunctional furocoumarins, especially 8-MOP, in photochemotherapy of some skin diseases such as vitiligo and psoriasis.

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