Dependence of Fluorescent Ability on Efficiency of Intersystem Conversion in Psoralens

N. E. Kovalskaia,[1,2] I. V. Sokolova,[1] and G. V. Mayer[1]

Results of theoretical research for seven psoralen molecules: psoralen, 5-methoxypsoralen, 8-methoxypsoralen, angelicin, pseudoisopsoralen, isopseudopsoralen, and allopsoralen, are presented. Schemes of photophysical processes in psoralens based on quantum chemical calculation by the INDO method are analyzed. Effects of isomerism and methoxysubstitution on the energy level diagram are demonstrated. The rate constants of intersystem and internal conversions are calculated. We obtained rather high intersystem conversion constant that influences on the fluorescent yield of psoralens.

INTRODUCTION

Psoralens are a group of naturally occurring or synthetic compounds with interesting photosensitizing, photobiological, and phototherapeutic properties [1]. Their biological activity increases strongly under the action of ultraviolet radiation (PUVA), which allows their use them for the treatment of psoriasis and other skin diseases [2–5].

We know some mechanisms of photoreactions that are very important in PUVA therapy. The mechanisms include the transition of electron, the transition of energy and two-stage photooxidizing processes [6].

In this paper we consider results of theoretical research on seven psoralen molecules: psoralen (PS), 5-methoxypsoralen (5-MOP), 8-methoxypsoralen (8-MOP), angelicin (Ang), pseudoisopsoralen (PIP), isopseudopsoralen (IPP), and allopsoralen (Allo) (Fig. 1).

QUANTUM CHEMICAL METHODS

The quantum chemistry method is used to study the photophysical properties of linear and angular psoralens with conjugated external carbonyl substitutents. The concepts and methods of quantum chemistry and the theory of nonradiative transitions in polyatomic organic molecules are the basis for our theoretical approach. The quantum chemical algorithms and programs are based on a semiempirical method of intermediate neglect of differential overlapping (INDO) involving particular spectroscopic parametrization [7,8].

A computer program is developed for calculating the matrix elements of the spin-orbital interaction operator, which makes it possible to estimate the rate of singlet-triplet conversion k_{ST}. Also we can to estimate of internal conversion [9].

We calculated k_{ST} by the formula:

$$k_{ST} \approx 10^{10} \, |\beta_{ST}|^2 \, 1/(ex\ n!) \tag{1}$$

where $n = \Delta E_{ST}/1200$, ΔE_{ST} is the energy gap between the S and T states and β_{ST} is the matrix element of spin-orbital interaction ($\approx 10\ cm^{-1}$ for the $\pi\pi \to n\pi$ conversion and $\approx 0.3\ cm^{-1}$ for the $\pi\pi \to \pi\pi$ conversion).

[1] Department of Photonics of Molecules, Siberian Physical Technical Institute by Tomsk State University, Novo-Sobornaya sq., 1, 634050, Tomsk, Russia.
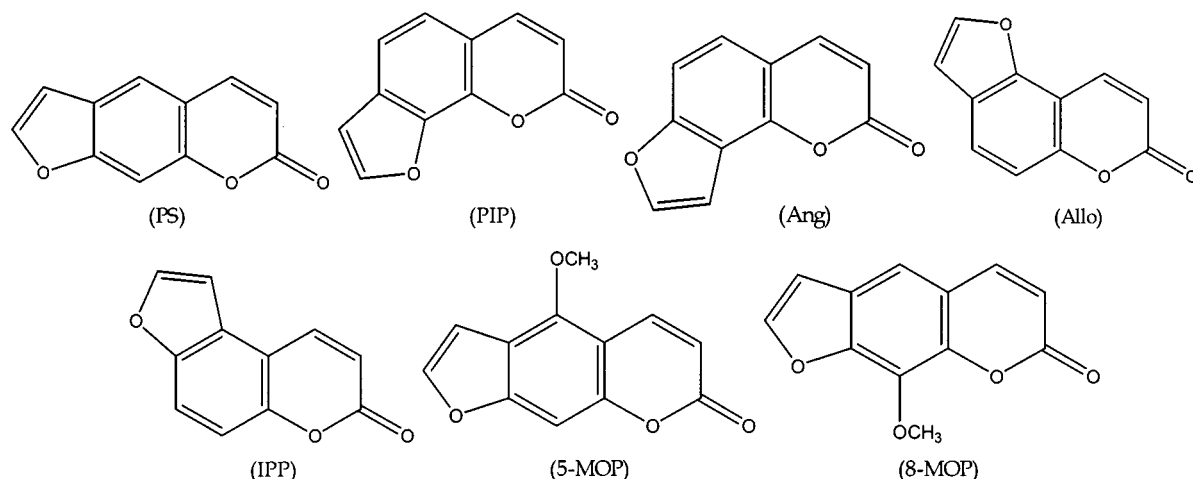[2] To whom correspondence should be addressed.

Fig. 1. Structure formulas of the tested psoralens.

DISCUSSION

Psoralen represents a coumarin molecule with an attached furan ring. The furan ring geometry was borrowed β-modification [10].

Quantum chemical calculations by the INDO method have been performed to determine the schemes of photophysical processes in psoralen molecules. It was shown that for all compounds the lower singlet excited state S_1 is a $\pi\pi^*$ type and state S_2-$n\pi^*$ type. Analysis of the electronic excited states shows that the intersystem conversion process is a basic channel of the excitation energy activation ($k_{ST} \sim 10^{10}$ to 10^{11} s^{-1}) for the molecules tested. This is due to the fact that in our systems the singlet and triplet of different orbital nature ($\pi\pi^*$ and $n\pi^*$ type) beside are located. Table I give the calculated oscillator strengths of the lower singlet excited states (f), rate of internal conversion k_{ic}, rate of intersystem conversion of electron transitions k_{ST} and radiation rate k_r.

From Table I, it can be seen that isomerization does not influence the oscillator strengths of the lower singlet

excited states but methoxysubstitution decreases the oscillator strengths.

Since our calculation was performed for isolated systems with ground state geometry the quantum fluorescence yields were very small. In actual practice, however, the intersystem conversion yield for the examined system (e.g., for 8-MOP and Ang) depends on the solvent [11]. This means that the nature of the medium in which psoralens are diluted in the skin is of great importance and the actual fluorescence quantum yields are somewhat greater. Therefore, intermolecular interaction (IMI) with various solvents are of great interest. These results were reported earlier [12].

In support of the energy level diagram obtained by us we compared the available experimental and theoretical date on positions of lower singlet and triplet energy levels [13]. The best agreement for the triplets was obtained for the calculations with special triplet parameterization. The energy of the T_1 ($\pi\pi^*$) state in this case was less than in the calculation with singlet parameters.

RESULTS

Schemes of photophysical processes in psoralens based on quantum chemical calculation are suggested. Also, efficient intersystem conversion which causes significant population of triplets is observed for the examined compounds ($k_{ST} \sim 10^{10}$ to 10^{11} s^{-1}). It may be a reason for the decreasing fluorescence yield. In addition, the internal conversion in psoralen molecules is fairly efficient. The internal conversion (IC) constant for the singlets is about 10^{10} to 10^{11} s^{-1} and for the triplets it is about 10^{10} to 10^9 s^{-1}. The IC constant for the $S_1 \rightarrow S_0$

Table I. The Calculated Constants of Photophysical Processes and Oscillator Strengths of the Lower Singlet Excited States by the INDO Method

Compound	f	k_{ic}	k_{ST}	k_r
PS	0.16	$6 \cdot 10^3$	$2 \cdot 10^{11}$	$1 \cdot 10^8$
PIP	0.18	$8 \cdot 10^3$	$3 \cdot 10^{11}$	$1 \cdot 10^8$
IPP	0.2	$1 \cdot 10^4$	$3 \cdot 10^{11}$	$1 \cdot 10^8$
Ang	0.12	$4 \cdot 10^3$	$2 \cdot 10^{11}$	$8 \cdot 10^7$
Allo	0.12	$9 \cdot 10^3$	$2 \cdot 10^{11}$	$8 \cdot 10^7$
8-MOP	0.015	$2 \cdot 10^4$	$5 \cdot 10^{10}$	$9 \cdot 10^6$
5-MOP	0.01	$1 \cdot 10^3$	$2 \cdot 10^{10}$	$7 \cdot 10^6$

transition is 10^3 to 10^4 s^{-1}. Finally, isomerization and methoxysubstitution influence the energy level diagram but do not influence the fluorescent yield.

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