

## PHOTOCHEMICAL SCISSION OF CINNAMIC ACID DIMERS: $\alpha$ -TRUXILLIC AND $\beta$ -TRUXINIC ACIDS

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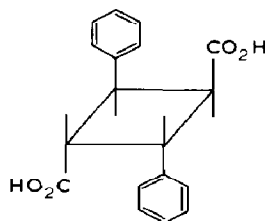
### Summary

Excited  $\alpha$ -truxillic acid and  $\beta$ -truxinic acid monomerize in solution to yield cinnamic acid with quantum efficiencies of 0.12 and 0.41, respectively. The photoscission proceeds *via* excited singlet and triplet molecules.

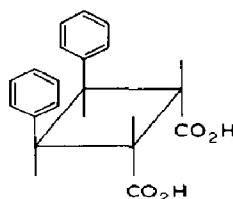
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### Introduction

The topochemical and photochemical aspects of the photodimerization of solid *trans*-cinnamic acid are well understood [1, 2]. In this reaction the stable  $\alpha$ -platelets yield  $\alpha$ -truxillic acid:



and the metastable  $\beta$ -needles produce  $\beta$ -truxinic acid:



exclusively [3]. Irradiation of solutions of dimeric cyclo-adducts with wavelengths shorter than 280 nm causes dimer splitting with formation of monomeric cinnamic acid [4a, b]. This reaction was studied to determine the quantum efficiency and elucidate the nature of the excited states involved in the monomer formation.

## Experimental

### Materials

*trans*-Cinnamic acid (Fisher, Reagent Grade) was twice recrystallized from methanol, m.p. 132 - 133 °C.

$\alpha$ -Truxillic acid was prepared by irradiation of a suspension of  $\alpha$ -*trans*-cinnamic acid in water as described by White and Dunathan [5]; and was twice recrystallized from methanol, m.p. 289 - 291 °C.

$\beta$ -Truxinic acid was prepared as described by Freedman *et al.* [6], m.p. 210 - 211 °C.

Absolute methanol (Baker and Adamson) and absolute ethanol (Publicker Industries, "Pharmco") were used without further purification, since a check of the absorbance and fluorescence of these solvents showed them to be suitable as supplied for fluorimetric use.

*trans*-Piperylene (Aldrich Chem. Co.) and *cis*-piperylene (J. T. Baker) were purified by four bulb-to-bulb vacuum distillations. About half of the original material was discarded.

### Apparatus

Absorption spectra were recorded on a Cary 14R spectrophotometer. Luminescence measurements were performed on a Hitachi-Perkin-Elmer MPF2A spectrofluorimeter thermostated at 25 °C. A Hitachi phosphorescence attachment supplied with this instrument was used to obtain low temperature luminescence measurements on samples in ethanol glass, which were contained in 3 mm o.d. cylindrical Spectrosil tubes. A rotating chopper which encircled the sample served to isolate the phosphorescence emission; in the absence of this chopper, total emission spectra were obtained.

### Quantum yield determinations

A 1.00 cm path length quartz reaction cell was held in a thermostated holder (maintained at  $25.0 \pm 0.1$  °C) on a specially constructed turntable (Fig. 1), permitting reproducible placement in the exciting radiation beam of either the reaction vessel or a 12 junction Eppley thermopile used to monitor intensity. Thermopile response was related to photons incident by means of ferrioxalate actinometry [7]. The radiation source was a 200 W Hanovia Xe-Hg lamp, light from which was passed through a Bausch and Lomb 500 mm grating monochromator set at  $265 \pm 3.2$  nm in the direct dimer photolysis.

### Analysis

The extent of the reaction was determined by differential spectrophotometry (irradiated solutions *vs.* dark blank), on the Cary Model 14R spectrophotometer with a 0 - 0.1 absorbance slidewire. Absorbance changes were measured at the wavelength of irradiation, and at the isosbestic point ( $\lambda = 247.5$  nm) for *cis-trans* isomerization of the cinnamic acid in methanol.

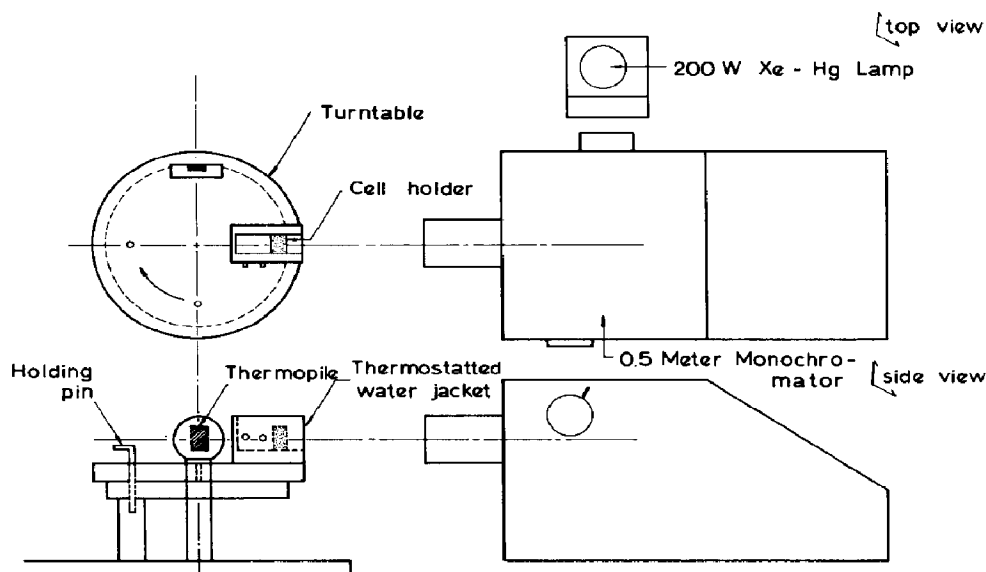


Fig. 1. Irradiation apparatus.

Absorbance of the dimer acids at these wavelengths varied linearly with concentration. Under the conditions of an irradiated run (*i.e.* in the presence of excess dimeric acid), the absorbance of cinnamic acid also varied linearly with concentration, notwithstanding that solutions of cinnamic acid alone in methanol exhibited deviations from Beer's law behavior as a result of dissociation.

## Results and Discussion

### *Quantum efficiencies of the photoscission reactions*

The absorption spectra of the dimer acids (Fig. 2) overlap with the near u.v. absorption band of cinnamic acid (Fig. 3); however, the absorptivity of the latter is an order of magnitude larger than those of the dimer acid at the wavelength of 247.5 nm. This wavelength was chosen for excitation and analysis, since it is isosbestic with respect to the geometrical isomers of the monomer. The absorbance changes measured at this wavelength *vs.* unirradiated blanks permitted reliable determinations of the fraction of radiation absorbed by dimer and amount of dimer reacted. Samples were periodically removed from exciting radiation and analyzed in the spectrophotometer. The quantum yield of scission,  $\Phi_r$ , was computed.

$$\Phi_r = \frac{0.5 \Delta A \times 3 \times 10^{-3} l}{(a_c - 0.5a_D) \times I_0 \times F \times \Delta t}$$

where

$\Delta A$  = absorbance increase at 247.5 nm,

$a_c$  and  $a_D$  are molar absorptivities of monomer and dimer, respectively,

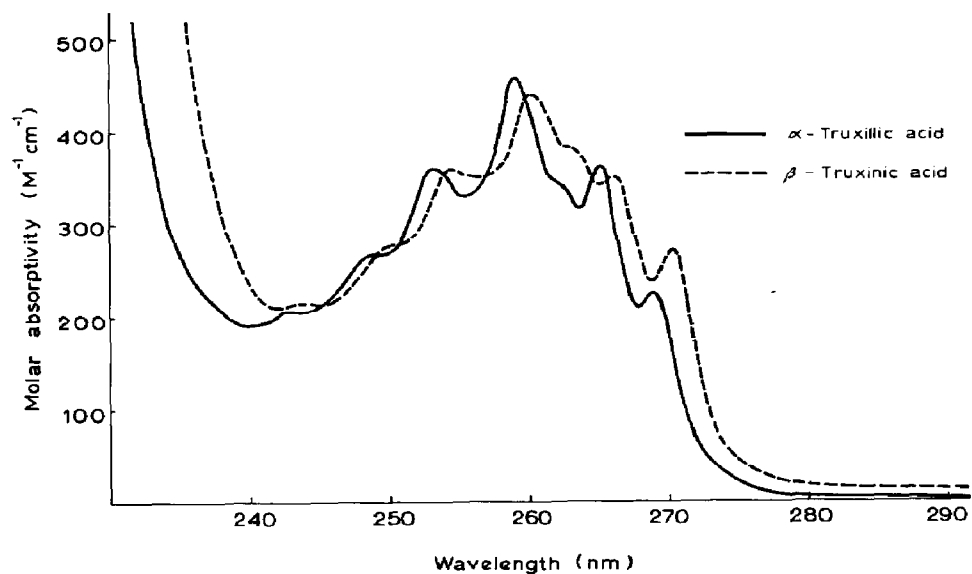


Fig. 2. Absorption spectra of  $\alpha$ -truxillic acid and  $\beta$ -truxinic acid in methanol.

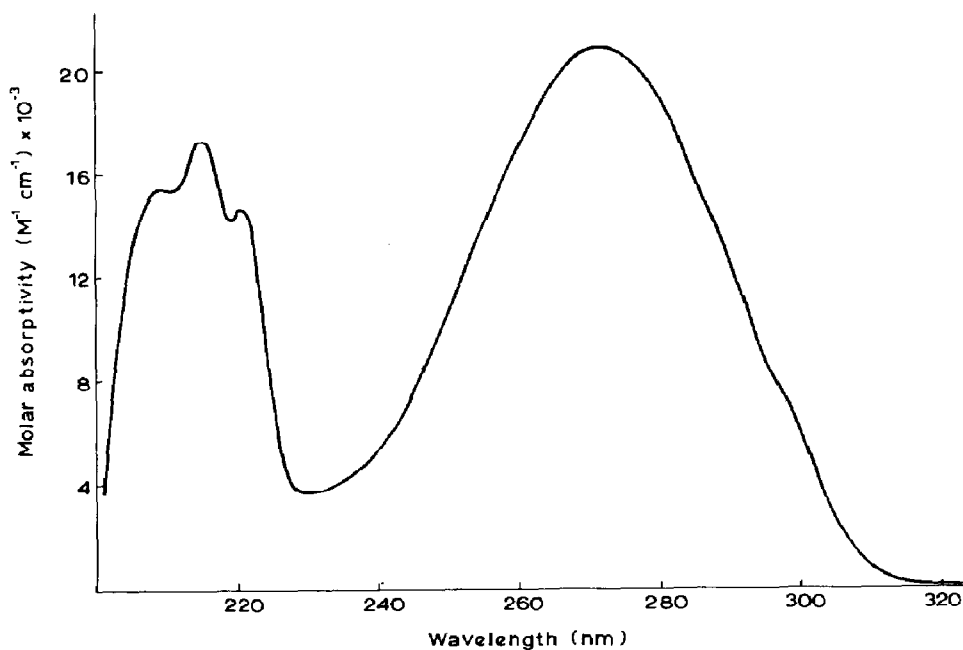


Fig. 3. Absorption spectrum of *trans*-cinnamic acid in methanol.

$I_0$  = incident intensity (inside front cell window),  
 $\Delta t$  = irradiation time interval,

$$\text{and } F = \left[ A_D^\circ - 0.5 a_D \left( \frac{\Delta A}{a_c - 0.5 a_D} \right) \right] \frac{1 - 10^{-A}}{A}$$

TABLE 1

Quantum yields of fluorescence, phosphorescence and of scission in absence of O<sub>2</sub>

Solute (1 mM)	$\Phi_{\text{Sciss.}}^{\text{a}}$	$F_{\text{rel.}}^{\text{a}}$	$\Phi_{\text{F}}^{298 \text{ K a,d}}$	$\frac{\Phi_{\text{F}}^{77 \text{ K b}}}{\Phi_{\text{F}}^{298 \text{ K}}}$	$\Phi_{\text{F}}^{77 \text{ K b}}$	$\frac{\Phi_{\text{P}}^{\text{b}}}{\Phi_{\text{F}}}$	$\Phi_{\text{P}}^{\text{b}}$
$\alpha$ -Truxillic acid	$0.123 \pm 0.009$	24.6	(0.032)	11 <sup>d</sup>	0.35 <sup>d</sup>	0.013	0.0045 <sup>e</sup> 0.0047 <sup>f</sup>
$\beta$ -Truxinic acid	$0.407 \pm 0.013$	14.6	0.019	19	0.36	0.016	0.0058 <sup>e</sup>

<sup>a</sup> Solvent: methanol.<sup>b</sup> Solvent: ethanol.<sup>c</sup> Based on  $\Phi_{\text{F}}$  (quinine sulfate/0.1 N H<sub>2</sub>SO<sub>4</sub>) = 0.58.<sup>d</sup> Calculated from  $\Phi_{\text{F}}^{77 \text{ K}}(\beta) = 0.36$ , and  $\Phi_{\text{F}}^{77 \text{ K}}(\beta)/\Phi_{\text{F}}^{77 \text{ K}}(\alpha) = 1.03$ .<sup>e</sup> Calculated from  $\Phi_{\text{F}}^{77 \text{ K}}$  and  $\Phi_{\text{P}}/\Phi_{\text{F}}$ .<sup>f</sup> Calculated from  $\Phi_{\text{P}}(\beta) = 0.0058$ , and  $\Phi_{\text{P}}(\beta)/\Phi_{\text{P}}(\alpha) = 1.24$ .

where

 $A_{\text{D}}^{\circ}$  = initial absorbance of dimer at 247.5 nm, $A$  = total absorbance of solution at 247.5 nm.

It may be noted (Table 1) that the quantum yield of scission for  $\beta$ -truxinic acid is  $3.3 \times$  larger than that of  $\alpha$ -truxillic acid which is 0.123 (molecule reacted/photon absorbed).

#### Luminescence of the photodimers

Fluorescence and phosphorescence spectra of the dimer acids are shown in Figs. 4 and 5. It should be noted that the fluorescence yield of  $\alpha$ -truxillic acid, exhibiting a lower photoscission efficiency than  $\beta$ -truxinic acid, is higher than that of the latter. The phosphorescence yields bear the opposite relationships to fluorescences. The larger intersystems crossing of  $\beta$ -truxinic acid concomitant with a larger photoscission yield suggests that the rate constant for scission of the excited triplet state is larger than that of the excited singlet state which has a higher population in excited  $\alpha$ -truxillic acid. To obtain more definitive information on excited states quenching experiments were performed.

#### Quenching by piperylene

Piperylene was found to quench both the fluorescence and scission rate of  $\alpha$ -truxillic acid in methanol. Both mixtures of *cis*- (43%) and *trans*-piperylene and *cis*-piperylene (containing less than 0.1% *trans*) were used in quenching. Stern—Volmer plots for quenching of scission and fluorescence yields gave overall (*cis* and mixture of piperylene) slopes (obtained by least squares

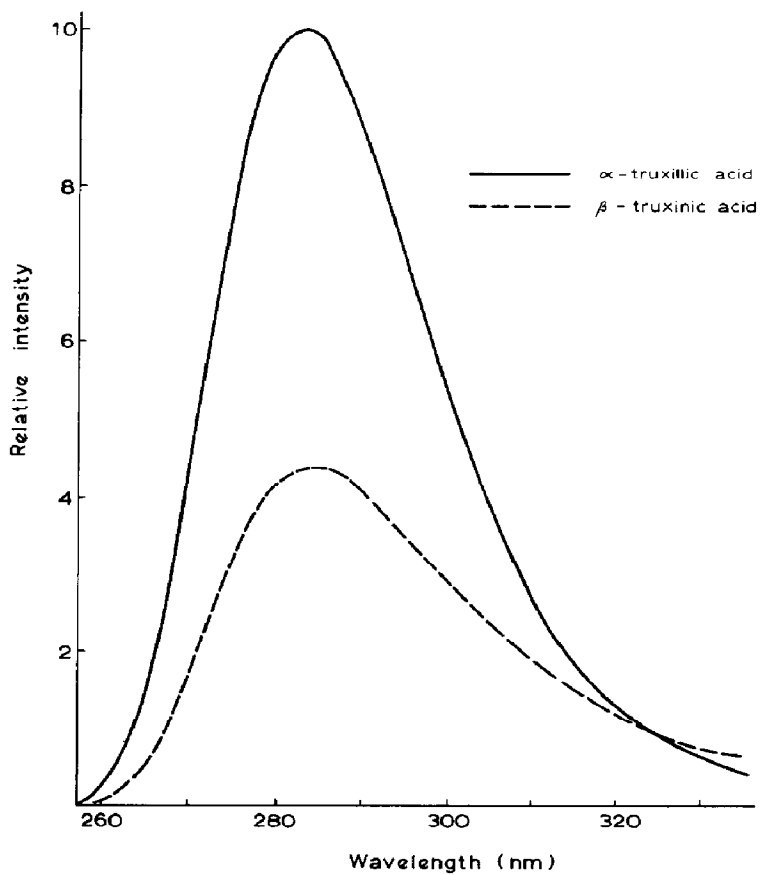


Fig. 4. Fluorescence spectra of  $\alpha$ -truxillic acid and  $\beta$ -truxinic acid in methanol at 25°C.

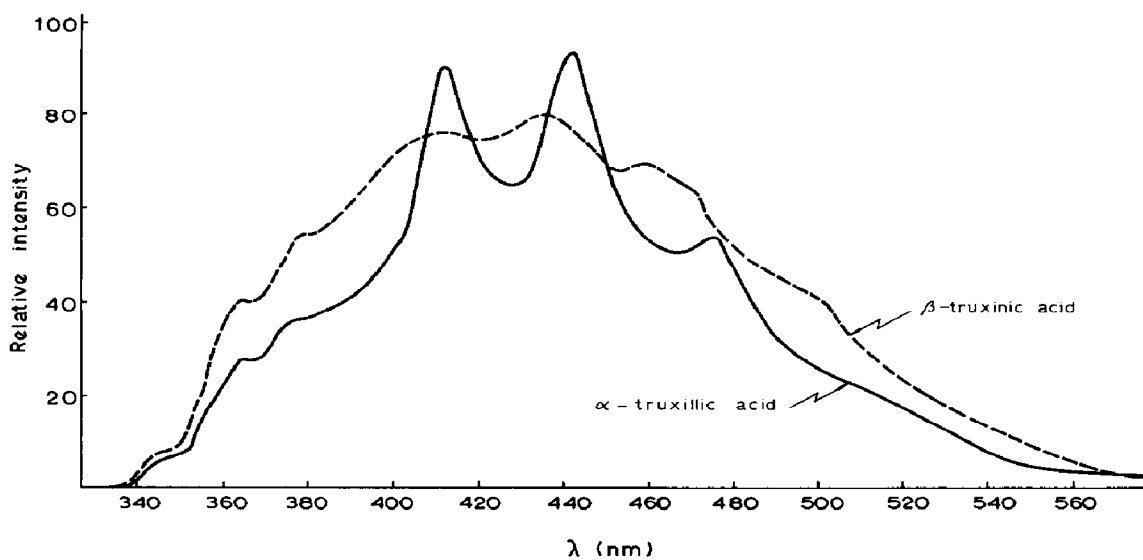


Fig. 5. Phosphorescence emission spectra of  $\alpha$ -truxillic and  $\beta$ -truxinic acids in EPA glass at 77 K.

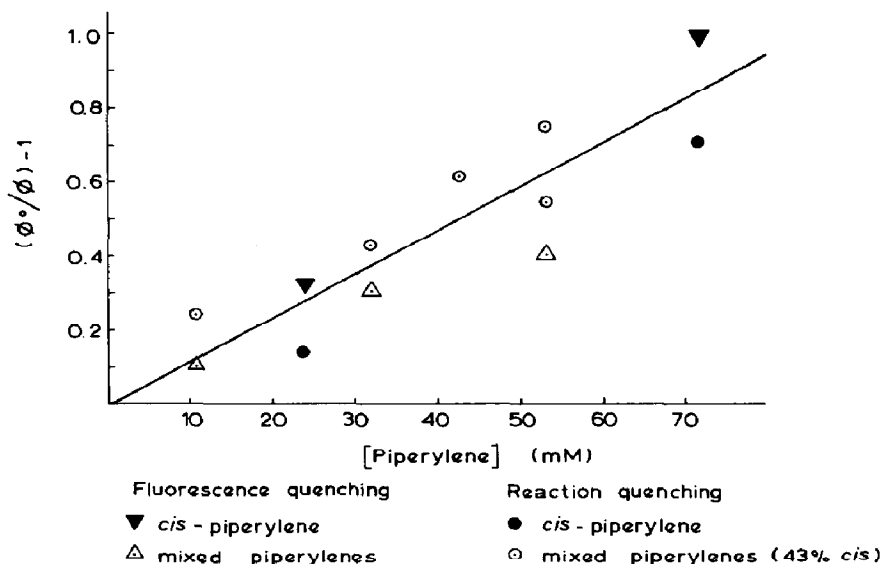


Fig. 6. Piperylene quenching of fluorescence and scission for  $\alpha$ -truxillic acid in methanol at 25 °C.

analysis) of  $12.1 M^{-1}$  and  $11.8 M^{-1}$  for fluorescence and reaction quenching, respectively. Figure 6 shows the quenching curve obtained by least squares analysis of both fluorescence and scission yield data. In view of the experimental error the coincidence of fluorescence and chemical quenching constants may be somewhat fortuitous. Nevertheless, these results, clearly show that most, if not all, of the scission reaction for  $\alpha$ -truxillic acid is singlet derived.

### Effect of oxygen

Fluorescence quenching of  $\alpha$ -truxillic acid and the less fluorescent

TABLE 2

Effect of oxygen on fluorescence and scission yields<sup>a</sup>

Solute	Solvent	[O <sub>2</sub> ] (mM)	Scission enhancement $\Phi_r/\Phi_r^0$	Fluorescence quenching $\Phi_F^0/\Phi_F$
$\alpha$ -Truxillic acid	MeOH	2.12 <sup>b</sup>	1.179	1.20
		3.80	1.261	—
		6.63	1.336	—
		10.13 <sup>c</sup>	—	2.18
		12.72	1.429	—
		19.72	1.421	—
		22.24	1.393	—
$\beta$ -Truxinic acid	MeOH	2.12 <sup>b</sup>	1.03	1.15
		10.13 <sup>c</sup>	0.788	1.84

<sup>a</sup> 1.0 mM dimer solutions.

<sup>b</sup> Air saturated solutions.

<sup>c</sup> Oxygen saturated solutions.

$\beta$ -truxinic acid by oxygen was determined for two well reproducible points (Table 2). Generally the oxygen quenching of fluorescence was more efficient than that of piperylene. It is noteworthy that oxygen at low concentrations enhances the scission efficiency but attenuates it at high concentration. In all cases reaction quenching by oxygen is less than fluorescence quenching. This means that a mechanism of fluorescence quenching in which oxygen enhances internal conversion of the excited singlet state to a non-reactive ground state must be ruled out. Instead, oxygen appears to catalyze crossing of the dimer fluorescent state to another state capable of undergoing scission. Product formation from this state appears more efficient than from the fluorescent state. It is reasonable to assume that this state is the dimer triplet. Now, a high concentration of oxygen crossing over of the excited triplet to the non-reactive singlet ground state effectively competes with intersystems crossing from excited singlet to excited triplet state. Consequently the quantum yield of scission is lowered.

### Conclusion

It appears that in the absence of oxygen the photoscission of  $\alpha$ -truxillic acid is mainly singlet derived while a considerable fraction of the splitting of  $\beta$ -truxinic acid is triplet derived. The scission of the triplet appears to have a higher rate constant than that of the singlet.

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