

Photochemical Reactions of the Substituent Groups of Cotton Cinnamate Fabric

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Synopsis

The extents to which the substituents of cotton cinnamate fabrics dimerize and undergo cis-trans isomerization upon irradiation with 2537 Å light were determined. It was shown that these photochemical reactions occur primarily on the surface of the fabric. Simple crosslinking via the truxillic and/or truxinic acid residues, although directly related to the increases in conditioned wrinkle recovery angles, was sufficient to produce fabrics with only moderate levels of wrinkle recovery properties.

INTRODUCTION

The two basic photochemical reactions of cinnamic acid, cis-trans isomerization and dimerization to truxillic and truxinic acids, have been investigated extensively; the former principally in dilute solution¹⁻⁴ and the latter in the crystalline state.^{5,6} Dimerization has also been shown to occur when the cinnamoyl groups are incorporated into a polymeric structure. The photodimerization of neighboring cinnamoyl substituents of poly(vinyl cinnamate) films has been demonstrated⁷ by the decrease in the number of double bonds measured by infrared absorption at 1635 cm⁻¹ and by saponification of the irradiated films followed by identification of α -truxillic acid via paper chromatography.⁸ The neighboring groups in cotton cellulose cinnamate might be expected to dimerize upon irradiation in a similar manner.

The possibility of using this photodimerization reaction as the basis for a delayed cure process for cotton fabric was examined earlier.⁹ Samples of cotton cinnamate fabric were prepared with varying degrees of substitution. These were irradiated with 2537 Å light for various periods of time. It was demonstrated that irradiation effected increases in the wrinkle recovery properties of the fabric.

There is considerable interest and question regarding the relative importance of crosslinking and resin deposition within the fiber as causative factors in the development of durable-press properties in the fabric. In many of the chemical finishing treatments for cotton cellulose, both phenomena are possible, each is difficult to assess, and the relation between them

and the resulting changes in fabric properties are unclear. In the cotton cinnamate fabrics, however, improvements in fabric properties effected by irradiation must be attributed to the photochemical reactions of the cinnamoyl substituents, resin deposition being eliminated as a possibility. It was of interest, therefore, to determine the extent to which the cinnamoyl groups in cotton cinnamate fabric underwent *cis-trans* isomerization and photodimerization, since the latter reaction results in the formation of "simple" crosslinks.

The study reported here is an investigation into the relative extents to which each of these basic photochemical reactions occurs in the cinnamoyl moiety when esterified to cellulose in cotton fabric.

EXPERIMENTAL

Materials

The preparation of the cotton cinnamate fabrics of degree of substitution (DS) 0.11, 0.34, 0.48, and 0.58 has been described.⁹ An authentic sample of α -truxillic acid was prepared according to a published procedure,⁶ mp 286–8°C (lit.⁶ 285–6°C).

Irradiation

A Rayonet Photochemical Reactor (Southern New England Ultraviolet Company, Middletown, Conn.) equipped with 16 lamps to generate light of wavelength 2537 Å was employed. The fabric samples were suspended in the reactor and irradiated in an atmosphere of air for periods of 1, 12, 24, and 48 hr. Solutions (10%) of methyl *trans*-cinnamate in methanol and hexane were irradiated in 15-ml quartz test tubes for periods of 1, 12, 24, and 48 hr.

Analytical Methods

The extents of *cis-trans* isomerization and photodimerization effected by irradiation were determined by gas-liquid chromatography (GLC) employing an Aerograph Autoprep Model A-700 gas chromatograph equipped with an F&M temperature programmer. A 6-ft OV-17 (Superlco, Inc., Bellefont, Pa.; 3% on Chromsorb W) column was used. The instrument was programmed from 100° to 320°C at a rate of 10°/min.

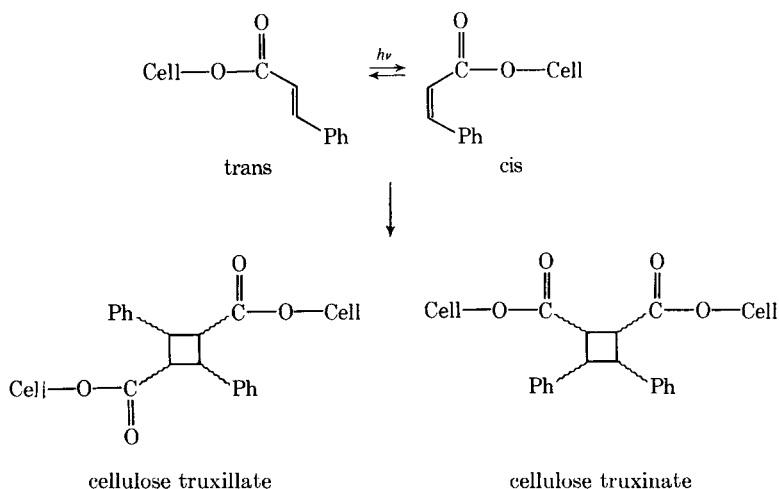
Irradiated fabric samples were saponified in a 20% methanolic solution of tetramethylammonium hydroxide (Aldrich Chemical Co., Inc., Milwaukee, Wis.) at 50°C for 16 hr; the photoproducts were identified via GLC as their methyl esters according to the general procedure for cellulose esters described by Berni et al.¹⁰

The distribution of cinnamate units in *cis*, *trans*, and dimer forms was calculated from GLC peak areas (measured on a du Pont 310 Curve Resolver, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.); the areas were corrected for detector response (methyl *trans*-cinnamate : methyl

α -truxillate, 1:0.75 (w/w), a 1:1 response being assumed for isomeric modifications).

RESULTS AND DISCUSSION

In addition to *cis*-*trans* isomerization, cinnamic acid is known to photodimerize via a 2 + 2 cycloaddition yielding truxillic and truxinic acids, of which there are 11 diastereomeric modifications. Incorporation of the *trans*-cinnamoyl moiety into a polymeric structure would not be expected to significantly alter its basic photochemical reactions. Dimerization of the cinnamoyl substituents of poly(vinyl cinnamate) has already been demonstrated,^{7,8} however, the extent to which *cis*-*trans* isomerization occurred was not reported. The potential photochemical reactions of the *trans*-cinnamoyl substituents of cellulose cinnamate are shown below:



That both photochemical reactions occur upon irradiation of cotton cinnamate fabric was demonstrated by saponification of the irradiated fabrics in 20% tetramethylammonium hydroxide solution followed by GLC identification of the photoproducts as their methyl esters.

Limitations of the Analytical Technique

Within each series, truxillic and truxinic acids have been shown to isomerize upon treatment with strong base¹¹⁻¹³ and also upon heating to relatively high temperatures.¹¹ In addition, the latter is reported to cause anhydride formation.¹¹ Fragmentation of α -truxillic acid upon distillation at 190-200°C has also been reported, *trans*-cinnamic acid and stilbene being detected among the products.¹⁴

Since basic hydrolysis was used to remove the dimer from the irradiated fabrics and column temperatures of about 300°C were used in the GLC determinations, it is probable that all or some of the isomerizations noted above occurred in the isolation and determination of the cinnamate resi-

dues. Fragmentation of the dimers on the column would render our technique worthless. Therefore, pure α -truxillic acid was dissolved in the tetramethylammonium hydroxide solution and injected into the gas chromatograph. It was eluted as a double peak, but there was no evidence of monomeric methyl *trans*-cinnamate or any other low molecular weight fragments.

Neutralization of the carboxylic acid groups of truxillic and truxinic acids is known to be stepwise, the second carboxyl group being neutralized only with excess alkali.¹⁵ Anhydride formation, after epimerization of a ring carbon bearing a carboxyl substituent, could account for the double peak due to α -truxillic acid. That this is not the case is indicated by the fact that the dimeric materials obtained upon saponification of the irradiated fabrics (necessarily removed from the cellulose polymer as the di-tetramethylammonium salt) and the dimers formed upon irradiation of methyl *trans*-cinnamate (where anhydride formation is very unlikely due to lack of contact with base) are both eluted as double peaks, although of different relative heights.

It can therefore be concluded that the two peaks represent two groups of methyl truxillates and/or truxinates of different polarities rather than a mixture of the methyl esters of the dimers and their anhydrides. The isomers of truxillic and/or truxinic acid which are originally formed upon irradiation of methyl *trans*-cinnamate or cellulose cinnamates are believed to be isomerized to the most stable configuration in the basic solution via epimerization of the ring carbons bearing the carboxyl groups. Thus, only the total percentage of dimer is reported.

Light Penetration

Evidently *cis*-*trans* isomerization and/or dimerization can occur in any cinnamate substituent which is electronically excited. Thus, the amount of *trans*-cinnamic acid remaining in a specific sample after irradiation, when compared with another sample in which all *trans*-cinnamoyl groups have the potentiality for absorption of incident light, can serve as a measure of the approximate depth of light penetration.

The amount of *trans*-cinnamic acid present at photoequilibrium in solution has been shown to be solvent dependent and directly related to the total acid concentration.²⁻⁴ Preceding studies utilized very dilute solutions (0.002–0.004*M*) in which dimerization is not likely to occur. In this study, 10% (0.62*M*) solutions were used in an attempt to obtain data at a cinnamate concentration comparable to that of the DS 0.11 fabric; i.e., this DS represents an 8% incorporation of cinnamate units. Dimerization, observed previously in water solution,¹⁶ did occur in these concentrated solutions; the results do not represent a photoequilibrium composition as the dimerization reaction is not photochemically reversible. They do, however, give us an approximate measure of the amount of *trans* isomer which would be present if all of the cinnamoyl substituents had the potentiality for electronic excitation.

TABLE I
Effect of Irradiation Time and Solvent on the Extent of Cis-Trans
Isomerization and Dimerization of Methyl *trans*-Cinnamate

Irradiation time, hr	Cis, %	Trans, %	Dimer, %
<i>n</i> -Hexane			
0	0	100	0
1	13.3	85.6	1.1
12	47.9	46.5	5.6
24	47.9	44.3	12.4
48	40.1	44.3	15.6
Methanol			
0	0	100	0
1	19.5	79.8	0.7
12	55.7	41.2	3.1
24	57.5	37.4	5.1
48	53.4	36.9	9.7
Neat			
24	16.5	76.9	6.6

As it is difficult to estimate whether the cellulose matrix resembles a polar or a nonpolar environment for the cinnamate groups, the solution irradiations were carried out in both methanol and hexane. Stirring during the irradiations did not affect the distribution of photoproducts. The results are given in Table I. The extents to which these same reactions occur on cotton fabric are given in Table II.

The substantially lower extents of isomerization of *trans*-cinnamate in fabrics (Table II) compared to the extents in solution (Table I) indicate that light penetration into the fabric is quite shallow. These data can be used to calculate an approximate value for the percentage of *trans*-cinnamoyl substituents actually subject to irradiation if it is assumed that the cellulose ester of *trans*-cinnamic acid behaves similarly to the methyl ester upon exposure to ultraviolet light. The resulting values are given in Table III. The overall range of proportion of cinnamate groups actually reached by the radiation is estimated to be 9% to 44%. It is evident from the values in Table III that the percentage of cinnamate groups reached by radiation decreases as the DS of the fabric increases: i.e., 33–44% at DS = 0.11, 19–22% at DS = 0.34, 14–19% at DS = 0.48, and 9–20% at DS = 0.58. As stated previously, the amount of *trans*-cinnamic acid present at photo-equilibrium is directly related to the initial concentration of cinnamic acid. The data used in the above calculations (Table III) were obtained using relatively concentrated solutions. Literature values are significantly lower for residual *trans*-cinnamic acid at equilibrium after irradiation of dilute solutions. With the lowest equilibrium value reported (28% *trans*-cinnamic acid²), estimations of the overall proportions of cinnamate groups

actually irradiated in the fabrics range from 6% to 32%. In any case, it is obvious that less than half of the substituents were within reach of the incident light, the percentage decreasing as the degree of substitution increased.

That the photochemical reactions occur on the surface of the fabric, as indicated above by the comparison of fabric data with the solution data,

TABLE II
Effect of Irradiation Time and Degree of Substitution on the
Extent of Cis-Trans Isomerization and Dimerization of the
Substituents of Cotton Cinnamate Fabric

Irradia- tion time, hr	Cis, %	Trans, %	Dimer, %	DS of crosslink ^a
DS 0.11				
0	0	100	0	0
1	8.0	84.3	7.7	0.009
12	8.9	76.7	14.4	0.016
24	9.9	73.8	16.3	0.018
48	9.9	75.4	14.7	0.016
DS 0.34				
0	0	100	0	0
1	3.1	94.1	2.8	0.010
12	5.0	88.3	6.7	0.023
24	5.1	87.3	7.6	0.026
48	4.7	88.2	7.1	0.024
DS 0.48				
0	0	100	0	0
1	2.4	95.0	1.7	0.008
12	3.8	92.0	4.2	0.021
24	4.5	89.9	5.6	0.027
48	4.4	89.3	6.3	0.021
DS 0.58				
0	0	100	0	0
1	2.7	95.3	2.0	0.016
12	2.3	94.9	2.8	0.024
24	3.3	93.1	3.6	0.030
48	5.1	88.9	6.0	0.035

^a Obtained by multiplying the fraction of cinnamoyl substituents which dimerized by the degree of substitution.

was confirmed by irradiating two fabric samples, DS 0.11 and 0.34, on only one side for 12 hr. In these cases, one side of the fabric was protected from irradiation by wrapping it around a Pyrex cylinder. The results, contrasted with those of the same fabrics irradiated on both sides, are given in Table IV. The shallow light penetration can be attributed to the tendency of the cinnamoyl groups in the outer regions of the fabric to shield those in the interior and/or to the opacity of the cotton fiber to ultraviolet light (via scattering).

TABLE III
 Estimation of Percentages of *trans*-Cinnamoyl Substituents
 Actually Reached by Irradiation and Percentages of
 Irradiated Substituents which Dimerized

Irradiation time, hr	Substituents ^a Irradiated, %		Dimer ^b (irradiated basis), %	
	Hexane ^c	Methanol	Hexane	Methanol
		DS 0.11		
12	44	40	33	36
24	43	42	38	39
48	44	39	33	38
		DS 0.34		
12	22	20	30	34
24	21	20	36	38
48	21	19	34	37
		DS 0.48		
12	15	14	28	30
24	17	16	33	35
48	19	17	33	37
		DS 0.58		
12	10	9	28	31
24	11	11	33	33
48	20	18	30	31

^a Calculated using $x = 100-a/100-b \times 100$, where a = percentage of residual *trans*-cinnamoyl substituents on fabric; b = percentage of residual methyl *trans*-cinnamate in solution at the same irradiation time; and x = percentage of cinnamoyl substituents actually irradiated.

^b Percentage of dimer formed on fabric divided by percentages of substituents irradiated, multiplied by 100.

^c Calculations based on irradiations in the indicated solution (see Table I).

TABLE IV
 Effect of One-Side Irradiation of Cotton Cinnamate
 Fabric on the Distribution of Photoproducts

Irradiated on:	Cis, %	Trans, %	Dimer, %
			DS 0.11
One side	4.6	90.3	5.1
Both sides	8.9	76.7	14.4
			DS 0.34
One side	1.9	96.1	2.0
Both sides	5.0	88.3	6.7

Photochemical Crosslinking

The fraction of cinnamate groups converted to dimer in the fabric is considerably greater than that converted in solution. The difference is particularly striking when one calculates from the data in Table II the percentage of dimerization on the basis of the fraction of substituents actually irradiated. These results are shown in Table III. The results are remarkably constant and significantly higher than those for dimerization

in solution. Dimerization in solution requires a collision between molecules, at least one of which is in an excited state—a difficult process unless one of the reactants is the solvent. On the other hand, the proximity of substituent groups in cellulose cinnamate facilitates dimerization. These results provide strong evidence that the cinnamoyl moieties are held in a definite and favorable relationship to one another when esterified to the cellulose polymer.

The percentage of cinnamate groups converted to dimer at any specific extent of irradiation decreases as the degree of substitution increases (Table II). At the extremes, a fivefold increase in the degree of substitution results in less than double the total number of crosslinks per pair of anhydroglucose units. The opposite might have been anticipated considering the close proximity required for dimerization. More effective screening of the incident ultraviolet light by the cinnamoyl substituents at

TABLE V
Effect of Irradiation Time and Degree of Substitution on the
Conditioned Wrinkle Recovery Angles (W + F) of Cotton
Cinnamate Fabrics

Irradiation time, hr	Degree of substitution					
	0 (blank) ^a	0 (control) ^b	0.11	0.34	0.48	0.58
0	180	179	188	214	217	218
1	173	192	210	220	223	221
12	180	191	227	225	239	239
24	185	173	224	243	243	239
48	171	186	228	230	233	240

^a Original print cloth.

^b Soaked in dimethylformamide/pyridine solution at 70°C for 3 hr.

the higher degrees of substitution or an uneven distribution of substituents throughout the accessible regions of the fiber with a higher concentration near the fabric surface could account for these results. These results are consistent with an esterification reaction occurring initially on the fabric surface, substitution taking place in the interior of the fabric and of the fiber only when the degree of substitution progresses to higher values.

The extent of dimer formation is a direct measure of the number of crosslinks introduced, although it is not possible to distinguish between inter- and intramolecular crosslinks. As noted in the introduction, irradiation of the cotton cinnamate fabrics effected improvements in the wet and conditioned wrinkle recovery angles. The conditioned wrinkle recovery data are reproduced in Table V. The greatest increases effected by irradiation were realized at the lowest degree of substitution, even though the highest wrinkle recovery angles occurred at the higher degrees of substitution; the latter was the result of the combined contributions of cinnamoyl substitution¹⁷ and crosslinking to wrinkle recovery values.

As already noted, the highest percentage of substituents dimerized upon irradiation also occurred for the cotton cinnamate having the lowest degree of substitution. Comparison of the trends in Tables II and V shows the direct relationship between the increases in wrinkle recovery angles and the introduction of crosslinks via the dimerization of the cinnamoyl substituents. The wrinkle recovery angles attained in this study, however, are low compared to those resulting from treatments where polymer deposition is also a possibility.¹⁸ Thus, simple truxillic and/or truxinic acid crosslinking, although directly related to the increases in wrinkle recovery angles, is sufficient to produce fabrics with only moderate levels of wrinkle recovery properties.

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