

cis-trans ISOMERIZATION OF ESTERS OF HYDROXYCINNAMIC ACIDS

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In a preceding paper [1] we discussed the spectral properties of the cis and trans isomers of the free hydroxycinnamic acids most widely distributed in nature (p-coumaric, caffeic, and ferulic acids). However, in plants the hydroxycinnamic acids are mainly present in the form of esters with quinic acid or with carbohydrates and are rarely in the glycosylated form. In view of the biological importance of cis-trans isomerization and the absence of information on the properties of the isomeric esters, we have studied the behavior of some compounds of this type on UV irradiation. Chromatographically pure samples of 3-O-caffeoylquinic (chlorogenic), 5-O-caffeoylquinic (neochlorogenic), and 3-O-feruloylquinic acids and 3-p-coumaroylglucose were studied. 0.01 M solutions of the substances in 50% ethanol were irradiated with shortwave UV light (OKUF-5M) at ~366 mμ 10 cm from the source for 4 hr. In each case, the paper-chromatographic separation of the photolysis products in 2% acetic acid showed a second spot with a higher R_f value. In contrast to the initial compounds, the fluorescence of the products obtained appeared only 1-2 min after the start of illumination with filtered UV light. The spots of the substances were cut out from the chromatograms and eluted with 50% ethanol. Irradiation with UV light of the eluates of the upper and lower spots led to the formation of mixtures of both compounds in each case. In the UV region of the spectrum the photolysis products had absorption maxima at somewhat shorter wavelengths (table).

Compound	R _f	UV spectrum, λ _{max} , mμ	Fluorescence		
			0 min	after 1-2 min	in ammonia vapor
trans-Chlorogenic acid	0.65	245 (299) 326	Blue	} Blue	} Greenish-blue
cis-Chlorogenic acid	0.76	240 (290) 315 (325)	Does not fluoresce		
trans-Neochlorogenic acid	0.70	245 (299) 326	Blue	} Blue	
cis-Neochlorogenic acid	0.78	240 (291) 310	Does not fluoresce		
trans-Feruloylquinic acid	0.66	245 (290) 318	Blue	} Blue	} Light blue
cis-Feruloylquinic acid	0.77	235 (285) 306	Does not fluoresce		
trans-p-Coumaroylglucose	0.68	230 (285) 310	} Does not fluoresce	} Blue	} Blue
cis-p-Coumaroylglucose	0.79	235 (285) 306			

*2% acetic acid; ascending chromatography; "Goznak" paper.

The information obtained shows that the compounds formed on photolysis are the cis isomers of the corresponding starting materials. Consequently, esters of hydroxycinnamic acids, which exist as the more stable trans-forms, are capable of forming the cis isomers on UV irradiation.

REFERENCE

1. L. I. Dranki and T. A. Shubert, DAN SSSR, 185, 705, 1969.

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