

Ionization Constants and Ultraviolet Spectra of Fluoro and Trifluoromethyl *trans*-Cinnamic Acids

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The *o*-, *m*- and *p*-trifluoromethyl *trans*-cinnamic acids have been prepared by the Doebner modification of the Knoevenagel reaction. The apparent ionization constants of these acids and their fluoro analogs in 50% ethanol-water have been measured and compared with the ionization constant of *trans*-cinnamic acid. The ultraviolet spectra of these compounds have also been measured.

RECENTLY, we reported (4) rate and equilibrium data for *o*-, *m*-, and *p*-fluoro and trifluoromethyl-substituted phenylpropionic acid and ionization constants in various media.

As part of this study, the corresponding *trans*-cinnamic acids by condensation of the appropriately substituted benzaldehyde with malonic acid in the presence of piperidine in pyridine solvent were prepared. The fluoro compounds have been described previously (1-3). The trifluoromethyl analogs are, to our knowledge, new compounds are the data concerning them are shown in Table I.

The apparent ionization constants were measured for six fluorine-containing cinnamic acids in 50% ethanol-water solution at 25° and compared with values for *trans*-cinnamic acid under the same conditions. The results, obtained by

potentiometric titration, are shown in Table II. The slightly enhanced acidity of all of these compounds relative to cinnamic acid reflects the electron-attracting ability of the F and CF₃ groups. The observed order of acidity (*o* > *m* > *p*) for the fluoro compounds correlates with the diminution of the inductive effect with increasing distance from the carboxyl group. The trifluoromethyl compounds are somewhat more acidic than their fluoro counterparts with the *p*-CF₃ analog showing the greatest effect.

The maxima observed in the ultraviolet region for these acids in 95% ethanol solution are listed in Table III. All exhibit hypsochromic shifts relative to *trans*-cinnamic acid with the fluoro analogs showing the same trend found in the phenylpropionic acid series (4). The trifluoromethyl cinnamic acids fail to follow this trend.

Table I. Trifluoromethyl Cinnamic Acids

Compound	Yield (%)	M.P. ^a	Analysis			
			Calcd.		Found	
			C	H	C	H
<i>o</i> -CF ₃	28	199°	55.56	3.26	55.38	3.45
<i>m</i> -CF ₃	43	132-3°	55.56	3.26	55.40	3.32
<i>p</i> -CF ₃	57	230-1°	55.56	3.26	55.43	3.49

^a M.P.'s were determined on a Fisher-Johns block and are uncorrected.

Table II. Apparent Ionization Constants for Substituted *trans*-Cinnamic Acids in a 50% Ethanol-Water Solution at 25°.

Substituent	K × 10 ⁶	pK
H	2.40	5.62
<i>o</i> -F	5.01	5.30
<i>m</i> -F	2.82	5.55
<i>p</i> -F	2.57	5.59
<i>o</i> -CF ₃	5.75	5.24
<i>m</i> -CF ₃	5.13	5.29
<i>p</i> -CF ₃	8.51	5.07

Table III. Ultraviolet Absorption Data for Substituted *trans*-Cinnamic Acids^a

Substituent	λ _{max} , mμ
H	272
<i>o</i> -F	264
<i>m</i> -F	266
<i>p</i> -F	269
<i>o</i> -CF ₃	265
<i>m</i> -CF ₃	263
<i>p</i> -CF ₃	267

^a Spectra were obtained in 95% ethanol.

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