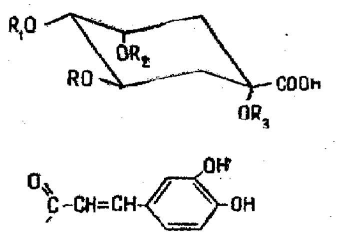
A SPECTROSCOPIC INVESTIGATION OF THE PHENOLCARBOXYLIC ACIDS OF CYNARA SCOLYMUS

L. I. Dranik

Khimiya Prirodnykh Soedinenii, Vol. 2, No. 5, pp. 303–306, 1966

In an investigation of hydroxycinnamic acids in the UV region of the spectrum, it was found that the dihydroxycinnamic acids and their esters (depsides) have similar absorption maxima at 325–330 mμ in neutral alcoholic solution [1, 2]. However, more detailed information on the use of UV spectroscopy to establish structural features of these compounds is rather limited at the present time.



Phenylcarboxylic acids of the artichoke: cynarin $R_1 = R_3 = K$, $R = R_2 = H$; chlorogenic acid $R = K$, $R_1 = R_2 = R_3 = H$; neochlorogenic acid $R_2 = K$, $R = R_1 = R_3 = H$; 4-caffeylquinic acid $R_1 = K$, $R = R_2 = R_3 = H$; 1-caffeylquinic acid $R_3 = K$, $R = R_1 = R_2 = H$; quinic acid, $R = R_1 = R_2 = R_3 = H$, K–caffeyl.

In a study of the phenylcarboxylic acids (scheme 1) that we have isolated from the fresh leaves of Cynara scolymus L. (artichoke) we have obtained UV spectra using ionizing and complex-forming reagents (see table).

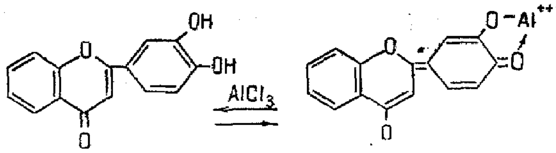
In all the cases considered, an absorption maximum was observed in the long-wave region (band I) at 325–328 mμ in neutral alcoholic solution. There was an absorption maximum in the short-wave region of the spectra of these compounds at 235–245 mμ (band II).

The addition of fused sodium acetate to an alcoholic solution of the depsides caused a slight bathochromic shift (1–10 mμ) in the maximum of band I. However, in the case of caffeic acid a hypsochromic shift of the maxima of bands I and II was found, apparently as a consequence of the ionization of the free carboxy group conjugated with the aromatic system [2].

Sodium ethoxide ionizes not only the phenolic hydroxyls, causing a bathochromic shift, but also the conjugated carboxy group, causing a hypsochromic shift [2]. In esters, the –COOH group is blocked and therefore a considerable bathochromic shift (50–55 mμ) of absorption band I takes place in the presence of this reagent because of the ionization of only the phenolic hydroxyls conjugated with the carbonyl group. In the free hydroxycinnamic acids, as can be seen with, e.g., caffeic acid, there are the competing effects of the conjugated –OH and –COOH groups, in consequence of which the observed bathochromic shift is somewhat decreased. Caffeic acid is unstable in alkaline solution and therefore to obtain reliable results the spectrum must be recorded immediately after the addition of the sodium ethoxide.

The spectra of the phenylcarboxylic acids investigated with boric acid and sodium acetate are informative. In the case of the depsides, a bathochromic displacement of the absorption maxima of both band I (22–25 mμ) and band II is found, but in the spectrum of caffeic acid there is a slight hypsochromic shift (5 mμ).

It is known that in the flavonoids an o-dihydroxy grouping in the B ring is shown by a bathochromic shift of the maximum of the long-wave absorption band in the presence of boric acid and sodium acetate or in the presence of aluminum chloride. These bathochromic shifts are the result of the formation of a complex at the o-dihydroxy groupings [3, 4]. The mechanism of the formation of these complexes, for example, with aluminum chloride, is as follows:



In view of these results, an attempt to use complex-forming reagents to observe the o-dihydroxy grouping in caffeic acid and its esters was made. When complexes of phenylcarboxylic acids with boric acid in the presence of sodium acetate were studied spectroscopically, it was found that practically no changes occurred in the spectrum of caffeic acid while there were considerable bathochromic shifts in the maxima of absorption band I of the esters. These phenomena are probably due to the fact that in free caffeic acid, because of salt formation at the carboxy group with the sodium acetate, the conjugation of the complex with the carbonyl grouping is weakened. In the esters, the carboxy group is blocked by the quinic acid, salt formation is excluded, and the conjugation of the boron complex at the o-dihydroxy grouping with the carbonyl is retained.

The appearance of three strong absorption bands in the spectra of all the compounds studied was observed in the presence of aluminum chloride. This is probably connected with the formation of a conjugated aluminum complex at the o-dihydroxy grouping which possesses strong chromophoric properties.

Experimental

The UV spectra of the compounds studied were obtained on a SF-4 spectrophotometer in cells with an absorption layer 1 cm thick. Chromatographically pure compounds were used for the investigation. The initial solutions of the compounds were 0.001 M in absolute ethanol.

Spectroscopic Characteristics of the Phenylcarboxylic Acids of the Artichoke

Compound	Bands	Alcoholic solution		Alcoholic solution + CH_3COONa			Alcoholic solution + C_2H_5ONa			Alcoholic solution + H_3BO_3 + CH_3COONa			Alcoholic solution + $AlCl_3$	
		λ_{max}	log ε	λ_{max}	log ε	Δλ	λ_{max}	log ε	Δλ	λ_{max}	log ε	Δλ	λ_{max}	log ε
Cynarin	I	325	4.43	332	4.40	7	375	4.30	50	349	4.30	24	360	4.81
	II	245	4.26	—	—	—	265	4.13	—	254	4.32	9	315	4.81
													240	4.95
Chlorogenic acid	I	325	4.11	330	4.08	5	380	4.23	55	350	4.23	25	360	4.82
	II	240	3.92	—	—	—	260	3.96	20	255	4.01	10	315	4.82
													240	4.93
Neochlorogenic acid	I	328	4.10	329	4.03	1	371	4.19	43	350	4.21	22	360	4.83
	II	245	3.89	—	—	—	265	3.95	15	255	4.03	10	315	4.83
													240	4.92
4-Caffeylquinic acid	I	328	4.11	335	4.06	7	375	4.20	47	350	4.19	22	360	4.82
	II	246	3.90	—	—	—	265	4.00	20	255	3.96	10	315	4.82
													240	4.92
1-Caffeylquinic acid	I	327	4.12	337	4.05	10	380	4.21	53	350	4.20	23	360	4.81
	II	245	3.89	—	—	—	265	3.97	20	256	4.00	11	315	4.81
													240	4.92
Caffeic acid	I	325	4.37	310	4.28	−15	360	4.09	35	320	4.29	−5	360	4.81
	II	(299)	—	280	4.31	—	250	4.03	—	295	4.20	—	315	4.81
		235	4.24										240	4.95

Spectrum in absolute ethanol. 0.2 ml of the initial solution was diluted with absolute ethanol to 10 ml, giving a solution with a concentration of 2×10^{-5} M.

Spectrum with sodium acetate. 0.2 ml of the initial solution was diluted with absolute ethanol to 10 ml, and an excess of fused sodium acetate was added. The spectrum was determined after the solution had been shaken and allowed to stand for 15–20 min.

Spectrum with sodium ethoxide. 0.2 ml of the initial solution was treated with 2 ml of 0.01 M sodium ethoxide, and the volume was made up to 10 ml with absolute ethanol.

Spectrum with boric acid and sodium acetate. 0.2 ml of the initial solution was treated with 2 ml of 4% boric acid, the solution was made up to 10 ml with absolute ethanol and an excess of sodium acetate was added. The spectrum was determined after the solution had been shaken and allowed to stand.

Spectrum with aluminum chloride. 0.2 ml of the initial solution was treated with 2 ml of 0.01 M aluminum chloride and made up to 10 ml with absolute ethanol.

Summary

Spectroscopic investigations in the UV region of the phenolcarboxylic acids that we have isolated from the leaves of *Cynara scolymus* have been carried out. It has been found that:

1. Free caffeic acid can be distinguished from its esters by the changes in the UV spectra under the influence of sodium ethoxide and sodium acetate.

2. An o-dihydroxy grouping in esters can be detected from the bathochromic shift observed with boric acid in the presence of sodium acetate.

3. An o-dihydroxy grouping can be detected both in esters and in the free acid under the influence of aluminum chloride.

REFERENCES

1. K. Herrmann, Die Pharmazie, no. 5, 266, 1958.

2. L. Jurd, Arch. Biochem. and Biophys., **66**, 284–288, 1957.
3. L. Jurd, Arch. Biochem. and Biophys., **63**, 376–381, 1956.
4. L. Jurd and T. A. Geissman, J. Org. Chem., **21**, no. 12, 1395–1401, 1956.

4 January 1966

Khar'kov Chemical and Pharmaceutical Scientific Research Institute