Cotton Effects in Some ω-Substituted α-Amino Acids*

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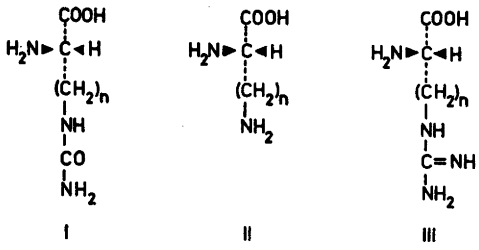
The recent availability of instruments permitting the measurement of optical rotatory dispersion curves down to nearly 200 mμ has made it possible to reach the region of the $n \rightarrow \pi^*$ transition of the carboxyl group at about 210 mμ. A series of α-amino acids has been measured in water and acid down to 210 mμ by Dirkx and Sixma [1] and it has been shown that all L-amino acids give positive Cotton Effect curves of which one extremum is reached. These results were confirmed and extended in one of our laboratories.[2] A short series of α-amino acids has also been measured by Gaffield [3] down to a lower wavelength limit of 190 mμ and covering the whole C. E.

The finding [4] several years ago of an unexpected difference between the plain negative dispersion curve of L-albizziine (I, $n = 1$), and the plain positive curve of higher homologues of the same series (I, $n = 2, 3, 4$) in the wave-length region of 290–600 mμ has prompted an extension of these measurements to shorter wavelengths. We now report measurements of a series of α,ω-diamino-acids (II) and of ω-guanidino-α-amino acids (III) down to about 210 mμ.



The measurements were performed on solutions in water, 1.1 N HCl, and 0.5 N KOH and the results are presented in Table 1. It appears that all homologues of the ω-ureido series (I) exhibit a positive Cotton Effect with the first extremum at about 224 mμ in acid (Fig. 1) and 213 mμ

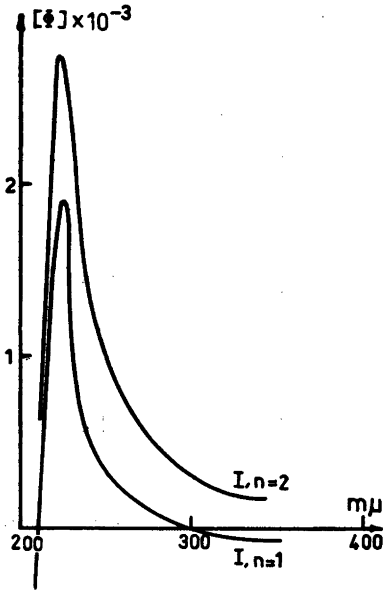


Fig. 1. Rotatory dispersion curves of L-albizziine and L-norcitrulline in 1.1 N HCl.

in aqueous solution (Fig. 2), whereas no extremum was reached in alkali. It should be noted, however, that only in the neutral solution of albizziine (I, $n = 1$) is the positive Cotton Effect superimposed on a strong negative background as shown

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Note added in proof: After the present paper was submitted for publication, Iizuka and Young (*Biochem.* 3 (1964) 1519) published a careful study of twenty L-amino acids at pH 1. All showed positive C.E. curves with the peak located around 225 mμ.

Table 1. Rotatory dispersion data for ω-substituted L-α-amino acids in water, acid, and alkali. pk, peak; ! indicates the lowest wavelength measured; *i.e.*, the peak was not reached.

Amino Acids	Formula	Water [Φ]	Water λ (mμ)	1.1 N HCl [Φ]	1.1 N HCl λ (mμ)	0.5 N KOH [Φ]	0.5 N KOH λ (mμ)
L-Albizziine (L-2-Amino-3-ureidopropionic acid)	I, $n = 1$	− 810	221	+ 1900 pk	224	+ 504!	222
L-Norcitrullin (L-2-Amino-4-ureidobutyric acid)	I, $n = 2$	+ 965 pk	213	+ 2740 pk	222	+ 1825!	222
L-Citrullin (L-2-Amino-5-ureidopentanoic acid)	I, $n = 3$	+ 1550 pk	210	+ 2740 pk	224	+ 1005!	223
L-Homocitrullin (L-2-Amino-6-ureidohexanoic acid)	I, $n = 4$	+ 1550!	213	+ 2820 pk	224	+ 1165!	227
L-2,3-Diaminopropionic-acid monohydrochloride	II, $n = 1$	+ 1070 pk	208	+ 1460 pk	224	+ 655!	227
L-2,4-Diaminobutyric acid monohydrochloride	II, $n = 2$	+ 855 pk	213	+ 1600 pk	223	+ 1160!	227
L-Ornithine monohydrochloride (L-2,5-Diaminopentanoic acid monohydrochloride)	II, $n = 3$	+ 1520 pk	217	+ 2200 pk	223	+ 1000!	227
L-Lysine monohydrochloride (L-2,6-Diaminohexanoic acid monohydrochloride	II, $n = 4$	+ 1420 pk	211	+ 2160 pk	224	+ 1010!	226
L-2-Amino-3-guanidinopropionic acid monohydrochloride	III, $n = 1$	+ 4560!	212	+ 3260 pk	223	+ 650!	228
L-2-Amino-4-guanidinobutyric acid monohydrochloride	III, $n = 2$	+ 3660!	211	+ 3450 pk[a]	221	+ 1540!	227
L-Arginine monohydrochloride (L-2-Amino-5-guanidinopentanoic acid monohydrochloride	III, $n = 3$	+ 1950!	213	+ 2650 pk	222	+ 1215!	227
L-2-Amino-6-guanidinohexanoic acid monohydrochloride	III, $n = 4$	+ 1528!	214	+ 2600 pk	221	+ 950!	227

[a] Measured in 0.5 N HCl.

in Fig. 2.* The molecular rotations at the peak in water increase as n increases; the peak rotations are generally considerably greater in acid than in water.

Similar results were obtained with the homologous series of L-α,ω-diamino acids (II, $n = 1, 2, 3, 4$).

The third series comprised the four L-α-amino-ω-guanidino acids (III, $n = 1, 2, 3, 4$) all of which exhibited well-developed Cotton Effects in acid solution, whereas no extremum was reached in neutral or alkaline solution. Contrary to what was found for the first two series (I and II), a *decrease* in molecular rotation at the peak at the lowest wave-length measured is observed as n increases.

The present results substantiate the previous evidence [1-3] that L-amino acids in general exhibit positive Cotton Effects in neutral or in acid solution with the

* This background rotation is clearly what was seen in the (apparently anomalous) longer wave-length curve reported previously.[4] The pattern is somewhat similar to that exhibited by L-proline and L-hydroxyproline (*cf.* Ref.[1]).

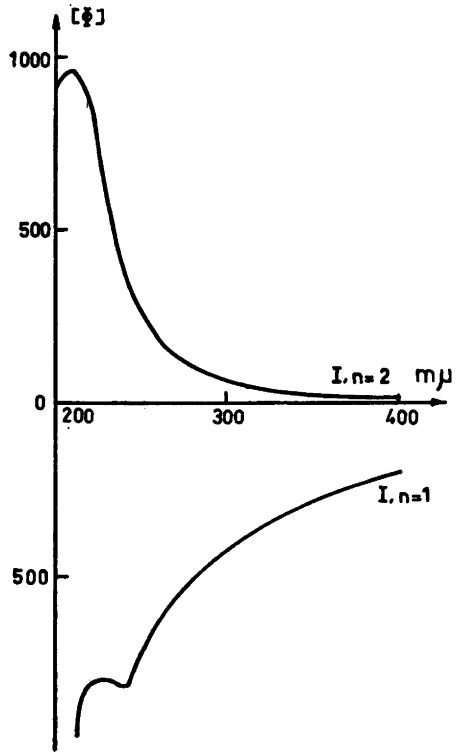

Fig. 2. Rotatory dispersion curves of L-albizziine and L-norcitrulline in water.

first extrema located at about 215 mμ or 223 mμ, respectively.

Experimental. Rotatory dispersion curves were measured with the Bellingham and Stanley/Bendix-Ericsson "Polarmatic 62" automatic recording spectropolarimeter, modified as previously described.[2] The measurements were performed at 18–25° in a 0.1 dm cell; the concentrations were about 1 mg/ml in water and 1.1 N HCl and about 2 mg/ml in 0.5 N KOH. The wave-length range studied was 400–200 mμ and the results are expressed as molecular rotations (Φ).

L-Citrulline, and the hydrochlorides of L-lysine, L-ornithine, and L-arginine were commercial preparations. L-Albizziine and L-2,3-diaminopropionic acid hydrochloride were prepared in the laboratories of one of the authors (A.K.).

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The Purification of an Alkaline Phosphatase from Baker's Yeast

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The occurrence in baker's yeast extract of several phosphatases with different enzymatic properties has been reported.[1-3] However, no alkaline phosphatase has previously been purified and investigated extensively. This paper describes the purification of an alkaline phosphatase from baker's yeast. The enzyme has a rather high activity towards O-monophosphate esters (*p*-nitrophenyl phosphate, phenyl phosphate, sodium β-glycerophosphate, threonine phosphate, serine phosphate, and different O-phosphorylated serine peptides).

The alkaline phosphatase activity was measured by incubating the enzyme with the substrate *p*-nitrophenyl phosphate

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