43. *Optical Rotatory Dispersion. Part X.*[1] *Amino-acids.*

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The rotatory dispersion of a series of L-amino-acids has been investigated. These give positive Cotton effects with peaks at about 216 mμ, which show a significant change in 0·5M-hydrochloric acid. A few D-amino-acids have also been examined.

SEVERAL studies of the optical rotatory dispersion curves of α-amino-acids have been described,[2] but these have all been carried out with instruments which did not permit the measurement of the curves below about 250 mμ The chromophore of longest-wavelength absorption in amino-acids is the carboxyl group, the $n \longrightarrow \pi^*$ transition of which occurs at about 220 mμ, and the plain rotatory dispersion curves measured with the older instruments have not reached the region of this absorption band.

Recently a new instrument has become available [3] (the Bellingham and Stanley/Bendix-Ericsson " Polarmatic '62 ") which permits the measurement of rotatory dispersion curves down to nearly 200 mμ. We have therefore measured these curves for a series of amino-acids in water and in 0·5M-hydrochloric acid, and in many cases have been able to show the existence of a Cotton effect at about 215 mμ. These results are given in Table 1. Values for a few pairs of enantiomers are compared in Table 2. The Figure shows the curves obtained for L- and D-alanine in 0·5M-hydrochloric acid.

Attempts at the theoretical interpretation of these results seem premature, but it is clear that all L-amino-acids (unless they have unusual substituents in the neighbourhood of the α-amino-acid group, or other chromophores absorbing at a higher wavelength) will show positive Cotton effects with a peak at 216 mμ or less. Furthermore, the change from water to 0·5M-hydrochloric acid as solvent is generally accompanied by an increase in molecular rotation of 1000—1500° at the peak, and a shift of the wavelength of this peak from about 215 mμ to about 225 mμ; cf. the Lutz–Jirgensons rule for rotations at the *D*-line.[4]

In those cases where the first extremum of the Cotton effect is not reached, aqueous

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[1] Part IX, Klyne, *Experientia*, 1964, **20**, 349.

[2] Djerassi, " Optical Rotatory Dispersion," McGraw-Hill, New York, 1960; Izumiya, Winitz, Birnbaum, and Greenstein, *J. Amer. Chem. Soc.*, 1956, **78**, 1602; Strem, Krishna-Prasad, and Schellman, *Tetrahedron*, 1961, **13**, 176.

[3] Gillham and King, *J. Sci. Instr.*, 1961, **38**, 21; Jennings, *Biochem. J.*, 1963, **86**, 16P.

[4] Lutz and Jirgensons, *Ber.*, 1930, **63**, 448; 1931, **64**, 1221.

TABLE 1.

Rotatory dispersion data for L-amino-acids in water and in 0·5M-hydrochloric acid. pk, peak; ! indicates the lowest wavelength measured, *i.e.*, the peak was not reached

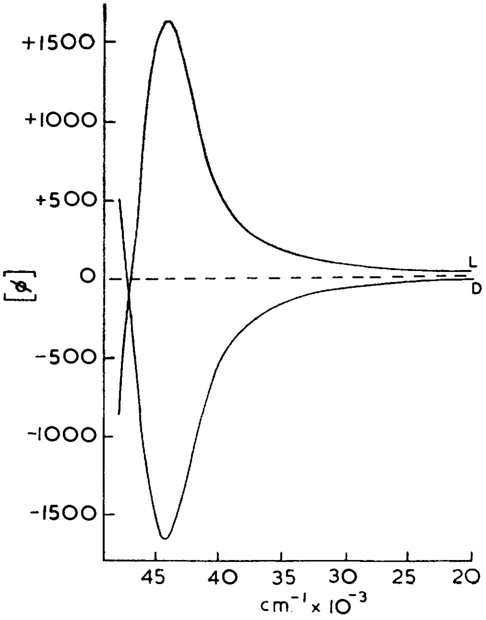
	In water		In 0·5M-HCl	
Amino-acid	[ϕ]	λ (mμ)	[ϕ]	λ (mμ)
L-Alanine	+750 pk	216	+1610 pk	224
L-Valine	+1390 pk	213	+2720 pk	223
L-Leucine	+1420 pk	213	+2770 pk	223
L-Isoleucine	+1830 pk	210	+2880 pk	224
L-Serine	+1070 pk	216	+2080 pk	224
L-Threonine	−40 pk	218	+1730 pk	225
L-Cysteine hydrochloride	+1670!	224!	+2110 pk	228
L-Cystine	*		+840 pk	231
L-Methionine	+230!	230!	+1560!	226!
L-Aspartic acid	+1110 pk	214	+1610 pk	222
L-Asparagine	+510!	210!	+1020 pk	224
L-Glutamic acid	+1460 pk	216	+2550 pk	224
L-Glutamine	+1470!	213!	+2710 pk	225
L-Tryptophan	+120!	298†!	+610!	302!
L-Histidine hydrochloride	+2010!	230!	+4300!	226!
L-Lysine hydrochloride	+1630 pk	213	+2590 pk	221
L-Arginine hydrochloride	+2460!	208!	+2870 pk	224
L-Proline	−1630!	215!	+410 pk	225
L-Hydroxyproline	−1580!	220!	+400 pk	224
L-Phenylalanine	+3240!	222!	+5180 pk	224
L-Tyrosine	*		+3320 pk	233

* Compound insufficiently soluble in water; not measured. † Absorption too high for measurements to be made below about 300 mμ.

TABLE 2.

Comparison of the molecular rotations of L- and D-amino-acids at the first extremum of the Cotton effect (pk = peak; tr = trough; ! = lowest wavelength measured. The values of the *wavelengths* of the first extrema are quoted in Table 1).

Amino-acid	In water [ϕ]	In 0·5M-HCl [ϕ]	Amino-acid	In water [ϕ]	In 0·5M-HCl [ϕ]
L-Alanine	+750 pk	+1610 pk	L-Serine	+1070 pk	+2080 pk
D-Alanine	−740 tr	−1590 tr	D-Serine	−1150 tr	−2170 tr
L-Phenylalanine	+3240!	+5180 pk	L-Threonine	−40 pk	+1730 pk
D-Phenylalanine	−3040!	−5040 tr	D-Threonine	0 tr	−1710 tr



Rotatory dispersion curves of L-Alanine (L) and D-Alanine (D), in 0·5M-hydrochloric acid. (These curves are direct machine tracings.)

solutions of L-amino-acids show a steeply rising plain positive rotatory dispersion curve. The only exceptions to this general pattern of behaviour are the cyclic compounds proline and hydroxyproline, which give plain negative curves in aqueous solution (cf.[5]). However, these curves have inflections at about 220 mμ, which may be attributed to a small positive Cotton effect superimposed on a strong negative background. In 0·5M-hydrochloric acid these compounds behave normally, and have positive Cotton effects of small magnitude.

Parallel studies with an instrument of different type [6] have been carried out by Dr. J. P. Dirkx in Amsterdam; [5] the results are in general in fair agreement. We are greatly indebted to Dr. Dirkx for exchange of information regarding this work.

[*Note added in Proof.*—Gaffield [7] has recently described the O.R.D. curves of a short series of amino-acids measured with a Carey spectrophotometer down to 190 mμ.]

EXPERIMENTAL

Rotatory dispersion curves were measured with the Bellingham and Stanley/Bendix-Ericsson " Polarmatic '62 " automatic recording spectropolarimeter, which has been modified in this Department as follows. The compensating Faraday-cell current (linearly proportional to rotation at any one wavelength) is attenuated by a cam-driven potentiometer system. This compensates for the wavelength variation of the Verdet constant of the silica compensating slug. The rotation scale is now linear and independent of wavelength, and rotation is plotted directly against a linear wave-number scale.

Condition.—l = 0·1 dm., t, 18—25°; C, 1 mg./ml. or less, in water, or in 0·5M-HCl. Wavelength range, 500—200 mμ. Results are expressed as molecular rotations [ϕ].

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[5] Dirkx and Sixma, *Rec. Trav. chim.*, 1964, **83**, 522; Dirkx, Thesis, Amsterdam, 1962.
[6] Dirkx, van der Haak, and Sixma, *Analyt. Chem.*, 1964, **36**, 1988.
[7] Gaffield, *Chem. and Ind.*, 1964, 1460.