LXVIII.—*The Rotation of Aspartic acid.*

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LANDOLT (*Ber.*, 1880, **13**, 2334) and Becker (*Ber.*, 1881, **14**, 1035) ascribe to the aspartic acid, obtained from ordinary lævo-asparagine, a lævorotation in aqueous solution. Piutti (*Ber.*, 1886, **19**, 1691), however, comparing the derivatives of ordinary asparagine and dextro-asparagine, found that the ordinary asparagine yielded, on boiling with hydrochloric acid, a *dextro*-aspartic acid, which in its turn, when treated with nitrous acid, gave ordinary lævo-malic acid; whilst, on the other hand, the dextro-asparagine gave a lævo-aspartic acid convertible into a dextro-malic acid.

In the course of an investigation into the conditions of formation of the two active chlorosuccinic acids, I have been led to examine aspartic acid, concerning which the foregoing contradictory statements are on record. My results lead me to support the observations of Piutti. Two samples of aspartic acid, prepared from ordinary asparagine, and a third commercial sample, presumably from the same source, were all dextrorotatory. This dextro-acid also gave the ordinary lævo-malic acid when treated with nitrous acid. Moreover, the solubility of the dextro-acid in water was much less than that indicated by Becker's numbers. In his determinations of the rotation, the values of p , the number of grams of acid in 100 grams of solution, increase from 1.201 to 2.802, while $[\alpha]_D$ increases from -3.87° to -4.71° . This is stated to be at the ordinary temperature. The solubility of aspartic acid given by Pasteur is, however, only 1 part in 364 parts of water at 11° ; and by Guareschi (*Jahresber.*, 1876, 777) as

1	part	in	256.4	parts	of	water	at	10° ,
1	„		222.2	„		„		20,

whilst the solubility in my own determination was found to be 1 part in 236 at 17° , corresponding with a maximum value for p of only 0.42 at this temperature. The solubility at 17° , calculated from Engel's formula (*Compt. rend.*, 1888, **106**, 1736), is 0.585 gram in 100 grams of water.

In dilute acid and alkaline solutions this dextro-acid gave rotations similar to those observed by Becker, and also, earlier, by Pasteur and Landolt, being dextrorotatory in acid solution and lævorotatory in alkaline.

1. The first sample of aspartic acid was prepared by boiling asparagine with dilute hydrochloric acid (Schiff's method, *Ber.*, 1884, **17**, 2929). The asparagine employed gave $[\alpha]_D = -4.80^\circ$ at

18° for $c = 2.00$, $l = 50$ cm., and $\alpha = 0.48^\circ$. The aspartic acid obtained gave the following values for its specific rotation.

$[\alpha]_D$.	c .	α .	l .	Temp.
+5.32°	0.3906	0.104°	50 cm.	21.0°
+5.01	0.4078	0.102	50 „	21.5
+4.67	0.4211	0.098	50 „	21.0

The acid was then purified by converting it into the copper salt, which, after recrystallisation, was decomposed with sulphuretted hydrogen (Hofmeister, 1877, *Annalen*, 189, 21). The purified acid gave the value

$[\alpha]_D$.	c .	α .	l .	Temp.
+6.08°	0.3902	0.119°	50 cm.	21.5°

so that there is a slight rise in the rotation, but its direction still remains the same.

The acid when treated with nitrosyl chloride gave a chlorosuccinic acid melting at 173—175°, and having a specific rotation $[\alpha]_D = -17.03^\circ$ at 22°, when $c = 4.19$. It is the same acid, therefore, as is given directly by asparagine, when it is treated in the same way; this had a rotatory power $[\alpha]_D = -19.67^\circ$ at 19.2° when $c = 9.2$.

The aspartic acid treated with nitrous fumes gave ordinary malic acid, of which the rotation in acetone was compared with that of a bought sample. The following values were obtained.

	$[\alpha]_D$.	c .	Temp.
Acid obtained from aspartic acid . . .	-4.76°	2.93	22.0°
Bought sample of malic acid	-5.33	2.93	19.5

2. The second sample of acid was prepared by boiling asparagine with dilute caustic soda instead of acid.

The asparagine employed gave the rotation $[\alpha]_D = -4.56^\circ$ at 17°; $c = 1.94$, $l = 50$ cm., and $\alpha = 0.44^\circ$; whilst the aspartic acid obtained from it gave the value

$$[\alpha]_D = +4.87^\circ; c = 0.406; \alpha = 0.039^\circ; \text{temp } 22.5^\circ.$$

3. The third sample bought from Kahlbaum gave

$$[\alpha]_D = +4.74^\circ; c = 0.408; \alpha = 0.097^\circ; \text{temp. } 21^\circ.$$

Rotation in Acid Solution.—A solution of the second sample of aspartic acid was made in dilute hydrochloric acid, the following being the molecular proportions.

Aspartic acid.	Hydrochloric acid.	Water.
1 mol.	13.1 mols.	198.6 mols.

For this solution, $[\alpha]_D = +25.3^\circ$ at 24°, Becker (*Ber.*, 1881, 14,

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1039) obtained the value $[\alpha]_D = +33.53$ for a solution of the proportions

Aspartic acid.	Hydrochloric acid.	Water.
1 mol.	12.5 mols.	151.8 mols.

Rotation in Alkaline Solution.—For this measurement, a portion of sample 1 was dissolved in dilute ammonia. The molecular proportions of the solution were

Aspartic acid.	NH ₃ .	Water.
1 mol.	2.18 mols.	315 mols.

This gave $[\alpha]_D = -10.39^\circ$ at 19.5° ; whilst Becker obtained the values

Aspartic acid.	NH ₃ .	Water.	$[\alpha]_D$ at 20° .
1 mol.	1 mol.	302 mols.	-9.17°
1 „	3 mols.	302 „	-9.39

All measurements of rotation were made by means of a Laurent half-shade polarimeter, using a 50-cm. tube.

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