27. *The Rotatory Dispersion of Organic Compounds. The First Oxidation Product of Ascorbic Acid.*

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This paper contains an account of work carried out at the suggestion of the late Prof. T. M. Lowry, F.R.S., to whom the author was greatly indebted.

It has been shown (Herbert, Hirst, Percival, Reynolds, and Smith, J., 1933, 1270, etc.) that ascorbic acid is reversibly oxidised by agents such as aqueous iodine to a lactone (2 : 3-diketogulonolactone), which in aqueous solution gradually changes into the corresponding acid. Some data on the mutarotation, absorption spectra, and rotatory power of such solutions were also given, and, together with measurements on the parent acid (Lowry and Pearman, J., 1933, 1444; Herbert, Hirst, and Wood, J., 1933, 1564), have been of service in elucidating the problems connected with this reactive substance. However, important deficiencies in these series of data are analyses of: (*a*) the rotatory dispersion of the aqueous lactone, and of the salt of the hydrated lactone; (*b*) mutarotation of the lactone in water. These are now supplied.

(a) *Rotatory Dispersion of the Lactone.*—This substance dissolved in water gives perfectly simple dispersion over the range 6708—3350 A. (see Table I). The wave-length from the Drude equation, 2152 A., is in good agreement with the value expected from examination of the absorption curve published by Herbert *et al.* (*loc. cit.*). The major contribution to the activity therefore finds its origin in the induced dissymmetry of the -CO-O- group under the influence of the asymmetry of the molecule.

Rotatory dispersion of the sodium salt. This compound has been shown to possess two absorption bands, at 2450 and 2950 A. (*loc. cit.*). Investigation over a limited range shows the probability of the inactivity of the low-frequency band (cf. Lowry, J., 1933, 1448). The rotatory dispersion of this salt is centred at 2316 A., in fair agreement with the value for the second absorption band (see Table II). Other cases of this inactivity of absorption bands are not unknown, but rather uncommon, the most striking example being afforded by the nicotinium ion.

(b) *Mutarotation of the Lactone.*—Solutions of this substance underwent mutarotation according to a unimolecular law, the course of the reaction being followed polarimetrically. Different preparations did not give quite reproducible values for the velocity constant, but a typical series of readings is appended (Table III).

A preliminary series for more dilute and acid solutions, previously given (*loc. cit.*), quoted negative final values for rotations, but in using concentrated solutions the trans-

TABLE I.

Rotatory Dispersion of the Lactone in Water at 20°.

$c = 4{\cdot}760$ g. of lactone per 100 c.c.; $l = 2$ dm.
$[\alpha] = 12{\cdot}242/(\lambda^2 - 0{\cdot}04630)$; $\lambda_0 = 2152$ A.

(Values corrected for slight initial errors, and for mutarotation effects.)

λ.	[α], obs.	[α], calc.	Diff.	λ.	[α], obs.	[α], calc.	Diff	λ.	[α], obs.	[α], calc.	Diff.
6708	31·2°	30·4°	−0·8°	5209	54·1°	54·5°	0·4°	3944	112·0°	112·0°	0·0°
6438	33·2	33·3	0·1	5153	55·9	56·0	0·1	3925	110·7	113·9	3·2
6362	34·5	34·2	−0·3	5086	57·8	57·8	0·0	3822	122·8	122·7	−0·1
6104	37·6	37·6	0·0	4800	66·5	66·5	0·0	3665	139·0	139·0	0·0
5893	41·1	40·8	−0·3	4602	73·5	74·2	0·7	3536	155·0	155·5	0·5
5782	42·6	42·6	0·0	4358	86·5	85·5	−1·0	3498	162·4	162·0	−0·4
5780	42·6	42·6	0·0	4290	89·8	89·0	−0·8	3490*	162·1	162·1	0·0
5700	44·0	44·0	0·0	4202	92·2	93·9	1·7	3356*	190·0	184·5	−5·5
5468	48·1	48·6	0·5	4130	98·5	98·5	0·0	3353*	192·0	185·0	−7·0
5461	48·6	48·6	0·0	4000	107·5	107·8	0·3				

* $l = 1$ cm.

TABLE II.

Rotatory Dispersion of the Sodium Salt in Water at 20°.

$c = 3{\cdot}879$ g. of salt in 100 c.c.
$[\alpha] = -5{\cdot}96/(\lambda^2 - 0{\cdot}0536)$; $\lambda_0 = 2316$ A.

λ.	[α], obs.	[α], corr.	λ.	[α], obs.	[α], corr.	λ.	[α], obs.	[α], corr.
6708	−13·40°	−14·99°	5780	−19·10°	−21·35°	5209	−24·48°	−27·38°
6438	−14·70	−16·42	5700	−19·70	−22·00	5153	−25·26	−28·20
6104	−16·78	−18·74	5468	−21·65	−24·20	5105	−25·90	−28·95
5893	−18·18	−20·30	5461	−21·52	−24·05	5086	−26·02	−29·10
5782	−18·80	−21·00	5219	−24·10	−26·92			

TABLE III.

Mutarotation of 2 : 3-Diketogulonolactone in Water at 20°.

$\lambda = 5461$ A.; $c = 4{\cdot}76$ g. of lactone per 100 c.c.; $\alpha_0 = 4{\cdot}62°$; $\alpha_{166} = -0{\cdot}01°$.
$k(\text{hr.}^{-1}) = (2{\cdot}303/t)\ .\ \log\ (\alpha_0 - \alpha_\infty)/(\alpha_t - \alpha_\infty)$; mean $k = 0{\cdot}0247$ hr.$^{-1}$.

Reading.	t, hrs.	α_t.	k.	Reading.	t, hrs.	α_t.	k.	Reading.	t, hrs.	α_t.	k.
1	0·20	4·59°	0·0242	8	2·70	4·28°	0·0282	15	53·0	1·48°	0·0214
2	0·25	4·60	0·0156	9	3·58	4·17	0·0283	16	70·0	1·02	0·0216
3	0·32	4·58	0·0238	10	23·25	2·72	0·0227	17	118·0	0·35	0·0216
4	0·77	4·52	0·0269	11	27·5	2·47	0·0227	18	125·0	0·28	0·0222
5	0·85	4·46	0·0393	12	29·5	2·38	0·0224	19	142·0	0·11	0·0257
6	1·37	4·45	0·0270	13	46·7	1·71	0·0212	20	149·0	0·07	0·0275
7	1·97	4·35	0·0296	14	50·0	1·58	0·0214				

$k(\text{hr.}^{-1}) = [2{\cdot}303/(t_2 - t_1)]\ \log\ (\alpha_1 - \alpha_\infty)/(\alpha_2 - \alpha_\infty)$; mean $k = 0{\cdot}0216$ hr.$^{-1}$.

Readings	1 & 11	2 & 12	3 & 13	4 & 14	5 & 15	6 & 16
k	0·0226	0·0224	0·0212	0·0212	0·0211	0·0213

parency was so poor after 150 hrs. that the measurements had to be abandoned, the rotation then being − 0·01°. For the same reason, the rotatory dispersion of the muta-rotated solution could not be investigated.

EXPERIMENTAL.

Preparation of Solutions of the Lactone.—Sodium hypochlorite (2*N*) was diluted slightly, and the amount of excess caustic alkali determined. Sufficient acid was then added to neutralise this, giving a solution of sodium chloride and hypochlorite only. Such mixtures evolved gas, and progressively decreased in titre, so iodometric estimation was necessary before use.

About 1 g. of very pure ascorbic acid, weighed into a 25 c.c. flask, was dissolved in water, and the calculated amount of oxidising agent run in dropwise and with efficient cooling. Measurements were then begun as soon as possible.

Absorption measurements, giving $\varepsilon_{max.} = 400$, showed that, when such concentrated solutions were used, some 4% of ascorbic acid remained unchanged, even when slight excess of hypochlorite was taken. The measurements of rotatory power should therefore be corrected to the higher figure given by Herbert *et al.* (*loc. cit.*) for dilute solutions through multiplication by a small factor. It should be pointed out, however, that the best value obtained, $[\alpha]_{5780} = 44{\cdot}8°$, was for a neutral 4% solution, whereas that of Herbert *et al.* was 46·8° for $< 1\%$ acid solution of lactone. The value given by them should be converted through multiplication by the M.W. factor 176/210·1, since the concentration was expressed as acid.

Readings of mutarotation and dispersion were taken on the same solution by reading the mercury yellow and green lines directly before or after any other line. Appropriate corrections for mutarotation were applied, and the resulting table shows $[\alpha]_{\lambda}^{20°}$ for t_0 in each case. Frequent checks of the accuracy of the time corrections were obtained by reading 10 duplicate lines at intervals.

Sodium Salt of the Keto-acid.—Two methods of oxidation were tried with similar results, and slight corrections had to be applied as before. After the oxidation, the necessary quantity of sodium carbonate or bicarbonate was added, but in every case it was impossible to produce a solution of sufficient concentration transparent to rays shorter than about 5086 A. for 2 dm.

SUMMARY.

(*a*) The rotatory dispersion of 2 : 3-diketogulonolactone is simple, with $\lambda_0 = 2152$ A.

(*b*) The rotatory dispersion of the corresponding sodium salt is also simple, with $\lambda_0 = 2316$ A. The first absorption band is probably inactive.

(*c*) The mutarotation of the lactone in water is analysed.

(*d*) It is shown that, in 4% solution, ascorbic acid needs an excess of oxidising agent for conversion into the lactone.

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