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Effect of food dyes on the photostability of aqueous solutions of L-ascorbic acid

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Summary

Aqueous solutions of L-ascorbic acid were irradiated with simulated sunlight in the presence of Amaranth (Food Red No. 9, C.I. 16185, E 123), Green S (Acid Green S, C.I. 44090, E 142) and Quinoline Yellow (Acid Yellow No. 3, C.I. 47005, E 104) and the residual drug assayed by spectroscopy. The stability of L-ascorbic acid in aqueous solution was diminished on the addition of E 104, this effect being reversed by the addition of mannitol, suggesting that this dye facilitated the photogeneration of hydroxyl radicals. The stability of L-ascorbic acid solution was also diminished by the separate addition of the other dyes tested. However, the incorporation of triplet quenching agents enhanced the stability of the substrate solutions, suggesting that the dyes acted as triplet sensitisers.

L-Ascorbic acid is used as a preservative in pharmaceutical preparations due to its antioxidant properties (Lachman, 1968a,b) and it is also employed for its vitamin properties as a chemotherapeutic agent (vitamin C). There are many such vitamin preparations which are coloured to render them more attractive to the purchaser. The colouring matter used is normally an approved food dye and in this context, E 123, 142 and 104 could well be used. The objective of the present work is to investigate whether the use of these colouring agents will facilitate the decomposition by photolysis of the active ingredient, L-ascorbic acid. The objective was achieved by measuring the rates of degradation of L-ascorbic acid in the presence of the test dyes against time, at 22 ± 1°C.

Amaranth (E 123) (B.D.H.), Green S (E142) (D.F. Anstead Ltd), Quinoline Yellow (E104), (Aldrich Chemical Co. Ltd), hydrochloric acid (F.S.A. Laboratory Supplies), 8-hydroxyquinoline (Hopkins & Williams Ltd), L-ascorbic acid (F.S.A. Laboratory Supplies), mannitol (Hopkins & Williams Ltd), methylene blue (B.D.H. Chemical Division), phosphotungstic acid (Hopkins & Williams Ltd), sodium acetate (B.D.H., G.P.R. grade), sodium metavanadate (Aldrich Chemical Co. Ltd) and zinc sulphate (Hopkin & Williams Ltd) were obtained from the indicated sources.

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TABLE 1

Photolysis of L-ascorbic acid in distilled water (0.2 mg / ml)

Irradiation time (h)	A_r	A_t	$A_r - A_t$	% remaining	Log (% remaining)	(% remaining)$^{-1}$
0	0.190	0.125	0.065	100	2.0000	0.0100
2	0.190	0.130	0.060	92.31	1.9652	0.0108
3	0.190	0.135	0.055	84.62	1.9275	0.0118
5	0.180	0.138	0.042	64.62	1.8104	0.0155
22	0.180	0.140	0.040	61.54	1.7892	0.0162
25	0.190	0.160	0.030	46.15	1.6642	0.0217
Correlation coefficients				−0.8776	−0.8929	−0.8928
k				1.65	0.024	3.57×10^{-4}

A_r, absorbance of reagent; A_t, absorbance of test.

Apparatus included a Cecil CE 373 linear readout spectrophotometer, Beckman DU 70 UV/visible spectrophotometer and a simulated sunlight irradiation apparatus (Evans et al., 1975).

The assay of L-ascorbic acid was carried out by a method adapted from that of Muralkrishna and Murty (1989) with the following modifications: sodium metavanadate was used in place of sodium vanadate, all volumes were scaled up by a factor of four and finally a 1 in 4 dilution of the phosphotungstic-metavanadate complex was made. Phosphotungstic acid and sodium metavanadate solutions were prepared in double-distilled water and buffer (pH 1.5) was made from sodium acetate solution and hydrochloric acid (Muralkrishna and Murty, 1989). Ascorbic acid standards were prepared 0.1–1.0 mg/ml in double-distilled water. A calibration graph was drawn and absorbance measurements were taken at 360 nm (correlation coefficient 0.9897, $p = 0.001$, three degrees of freedom).

The reaction order was determined by carrying out a linear regression analysis of plots of the percentage L-ascorbic acid remaining vs time, $\log_{10}$ (% L-ascorbic acid remaining) vs time and (% L-ascorbic acid remaining)$^{-1}$. The plot yielding the largest regression coefficient was deemed to represent the order of reaction (Florence and Attwood, 1981).

The calibration data show that there is a very good correlation for the Beer Lambert law plot of absorbance vs concentration of ascorbic acid. The choice of 360 nm by Muralikrishna and Murty (1989) was confirmed. However, comparison of the results with those accrued from measurements at more obvious wavelengths such as 262 and 290 nm showed that 360 nm was the optimal wavelength at which to carry out the assay. Table 1 shows that in the absence of any dyes or additives the photodegradation of ascorbic acid appears to follow first-order kinetics, which was supported by the two additional control experiments shown in Table 2. Previous workers (Blaug and Hajratwala, 1972) have reported that the stability of aqueous solutions of ascorbic acid are affected by such factors as pH, temperature, oxygen and contamination with metal ions. The addition of the dyes (E104, 123 and 142) caused a substantial diminution in stability of the L-ascorbic acid solution as indicated by a rise in the rate constant of the photodegradation reaction. In the cases of E 123 and 142 the increase in rate constant was from 0.020 to 0.052 whereas in the case of E 104 the rise was from 0.020 to 0.081.

It has been reported that L-ascorbic acid decomposition in aqueous solution was hydroxyl radical mediated (Blaug and Hajratwala, 1972), consequently a series of experiments was undertaken to test the effect of the addition of mannitol (in equimolar quantities with L-ascorbic acid), a known hydroxyl radical scavenger. It was expected that the addition of mannitol would bring about a reduction in the rate constant of the photodegradation reaction of L-ascorbic acid with

the added dyes. With the exception of E104 (k changes from 0.081 to 0.070) the dyes and mannitol produced an increase in the rate constant. This indicated that it was most unlikely that the dyes were acting as hydroxyl radical promoters. Some dyes have the property of acting as triplet sensitisers in photochemical reactions (Paleocrassus, 1974). This effect is brought about by the dye being easily raised to an excited triplet state by a modest input of light energy. The excited dye molecule can then transfer its acquired additional energy to the substrate molecule resulting in the decomposition of the latter. In order to pursue this hypothesis, methylene blue was used as an additive at the same concentration as the food dyes tested. The rate constant rose to 0.128; further evidence of this triplet sensitiser effect was obtained by using a mixture of methylene blue and 'zinc oxine'. The latter has been reported as a triplet quenching agent. Triplet quenching agents negate the effect of triplet sensitisers. As can be seen from Table 2, the addi-

TABLE 2

Photolysis results of ascorbic acid with dyes and additives

Ascorbic acid (0.2 mg/ml)	Correlation coefficients		Order of reaction	Rate constant (k)
	% ascorbic acid remaining	log (% ascorbic acid remaining)		
Control	−0.8776	−0.8929	1st	0.024
Control	−0.9783	−0.9896	1st	0.020
Ascorbic acid + E 142	−0.9749	−0.9915	1st	0.052
Ascorbic acid + E 123	−0.9664	−0.9826	1st	0.052
Ascorbic acid + E 104	−0.9820	−0.9999	1st	0.081
Ascorbic acid + E 142 + mannitol (0.2 mg/ml)	−0.9926	−0.9989	1st	0.065
Ascorbic acid + E 123 + mannitol (0.2 mg/ml)	−0.9987	−0.9991	1st	0.070
Ascorbic acid + E 104 + mannitol (0.2 mg/ml)	−0.9397	−0.9971	1st	0.070
Ascorbic acid + E 142 + zinc oxine (0.2 mg/ml)	−0.9901	−0.9951	1st	0.050
Ascorbic acid + E 123 + zinc oxine (0.2 mg/ml)	−0.9839	−0.9844	1st	0.032
Ascorbic acid + methylene blue	−0.7535	−0.9437	1st	0.128
Ascorbic acid + methylene blue + zinc oxine (0.2 mg/ml)	−0.7941	−0.9086	1st	0.093

Zinc oxine was prepared by reaction of zinc sulphate and 8-hydroxyquinoline (1:2 molar ratio). Each result represents the measurements at six time intervals after which more than 70% of the original amount of ascorbic acid had been decomposed and a duplicate experiment in each case. Dyes (E 104, 123 and 142) were used at a concentration of 10 mg/l.

tion of zinc oxine did reduce the rate constant from 0.128 to 0.093, however, this value was 4-times the rate constant of the control. This partial inhibition may have been due to an insufficient amount of the chelate (zinc oxine) being used but the limiting factor was the solubility of the former in the ascorbic acid solution. It does appear that both E 123 and 142 act as triplet sensitisers in the photochemical degradation of aqueous solutions of L-ascorbic acid under the test conditions used.

Aqueous L-ascorbic acid solutions coloured with the food dyes tested are less stable to light than the uncoloured solutions. No attempt was made to carry out the work in the absence of air as this would have been unrealistic in view of the manner in which L-ascorbic acid solutions would be used in normal practice.

References

Blaug, S.M. and Hajratwala, B., Kinetics of aerobic oxidation of ascorbic acid. *J. Pharm. Sci.*, 61 (1972) 556–562.

Evans, P.E., Sugden, J.K. and Van Abbe, N.J., Aspects of the photochemical behaviour of 1-hydroxypyridine-2-thione. *Pharm. Acta Helv.*, 50 (1975) 94–99.

Florence, A.T. and Attwood, D., *Physico-Chemical Principles of Pharmacy*, MacMillan, London, 1981, p. 459.

Lachman, L., Antioxidants and chelating agents as stabilizers in dosage forms. *Drug Cosm. Ind.*, 102 (1968a) 36–38,40,146–148.

Lachman, L., Antioxidants and chelating agents as stabilizers in dosage forms: II. *Drug Cosm. Ind.*, 102 (1968b), 43–51,146–149.

Muralkrishna, U. and Murty, J.A., Spectrophotometric determination of ascorbic acid in pharmaceutical preparations and fruit juices. *Analyst*, 114 (1989) 407–408.

Paleocrassus, S.N., Photocatalytic hydrogen production: Solar energy conversion alternative. *Sol. Energy*, 16 (1974) 45–51.