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LIGHT STABILITY OF VANILLIN SOLUTIONS IN ETHANOL

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ABSTRACT

Ethanolic solutions of vanillin, used as food flavouring are readily decomposed by the action of sunlight to 6,6'-dihydroxy-5,5'-dimethoxy-1,1'-biphenyl-3,3'-dicarbaldehyde (dehydrodi--vanillin). The decomposition is accompanied by the formation of a yellow colour and a slightly bitter taste. The U.S. Pharm--acopoeia (1975) spectroscopic assay of vanillin would be in--appropriate for samples contaminated with dehydrodivanillin, since the absorption maxima of vanillin are at 279 and 311 nm whereas the maxima for dehydrodivanillin are 279, 310nm with a shoulder at 337 nm.

DISCUSSION

The U.S. Pharmacopoeia (1975) recommends that vanillin solutions should be stored in light resistant containers [1], a requirement seldom observed with commercial preparations used for culinary purposes. Vanillin used for food flavouring is usually sold as an ethanolic solution, which assumes a yellow brown colour on on exposure to sunlight with the development of a slightly bitter taste. Irradiation of 0.8% w/v solutions of vanillin in degassed absolute ethanol by the method of Evans et. al. [2]. resulted in the formation of a brown colour within a few minutes, continued irradiation gave a precipitate of 6,6'-dihydroxy-5,5'-dimethoxy-1,1'-biphenyl-3,3'-dicarbaldehyde (dehydrodivanillin). This compound has also been prepared by the irradiation of aqu--ous solutions of vanillin in the presence of ferric chloride [3]. Alkaline solutions of vanillin rapidly assume a brown colour on irradiation with either sunlight or simulated sunlight as in Evans method[2]. Similar colour changes occur on irradiating ethanolic solutions of 3-methoxysalicylaldehyde but not on irradiating ethanolic solutions of 3,4-dimethoxybenzaldehyde. Consequently it appears that a hydroxy group attached to the aromatic ring is a prerequisite for this photochemical reaction.

In the light of Kiyirai's work [3] it appears that dehydro--divanillin is formed by the photooxidative coupling of two quinoid species, hence the brown colour formed initially may be due to a quinoid structure. In an attempt to prevent this photochemical reaction it was decided to study the effect of incorporating antioxidants prior to irradiation of the vanillin solutions. Tables 1 and 2 show that only 0.2 % w/v of sodium metabisulphite is effective and this antioxidant gives prot-

TABLE 1.

Chromatographic Study of Ethanolic Solutions of Vanillin with added Antioxidants during Irradiation

system	Vanillin 5% Control	Vanillin 5% + 0.05% B.H.A.	Vanillin 5% + 0.05% P.G.	Vanillin 5% + 0.2 % S.M.
Irrad. time for the appearance of decomp.	25 mins.	25 mins.	30 mins.	50 hours.

B.H.A = Butylated hydroxytoluene. P.G. = Propyl gallate. S.M. = Sodium metabisulphite.

TABLE 2.

Chromatographic Studies of the Decomposition of Ethanolic Solutions of Vanillin with Various Concentrations of Sodium Metabisulphite

System	Vanillin 5 % (control)	Vanillin 5% + 0.2% SM.	Vanillin 5% + 0.1% SM.	Vanillin 0.1% + 0.1% SM.
Irrad. time for appearance of decomp.	25 mins. (light yellow solution)	24 hours (yellow solution)	2.5 hours (yellow solution)	166 hours (clear solution + hazy ppt)

-ection from decomposition for up to 50 hours, which is equivalent to several months of shelf life. Table 3 shows that photochemical decomposition of vanillin is dependent on concentration as well as time. Comparison of the uv. absorption

TABLE 3.

Uv. Absorption of Irradiated Ethanolic Solutions of Vanillin at 311 nm

Time	5.0 % Vanillin		2.5 % Vanillin		0.05 % Vanillin *	
Hrs.	Absorb.	Colour	Absorb.	Colour	Absorb.	Colour
0	0.301	C	0.212	C	0.331	C
0.25	0.296	L Y	0.211	C	0.324	C
0.5	0.372	L Y	0.255	C	0.361	C
1.0	0.341	Y	0.410	L Y	0.363	C
2.0	0.760	Y	0.383	L Y	0.386	C
4.0	0.493	Y	0.182	L Y	0.266	L Y
8.0	0.350	Y	0.163	L Y	0.380	L Y
24.0	0.311	Y + ppt	0.192	Y	0.368	L Y
48.0	0.313	O + ppt	0.162	O	0.318	Y
72.0	0.277	O + ppt	0.169	O	0.261	Y
144.0	0.372	O + ppt	0.240	O + ppt	0.173	O
168.0	0.427	O + ppt	0.239	O + ppt	0.162	O

* serial dilutions made prior to measurement on the spectrometer.

C = colourless, L Y = light yellow, O = orange, Y = yellow, ppt = precipitate.

curves of vanillin and dehydrodivanillin shows that they have too much overlap to make the U.S.P. (1975) assay of vanillin appropriate for samples contaminated with dehydrodivanillin.

EXPERIMENTAL

6,6'-Dihydroxy-5,5'-dimethoxy-1,1'-biphenyl-3,3'-dicarbaldehyde

Vanillin (0.5 g., 0.00328 mole) was suspended in hydrochloric acid (0.5 %; 170 cm^3), ferric chloride solution (1 %; 10 cm^3) added and the mixture heated under reflux for 0.5 hr. After cooling to 0^oa solid precipitated which was collected and recrystallised from benzene cyclohexane mixture (1:10), mp. 304 - 306^o (Lit[4] 304 -306^o). Yield 0.07 g. (14%).

6,6'-Dihydroxy-5,5'-dimethoxy-1,1'-biphenyl-3,3'-dicarbaldehyde (photolysis of vanillin)

Vanillin (2 g., 0.031 mole) in degassed absolute ethanol (250 cm^3) was irradiated by Evans method[2] for 72 hrs. The solvent was removed under reduced pressure and the residue extracted with ether (2 x 20 cm^3). The ether extract was diluted with petroleum ether (40-60) and the mixture cooled to give a precipitate, which was collected and re-crystallised from benzene cyclohexane mixture (1:10), mp 304 -306^o. Yield 0.072 g. (7.2 %) ir (nujol mull) 3500 - 3100, 1685, 1603, 840, 740 cm^{-1}. n.m.r ($DMSO_{d6}$) δ 9.90^*(2H,s), 9.82 (2H,s), 7.41 (4H,s), 3.90 (6H,s) * disappears on deuteration. Recovered vanillin 1.68 g. Intractable tar 0.2 g.

Photochemical decomposition of 3-methoxysalicylaldehyde

3-Methoxysalicylaldehyde (2 g., 0.013 mole) in degassed ethanol (250 cm^3) was irradiated as above for 72 hrs. After 2 hrs irradiation a brown colour had developed but on working up the reaction mixture only an itractable tar was recovered (1.9 g.)

Attempted photolysis of 3,4-dimethoxybenzaldehyde

3,4-Dimethoxybenzaldehyde (5 g., 0.030 mole) in degassed absolute ethanol (250 cm^3) was irradiated as above and on working up the reaction mixture only the starting material was recovered (4.9 g.)

Ultra violet absorption measurements

The uv spectra in ethanol were run for both vanillin and dehydrodivanillin on a Unicam S.P. 800 spectrometer. The absorption maxima were at wavelengths of 279 and 311 nm for vanillin and 279, 310 nm (shoulder at 337 nm) for dehydrodivanillin. Beer Lambert law plots for both compounds were satisfactory. The photochemical stability of vanillin was assessed by irradiating solutions in degassed absolute ethanol (5.0, 2.5, and 0.5 % w/v) in stoppered Q&Q tubes (15 cm x 2.5 cm int. dia.). Uv absorption measurements were taken at 311 nm at intervals between zero and 168 hrs. Chromatographic assessment of the photochemical degradation of vanillin was carried out by placing samples of the irradiated solutions on strips of Whatman No 1 paper and developing the chromatogram with acetone. After careful drying the paper strips were sprayed with Brady's reagent, showing two spots, the faster moving one being due to vanillin and the other due to dehydrodivanillin. This method was used to give a qualitative estimate of the minimal period of irradiation before decomposition could be detected, with and with-

-out antioxidants. The results of duplicate experiments appear in Tables 1 and 2.

Studies of the suitability of the U.S. Pharmacopoeia (1975) assay of vanillin were carried out using freshly prepared solutions in degassed absolute ethanol and those after 0.5 hr irradiation. The only change in the spectrum of vanillin after irradiation was the emergence of a shoulder at 337 nm.

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