Photooxidation, reduction of the ferric ion-glucose complex

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Summary. Ferric ions in an acid solution of glucose are reduced by irradiation with light of wavelengths less than 400 nm. The action spectrum for this reaction and the oxidation products of glucose have been determined.

In addition to their intrinsic interest, the photooxidations and reductions of metal ion complexes have recently received attention as a possible means of utilizing solar energy[1]. However, frequently in these complexes, photooxidation or reduction of the metal ion only occurs at short wavelengths not present in significant amounts in the solar spectrum on earth[2-5].

It has been reported that ferric ions are chelated by sugars[6-8] and absorption spectra of these complexes display maxima at about 350 nm. In addition, it is known that in a 1:1 ferric ion-glucose complex in acid aqueous solution ferric ions are thermally reduced[8]. Complexes in which the metal ion undergoes a thermal reduction also frequently display photooxidation reductions when excited by light in an appropriate charge transfer band[4]. It was therefore of interest to see if the ferric ion-glucose complex displays any photoreaction at wavelengths greater than about 300 nm.

Material and methods. $Fe(ClO_4)_3 \cdot 6\,H_2O$ (99% min. assay) was obtained from P.C.R. Inc. Other solvents and reagents were AR grade. The difference in absorption spectrum between aqueous solutions of 2×10^{-4} M ferric perchlorate and 2×10^{-4} M ferric perchlorate plus 0.2 M glucose acidified to pH 2 with perchloric acid was determined with a Beckman Acta CV Spectrophotometer.

Acidified and deoxygenated solutions of 2×10^{-4} M ferric perchlorate plus 0.2 M glucose were photolyzed with a 200 W HBO super high pressure mercury arc through a Bausch and Lomb monochromator (bandpass 10 nm). The concentration of the ferric ion remaining at different stages of the irradiation was determined by the absorption of the ferric thiocyanate complex formed following the addition of ammonium thiocyanate to aliquots of the photolyzed sample. The rate of decrease of ferric ion concentration was first order and the rate constants, k_λ, at wavelengths of 298 nm, 312 nm, 333 nm, 365 nm and 405 nm were measured. The relative light intensity incident on the solutions at each wavelength were measured with a Hilger vacuum thermopile and from these the relative number of quanta/sec, Q_λ, were obtained.

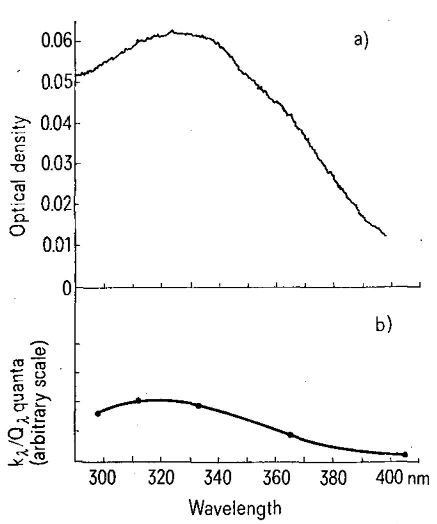
The glucose oxidation products resulting from exposure of an aqueous solution of 10^{-3} M ferric perchlorate and 0.2 M glucose at pH 2 to sunlight behind pyrex glass (wavelengths > 320 nm) were determined by chromatography of their 2,4-dinitrophenylhydrazine derivatives. These were prepared by adding a saturated solution of 2,4-dinitrophenylhydrazine (DNPH) in hydrochloric acid to the reaction mixture and standing cold for 1 h. (Glucose does not form a derivative under these conditions.)

Results and discussion. The absorption spectrum of the ferric ion-glucose complex obtained by subtracting the spectrum of a 2×10^{-4} M ferric perchlorate solution from the spectrum of a 2×10^{-4} M ferric perchlorate plus 0.2 M glucose solution is shown in figure 1, a. The action spectra (k_λ/Q_λ plotted against λ) for the deoxygenated 2×10^{-4} M

Table 1. Chromatography data of DNPH derivatives of products of glucose oxidation

R glyoxal a	b	c	d
1.05	1.14	1	1.05
1	1	0.90	1
0.89	0.83	0.84	0.89
0.78	0.66	0.77	0.76
0.61	0.52	0.60	0.50
0.45	0.44	0.55	–
0.31	0.38	0.51	–
0.23	0.26	0.34	0.20
0.13	0.12	0.24	0.08
0.04	–	0.14	0.00

Solvent systems used: a) benzene/tetrahydrofuran (80:20); b) benzene/tetrahydrofuran (93:7); c) toluene/ethyl acetate (1:1); d) benzene/tetrahydrofuran (80:20), from thermal oxidation[8].



a Absorption spectrum of the ferric ion-glucose complex. *b* Action spectrum for ferric ion and glucose minus action spectrum for ferric ion alone.

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ferric perchlorate solution and the 0.2 M glucose plus 2×10^{-4} M ferric perchlorate solution were determined. From these the 'difference' action spectrum was obtained and is shown in the figure, b.

The 'difference' action spectrum and the absorption spectrum of the complex are similar, suggesting that excitation of a charge-transfer band of the ferric ion-glucose complex is responsible for the reduction of the ferric ion.

We observe that this reduction can be induced by light at wavelengths present in the solar spectrum on earth and although glucose is oxidized in the process it can be replaced cheaply. It is therefore possible to envisage a photochemical fuel cell based on the ferric ion-glucose complex making use of light at wavelengths < 400 nm. Table 1 shows the chromatographic properties of the 2,4-dinitrophenylhydrazine derivatives of glucose photooxidation while table 2 gives some literature values[9,10].

Table 2. Literature values for $R_{glyoxal}$ of DNPH derivatives

Compound	Solvent systems* a[9]	b[9]	c[10]
Glyoxal	1	1	1
Pyruvaldehyde	1.05	1.17	–
Hydroxypyruvaldehyde	0.87	0.5	0.92
Glycolaldehyde	0.32, 0.45	0.14, 0.26	0.48
5(hydroxymethyl)furfural	0.45, 0.48	0.18, 0.27	0.60
Erythrose	0.81	0.39	–
Mesoxaldehyde	–	0.64, 0.43	–
Glyceraldehyde	0.09	–	–
Dihydroxyacetone	0.15	–	0.31
D-glucosone	0.05	–	0.13

* Solvent systems as in table 1.

All values are relative to glyoxal. For comparison, the chromatographic data from the thermal oxidation of glucose with ferric perchlorate[8] is given in the 4th column of table 1.

Apart from the compound, $R_g = 0.50$, all of the products observed in the thermal oxidation appear in the photochemical oxidation, within the experimental errors of the chromatography. There are also traces of 3 compounds not observed in the thermal oxidation.

Based on this chromatographic data, the presence of the following compounds can be reasonably inferred. (Experimental chromatographic R_g values from table 1 are given in parenthesis.)

Glyoxal	(a = 1, b = 1, c = 1)
Glycolaldehyde	(a = 0.31, 0.45, b = 0.12, 0.26, c = 0.5)
Glucosone	(a = 0.04, c = 0.14)
Erythrose	(a = 0.78, b = 0.38)
Pyruvaldehyde	(a = 1.05, b = 1.14, c = 1)
Hydroxypyruvaldehyde	(a = 0.89, b = 0.52, c = 0.90)

The principal products are glyoxal, pyruvaldehyde and hydroxypyruvaldehyde. The method of isolating products does not detect any nonketonic compounds, but as the total yield of products was in the order of a few mg, in the presence of vast excesses of glucose (necessary to ensure that the ferric ions are fully complexed) no other method appeared practical.

The DNPH derivatives of glucosone, glyoxal, erythrose, pyruvaldehyde and hydroxypyruvaldehyde were all clearly isolated from the thermal oxidation[8] and their assignment as photooxidation products of glucose in this work, although based only on chromatography, indicates that similar reaction-paths are followed by the thermal and photochemical oxidations.

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Eubotriol and eubol, new diterpenes from *Sideritis euboea*[1]

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Summary. 2 new diterpenes Eubotriol (ent-kaur-16-ene-7α, 15β, 18triol) (**I**), and eubol (ent-kaur-16-ene-7α-acetoxy-15β, 18 diol) (**II**) have been isolated from Sideritis euboea Helder.

Recently[2] we reported the isolation of 5 tetracyclic isokaurene diterpenes from the aerial part of Sideritis euboea Helder (Labiatae), a species growing in Euboea, (Greece). They were identified with siderol[3], epoxysiderol[4], isolinearol[5], sideridiol[3], sideroxol[6], which are already known. We describe now 2 minor components, eubotriol (**I**) and eubol (**II**), isolated from the same extract by chromatography on silica gel: (**II**) appeared in the cyclohexane-Et_2O 1:1 fraction, (**I**) in the Et_2O-AcOEt 1:3 fraction.

Eubotriol (**I**) $C_{20}H_{32}O_3$, m.p. 193–194 °C (bright prisms from AcOEt), gave a negative TNM test; IR (nujol) 3600–3350 (OH), 1655 and 897 cm^{-1} ($C{=}CH_2$); MS[7] 302 ($M{-}H_2O$), 287 ($M{-}H_2O{-}CH_3$), 272 ($M{-}OH{-}CH_2OH$), 254 ($M{-}H_2O{-}OH{-}CH_2OH$), 109 m/e (ring A, $C_6H_7Me_2$); NMR (100 MHz, pyridine-d_5) 0.92 (s, 4α–CH_3), 1.05 (s, 10α–CH_3), 2.80 (m, 13α–H), 3.47 and 3.63 (q_{AB}, J 11 Hz, 4β–CH_2OH), 4.23 (t, ~ 2 Hz, 7α-H), 4,45 (t, J 1 Hz, 15β–H), 5.19 and 5.44 δ (br s, $W^1/_2$ 3 Hz, $C{=}CH_2$).

The spectra of eubotriol (typical of an ent-kaur-16-ene skeleton with an oxygenated function on C-15) and the physical constants are in perfect agreement with those reported for ent-kaur-16-ene-7α, 15β, 18-triol (**I**), previously obtained[8,9] as a by-product during the partial synthesis of sideritriol[8], another natural diterpene from

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[1] This work was supported by National Research Council (C.N.R.), Roma.

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