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The amylose–iodine complex

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ABSTRACT

The nature of the amylose–iodine complex has been re-examined. Anhydrous V-amylose can absorb ~ 30% of its weight of iodine vapour to form an unstable complex. In aqueous solution, this complex is also unstable and its properties are consistent with a model in which helices of ~ 50 α-D-glucopyranosyl residues containing iodine alternate with segments of randomly coiled amylose chain. Free iodine is also present in the solution. For the solution, the absorption spectrum is a composite of those of the complex and an aqueous solution of iodine, and the shoulder at 485 nm is due to overlap. The importance of water in forming the blue complex is demonstrated.

INTRODUCTION

The blue complex that iodine forms with amylose is well known and its nature was established by Rundle and his coworkers[1–7]. Rundle and French[3] showed that the amylose in the complex assumes a six-fold helical conformation, with iodine within the cavity of the helix. Amylose can form similar complexes with many other substances and they are termed amylose-V complexes. The formation of an amylose–butanol complex is used to separate amylose from amylopectin in granular starches[8]. The complexing agent can be removed to leave the amylose helix intact and drying then yields anhydrous V-amylose which has a characteristic X-ray diffraction pattern[4,9]. Rundle and French[3] found that, on exposure to iodine vapour, anhydrous V-amylose absorbed ~ 26% of its weight of iodine.

Electron microscopy of crystalline V-complexes[10,11] showed that the rectangular platelets of the complex are composed of aggregates of lamellae each ~ 10 nm thick. The axis of the helix is perpendicular to the lamellae surfaces and there is extensive folding of the amylose chain within the lamellae. In single crystals of many synthetic linear polymers such as polyethylene, a similar structure is observed[12]. In general, the fold surface in polymer crystals is considered to be a

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region of considerable molecular disorder and is regarded as an amorphous layer which may contain sharp folds or loose loops or free ends, or a combination of these features[13]. The question arises as to whether the helical structure is maintained within a fold. Jane and Robyt[14] showed that alpha-amylases can hydrolyse the amorphous region in amylose to leave an amylodextrin having a dp that accords with a helix 10 nm in length. The selective action of the enzyme suggests that the amorphous layer has a structure which is different from that of the crystalline region, but little is known of the nature of the amorphous layer.

Like anhydrous V-amylose, a product prepared by treating retrograded amylose with methanol, absorbed a considerable amount of iodine vapour to form a strongly coloured complex[15]. When the anhydrous V-amylose–iodine complex was prepared for purposes of comparison, it became clear that its properties differed in some important respects from those published[3] and a re-investigation was undertaken, the results of which are now reported.

EXPERIMENTAL

Potato amylose, obtained from Aldrich, was insoluble in water, but dissolved in M KOH and Me_2SO.

Preparation of V-amylose.—A solution of amylose (1 g) in Me_2SO (30 mL) was diluted to 800 mL with water, then heated to 95°, and butan-1-ol (120 mL) was added gradually with constant stirring. The solution was stored at room temperature for at least 24 h, the butanol complex was isolated by centrifugation and dissolved in boiling air-free water, the solution was filtered, and the complex was reprecipitated by the above procedure. The purified complex was washed two or three times with small quantities of methanol, then treated with boiling AR methanol (2×50 mL) for 45 min, followed by filtration. The complex was then treated with boiling, freshly prepared anhydrous methanol (100 mL) for 1 h with prevention of the ingress of moisture. The anhydrous amylose was filtered, most of the residual methanol was removed by drying in vacuo, and the amylose was reduced quickly to a coarse powder, then dried to constant weight over phosphorus pentaoxide at 30°.

The resulting anhydrous amylose (*a*) gave an X-ray diffraction pattern that accorded with recorded data[9]; (*b*) had a dp of 2160, determined by measuring the limiting viscosity number in M KOH and using the relationship[16] $[\eta] = 1.18 \times 10^{-5} [M_w]^{0.89}$; (*c*) had an iodine-binding capacity[17] of 20.2 at 25°; and (*d*) had a carbohydrate content of 101.5%, as determined using the phenol–H_2SO_4 method[18]. When the anhydrous amylose was kept at 30°/10^{-4} torr for 1 h, there was no detectable loss in weight and only a trace of water was evolved, but no butanol or methanol (IR spectroscopy).

Iodination of anhydrous V-amylose.—Amylose (0.2–0.3 g) was exposed to iodine vapour in the presence of phosphorus pentaoxide at 30° until the increase in weight became constant (after ~ 30 days). There was no gain in weight in the absence of iodine. The most suitable temperature for iodination was 30°; at higher

temperatures, the rate of iodination increased, but some degradation of the amylose occurred as a result of reaction with the iodine.

Spectrophotometry.—Solutions were examined over the range 190–800 nm at 23°, using 10-mm silica cells with water in the reference cell except where otherwise stated. In order to ensure that small changes were not due to variations in instrument performance, the variability of the instrument was monitored on the basis of the absorbance at 536.7 nm of a holmium glass filter. The mean value obtained was 0.343 with a standard deviation of $\pm 2.54 \times 10^{-3}$, which is well within the limits of variation for the solution of the complex.

X-ray diffraction.—A Philips X-ray diffractometer, using Ni-filtered Cu-K_α radiation, was employed. Samples were held on a strip of sellotape within the sample holder, and a drying agent was placed in the sample chamber of the instrument.

RESULTS AND DISCUSSION

The fully iodinated amylose complex was dark red-violet, turned black when moistened with water, and dissolved in cold water to yield a deep-blue solution. The iodine in the solid complex could be extracted with hydrophilic solvents such as methanol, but hydrophobic solvents such as carbon tetrachloride removed only a small proportion. The mean value, from fourteen separate experiments, for the increase in weight due to absorption of iodine was $28.50 \pm 1.3\%$, with a highest value of 30.11%. Iodination of amylose from laboratory-grade potato starch (not soluble starch), isolated using the procedure outlined in this paper, gave a value of 30.03% which was included in the above results.

The complex was unstable and gave off iodine vapour, but it could be stored satisfactorily over phosphorus pentaoxide and iodine crystals.

Loss of iodine from the solid complex.—When the solid complex (29.78% of iodine) was stored at 30° over phosphorus pentaoxide and a small amount of anhydrous V-amylose (replaced occasionally), the loss of iodine, determined gravimetrically during 56 days, was as shown in Fig. 1. The iodine content after 56 days was 17.74%, which declined to 15.88% after 378 days.

When the solid complex (28.77% of iodine) was stored at 23° over phosphorus pentaoxide at $\sim 10^{-1}$ torr, the iodine content (Fig. 2) after 67 h was 19.24%. The temperature was then raised to 34° and, after 115 h, the iodine content had fallen to 18.02%. Thus, ~40% of the iodine in the complex may be removed readily.

The ease with which iodine is lost shows that the binding is weak. Moreover, loss of iodine from locations near to the ends of a helix would be expected to occur more rapidly than from the centre of a helix.

The iodine content (28.5%) of the V-amylose–iodine complex is somewhat higher than that (26%) reported by Rundle and French[3], which corresponds to one iodine molecule for each turn of the helix. In such an arrangement, the iodine molecules do not completely fill the space available.

Using the van der Waals radius of an iodine molecule (6.97 Å), it can be

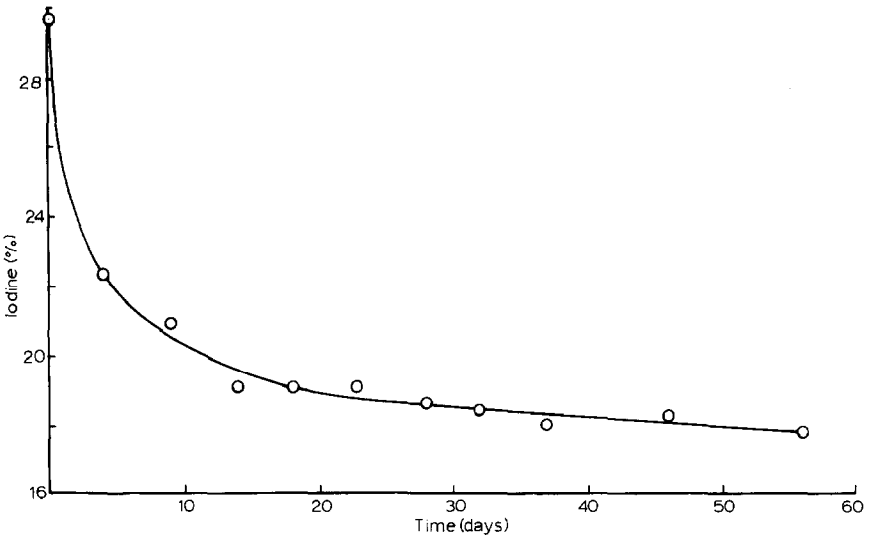

Fig. 1. Loss of iodine from the amylose–iodine complex at 30°, using anhydrous V-amylose to absorb the iodine vapour.

calculated that the maximum iodine content is 30%, a value close to that found experimentally in this study.

However, from X-ray studies of the amylose–iodine complex and other similar iodine complexes, West[19] has determined the average interatomic spacing of the iodine atoms to be 3.10 Å. Using this value and repeating the calculation, the maximum iodine content becomes 33.7%.

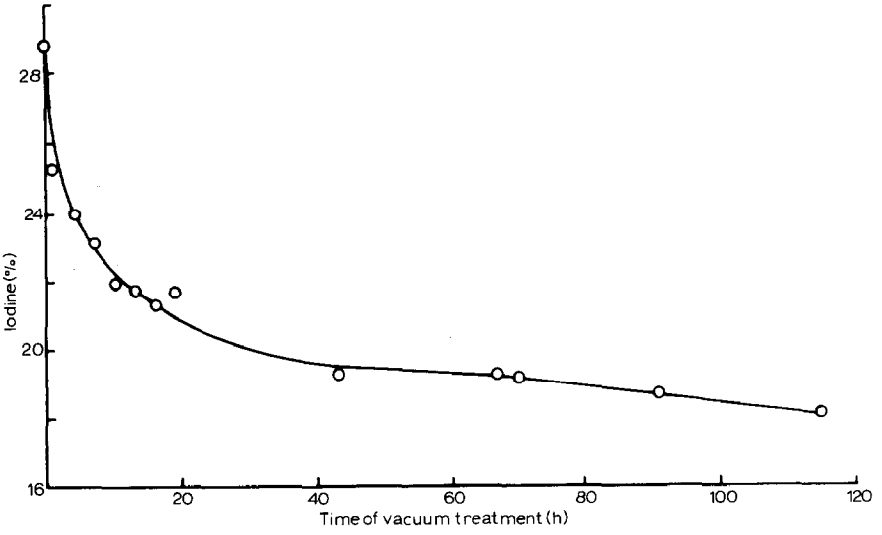

Fig. 2 Loss of iodine from the amylose–iodine complex at 23° and $\sim 10^{-1}$ torr.

TABLE I

Change in the absorbance of a solution (0.1184 g L^{-1}) of an amylose–iodine complex solution contained in a sealed vessel

Days	λ_{max}	Absorbance	λ_{max}	Absorbance	λ_{max}	Absorbance
0	566.6	0.654	354.2	0.337	203.6	1.633
2	568.8	0.635	353.4	0.300	203.0	1.542
4	569.4	0.680	353.4	0.317	203.2	1.508
7	569.4	0.714	352.2	0.330	202.8	1.493
11	569.8	0.733	353.0	0.338	202.4	1.467
14	570.2	0.745	352.4	0.343	202.6	1.459
18	570.4	0.740	353.4	0.337	201.6	1.407
21	572.2	0.728	352.8	0.343	203.2	1.458
25	570.4	0.752	353.2	0.345	201.4	1.422
30	569.8	0.771	352.0	0.350	201.2	1.373
35	570.0	0.871	352.0	0.426	200.2	1.436
39	569.2	0.794	352.8	0.370	199.0	1.486
42	569.8	0.889	352.2	0.421	199.0	1.429
44	569.4	0.860	351.4	0.378	199.0	1.424
49	571.0	0.902	352.2	0.395	199.0	1.399

The above calculations assume that the amylose is completely helical in structure and is able to accommodate the maximum number of iodine molecules. This structure would require iodine to be present in both the amorphous (i.e., folds) and crystalline regions. No information on this point is available at present.

Stability of the complex in solution.—The complex is readily soluble in cold water to yield a deep-blue solution. However, the instability of the solid complex is also paralleled in aqueous solution, which gives rise to free iodine and thence to products of hydrolysis. The ease with which iodine is lost from the complex can be shown by bubbling nitrogen through the solution which soon becomes colourless.

When a solution of the complex was stored in a closed vessel, there was a progressive change in the absorption spectrum. Table I shows the results for a complex containing 28.45% of iodine in aqueous solution at 0.1184 g L^{-1} and at 23°; λ_{max} 566 nm is due to the complex and λ_{max} 203 nm. represents unresolved peaks from species arising from the hydrolysis of iodine. Since the concentration of the complex slowly increases, whereas that of the ionic iodine species decreases, the complex must be formed at the expense of the products of hydrolysis of the iodine.

A similar experiment, using the same solid complex and a solution (0.0872 g L^{-1}) to which potassium iodide was added to 0.01 M, gave the results in Table II. The absorption peaks at 349 and 288 nm are due to the I_3^- ion[20]. The peak formerly observed at 202 nm has been obliterated by intense absorption due to the I^- ion.

The absorption at 556 nm due to the complex is remarkably constant having a mean value of 1.108 ± 0.016. Thus, when a solution is prepared from the solid complex, molecular iodine within the helix is slowly converted into I_3^- ions so that

TABLE II

Change in the absorbance of the complex used in Table I, but with the solution (0.0872 g L^{-1}) made 0.01 M with respect to added I^- ions

Time	λ_{max}	Absorbance	λ_{max}	Absorbance	λ_{max}	Absorbance
0 (h)	556.0	1.111	349.4	1.086	288.6	1.291
1 (h)	557.2	1.112	349.4	1.080	288.4	1.280
3 (h)	555.6	1.127	348.8	1.078	288.6	1.272
2 (d)	556.4	1.104	349.2	1.041	288.4	1.233
7	555.8	1.130	349.2	1.041	288.8	1.192
18	556.4	1.108	349.2	0.987	289.0	1.116
23	555.8	1.122	349.6	0.976	288.8	1.108
32	556.2	1.122	349.4	0.965	288.8	1.088
37	555.8	1.102	349.0	0.959	288.6	1.081
42	556.3	1.101	349.5	0.957	288.7	1.081
46	557.4	1.079	349.2	0.956	289.5	1.083
51	556.7	1.079	350.1	0.949	289.1	1.072
72	556.4	1.108	349.4	0.912	289.0	1.012

the helix contains a mixture of I_2 and I_3^- species. If sufficient I^- ions are available, the change is rapid, and the helix and its contents become stabilised.

The instability in the solution of the complex limits the study of the properties and only trends can be discerned.

The role of the iodide ion.—In the absence of I^-, the formation of a complex cannot take place. Claims[3] that I^- was not necessary appear to have overlooked its formation by hydrolysis of iodine[21].

$$I_2 + H_2O \rightleftharpoons I^- + H^+ + HOI$$

$$3I_2 + 3\,H_2O \rightleftharpoons IO_3^- + 5\,I^- + 6\,H^+$$

$$I_2 + H_2O \rightleftharpoons H_2OI^+ + I^-$$

If acid is added to an aqueous solution of iodine in order to suppress the formation of I^-, then the formation of the blue complex is also suppressed[22,23].

The absorbance at the λ_{max} is increased greatly by the addition of potassium iodide. Kuge and Ono[23] found that the absorbance passed through a maximum when the concentration of iodide was 5×10^{-3} M. Banks et al.[24] found that the iodine-binding capacity of amylose also passed through a maximum at 10^{-2} M KI. With high concentrations of iodide, λ_{max} shifts to shorter wavelengths[23].

Table III shows the effect on the absorbance of adding potassium iodide to a solution of a complex containing 28.77% of iodine when (*a*) $[I^-]/[I_2] = 1$ and (*b*) the solution was 10^{-2} M with respect to iodide ions.

The changes observed in the spectra may be ascribed to the increased concentration of I_3^- and I^- in solution. Although the trend in the results is as expected, the values for the absorbances are much smaller than anticipated. This situation is

TABLE III

Changes in the absorption spectrum [a] of a solution (0.0674 g L^{-1}) of the amylose–iodine complex brought about by the addition of I^- ions

No added KI		$[I^-]/[I_2]=1$		$[I^-]=10^{-2}$ M	
λ_{max}	Absorption	λ_{max}	Absorption	λ_{max}	Absorption
576.2	0.240	578.4	0.323	566.4	0.596
352.4	0.129	352.4	0.162	347.0	0.349
195.2	0.649	225.2	1.125	290.8	0.320
		193.8	1.406	227.1 [b]	1.356
				194.7 [b]	1.440

[a] ϵ values at 576.2, 578.4, and 566.4 nm: 405, 545, and 1005 m^2 mol^{-1}, respectively. [b] These peaks were resolved only by diluting the complex solution 1:100.

shown clearly when the values for the molar extinction coefficients (ϵ) are compared with the published[25] value of 3630 for λ_{max} for the comparable peak.

The stoichiometry of the complex in solution.—It is widely accepted that the iodine chain is negatively charged and may be regarded as being composed of I_3^- ions and iodine molecules. Among recent proposals for the identity of the unit, the I_5^- ion[26] and the I_7^- ion[27] have been suggested. The absence of agreement may indicate that the composition of the unit is variable and may be influenced by the concentration of the iodide ion and the dp of the amylose.

Cesaro et al.[28] proposed that the formation of the complex is initiated by an I_3^- ion binding to the randomly coiled amylose chain and promoting some local formation of helices. Propagation proceeds by the attraction of iodine molecules to the I_3^- ion and their conversion into ion-induced dipoles. It was assumed that this stacking interaction is limited to second neighbours on both sides of the I_3^- ion. The theoretical treatment is based upon the matrix method of Zimm and Bragg[29] for helix–coil transitions in polypeptides. The model can predict most of the experimental data.

The conclusion that 7–8 glucose residues at the ends of the amylose chain do not participate in binding iodine accords with findings noted below.

Minick et al.[30] consider that complex formation does not require negatively charged ionic species and that only neutral iodine molecules are involved. Based, in part, upon quantum-mechanical (INDO CI) calculations to predict the wavelengths of the absorption peaks of such species as I_4, I_6, I_8, etc., with an inter-iodine distance of 3.0 Å, the unit $(C_6H_{10}O_5)_{16.5}I_6$ was identified as being responsible for the colour of the complex.

This approach is based on the conclusion[31] that, when iodine is dissolved in water, hydrolysis to yield I^- and other negatively charged ions does not take place, so that these ions need not be considered. However, the results now reported demonstrate that, when the complex is dissolved in water, hydrolysis of iodine does occur. Thus, when a stream of oxygen-free nitrogen was passed through a solution (0.1360 g L^{-1}) of a complex having an iodine content of 28.77% for 100 min at 23°,

TABLE IV

Changes in the absorption spectrum of the amylose–iodine complex brought about by bubbling a stream of nitrogen through the solution until it was almost colourless

Before treatment		After treatment	
λ_{max}	Absorbance	λ_{max}	Absorbance
569.0	0.611	224.2	0.296
355.0	0.289	194.8	0.406
202.8	1.817		

the absorption spectrum (Table IV) changed to that of the iodide ion[20] which must have been formed by hydrolysis of iodine molecules in the complex.

The role of water.—The solid complex changes colour from dark red-violet to dark blue or black when moistened with water. Meyer and Bernfeld[32] claimed that water was indispensable for complex formation, but this claim was refuted by Rundle and French[3].

When equal volumes of 10^{-2} M I_2 and 10^{-2} M KI in methyl sulfoxide and 1% amylose in methyl sulfoxide were mixed, no change in the colour was observed, but the addition of sufficient water caused the development of an intense blue colour. A similar result was reported by Peticolas[33] and Ono et al.[34].

When granular anhydrous V-amylose was treated with 10^{-2} M I_2 and 10^{-2} M KI in methanol for 24 h at room temperature, the resulting powder, after drying, contained V-amylose, I_2, and I^- ions. Although this method of preparation ensures that at least some of the I_2 and I^- ions are present within the helices, the powder had a brown colour that was unaffected on treatment with non-aqueous solvents. However, when the powder was treated with water, it changed immediately to a dark blue-black product and a blue solution. Thus, for the blue colour of the complex to develop, V-amylose, iodine, iodide ion, and water are necessary.

Rundle and coworkers[6,35] considered that the glucose residues in the helix were polar and could induce dipoles in the iodine molecules, which, together with resonance along the iodine chain, was considered to be responsible for the colour. However, Murakami[36] considered that the colour arose from electron transfer from the oxygen atoms of the amylose to the iodine molecules. From an IR study of the complex, Greenwood and Rossotti[37,38] concluded that there was some iodine–oxygen interaction. However, the experimental evidence presented here indicates that interaction of the helix and iodine is insufficient to promote the formation of the blue colour of the complex and that water is primarily responsible for the change.

The role of the amylose in complex formation appears to be the provision of a channel that can accommodate a linear array of iodine atoms.

Iodide ions readily react with iodine molecules to give I_3^- ions, which confers a negative charge on the linear array, although the exact nature of the charged moiety is still unresolved. Saenger[39] suggested that these units are linked by bonds which involve the $5p_x$ orbitals, thereby facilitating electron delocalisation.

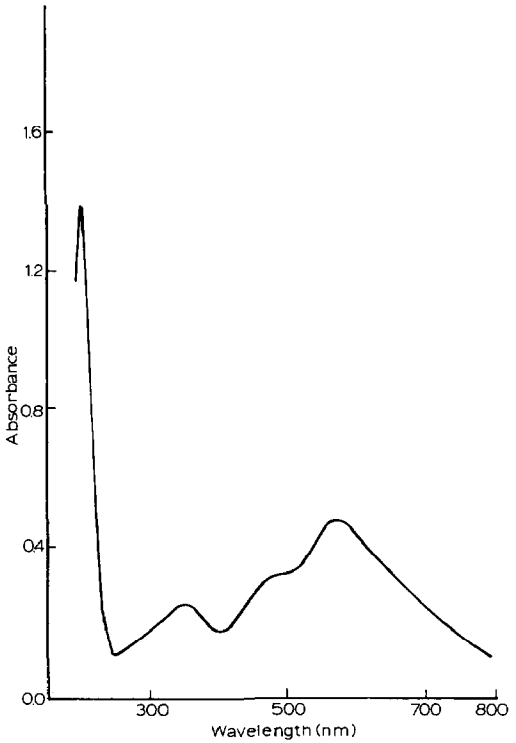

Fig. 3. The absorption spectrum of an aqueous solution (0.1376 g L^{-1}) of the amylose–iodine complex with 28.77% of iodine.

Because of the negative charge on the iodine chain, the helices will repel each other and attract positively charged ions and water molecules. Since the concentration of water molecules is high, each helix acquires a sheath of water molecules, the electric potential within the helix is lowered by dipole–ion interaction, the electron energy levels of the iodine atoms are perturbed, and the blue colour develops. This dipole–ion interaction makes the complex readily soluble in cold water, whereas V_a-amylose is only slightly soluble. In addition, water facilitates hydrogen bonding between units of the helix, thereby stabilising the helix and the complex.

Spectrophotometry.—Fig. 3 shows the absorption spectrum of an aqueous solution of a complex with an iodine content of 28.77%. The λ_{max} (574 nm) of the peak responsible for the colour of the complex is much shorter than the published[40] value (624 nm). The λ_{max} increases with the amount of iodine bound and the dp of the amylose.

Banks et al.[40] showed that, when the iodine reagent was added to a solution of amylose, λ_{max} changed from 605 nm for 3.7 mg of I_2/100 mg of amylose to 624 nm for 19.5 mg of I_2/100 mg of amylose. Banks et al.[41] also showed, for a series of enzymically synthesised amyloses, that λ_{max} for the complex was a function of the dp (Table V).

TABLE V

Absorption (λ_{max}) of solutions of amylose–iodine complexes for a series of enzymically synthesised amyloses of various dp (data from Banks et al.[41])

Sample	1	2	3	4	5	6	7	8	9	Amylose
Dp	22.2	28.9	31.3	36.4	50.7	71	93	105	134	1500
λ_{max}	496	524	530	546	574	588	595	606	610	642

The complexes are usually prepared by adding iodine–iodide reagent to an aqueous solution of amylose. Each amylose molecule is considered to be present as a random coil which is forced into a helical conformation by the iodine[42]. The length of each helix will depend on the size of the amylose molecule. In the solid complex, however, the iodine molecules are already contained within helices that are ~10 nm long, corresponding to ~75 glucose residues. Thus, when the complex is dissolved, it will behave as though it had been derived from amylose with a dp of ~75. Iodine molecules near the ends of helices will pass readily into solution and the light-absorbing characteristics of the solution will be determined by the length of helix that accommodates those iodine molecules that remain. If 75% of the original iodine remains in the helix, then its effective length becomes 7.5 nm, corresponding to a dp of ~56.3. Using the data in Table V, this dp corresponds to λ_{max} 575 nm, which is in good agreement with experimental results (λ_{max} 574 nm).

As noted above, on storage of a complex in vacuo, the iodine content was reduced from 28.77 to 18.02% and the λ_{max} data changed as shown in Table VI for solutions of the complexes. Based on the data in Table V, λ_{max} at 576.6 and 564.2 nm correspond to dp 58.1 and 47.8, respectively. If the iodine content of 28.77% corresponds to a dp of 75 in the solid state, then, on dissolution, the dp of the helix is effectively reduced from 75 to 58.1, a 22.5% reduction, which implies that 22.5% of the original iodine content of the complex passes into solution. The ratio of the dp values and absorbances before and after vacuum treatment were 0.822 and 0.816, respectively, and this agreement is consistent with the views set out above.

The model for the complex proposed by Cesaro et al.[28] led to the conclusion that 7–8 glucose residues at the chain ends did not bind iodine. The reduction

TABLE VI

The absorption spectra of a solution (0.134 g L^{-1}) of an amylose–iodine complex before and after vacuum treatment, which reduced the iodine content from 28.77 to 18.02%

28.77% I_2		18.02% I_2	
λ_{max}	Absorbance	λ_{max}	Absorbance
576.6	0.653	564.2	0.533
355.0	0.293	353.6	0.232
199.4	1.015	202.0	1.018

noted above in the effective helix length from 75 to 58 glucose residues, when iodine from the complex passes into solution, accords with this conclusion.

The influence of free iodine in the solution of the complex.—The absorption spectrum of an aqueous solution of iodine shows three prominent peaks at 460, 350, and 286 nm. The peak at 460 nm is attributed[43] to the iodine molecule and the others to I_3^-. Pfannemuller et al.[44] suggested that the shoulder at ~485 nm arises from an interaction of iodine with the hydroxyl groups of the amylose and reflects the presence of free iodine. That this shoulder arises from the overlap of the peaks at 580 and 460 nm of the complex and free iodine, respectively, was demonstrated as follows.

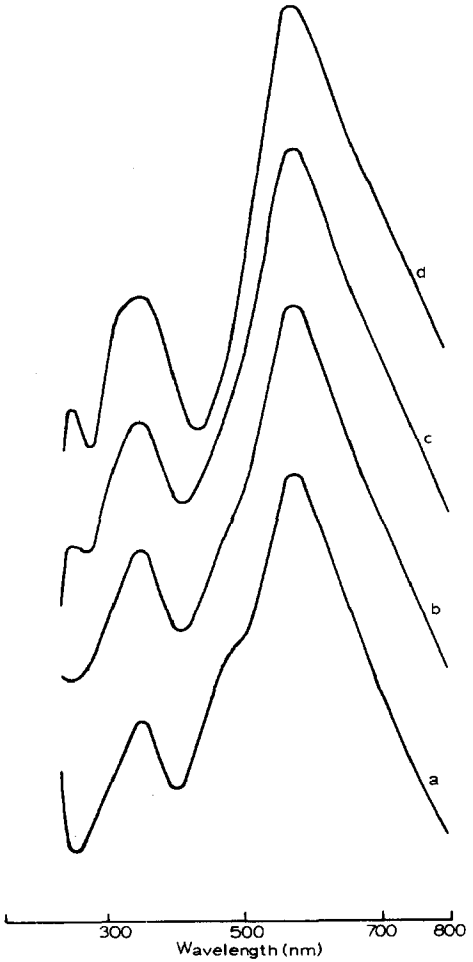

Fig. 4. Changes in the absorption spectrum of the amylose–iodine complex with progressive increase in the concentration of aqueous iodine in the reference cell: (a) water only; (b) 10% of I_2; (c) 20% of I_2; (d) 40% of I_2.

Fig. 4 shows that this shoulder disappeared from the absorption spectrum of the complex when the concentration of iodine in the reference cell was increased up to 40%, leaving what is probably the true spectrum of the complex in the range 300–800 nm; the small peak at 254 nm is a trough from the inverted spectrum of the iodine solution.

Likewise, when the iodine content of a solution of the complex was increased progressively, the shoulder at 485 nm became more prominent and finally developed into a peak at 470 nm, with the original peak at 564 nm being converted into a shoulder (Fig. 5).

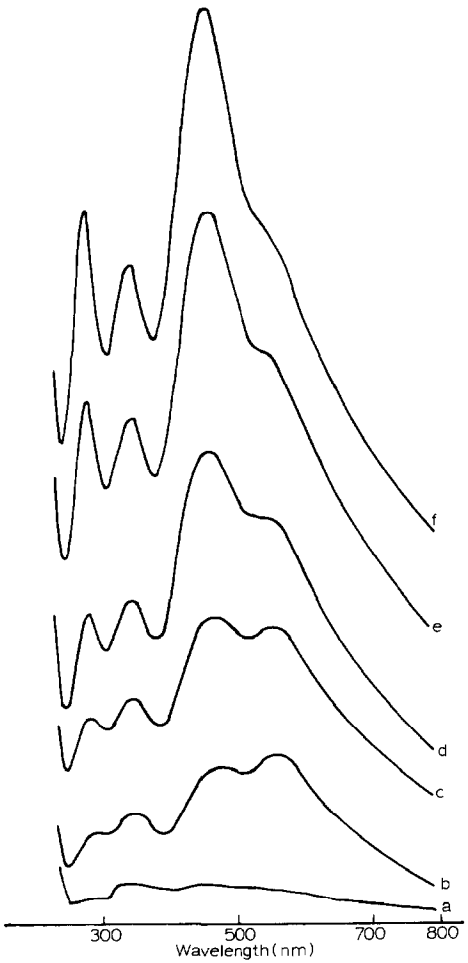

Fig. 5. Changes in the absorption spectrum of the amylose–iodine complex with progressive increase in the amount of added iodine. To a solution (2 mL) of the complex (0.1456 g L^{-1}) was added saturated aqueous iodine, and the volume was made up to 10 mL: volume of aqueous iodine added: (a) nil; (b) 1 mL; (c) 2 mL; (d) 4 mL; (e) 6 mL; (f) 8 mL:

The foregoing results present a picture of the solid amylose–iodine complex that differs in many respects from that which is widely accepted. Anhydrous V-amylose is a porous solid that can absorb a variety of organic and inorganic vapours. Thus, iodine molecules will enter and fill the space in the helices. However, the results do not accord with the formation of a stoichiometric complex and the widely held view of one iodine molecule for each turn of the helix. The bonding between iodine and amylose is weak, so that iodine is readily lost by the complex. On the other hand, water vapour is rapidly and strongly absorbed by amylose.

The evidence from the above study indicates that, in the solid complex, the iodine is present in the helix as iodine molecules, although Teitelbaum et al.[26] have presented evidence that it is the I_5^- ion. The two conclusions are not necessarily incompatible, since the iodide ion necessary for the formation of I_5^- ions in the solid complex was considered[26] to be produced by the hydrolysis or alcoholysis of the iodine, whereas the amylose studied here was rigorously freed from water and alcohols.

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