5-1962

Complexing of Sugars and Polyhydroxy Alcohols with Molybdenum (VI)

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COMPLEXING OF SUGARS AND POLYHYDROXY ALCOHOLS WITH MOLYBDENUM (VI)

by

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A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Chemistry

UTAH STATE UNIVERSITY
Logan, Utah

1962

ACKNOWLEDGMENT

The author wishes to express great appreciation to Dr. J. T. Spence for his continued guidance and cordial instruction during the course of this study.

Grateful acknowledgment is also made to Dr. Garth Lee and Dr. G. O. Larson for their reviewing of this thesis. Thanks are also due to Mr. S. F. Yang for his encouragement and help.

I am indebted to Utah State University Research Council, and to Research Corporation for financial support.

Su Chin Kiang

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INTRODUCTION

Molybdenum is very important in the life processes of both plants and animals. It acts as a catalyst in promoting and controlling many biological reactions in living cells, but exactly what it does and how it functions are not well understood. In the past because of the obvious complexity of the reactions concerned and the extremely minute quantities of molybdenum involved, its presence was long undetected. Lately, molybdenum has drawn special attention on account of its effects on metabolic processes, particularly of plants. In this regard, molybdenum has been shown to be present in four enzymes: nitrate reductase (33), xanthine oxidase (39), aldehyde oxidase (28), and hydrogenase (41).

In living cells, carbohydrate metabolism occurs. These carbohydrates are mainly hexoses or phosphate derivatives of hexoses. In addition, many biochemical compounds contain ribose or a derivative as part of the molecule (ATP, adenosine, FAD, DNA, RNA, etc.). These compounds may complex with molybdenum and it is of interest to determine if the sugar moiety is involved. Since molybdenum(VI) forms complexes with organic oxygen, nitrogen, and sulfur compounds, it seems reasonable that there may be complexes of molybdenum with many sugars and sugar alcohols. Some complexes of molybdenum and organic compounds have been found, such as those with α -hydroxy organic acids (37), polyhydroxy organic compounds (38), riboflavin (44), adenosine triphosphate (6), ethylenediaminetetracetic acid (35), and polyhydric phenols (10).

There is no quantitative data available on the stability constants (5)

for any molybdenum complex with sugars or polyalcohols. The determination of stability constants is of great importance in the study of complex compounds, since this is a promising approach to a knowledge of their structures and possible modes of operation in biochemical systems.

REVIEW OF LITERATURE

Complexing tendencies of polyhydroxy organic compounds

Traube and Kuhbier (46) in 1932 first investigated ferric-mannitol complexes which were precipitated as barium salts by barium chloride. Barium could be replaced by calcium. Also, barium salts of sorbitol, glycerol and the calcium salt of the sorbitol complex were prepared. Aluminum and chromium were also substituted for iron in the preparation of mannitol complexes. In 1933, the same authors obtained complex compounds of trivalent iron, chromium, and aluminum, antimony, and bismuth, in the form of calcium, barium and selenium salts, by the reaction with and aqueous alkali solution of an aliphatic polyhydric alcohol containing at least three hydroxyl groups on three adjacent carbon atoms (such as mannitol, glycerol, erythritol, xylitol, sorbitol or dulcitol) with a salt or hydroxide of trivalent iron, chromium, aluminum, antimony or bismuth and precipitation of the complex compounds formed by the addition of an alkali earth metal salt or hydroxide. Kubota (25) reported copper polyalcohol complexes. He stated that mannitol formed complexes most readily, followed by glycerol, ethylene glycol, pentaerythritol and pinacol. Some of the copper complexes of polyalcohols were isolated and analyzed by Lieser and Ebert (26). They determined the composition of the complex. For example, the molar ratios of polyol to copper are: glycol, 1:1; glycerol, 1:1.5; adonitol, 1:2.5; hexitol, 1:3; erythritol, 1:2. Böeseken (7) reviewed the complexes of boric acid with polyols. He stated that aliphatic polyols with adjacent hydroxyl groups complex with boric acid if

they are cis forms. Complex formation between mannitol with molybdenum was studied by Frey (19), Rimbach (40), and Tanret (43). Frey described a method for the preparation of a solid mannitol-molybdenum complex. Rimbach found an increase in acidity of glycol and glycerol solutions upon addition of molybdic acid. Tanret (43) found that the optical rotation of mannitol was affected by ammonium molybdate, the specific rotation of mannitol changing from -0.25 to 52.5 degrees of arc by addition of molybdate. The molar ratio of molybdate to mannitol in the complex was determined as being 2.0. Lately, Richardson (38) found that molybdic acid prepared by ion exchange formed complexes with erythritol, gluconic, galactonic and arabonic acid. No tendency to form a complex was shown by glycerol, inositol and pentaerythritol. His work indicated that molybic acid or molybdate ions complex only with linear polyhydroxy compounds containing four or more hydroxyl groups on adjacent carbon atoms. A recent paper by Bourne, Huston and Weigel (8) reported studies on complexes between molybdate and acyclic polyhydroxy compounds by an inophoresis method. They concluded that the complexes had a maximum stability at acidic pH values and were decomposed by alkali. The Ms values (distance of migration of compound divided by distance of migration of sorbitol) of polyhydroxy compounds were determined, and they concluded that there was complex formation when Ms was larger than 0.1.

Complexes of molybdate with polyhydroxy phenols were investigated by Buchwald and Richardson (10) in 1959. The nature of the colored complexes of molybdate with polyhydroxy phenols were determined spectrophotometrically. A 2:1 catechol : molybdate complex was indicated over a pH range of 2 to 7. With gallic acid at pH 4 to 7, a 2:1 ratio of phenolic compound to molybdate

was found, whereas at lower pH the ratio was 1:2. A ratio of 1:1 at lower pH and 2:1 at higher pH values was found for 3,4-dihydroxybenzoic acid. In the same year a study of the chelate forming reaction between some phenolic compounds and anions formed by molybdenum(VI), tungsten(VI), vanadium(V), bismuth(III) and tin(IV) was made by Halmekoski (20). The phenolic compounds he used were catechol, 3,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzoic acid, pyragallol, gallic acid and other phenolic compounds. The more ionic phenolic chelates had higher migration rates in paper electrophoresis and lower Rf values in paper chromatography. After chelating with molybdate, tunsten, vanadiate or phosphomolybdate anions, 3,4-dihydroxybenzaldehyde, 3,4-dihydroxybenzoic acid, pyrogallol and 3,4,5-trihydroxybenzoic acid showed new absorption maxima. Borate and arsenite produced few changes and molybdate no change in the spectrum of catechol. Also, some formation constants of the chelates were determined spectrophotometrically.

Traube and Kublier (45) also investigated sugar complexes, such as barium-ferric glucose, mannose, maltose, lactose, saccharose, galactose, arabinose, glucose oxime, fructose oxime, mannose methoxime, gluconate, glycerate, erythrate, arabonate and amygdalin, etc. The corresponding sodium-ferric gluconate was also made. Lieser and Ebert (26) found copper complexes with sugars and their derivatives. The molar ratios of copper to sugar were: methyl xyloside, 1.5:1; methyl glucoside, 2:1; glucose, galactose, fructose 2:1; leveglucosan, 1.5:1; maltose, lactose, saccharose 3:1; and inositol, 3:1. Böeseken (7) concluded that aromatic hydroxy compounds complex with boric acid if they have only ortho dihydroxy

benzene structures. Also, he studied the rate of reaction of boric acid with many sugars. In 1952, Consden and Stanier (12) determined the mobilities of sugars in borate at various pH values on paper. Borate ionophoresis was studied extensively by Foster (16). Baker (4) found a method for separation of different pairs of sugars due to the different rates of elution of the sugars from charcoal columns impregnated with borate and molybdate. Use of molybdate complexes in paper ionophoresis was studied for sugars by Frahn and Mills (18), and paper ionophoresis of a number of cyclic carbohydrates in molybdate solution at pH 5.0 was made by Bourne, Hutson and Weigel (9) in 1960. The latter workers concluded that aldoses with a six membered ring system form complexes with molybdate if they possess three hydroxyl group in a cis-cis 1,2,3 triol arrangement. McDonald (29) reported the complexes of sucrose and α-methyl-D-galactoside, which contain one active diol group per molecule, and cis or trans- 1,2 cyclohexanediol with copper. In these complexes, the ratio of copper to diol was 2:1.

Complexing tendencies of other biochemical compounds

It has been shown that molybdenum functions as a part of enzymatic systems, being present in aldehyde oxidase, nitrate reductase, xanthine oxidase and hydrogenase. Molybdenum could be attached to the protein part (apoenzyme) of these enzymes or to the coenzyme, FAD. Therefore, it will be of interest to review briefly how metals in general are tied up in biochemical systems. It is known that some substances in biochemical systems bind metals with an extreme avidity (1). For example, the porphyrins bind iron and vitamin B_{12} binds cobalt very strongly.

Amino acids and peptides form a family in which the metal is also tightly bound, but with less avidity than the extreme cases just stated. A series of constants for amino acid complexes were determined by Albert (3) and the order of preference for various metallic ions was: copper, nickel, zinc, cobalt,cadmium, iron manganese and magnesium. No investigation for molybdenum has yet been reported. Some peptides were investigated by Dobbie and Kermack (14) and further explored by Rabin (36), and were found to have less avidity for metals than the amino acids.

The nucleotides in cells also combine with metals, but little work has been done to determine their constants. Smith and Alberty (42) first studied the formation of complexes of adenosine-5-mono, di- and triphosphate, orthophosphate and creatine phosphate with calcium, magnesium and manganese. Wazer and Callis (47) studied the complexing ability of phosphate and concluded that the orthophosphate complexes of alkali metals and alkaline earth metals were weaker than the corresponding complexes of chain or ring phosphates. Blum and Chambers (6) investigated the interaction of adenosine triphosphate with molybdate and concluded that a complex was formed.

Purines, pterines and riboflavin have avidities for metals similar to those of the amino acids. The potentiometric titration technique was used in a study of the behavior of adenine toward metal ions by Calvin and Wilson (11), and the formation constants were determined by Harkins and Freiser (21). The logarithm of the first stability constant found for copper with adenine was about 8 and those for nickel and cobalt about 5. Liquier-Milward (27) isolated the 1;1 cobalt adenine complex and

Albert (2) titrated adenine in the presence of copper (II) and cobalt (II) and concluded that a weak complex was formed with copper.

Albert (2) discovered that riboflavin could form stable chelation compounds with metals on the basis of titration data. The first partial stability constants of the complexes when one atom of the metal is bound to one molecule of riboflavin were determined for the complexes of riboflavin with iron (II), copper (II), nickel (II), zinc (II), and cobalt (II) as being 7.1, 6.5, 4.1, 5.6, and 3.9, respectively. The overall stability constants (two riboflavin for one metal) were not obtained because of the insolubility of these complexes. However, Hemmerich and Fallab (22) criticized Albert's work and concluded that riboflavin forms only weak copper (II) complexes with a stability constant of log K smaller than 4.0. Tocatlian (44) reported the interaction of riboflavin with molybdenum in 1960. He concluded that molybdenum (VI) formed a very strong complex with the riboflavin molecule, which was in accordance with the general formula (riboflavin)$(metal)_2$ found by Foye and Lange (17) for a number of other solid metal complexes of riboflavin.

Niericker and Treadwell (34) prepared a solid complex of 8-hydroxyquinoline with molybdenum. Metal chelate stability constants of 8-hydroxyquinoline have been measured by Johnson and Freiser (24). Their results indicated that for 8-hydroxyquinoline and analogous substances, five membered ring chelates were more stable than chelates having six membered rings.

Scope of the present work

As can be concluded from this survey, very little has been done with molybdenum complexes with important biochemical compounds. This work is urgently needed (1) since molybdenum plays an important role in biochemical reactions. Complexes of sugars and polyols with molybdenum, as stated before, were found by Bourne (8, 9). The complexing tendencies of sugars and polyols could be observed from the Ms values in their work, which appeared when this investigation was nearly complete, but the formation constants and molar ratios were not determined.

EXPERIMENTS

Materials

Molybdenum (VI). Sodium molybdate (Baker certified, 99.5%) was used in the present work after drying at 105°C for 24 hours. Purity was determined to be 99.7% by the ∝-benzoinoxime method (44).

Mannose, ribose, arabinose, xylose, lyxose, erythrose, arabitol, dulcitol, adonitol, ∝ -methyl-D-mannopyranoside, ∝ -methyl-D-glucopyranoside, and 2-deoxy-D-ribopyranoside. These compounds were purchased from Nutritional Biochemicals Corporation, Cleveland, Ohio, and were used without any further treatment.

	Melting point (literature reported) °C	Melting point °C
mannose	132	130 - 131.5
ribose	86 - 87	85.5 - 87.0
arabinose	155.5 - 156.5	156 - 157
xylose	153 - 154	151 - 152
lyxose	106 - 107	112 - 115
arabitol	103	103
dulcitol	188.5	186 - 188
adonitol	102	101 - 99
∝ -methyl-D-mannopyranoside	194	192 - 194
∝ -methyl-D-glucopyranoside	168	167 - 168

Mannitol. Purchased from Fisher Science Company, and used without treatment; melting point 166.5 - 167° C; reported melting point 166 - 168° C.

Glucose, sorbitol. Purchased from Eastman Kodak Company and used without treatment. Reported melting point: anhydrous sorbitol, 110 - 111° C, hydrate 75° C and 87 - 95° C from alcohol; glucose 146° C. Melting points of the samples used were 146 - 148° C for glucose and 93 - 94.5° C for sorbitol.

Galactose. Anhydrous form purchased from Chemical Commerce. It was used without treatment. Reported melting point 165° C, and melting point of the sample 158 - 160° C.

Adenosine, ATP (adenosine triphosphate), AMP (adenosine monophosphate). Purchased from Nutritional Biochemical Corporation, Cleveland, Ohio. Used without further purification.

Adenine sulfate. Purchased from the Matheson Corporation, Joliet, Illinois. Used without treatment.

Instrumental Work

pH measurement. pH determinations were made with a Beckman, model GS, pH meter and a Colman Model 28 pH meter, duly calibrated against Beckman standard buffers of pH 6.8 and 4.0, respectively.

Polarimetric measurements

A Schmidt & Haensch polarimeter was used for polarimetric measurements. This instrument reads to $\pm$.01 degrees of arc, and the precision is of the order of $\pm$.02 degrees of arc. During the experiments, the temperature was kept at 25° C $\pm$.2° C. Jacketed tubes of 40 cm. and 20 cm. were used. The sodium lamp was used as light source with a wavelength of 5890 Å.

Methods for determination of molar ratios. Job's method of continuous variations (13, 23) was successfully adapted to polarimetric studies. The sum of the concentration of the metal ion and complexing compound is kept constant and their relative proportion is changed. Considering the formation of a complex MXn, where M is a metallic ion and X is a complexing agent:

$$M + nX \rightleftharpoons MXn$$

At equilibrium,

$$K = \frac{(M)\,(X)^n}{(MXn)}$$

where ( ) represents activities, approximately equal to concentration.

Let

$$Cm + Cx = C$$

$$Cx = fC$$

where f is the molar fraction of the ligand in the mixture, Cx is the total concentration of ligand, Cm is the total concentration of the metal and C is the total concentration of both ligand and metal (constant), then,

$$(X) = Cx - n(MXn) = fC - n(MXn)$$

$$(M) = Cm - (Mxn) = (1 - f)C - (MXn)$$

$$(MXn) = \frac{[(1-f)C - (MXn)]\,[fC - n(MXn)]^n}{K}$$

$$K\,\frac{d(MXn)}{df} = [f\,C - n(MXn)]^n\,[-C - d(MXn)/df] + [(1 - f)C - (MXn)]\,[C - n\,d(MXn)/df]\,n\,[fC - n(MXn)]^{n-1}$$

If $d(MXn)/df = 0$, (maximum concentration of MXn), then

$$fC - n(MXn) = 0,$$

and $(1-f)C - (MXn) = 0,$

so $n = f/(1-f)$

In other words, for a constant total concentration of metal and complexing agent, the concentration of complex is greatest when the metal and complexing agent are brought together in the ratios in which they exist in the complex. Therefore, plotting a physical property of the complex which changes with concentration of complex present, such as its absorption or

optical rotation, imposing the restriction that Cm + Cx = C(total concentration of metal and complexing agent being constant), a maximum is obtained at the point where the metal ion and the complexing agent are present in the same ratio as in the complex.

Molar ratio method (32). The concentration of one component, for instance the metal ion, is kept constant and the amount of complexing agent is varied. The observed optical rotation of the different mixtures is plotted against the concentration ratio of complexing agent to metal. As the ratio of complexing agent per constant quantity of metal increase, the more complex is formed and consequently the optical rotation change is greater. The optical rotation stops changing at a point where any further addition of complexing agent has no effect; that is, a point where essentially all the metal has combined with the complexing agent. The extent of the curvature of the plot depends, of course, on the degree of dissociation of the complex. The stoichiometric formula of the complex can be found by extrapolation of the straight line portions of the graph. The point at which these lines intersect corresponds to the ratio of ligand to metal in the complex. For example, for a complex having the molar ratio of 1:1

$$(MX) = C\,(\alpha/\alpha m)$$

$$(M) = (X) = C - (MX) = C\,(1 - \alpha/\alpha m)$$

$$K = \frac{(M)\,(X)}{(MX)} = \frac{(1 - \alpha/\alpha m)^2}{\alpha/\alpha m}\,C$$

where ( ) represents the concentration, C, initial concentration of ligand and metal; α represents the observed optical rotation and αm, the maximum optical rotation obtained by extrapolation.

Since α/α_m depends on C, because the degree of dissociation of the complex increases with increasing dilution, it is advisable to determine K at a number of values of C. The agreement among the values of K thus found gives a valuable indication of the reliability of their mean. The best values are generally secured when α/α_m is between about 0.7 to 0.9 (30).

Technique. The required amounts of complexing agents and the metal salt were weighed precisely, and the respective solutions were prepared by dissolving the weighed quantities in buffer or water and diluting to the mark in volumetric flasks. These stock solutions of known molarity were used in preparing the different mixtures required. Precautions were taken to prevent alteration of the solution (such as keeping it in the dark, at right pH, not longer than necessary). Before taking any readings, the stock solutions were allowed to stand for one day to allow any mutarotation to occur.

The desired amount of stock solution of complexing agent and metal salt was pipetted into flasks containing the correct amount of buffer or water. The pH of the resultant solution was measured with the pH meter. The temperature of the solution was also measured in the jacketed polarimetric tube, before and after readings were taken. The solutions were buffered with sodium acetate-acetic acid or sodium monochloroacetate-monochloroacetic acid.

Comparison of continuous variations and molar ratio methods. There are several advantages of the molar ratio method over the continuous variations method:

(a) The amount of one of the reactant is held constant, which simplifies the preparation of solutions.

(b) It is suitable for higher ratio complexes. In the continuous variations method, the ratios of 4:1, 5:1, 6:1 are 0.8, 0.83, 0.857 and an error of 2% in preparation of solution or in the estimation of the position of the maximum is sufficient to produce a unit change in observed molar ratio. Six to 10% error is necessary to produce a unit change in the molar ratio method.

(c) In the continuous variations method, the relative concentration of a particular complex is decreased with increasing divergence of the molar ratio from 1:1. This increases the dissociation which affects the localization of the maximum of the complexes.

Several advantages of continuous variations method over the molar ratio method are:

(a) It is applicable to a system (by carefully choosing conditions), in which more than one compound is formed from a given pair of components.

(b) If the dissociation constant of the complex is too large, the molar ratio plot will become a smooth continuous curve and it will be impossible to locate the "stoichiometric" point. This does not occur with the continuous variations method.

(c) It facilitates the use of small volumes when one of the reagents is available in limited supply.

Polarographic measurements

Polarographic waves were obtained with a Sargent Polarograph, Model XV. The half wave potentials reported were obtained by extrapolations of

the nearly vertical portions of a wave to intersect extension of the residual current and diffusion current plateaus. The projection of the midpoint of nearly vertical segment onto the voltage axis gives the half wave potential.

Air was removed from solutions prior to electrolysis at the dropping mercury electrode with nitrogen gas which had been deoxygenated by passing through a vanadyl sulfate-amalgated zinc purification train (31). The cell used was an H-cell, containing a reference saturated calomel electrode connected to the dropping mercury electrode by an agar bridge.

Spectrophotometric measurements

For spectrophotometric measures the Beckman quartz spectrophotometer, Model DU, and the Perkin-Elmer recording ultraviolet spectrophotometer, Model 4000, were used. The curvettes used in all cases were 1 cm. in length, and 3 ml. capacity.

Ion exchange method

An ion exchange method may be used for the quantitative determination of formation constants of metal chelates and metal complexes. This method has several advantages: a very low concentration of material may be employed; it is suitable for water-soluble chelates, particularly in cases where the formation constants is so high that only traces of free metal ion can exist in equilibrium with the chelating agent; sugar-molybdenum complexes may be investigated at higher pH values where the optical rotations are very low.

The synthetic organic anion exchanger, Dowex 2x8, 100 - 200 mesh, in

the chloride form was used. The resin was washed before use with sodium hydroxide and then hydrochloric acid. The pH of the solution was adjusted by hydrochloric acid. A column process was not used because molybdenum blue formed in the column before the washing effluent was free from excess sugar. Rather, a batch process using two flasks was used. One of the flasks contained a known amount of sugar (mannose) and the anion exchanger and the other flask had the same amount of sugar, the anion exchanger and molybdate, the sugar being in excess. After shaking for three hours, they were centrifuged and the concentration of the sugar in solution in both flasks were determined. The results indicated that there was no significant difference in concentration of mannose after and before shaking with the anion exchanger. N,N-diethyl amino.HCl ethylcellulose, anion exchanger, was also used for this investigation, but it gave the same result as the other exchanger. Probably the weak negatively charged complex was broken down and the molybdenum anion species adsorbed by the exchanger.

Redox potential measurements

Complex formation will affect the redox potential for a metal in solution. Thus the reduction potential of a metal ion in equilibrium with ligand is usually decreased by complex formation. The reduction potential of the Mo(VI)-Mo(V) couple has been determined against a hydrogen electrode and a calomel electrode over a range of hydrochloric acid concentration from 8N to smaller than 0.01M by El-Shamy (15). His method, with little modification was used. It involved the following cell:

$$\text{Au} \mid \text{Mo(VI), Mo(V), HCl(1M)} \;\vdots\; \text{HCL(1M), } Hg_2Cl_2 \mid \text{Hg}$$

under nitrogen atmosphere

$$E = E^{\circ} - 0.59 \log \left([Mo(VI)] / [Mo(V)] \right) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$K = \frac{[L]\,[Mo(VI)]}{[C]}$$

$$[Mo(VI)] = [C]\,K / [L] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where $[L]$ = concentration of complexing agent

$[C]$ = concentration of complex

Substituting equation (2) into (1),

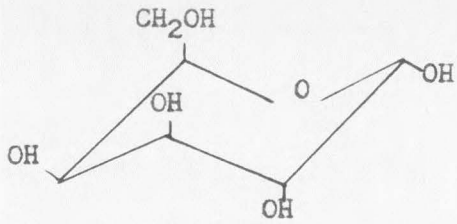
$$E = E^{\circ} - 0.059 \log \frac{[C] \cdot K}{[L]\,[Mo(V)]}$$

When the concentration of molybdenum (VI) and molybdenum (V) are the same, the electrode potential of the system will equal the standard potential of the system at the temperature of 25° C. This allows determination of E° . K value and then can be calculated by knowing concentrations of ligand, complex and molybdenum (V) (ligand is in large excess). In order to prepare the cell, a solution of sodium hydroxide free from oxygen was introduced into the solution of molybdenum (V). A brown precipitate formed. This precipitate may be quinquevalent molybdenum hydroxide, and the standard electrode potential could not be obtained at these concentrations. Lower concentrations could not be used because of the time necessary to reach equilibrium.

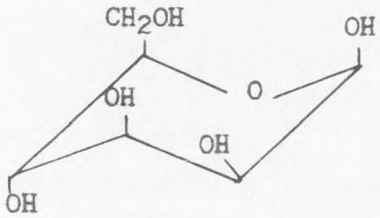
pH titrations

All metal chelates may be considered as formed by the displacement of one or more acidic protons of the chelating agent by a metal ion. Thus the addition of the complexing agent to a solution of metal salt causes a drop in the pH. Titration curves of mixtures of mannitol and sodium

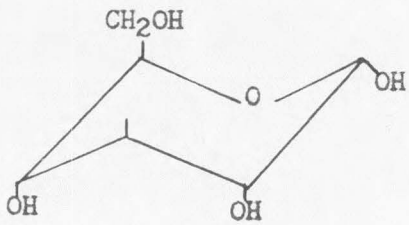
molybdate with hydrochloric acid were obtained. Due to the great complexity of the curves, however, a reasonable interpretation was impossible. This complexity is due to the reaction of molybdate with protons to form dimers, tetramers, etc.



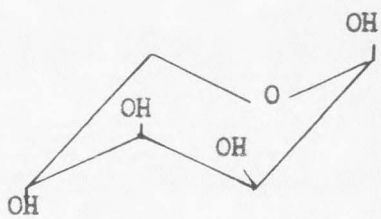
α -D-galactose



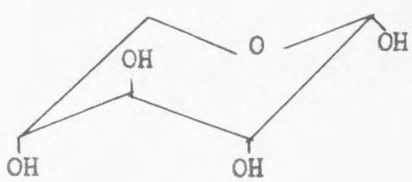
β -D-mannose



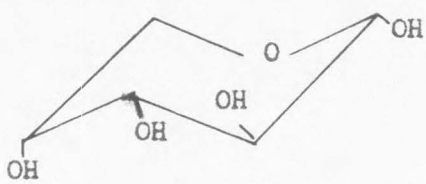
α -D-glucose



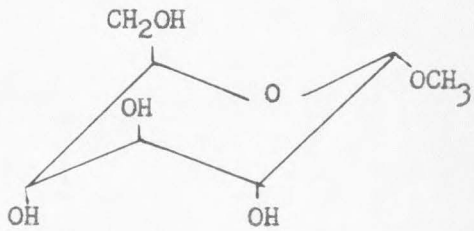
β -D-lyxose



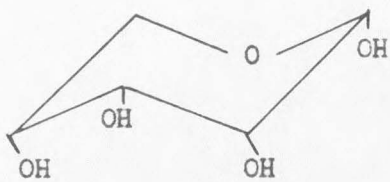
α -D-xylose



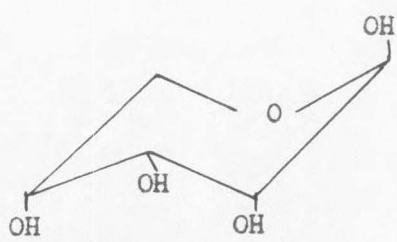
α -D-arabinose



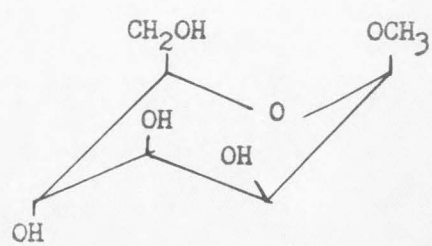
α -methyl-D-glucopyranoside



α -D-ribose



β -D-ribose



α -methyl-D-mannopyranoside

Figure 1. Structural formulas

RESULTS

Polarimetric studies

The effect of pH on the specific rotation of the polyol-molybdenum (VI) complexes is shown in Figure 2. The pH values were adjusted by hydrochloric acid. At a very low pH, molybdenum blue is formed. For instance, in the case of mannitol, this pH is around 0.5. From the figure, the optical rotation increases with increasing acidity. This may be interpreted as indicating that the complex is stronger at lower pH values.

Table 1. Effect of pH on the specific rotation of sorbitol-molybdenum (VI) complex[a]

pH	Degrees of arc $[\alpha]$
0.62	43.7
1.1	61.8
1.4	75.6
1.8	75.8
2.4	71.2
2.9	60.3
3.7	36.5
4.7	15.95
5.5	12.4
6.7	8.8
7.6	0.16

[a]Molar ratio of sorbitol to molybdenum (VI) 1:1.
Length of tube 20 cm.
Temperature 25° ± .2° C.
Wavelength 5890 Å.

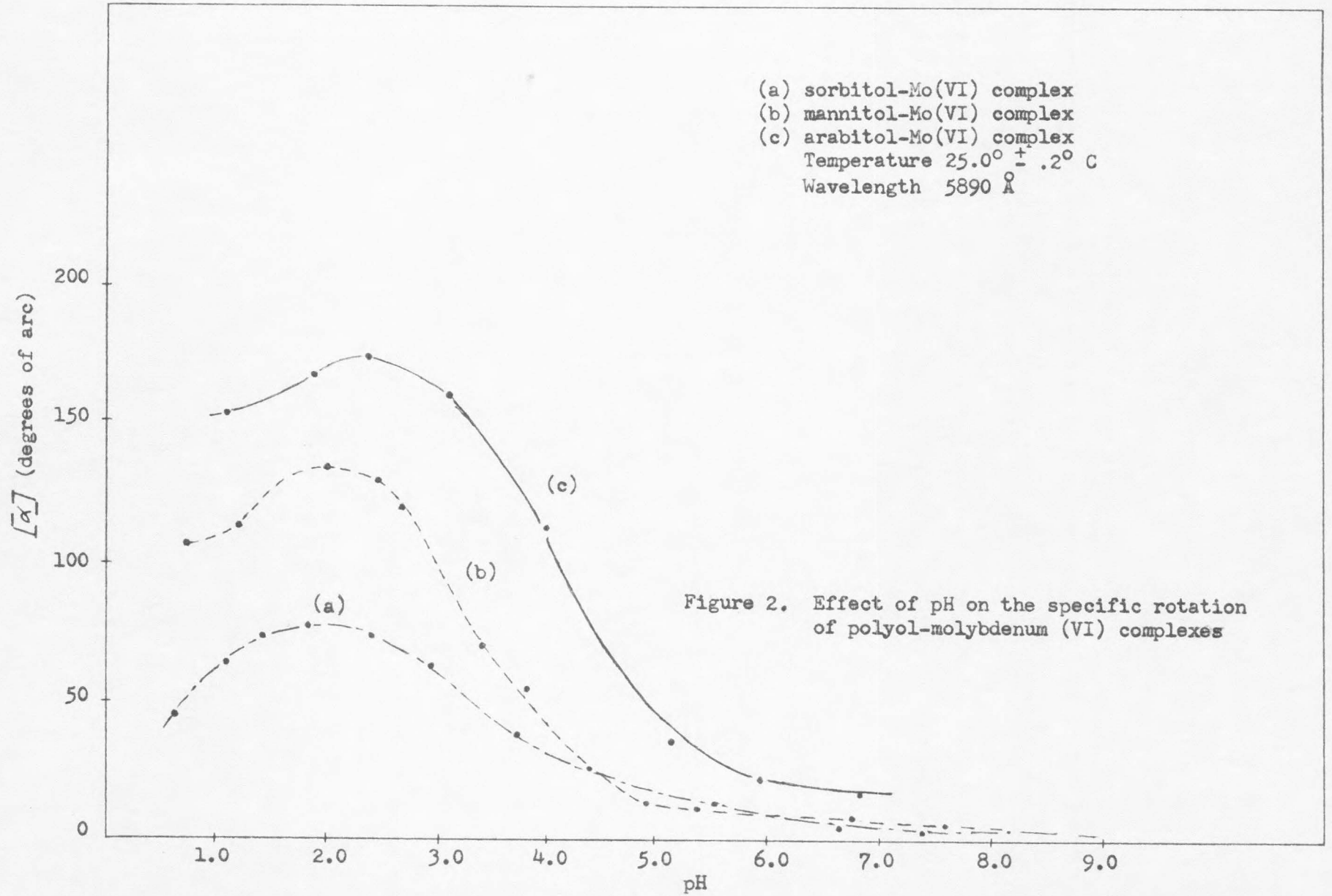


Figure 2. Effect of pH on the specific rotation of polyol-molybdenum (VI) complexes

The effect of pH on the specific rotation of the sugar-molybdenum (VI) complexes is shown in Figure 3. The specific rotation of the complex changes with different acidity, and there is maximum around pH 5.0 where the complex is stronger. Below a certain pH, molybdenum blue also is formed.

Table 2. Effect of pH on the specific rotation of mannitol-molybdenum (VI) complex[a]

pH	Degrees of arc $[\alpha]$
0.75	107.4
1.20	112.0
2.00	134.3
2.70	119.6
3.40	68.2
3.85	54.9
4.30	24.7
4.90	15.4
5.40	14.3
6.75	6.03
7.35	4.67
8.50	3.19

[a]Molar ratio of mannitol to molybdenum (VI) 1:2.
Length of tube 20 cm.
Temperature 25° ± .2° C.
Wavelength 5890 Å.

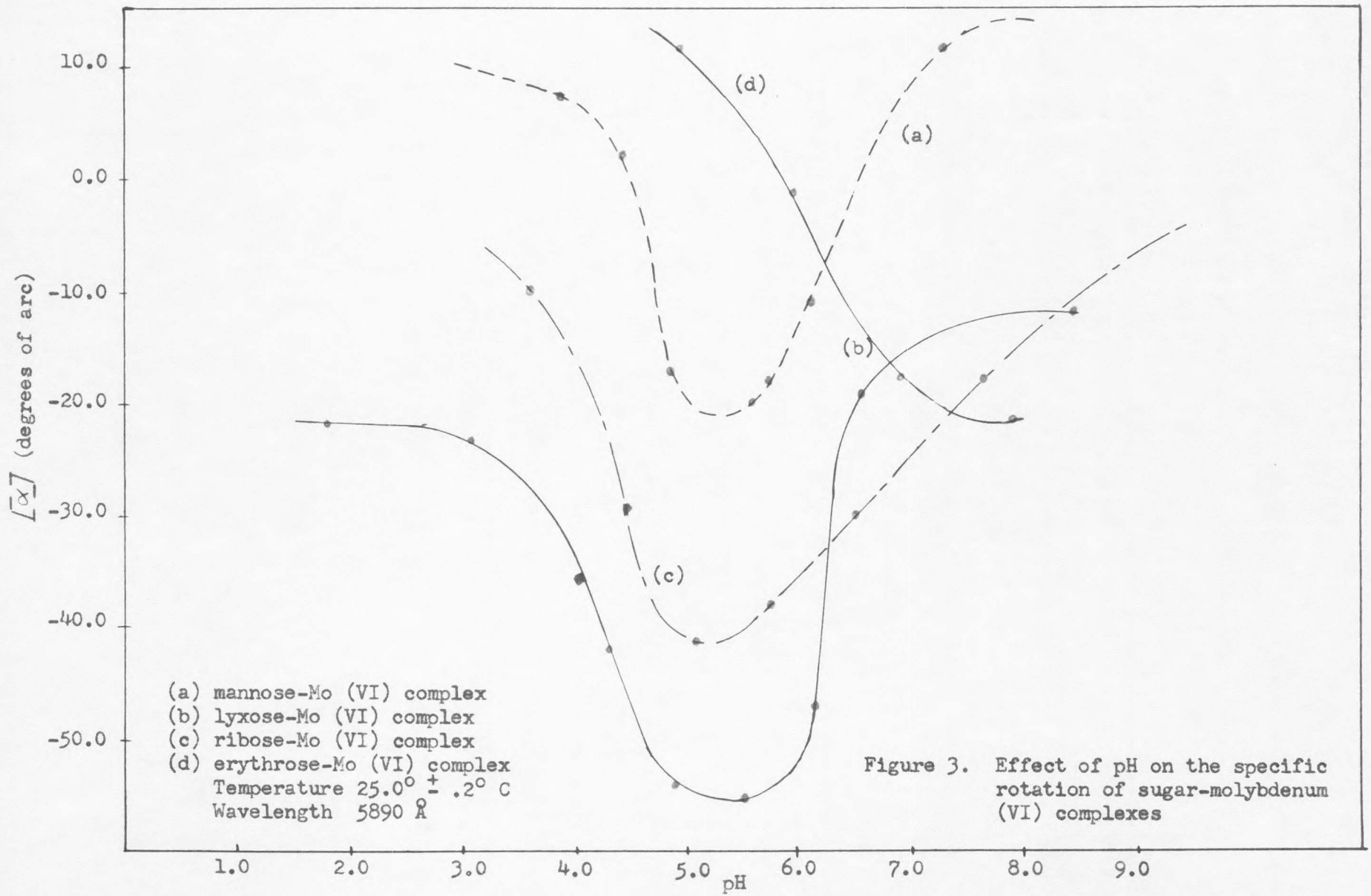


Figure 3. Effect of pH on the specific rotation of sugar-molybdenum (VI) complexes

Table 3. Effect of pH on the specific rotation of arabitol-molybdenum (VI) complex [a]

pH	Degrees of arc $[\alpha]$
1.20	154.0
1.90	167.0
2.40	174.0
3.10	160.5
4.00	112.0
5.10	32.9
5.90	25.0
6.80	7.9

[a]Molar ratio of arabitol to molybdenum (VI) 1:1.
Length of tube 20 cm.
Temperature 25° ± .2° C.
Wavelength 5890 Å.

Table 4. Effect of pH on the specific rotation of mannose-molybdenum (VI) complex[a]

pH	Degrees of arc $[\alpha]$
3.9	6.93
4.5	1.94
5.0	-19.75
5.6	-19.90
5.7	-17.70
5.9	-15.30
6.1	-11.10
7.3	12.20
8.0	13.90

[a]Molar ratio of mannose to molybdenum (VI) 1:1.
Temperature 25.0° ± .2° C.
Wavelength 5890 Å.
Length of tube 20 cm.

Table 5. Effect of pH on the specific rotation of ribose-molybdenum (VI) complex[a]

pH	Degrees of arc $[\alpha]$
1.8	-22.0
3.1	-23.0
4.3	-42.0
4.8	-54.2
5.5	-55.7
6.2	-47.0
6.5	-19.0
8.4	-12.0

[a]Molar ratio of ribose to molybdenum (VI) 1:1.
Temperature 25.0° ± .2° C.
Length of tube 20 cm.
Wavelength 5890 Å.

Table 6. Effect of pH on the specific rotation of lyxose-molybdenum (VI) complex[a]

pH	Degrees of arc $[\alpha]$
3.60	-10.34
4.30	-29.30
5.10	-41.30
5.75	-38.00
6.50	-30.00
7.60	-17.70

[a]Molar ratio of lyxose to molybdenum (VI) 1:1.
Temperature 25.0° ± .2° C.
Wavelength 5890 Å.
Length of tube 20 cm.

Table 7. Effect of pH on the specific rotation of erythrose-molybdenum (VI) complex[a]

pH	Degrees of arc $[\alpha]$
5.0	10.96
6.0	- 1.52
6.9	-18.54
7.9	-21.60

[a]Molar ratio of erythrose to molybdenum (VI) 1:1.
Temperature 25.0° ± .2° C.
Length of tube 20 cm.
Wavelength 5890 Å.

Besides the above compounds, the following compounds gave little or no change in optical rotation in the presence of molybdenum:

Polyols	Sugars and derivatives
ribitol	glucose
dulcitol	galactose
	arabinose
	xylose
	2-deoxy-D-ribopyranoside
	α-methyl-D-glucopyranoside
	α-methyl-D-mannopyranoside

All polyols except ribitol and dulcitol, which are meso forms and optically inactive, complex with molybdenum (VI). Richardson (37) has concluded that the polyols complex with molybdenum (VI) if they possess four or more hydroxyl groups on adjacent carbons. Their ability to complex with molybdenum (VI) was also shown in Bourne's work (8).

Analysis of the results with the sugars revealed that aldohexoses and aldopentoses with a pyranoside ring form complexes with molybdenum (VI) if they possess three hydroxyl groups in a cis-cis (axial, equatorial, axial), 1,2,3 triol arrangement. This is represented by the structures of mannose, ribose, and lyxose. Substitution or replacement of one of the hydroxyl groups of this system destroys the ability to form a complex. This is proven by α-methyl-D-mannopyranoside and 2-deoxy-D-ribopyranoside which do not complex with molybdenum (VI), and the fact that α-methyl-D-ribopyranoside does complex with molybdenum (VI), as shown in Bourne's work, since this compound still has 2(ax), 3(eq), 4(ax) triol system. This may apply to all pentoses and hexoses having the same relative positions as those of the cis-cis triol, 1(ax), 2(eq), 3(ax) system.

Table 8. Effect of concentration of chloroacetic acid buffer on sorbitol-molybdenum complex[a]

Concentration of buffer (molar)	Degrees of arc α
0.5	3.66
1.0	3.21
1.5	2.83
2.0	2.57
3.0	2.09

[a] Concentration of sorbitol 0.2M.
Concentration of molybdenum (VI) 0.2M.
pH 2.7 chloroacetic acid buffer.
Temperature 25.0° ± .2° C.
Wavelength 5890 Å.
Length of tube 20 cm.

The effect of concentration of buffer on mixtures of sorbitol-molybdenum is shown in Figure 4. There may be a weak complex formed between molybdenum (VI) and the buffer. At a certain concentration of a buffer, optical rotation of a ligand (sugars or polyols) increases directly with its concentration. This means there is no interaction between the buffer and polyols and sugars.

Table 9. Molar ratio sorbitol-molybdenum (VI) complex[a]

Molar ratio of sorbitol/Mo	Degrees of arc α
0.1	0.43
0.2	1.01
0.4	2.29
0.5	2.62
0.6	2.80
0.8	2.98
1.0	2.98
1.2	2.97
1.5	2.93

[a]Concentration of molybdenum (VI) 0.25 M.
Length of tuber 20 cm.
Wavelength 5890 Å.
pH 3.2 in chloroacetic acid buffer.
Temperature 25.0° C.

This investigation of the molar ratio of the two components of the complex was made by Job's continuous variations method or the molar ratio method. Figure 5 shows the molar ratio plot of sorbitol-molybdenum (VI) complex in chloroacetic acid buffer of pH 3.2. The concentration of molybdenum (VI) is kept constant, and the concentration of sorbitol is varied. From the figure, the optical rotation increases with the increasing molar ratio of sorbitol to molybdenum. Extrapolating the straight line portions,

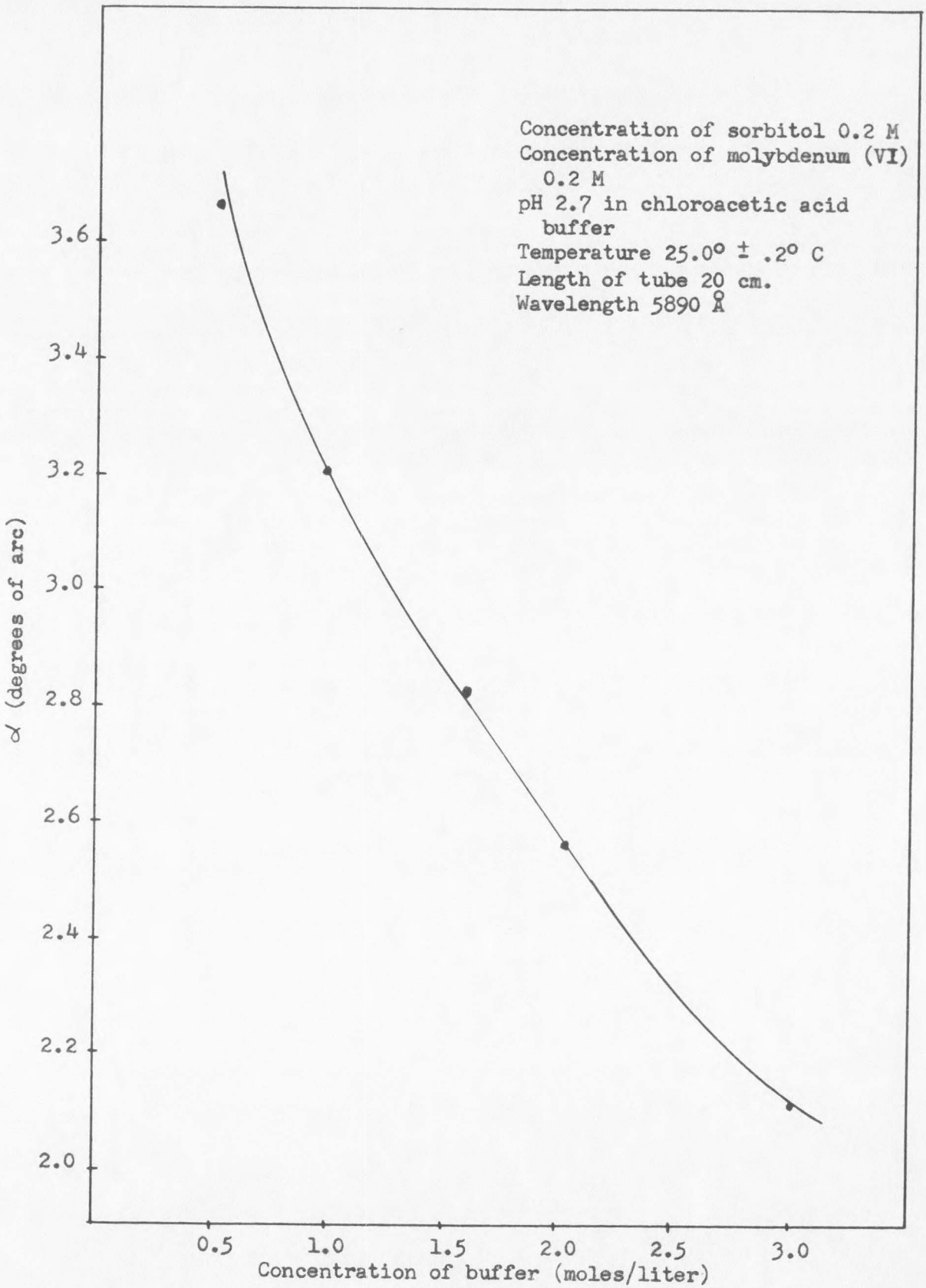


Figure 4. Effect of concentration of buffer on sorbitol-molybdenum (VI) complex

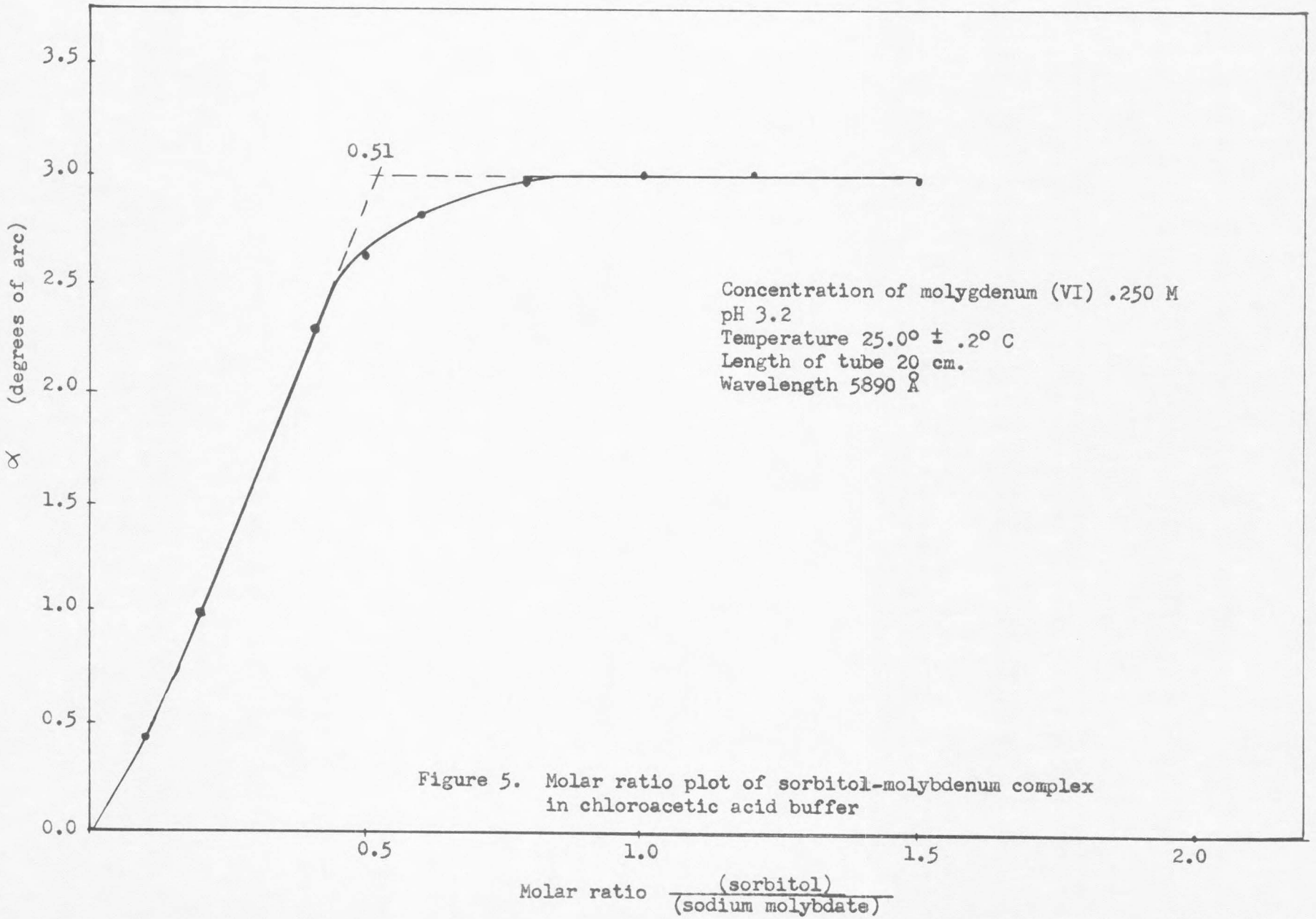


Figure 5. Molar ratio plot of sorbitol-molybdenum complex in chloroacetic acid buffer

there is an intersection at molar ratio 0.51 which is the ratio in the complex. Therefore the molar ratio of sorbitol to molybdenum (VI) in its complex is 1:2. Figure 6 is a molar ratio plot of mannitol-molybdenum (VI) complex, at a pH of 3.0 in chloroacetic acid buffer. The figure shows that the molar ratio of mannitol to molybdenum (VI) is 1:2 again.

The continuous variations plot of arabitol-molybdenum (VI) complex is shown in Figure 7. The total concentration of arabitol and molybdenum (VI) is constant, and the relative proportion of two components is varied. The pH is kept constant at 2.2 in all solutions by chloroacetic acid buffer. The optical rotation at first increases as more complex is formed and then falls off. The maximum occurs at approximately 0.6. Therefore the ratio of arabitol to molybdenum (VI) probably is 1:2. (The theoretical value would be .67). Bourne and coworkers indicated the ratio of arabitol to molybdenum (VI) was 1:2, although their data also did not show the ratio at 2.0 exactly but at 1.75.

Table 10. Molar ratio mannitol-molybdenum (VI) complex[a]

Molar ratio of mannitol/Mo	Degrees of arc α
0.12	1.46
0.25	2.94
0.40	4.64
0.50	5.53
0.60	5.80
0.80	5.87
1.00	5.90
1.20	5.90
1.50	5.90

[a]Concentration of molybdenum (VI) 0.250M.
Length of tube 20 cm.
pH 3.0 in chloroacetic acid buffer (2M).
Wavelength 5890 Å.
Temperature 25.0° C.

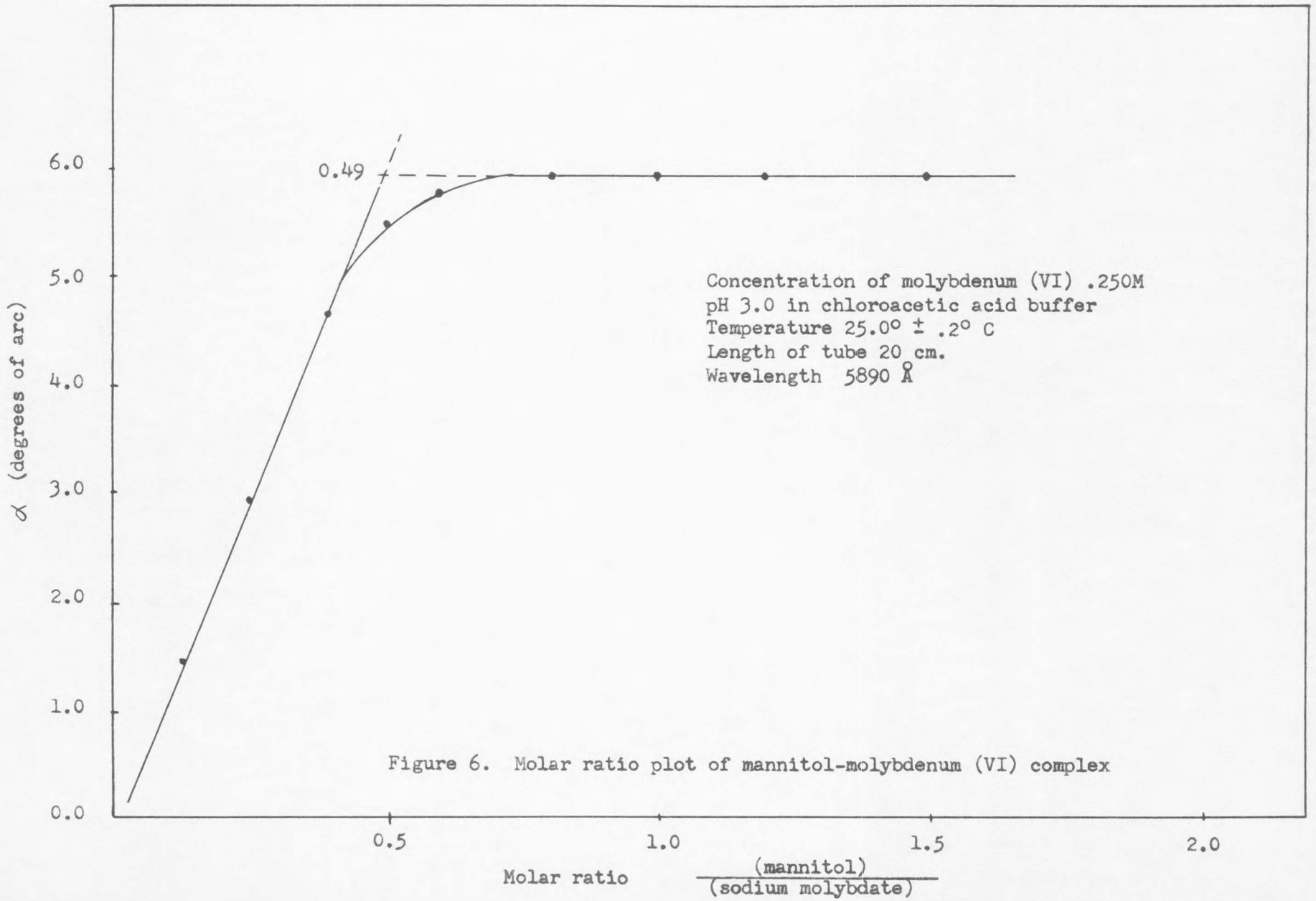


Figure 6. Molar ratio plot of mannitol-molybdenum (VI) complex

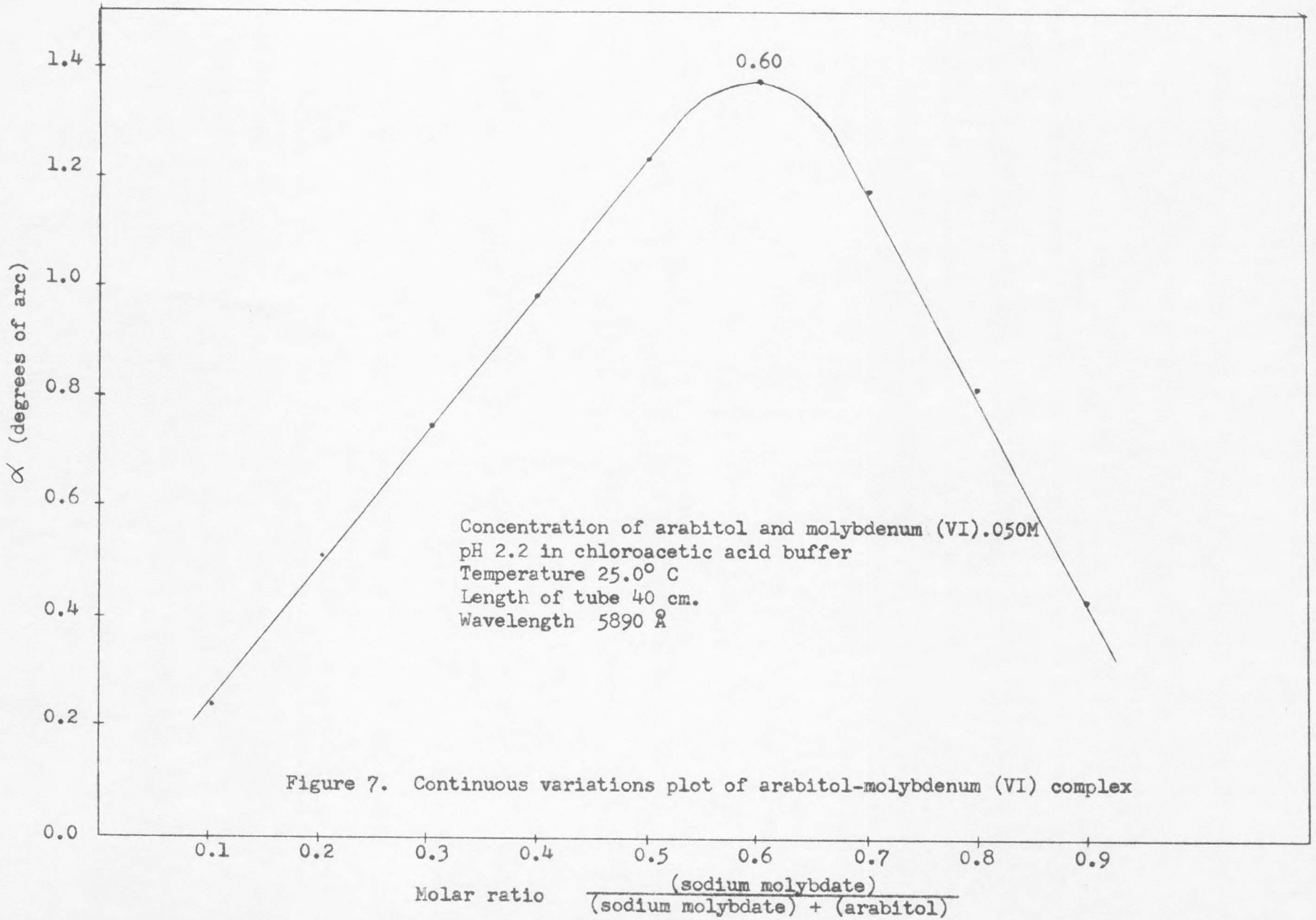


Figure 7. Continuous variations plot of arabitol-molybdenum (VI) complex

Table 11. Continuous variation arabitol-molybdenum (VI) complex[a]

Molar ratio of arabitol/ (arabitol + Mo)	Degrees of arc α
0.1	0.24
0.2	0.53
0.3	0.74
0.4	0.99
0.5	1.23
0.6	1.38
0.7	1.18
0.8	0.83
0.9	0.43

[a]Concentration of arabitol and molybdenum (VI) 0.050 M.
Length of tube 40 cm.
Temperature 25.0° C.
pH 2.2 in chloroacetic acid buffer (2M).
Wavelength 5890 Å.

The continuous variations plots of molybdenum (VI)-sugar complexes were determined. Figures 8, 9, 10, 11, and 12 are the continuous variations plots of the mannose-molybdenum (VI) complex at pH 4.4, 4.8, 5.1, 5.4, and 5.7, respectively. The maximum occur at 0.43, 0.43, 0.41, 0.41, and 0.39 in Figures 8, 9, 10, 11, and 12, respectively. From these results, the molar ratio of the two components in the complex is independent of pH over the range tested. This method was not applicable to the complex in higher pH because of insignificant optical rotations and at lower pH values because molybdenum blue is formed.

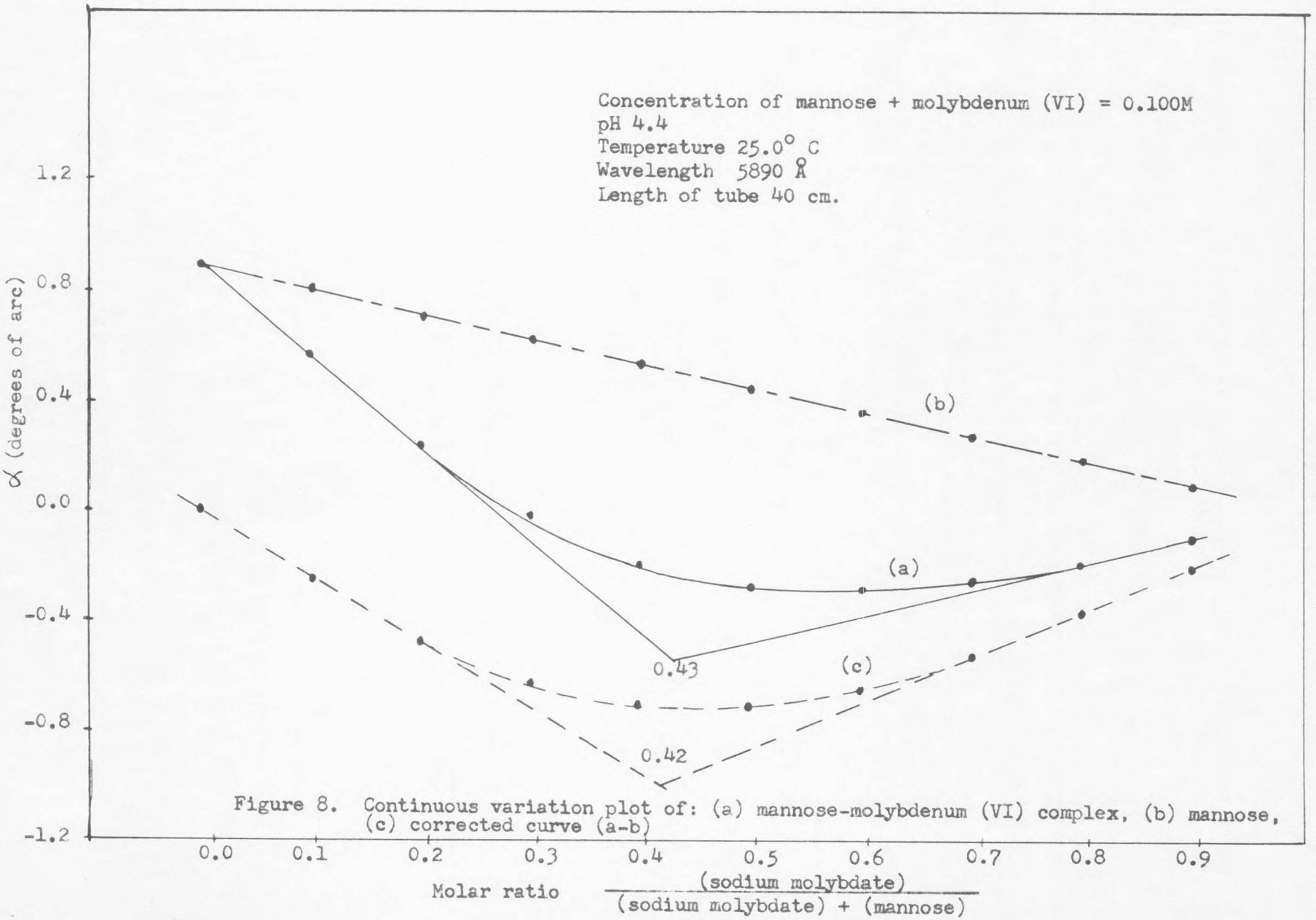


Figure 8. Continuous variation plot of: (a) mannose-molybdenum (VI) complex, (b) mannose, (c) corrected curve (a-b)

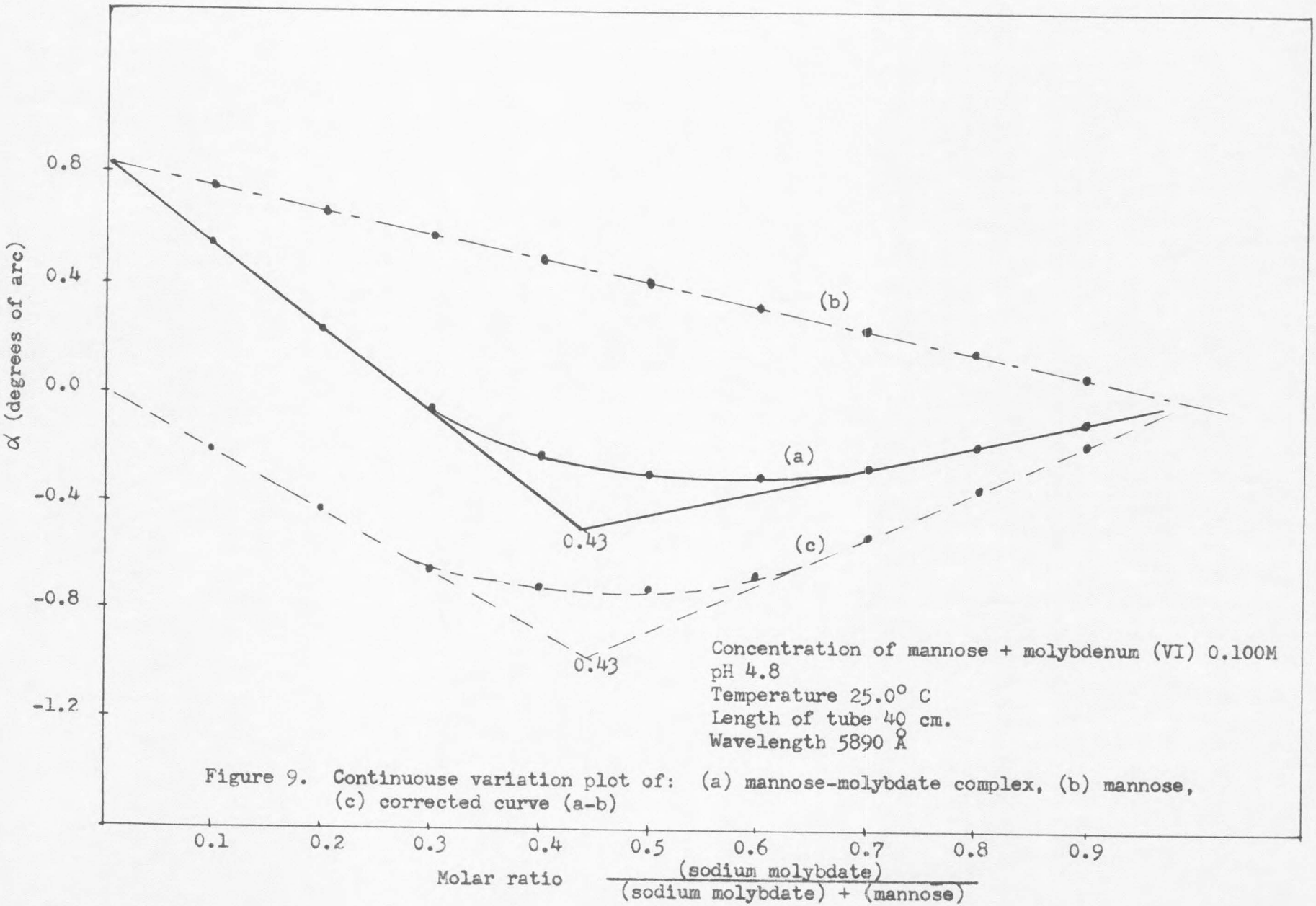


Figure 9. Continuouse variation plot of: (a) mannose-molybdate complex, (b) mannose, (c) corrected curve (a-b)

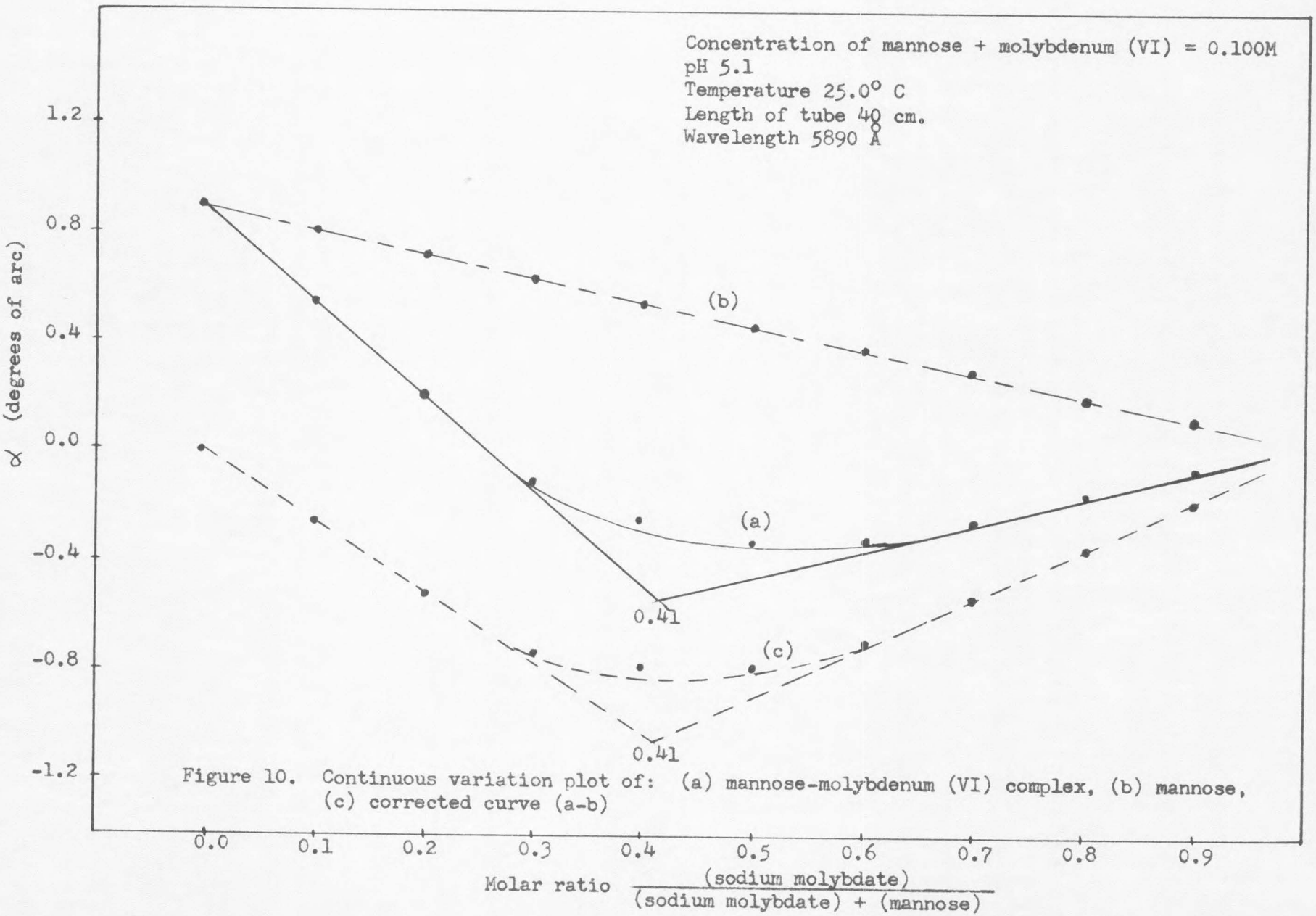


Figure 10. Continuous variation plot of: (a) mannose-molybdenum (VI) complex, (b) mannose, (c) corrected curve (a-b)

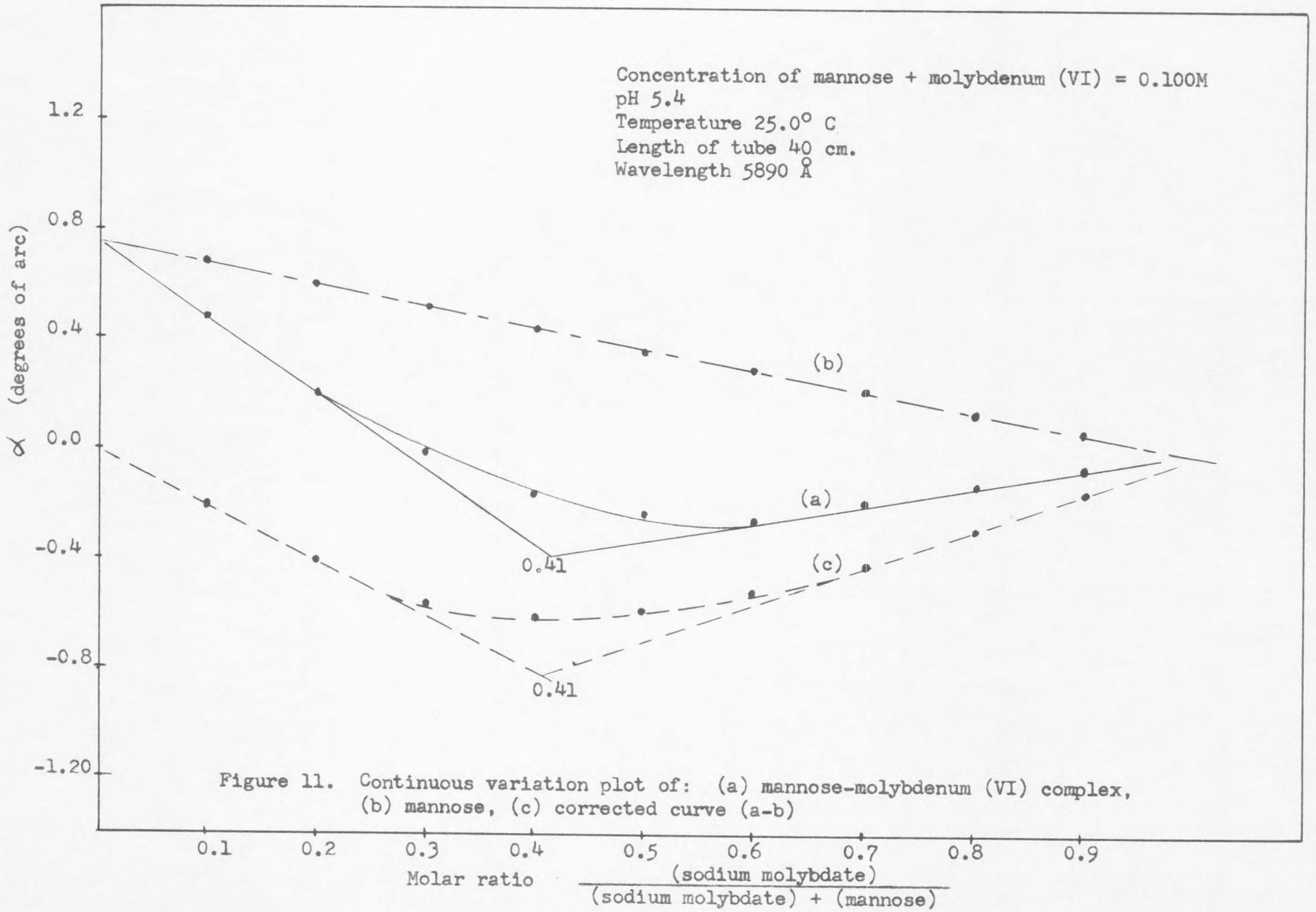


Figure 11. Continuous variation plot of: (a) mannose-molybdenum (VI) complex, (b) mannose, (c) corrected curve (a-b)

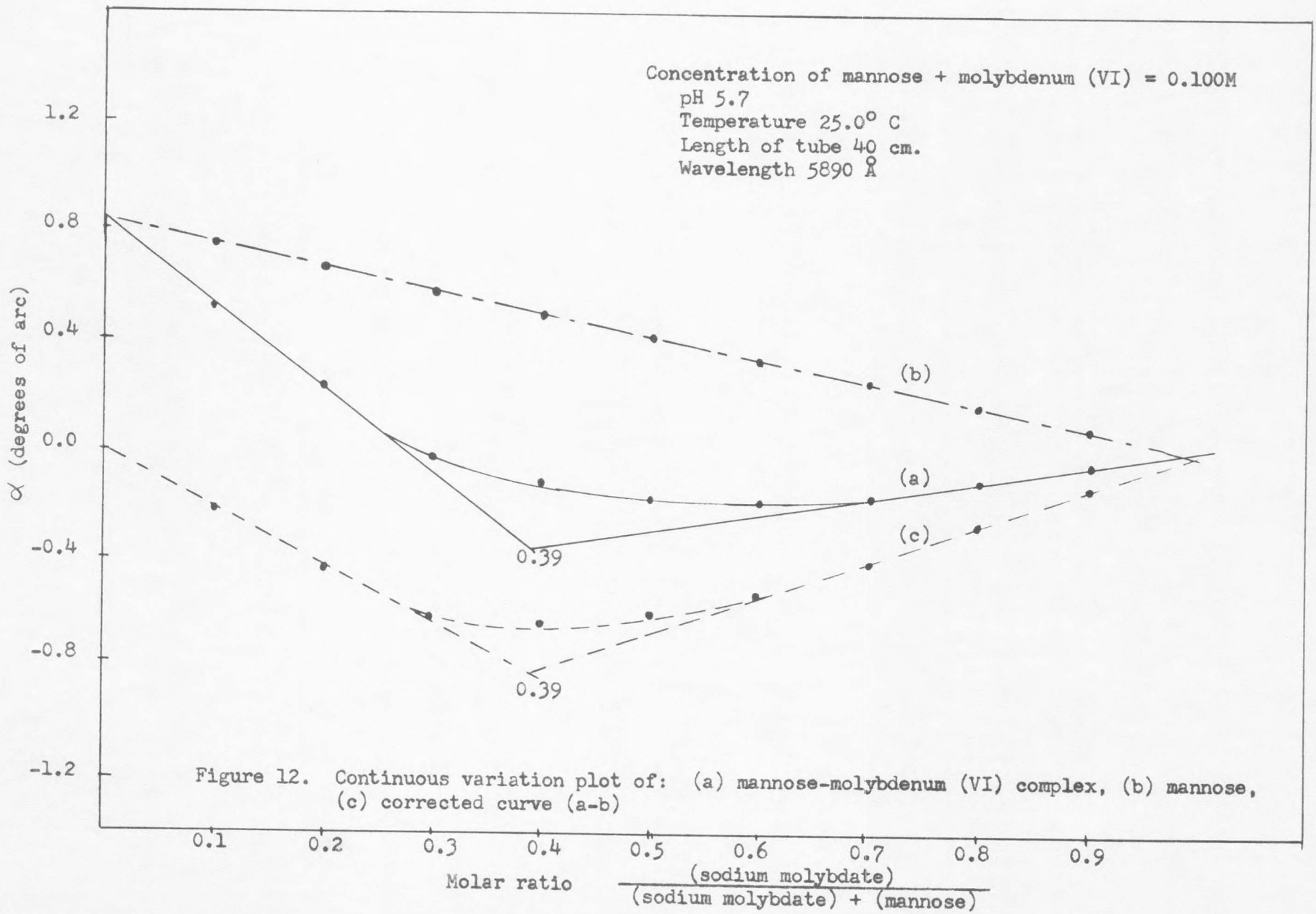


Figure 12. Continuous variation plot of: (a) mannose-molybdenum (VI) complex, (b) mannose, (c) corrected curve (a-b)

Table 12. Continuous variations mannose-molybdenum (VI) complex at pH 4.4 [a]

Molar ratio of Mo/(Mo+mannose)	α Degrees of arc		
	Mannose-molybdenum (VI) complex	Mannose	Corrected complex
0.0	0.89	0.89	0.00
0.1	0.56	0.80	-0.24
0.2	0.24	0.71	-0.47
0.3	0.00	0.62	-0.62
0.4	-0.17	0.53	-0.70
0.5	-0.27	0.44	-0.71
0.6	-0.28	0.36	-0.64
0.7	-0.26	0.27	-0.53
0.8	-0.18	0.18	-0.36
0.9	-0.11	0.10	-0.21

[a] Total concentration of mannose and molybdenum (VI) 0.100M.
Length of tube 40 cm.
pH 4.4 in acetate buffer 3M.
Wavelength 5890 Å.

Table 13. Continuous variations mannose-molybdenum (VI) complex at pH 4.8 [a]

Molar ratio $\frac{(Mo)}{(Mo)+(mannose)}$	α Degrees of arc		
	Mannose-molybdenum (VI) complex	Mannose	Corrected complex
0.0	0.82	0.82	0.00
0.1	0.54	0.76	-0.22
0.2	0.23	0.67	-0.44
0.3	-0.06	0.58	-0.64
0.4	-0.21	0.50	-0.71
0.5	-0.29	0.42	-0.71
0.6	-0.33	0.32	-0.65
0.7	-0.28	0.24	-0.52
0.8	-0.19	0.16	-0.35
0.9	-0.10	0.07	-0.17

[a] Total concentration of mannose and molybdenum (VI) 0.1000M.
pH 4.8 in acetate buffer 3M.
Length of tube 40 cm.
Temperature 25.0° C.
Wavelength 5890 Å.

Table 14. Continuous variations mannose-molybdenum (VI) complex at pH 5.1[a]

Molar ratio $\frac{(Mo)}{(Mo)+(mannose)}$	α Degrees of arc		
	Mannose-molybdenum (VI) complex	Mannose	Corrected complex
0.0	0.89	0.89	0.00
0.1	0.54	0.80	-0.26
0.2	0.21	0.72	-0.51
0.3	-0.10	0.63	-0.73
0.4	-0.22	0.54	-0.76
0.5	-0.32	0.46	-0.78
0.6	-0.32	0.37	-0.69
0.7	-0.25	0.29	-0.54
0.8	-0.15	0.20	-0.35
0.9	-0.07	0.12	-0.19

[a]Total concentration of mannose and molybdenum (VI) 0.1000M.
pH 5.1 in acetate buffer 3M.
Length of tube 40 cm.
Temperature 25.0° C.
Wavelength 5890 Å.

Table 15. Continuous variations mannose-molybdenum (VI) complex at pH 5.4[a]

Molar ratio $\frac{(Mo)}{(MO)+(mannose)}$	α Degrees of arc		
	Mannose-molybdenum (VI) complex	Mannose	Corrected complex
0.0	0.76	0.76	0.00
0.1	0.48	0.69	-0.21
0.2	0.21	0.61	-0.40
0.3	-0.02	0.53	-0.55
0.4	-0.16	0.45	-0.61
0.5	-0.21	0.37	-0.58
0.6	-0.25	0.30	-0.55
0.7	-0.19	0.22	-0.41
0.8	-0.13	0.14	-0.27
0.9	-0.07	0.07	-0.14

[a]Total concentration of mannose and molybdenum (VI) 0.1000M.
pH 5.4 in acetate buffer 3M.
Length of tube 40 cm.
Temperature 25.0° C.
Wavelength 5890 Å.

Table 16. Continuous variations mannose-molybdenum (VI) complex at pH 5.7 [a]

Molar ratio (Mo)/(Mo)+(mannose)	α Degrees of arc		
	Mannose-molybdenum (VI) complex	Mannose	Corrected complex
0.0	0.82	0.82	0.00
0.1	0.53	0.75	-0.22
0.2	0.23	0.67	-0.44
0.3	-0.03	0.59	-0.62
0.4	-0.10	0.50	-0.60
0.5	-0.17	0.42	-0.59
0.6	-0.19	0.33	-0.52
0.7	-0.17	0.24	-0.41
0.8	-0.11	0.16	-0.27
0.9	-0.06	0.07	-0.13

[a]Total concentration of mannose and molybdenum (VI) 0.1000M.
pH 5.7 in acetate buffer 3M.
Length of tube 40 cm.
Temperature 25.0° C.
Wavelength 5890 Å.

Table 17. Continuous variations ribose-molybdenum (VI) complex at pH 6.1 [a]

Molar ratio (Mo)/(Mo)+(ribose)	α Degrees of arc		
	Ribose-molybdenum complex	Ribose	Corrected complex
0.0	-1.06	-1.06	0.0
0.1	-1.05	-0.96	-0.09
0.2	-1.03	-0.86	-0.17
0.3	-0.98	-0.76	-0.22
0.4	-0.93	-0.65	-0.28
0.5	-0.82	-0.54	-0.28
0.6	-0.70	-0.43	-0.27
0.7	-0.54	-0.33	-0.21
0.8	-0.36	-0.22	-0.14
0.9	-0.19	-0.12	-0.07

[a]Total concentration of ribose and molybdenum (VI) 0.1000M.
pH 6.1 in acetate buffer 3M.
Length of tube 40 cm.
Temperature 25.0° C.
Wavelength 5890 Å.

Table 18. Continuous variations ribose-molybdenum (VI) complex at pH 5.7 [a]

Molar ratio $\frac{(Mo)}{(Mo)+(ribose)}$	α Degrees of arc		
	Ribose-molybdenum complex	Ribose	Corrected complex
0.0	-1.08	-1.08	0.00
0.1	-1.08	-0.97	-0.11
0.2	-1.08	-0.87	-0.21
0.3	-1.07	-0.77	-0.30
0.4	-1.00	-0.66	-0.34
0.5	-0.90	-0.55	-0.35
0.6	-0.74	-0.45	-0.29
0.7	-0.54	-0.34	-0.20
0.8	-0.36	-0.24	-0.12
0.9	-0.18	-0.14	-0.04

[a]Total concentration of ribose and molybdenum (VI) 0.1000M.
pH 5.7 in acetate buffer 3M.
Temperature 25.0° C.
Length of tube 40 cm.
Wavelength 5890 Å.

Table 19. Continuous variations ribose-molybdenum (VI) complex at pH 5.0 [a]

Molar ratio $\frac{(Mo)}{(Mo)+(ribose)}$	α Degrees of arc		
	Ribose-molybdenum (VI) complex	Ribose	Corrected complex
0.0	-1.12	-1.12	0.00
0.1	-1.12	-1.01	-0.11
0.2	-1.12	-0.90	-0.22
0.3	-1.12	-0.78	-0.34
0.4	-1.07	-0.67	-0.40
0.5	-0.90	-0.56	-0.34
0.6	-0.75	-0.45	-0.30
0.7	-0.57	-0.34	-0.23
0.8	-0.38	-0.22	-0.16
0.9	-0.20	-0.11	-0.09

[a]Total concentration of ribose and molybdenum (VI) 0.1000M.
pH 5.0 in acetate buffer 3M.
Length of tube 40 cm.
Temperature 25.0° C.
Wavelength 5890 Å.

Table 20. Continuous variations ribose-molybdenum (VI) complex at pH 4.5 [a]

Molar ratio (Mo)/(Mo)+(ribose)	α Degrees of arc		
	Ribose-molybdenum (VI) complex	Ribose	Corrected complex
0.0	-1.18	-1.18	0.00
0.1	-1.13	-1.01	-0.11
0.2	-1.12	-0.89	-0.23
0.3	-1.10	-0.77	-0.33
0.4	-1.02	-0.65	-0.37
0.5	-0.86	-0.54	-0.32
0.6	-0.69	-0.42	-0.27
0.7	-0.51	-0.30	-0.21
0.8	-0.33	-0.19	-0.14
0.9	-0.14	-0.07	-0.07

[a]Total concentration of ribose and molybdenum (VI) 0.1000M.
pH 4.5 in acetate buffer 3M.
Length of tube 40 cm.
Wavelength 5890 Å.
Temperature 25.0° C.

The same type of plot was made with ribose and lyxose. Figures 13, 14, 15, and 16 show the continuous variations plots of ribose-molybdenum (VI) complex at pH 6.1, 5.7, 5.0 and 4.5, respectively. Again, the maxima occur at the molar ratios 0.43, 0.41, 0.40, 0.39 in figures 13, 14, 15, and 16, respectively. For lyxose, Figure 17 shows the similar plot at pH 5.1 and the molar ratio of the complex in the plot is 0.47. From the above data, the molar ratio of sugar to molybdenum (VI) is probably 1:1. The slight departure from the theoretical value is not explainable.

An estimation of the value of the dissociation constants (K) of the complexes was made. Because the polarimeter reads only to $\pm$.01 degrees of arc, accurate values of K could not be obtained. For mannose-molybdenum (VI) complex, K is about 10^{-3}; ribose 10^{-2}; and lyxose, 10^{-3}. For polyol-

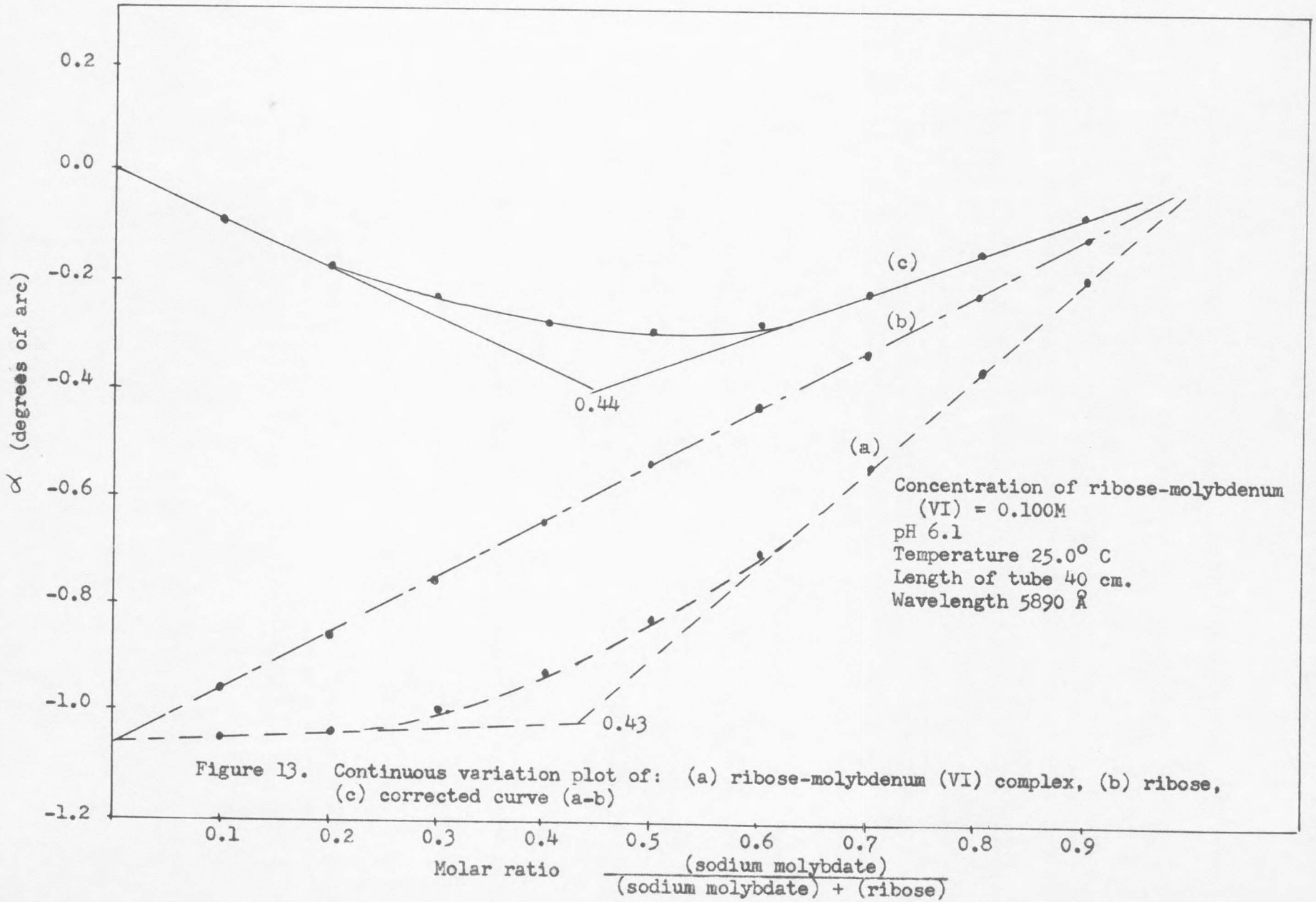


Figure 13. Continuous variation plot of: (a) ribose-molybdenum (VI) complex, (b) ribose, (c) corrected curve (a-b)

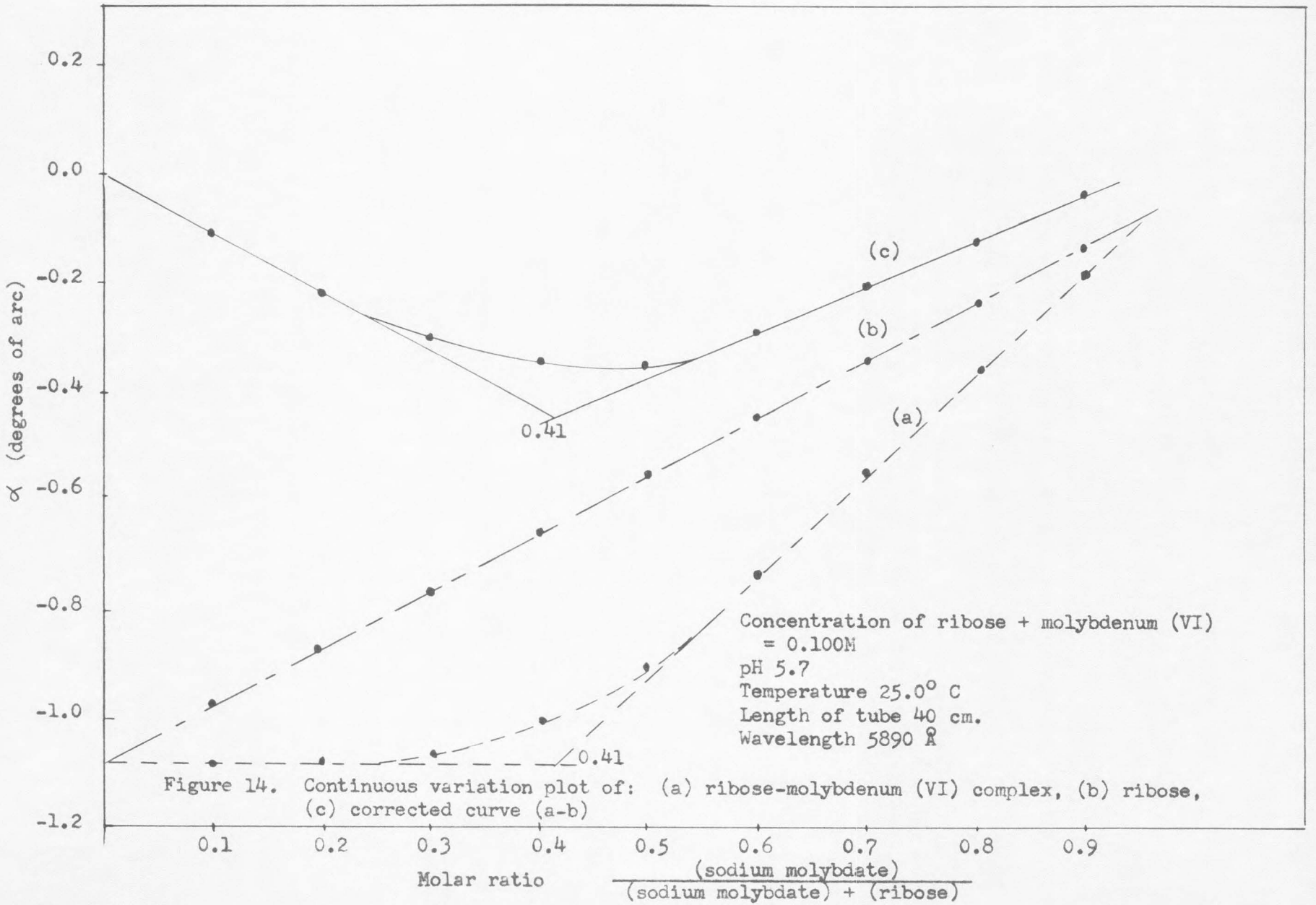


Figure 14. Continuous variation plot of: (a) ribose-molybdenum (VI) complex, (b) ribose, (c) corrected curve (a-b)

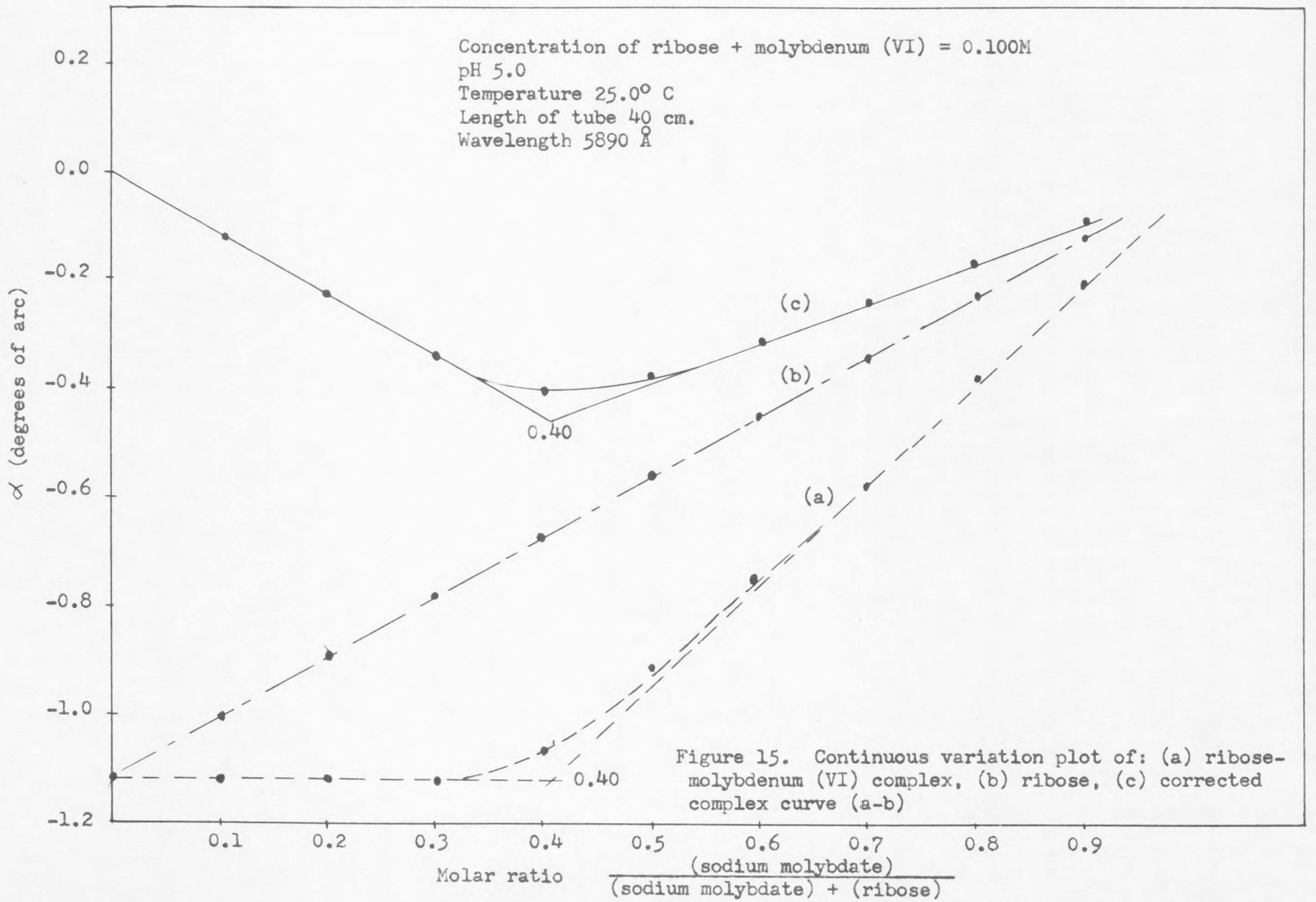


Figure 15. Continuous variation plot of: (a) ribose-molybdenum (VI) complex, (b) ribose, (c) corrected complex curve (a-b)

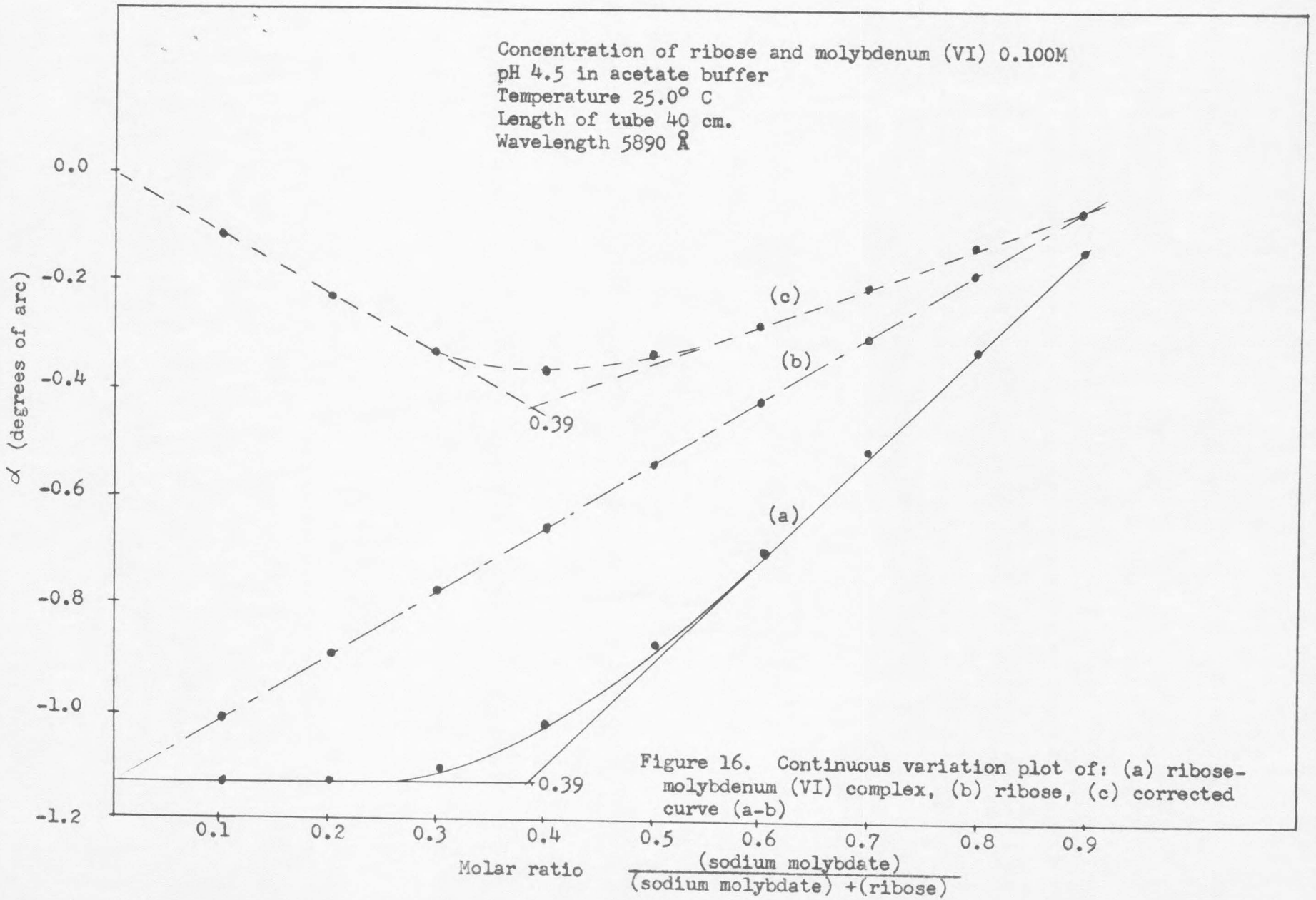


Figure 16. Continuous variation plot of: (a) ribose-molybdenum (VI) complex, (b) ribose, (c) corrected curve (a-b)

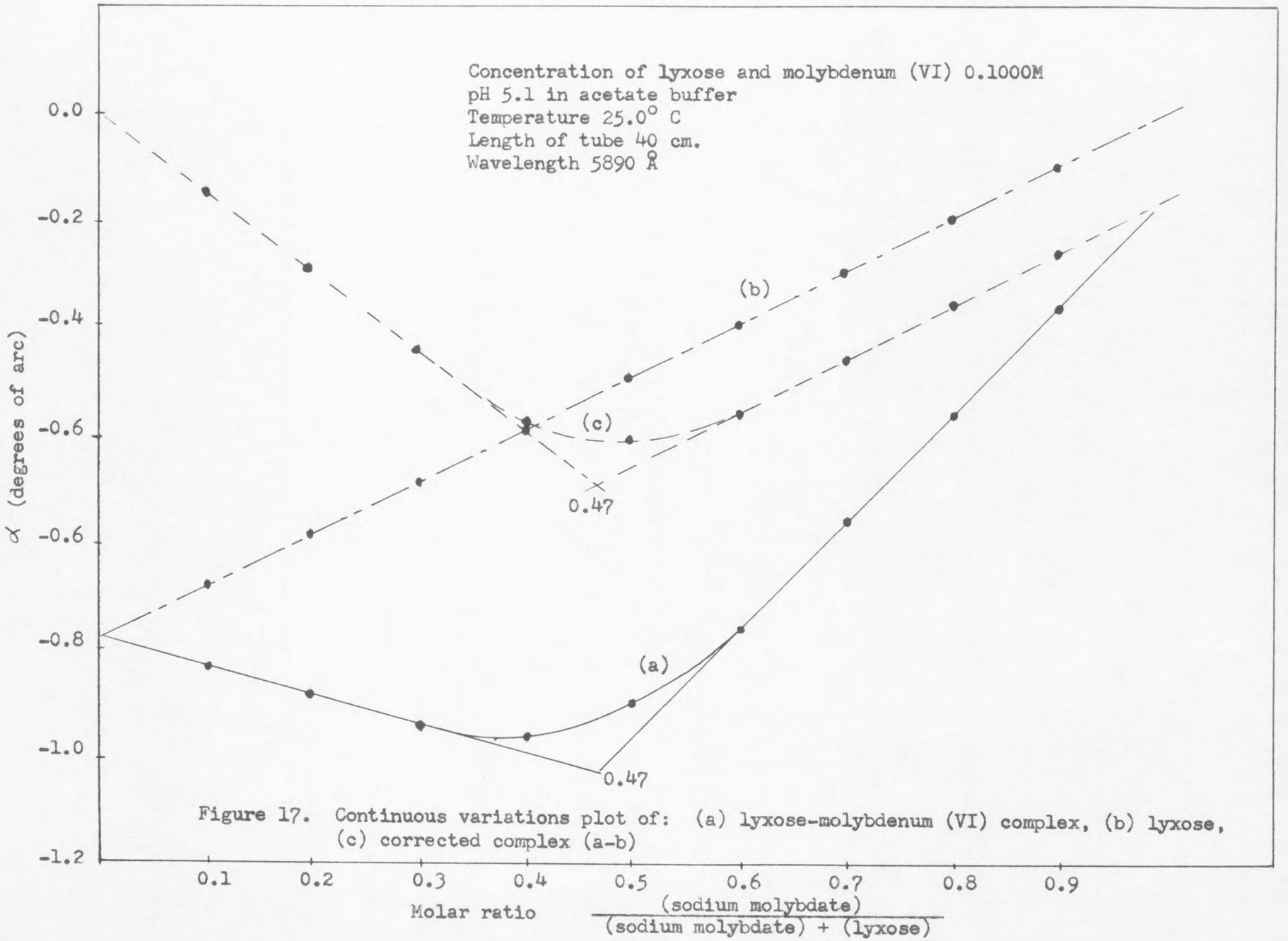


Figure 17. Continuous variations plot of: (a) lyxose-molybdenum (VI) complex, (b) lyxose, (c) corrected complex (a-b)

molybdenum (VI) complexes, K for sorbitol is about 10^{-4}; mannitol 10^{-5}; and arabitol 10^{-8}. In general, the sugar complexes are rather weak, and the polyol complexes somewhat more stable than the sugar complexes.

Table 21. Continuous variations lyxose-molybdenum (VI) complex at pH 5.1 [a]

Molar ratio (Mo)/(Mo)+(lyxose)	α Degrees of arc		
	Lyxose-molybdenum (VI) complex	Lyxose	Corrected complex
0.1	-1.02	-0.88	-0.14
0.2	-1.09	-0.79	-0.30
0.3	-1.13	-0.69	-0.44
0.4	-1.15	-0.59	-0.56
0.5	-1.10	-0.49	-0.61
0.6	-0.95	-0.39	-0.56
0.7	-0.75	-0.30	-0.45
0.8	-0.55	-0.20	-0.35
0.9	-0.35	0.09	-0.26

[a]Total concentration of lyxose and molybdenum (VI) 0.1000M.
pH 5.1 in acetate buffer 3M.
Length of tube 40 cm.
Temperature 25.0° C.
Wavelength 5890 Å.

Polarographic studies

(a) Adenine: On comparing reduction curves of sodium molybdate in chloroacetic acid buffer, pH 2.7, at 27.8° C with a mixture of molybdate and adenine sulfate under the same conditions, the difference in their half wave potentials was found to be very small and the waves were irreversible. A complex might be formed, but it is probably quite weak. Similar results were obtained for pH 4.8 under the same conditions.

(b) Adenosine: Polarographic waves of adenosine and its mixture with molybdenum at pH 2.7 and 4.8 were made. The shift in half wave

potential for adenosine was again small and the waves irreversible.

(c) AMP, ATP: Polarographic waves of ATP and AMP with and without molybdenum at pH 4.8 and 2.2 were obtained. There was no significant shift in half wave potentials and the waves were again irreversible.

(c) Polarographic waves of polyols and sugars with molybdenum gave only irreversible waves.

Spectrophotometric studies

In general, if complex formation or chelation occurs in aqueous solution between molybdate and a ligand, it is possible that it will result in a change in the ultraviolet or visible absorption curve.

In pH 4.8 sodium acetate buffer solution, the absorption spectra of adenine sulfate and the mixture of adenine sulfate and sodium molybdate were obtained. The results showed no change in the absorption spectrum. Also, the mixtures were tested at different pH's and the results were the same. Therefore, it was assumed no complex between adenine and molybdate is formed that has an absorption spectrum different from the sum of the components.

The complexes of sugar-molybdenum (VI) showed no absorption either in the ultraviolet or visible range, so the method was not applicable to them.

SUMMARY

The object of this study was to investigate complexes of sugars and poly-hydroxy alcohols with molybdenum (VI).

From the polarimetric studies it may be concluded:

(a) Molybdenum (VI) forms complexes with aldohexoses and aldopentoses which possess three hydroxyl groups in a cis-cis 1(ax), 2(eq), 3(ax) triol arrangement of the ring systems.

(b) Polyhydroxy alcohols which have four or more hydroxyl groups on adjacent carbon atoms complex with molybdenum (VI).

(c) Sugars complex with molybdenum (VI) more strongly around pH 5.0, while polyhydroxy alcohols do so near pH 2.0.

(d) The molar ratio of polyol to molybdenum (VI) in polyol-molybdenum (VI) complexes is 1:2, while the molar ratio of sugar to molybdenum (VI) in the sugar-molybdenum (VI) complexes is 1:1.

(e) The molar ratio for both complexes of polyols and sugars is independent of pH.

(f) The dissociation constants of the complexes could only be estimated. For sugar-molybdenum (VI) complexes, the value of K is about 10^{-3}, while for polyol-molybdenum (VI) it is approximately 10^{-5}. The approximate order of stability of sugar complexes is mannose lyxose ribose; while for polyol complexes it is arabitol mannitol sorbitol.

Little evidence could be found for complexes of adenine, adenosine, AMP and ATP with molybdenum (VI).

The present study on sugar-molybdenum (VI) and polyol-molybdenum (VI)

complexes is one approach to the problem, and the results agree with the work of Bourne and coworkers who used paper ionophoresis techniques.

The possibilities of the application of this investigation should be mentioned. A sugar having cis-cis 1(ax), 2(eq), 3(ax) triol configuration can be identified by addition of molybdenum (VI) and observation of the change in optical rotation, and this may prove of considerable value in carbohydrate chemistry.

Molybdenum is one of the important metals present in certain enzyme systems. The complexes formed between sugars or their derivatives and molybdenum may have some application to the enzyme systems, but this is not known yet, and will require further work. At present, it would seem that molybdenum (VI) is not bound to any molecules containing ribose (ATP, AMP, etc.) since these molecules do not possess the necessary cis-cis 1(ax), 2(eq), 3(ax) triol system.

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