

Starch – metal complexes and metal compounds

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Abstract

Recently, metal derivatives of starch evoked considerable interest. Such metal derivatives can take a form of starch compounds bearing metal atoms and metal carrying moieties either covalently bound or complexed. Starch metal complexes may have a character of either Werner, inclusion, sorption or capillary complexes. In this publication, preparation, structure, properties and numerous current and potential applications of those compounds as well as benefits resulting from the application and formation of the complexes are presented.

Keywords: capillary complexes, helical complexes, inclusion complexes, polysaccharides, sorption complexes, Werner complexes,

Running title: Starch metal compounds

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/jsfa.8820

INTRODUCTION

After cellulose, starch is the second polysaccharide commonly met in nature. In contrast to cellulose, it is widely used as an essential component of a human diet. Starch is usually utilized as a component of plants in their either raw state (chiefly as a component of some fruits and vegetables) or after processing (mainly seasoning, baking, frying). Also frequently starch is used after its isolation from a starchy material. Isolated starch is then used after specific processing, that is either converting it into pastes (pasting, gelatinization) or through physical,^{1,2} chemical³ and enzymatic⁴ modifications such as cutting their structure into shorter chains to form dextrans and finally α -D-glucose. Based on the behavior of starch on pasting and the crystalline character, starch spreads into tuber, cereal and sago (from the bark of sago palm) starch, called A-, B- and C-type starches, respectively.

Starch in plants is accompanied by various organic and mineral components. Their components and level depend on the botanical origin of the plant. On isolation of starch, the accompanying components can be removed but without destruction of its granules it always contains enzymes building starch from CO₂ and H₂O.

Starch is composed of two polysaccharides, amylose and amylopectin. Both are polymers of α -D-glucose. Amylose, a polysaccharide depending on its botanical origin has molecular weight (M_w) from 4 000 to 15 000 Da, that is it contains from 100 to 1400 D-glucose units bound to one another with the α -1 \rightarrow 4' bonds, so called glycosidic bonds, to form a linear structure. In some cases randomly branched amylose can be found. Its side chains are composed of 2-3 1 \rightarrow 4'-bound α -D-glucose units attached through 2 \rightarrow 1 and/or 3 \rightarrow 1 glycosidic bonds to the main linear chain.⁵

In the second polysaccharide component of starch – amylopectin - the main linear chain of the 1 \rightarrow 4' bound α -D-glucose units contains 1 \rightarrow 6' bound branches containing

from 15 to 30 1→4'-bound α -D-glucose units. The branches occur at every 9 – 10 glucose unit of the main chain. The M_w of amylopectin reaches from 500 to 100 000 kDa.

The amylose: amylopectin ratio in starch depends on the botanical origin of its source. Common native starch contains from 21 to 27 w% amylose and 73 to 79 w% amylopectin. For some technological requirements starch of high amylose content is more appreciated and in some others, starch of high content of amylopectin is beneficial. Since normal plants offering such kind starches are fairly random, starchy plants are genetically modified into starch of either higher content of amylose (so-called hylon starches) or higher content of amylopectin (so-called waxy starches). These problems are reviewed in numerous sources.⁶⁻⁹

Metal derivatives of starch are formed as a consequence of its interactions with metals, metal ions and non-ionized metal compounds involving the starch chemical nature and/or its macrostructure. The corresponding derivatives can be formed by (i) covalent bonding metal atoms and moieties, (ii) coordination forming Werner complexes in which amylose and amylopectin ligate the metal central atoms, (iii) starch surface sorption complexes, (iv) inclusion complexes involving ability of the polysaccharides to form helical structures and (v) capillary complexes holding metal compounds within capillaries between starch granules (Fig. 1).

Figure 1.

These problems have already been twice extensively reviewed in 1978¹⁰ and 1998.¹¹ This review continues both former collections of the data.

The complexes of the (i), (ii) and (iii) types employ the hydroxyl groups of the particular D-glucose mers of starch. The oxygen atoms of the rings as well as glycosidic bonds, usually accessible for protons and the anomeric carbon atom of the D-glucose rings, can accept solely some Lewis bases, provided they are situated in the terminal D-glucose units, that is, these corresponding mers are reducing sites of the polysaccharides. The hydroxyl groups of the mers have properties of the primary and secondary hydroxyl groups of alcohols. pK_a of those hydroxyl groups is above 12.¹² Thus, the hydroxyl groups are capable formation of salts, ethers and esters. The lone electron pairs at their oxygen atom are capable of playing a role of ligands of various Werner-type coordination compounds and proton acceptors in hydrogen bonds.

Numerical computations¹³ present charge density distribution (in a.m.u) on particular carbon, oxygen and hydrogen atoms in α -D-glucose and, hence, the preferences of particular hydroxyl groups for bonding metal atoms and metal atom containing moieties and particular oxygen atoms for coordinating to the central metal atoms in the Werner complexes.

Figure 2.

They are as follows:

Charge density distribution on the oxygen atoms:

$O3 > O4 > O2 > O1 > O6 > O_{\text{pyranose}}$

-0.53 -0.051 -0.048 -0.041 -0.040 -0.004

One can see that the negative charge density on the pyranose ring oxygen atom is practically negligible compared to the relevant densities on the remaining oxygen atoms.

Charge density distribution on the hydrogen atoms of the hydroxyl groups:

$H1 = H4 > H2 > H6 > H3$

.113 .009 .098 .095

O-H bond polarization as differences of the charge densities on the relevant oxygen and hydrogen atoms:

$4O-H > 1O-H > 3O-H > 2O-H > 6O-H$

.164 .154 .148 .147 .138

The results for O1, O4, H1, H4, 1O-H and 4O-H moieties are practically unessential as they are valid solely for terminal D-glucose units. In remaining D-glucose mers, if the steric factors are not involved, the preference for reactivity to form compounds with covalently bound metal atoms as well as coordination complexes declines in the order $3O-H > 2O-H > 6O-H$.

STARCH WITH COVALENTLY BOUND METALS

Like in alcohols, the hydroxyl groups of the D-glucose mers do not form salts with metal hydroxides. Attempts of the formation of starch-O-metal salts employed few strategies. Thus, starch could be reacted either in the granular, native form or after its pregelatinization. The latter source used to provide a higher rate and yield of metallation as the pregelatinization cancelled several intra and intermolecular interactions involving the hydroxyl groups. Metal alkoxides have been the most commonly used reagents.

Either relevant absolute alcohol or dry benzene was taken as a reaction medium. In such manner thallium(I) ethoxide gave thallated maize and potato starches¹⁴ and $Ti(OEt)_4$ formed $6-CH_2OTi(OEt)_3$ maize and potato starch derivatives.¹⁵ Optionally, solid state reaction of the reagents in the field of microwaves can be applied. At least in the syntheses of lanthanum starchates¹⁶ from soluble starch and $La(OPr-i)_3$ it appeared

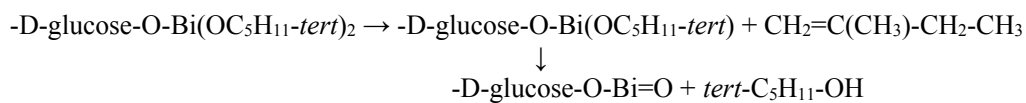
superior for its high rate and behavioral character in respect to the starch macrostructure. Depending on the reagent ratio and to a lesser extent on the other tested reaction conditions three products (**1-3**) (Fig. 3) could be isolated.

Figure 3.

The use of LaCl_3 as the reagent resulted in intensive production of dextrans.

The solid state reaction in the microwave oven was also applied for the synthesis of metal derivatives of pregelatinized potato starch with alkoxides of Mg, Cr(III), V(III), Mo(V) and W(V).¹⁷ Under such conditions starch formed O-Metal salts. The reaction was accompanied by the coordination of the introduced metal atoms to the OH groups being in the vicinity. In aqueous solutions chromium(III) and vanadium(III) salts hydrolyzed whereas the other derivatives were stable. Resulting compounds were less thermally stable than original pregelatinized starch.

For bismuth(III) derivatives of starch bismuth tri-*tert*-pentoxide was preferred reagent whereas for bismuth(V) derivatives NaBiO_3 appeared a more suitable. Both solid state reactions were carried out in the microwave oven.¹⁸ One D-glucose unit of starch could bound no more than two $\text{Bi}(\text{O-alkyl})_2$ groups. Reaction of starch with NaBiO_3 proceeded with crosslinking starch. Bismuthated derivatives were slightly less thermally stable than original starches. Their controlled thermal decomposition proceeded according to the scheme:



As proven, metal chlorides such as TiCl_4 ,¹⁹ BiCl_3 ,¹⁸ and LaCl_3 ,¹⁶ that is, salts of weak bases and strong acids hydrolyzed starch producing dextrans unless the reaction proceeds in anhydrous media. Thus, AsCl_3 and AlCl_3 were successfully applied for the synthesis of aluminum and arsenic(III) starchates carried out in benzene, toluene, carbon tetrachloride, cyclohexane or decalin.²⁰ Derivatives with such moieties as D-glucose-O- AlCl_2 , D-glucose-O AsCl_2 , D-glucose-O- $\text{Al}(\text{Cl})$ -O-glucose-D and D-glucose-O- $\text{As}(\text{Cl})$ -O-glucose-D were formed. They slowly hydrolyzed in water. Dextrinization accompanied these reactions. Ferric chloride did not react with starch and complexes of that salts were formed instead.^{21,22} Thus, starch ferrate was prepared by a slow, 2-4 day lasting roasting reduced iron powder in aqueous gel of starch at 37°C. The beneficial concentration of the gel in case of corn starch was 10 – 12%. The viscosity of the gel was crucial for the reaction rate. The starch ferrates contained D-glucose-O- $\text{Fe}=\text{O}$ and D-glucose-O- $\text{Fe}(\text{OH})$ -O-D-glucose moieties in whose, the 6- CH_2OH groups of the D-glucose mers were the most likely involved.²²

The strategies presented above have been applied for the preparation of metal derivatives of maltodextrins.²³

The ability of the hydroxyl groups of the D-glucose mers to esterification of acids was utilized in the esterification of inorganic acids bearing metal ions in their anions. It has been shown that the solid state reaction of starch either with boric acid, sodium borate or borax carried out in the field of microwaves produce borated starch. The borates were formed by the involvement of pairs of *cis*-hydroxyl groups of two D-glucose units at the C-2 and C-3 positions. Three of these groups formed intra- and inter-molecular ester bonds, while the fourth one formed a donor–acceptor bond via its lone electron pair on the oxygen atom and an empty orbital of the boron atom.²⁴

Similarly, starch selenites and selenates were prepared involving the solid state reaction

of starch with corresponding sodium salts of selenic(IV) and (VI) acids, respectively. Selenic(VI) salt is less reactive.²⁵ Subsequently, starch was silicated either with sodium metasilicates^{26,27} or silicic acid²⁸ Rashid²⁷ et al. suggested that solely amylopectin was esterified with sodium silicate whereas amylose did not react. Reactions with sodium tetrahydrozincate²⁸ and ammonium tetrachlorocuprate³⁰ provided corresponding esters. It has been shown that replacing convectional heating with the microwave heating essentially reduced the reaction time and depolymerization of starch.³¹ Successful solid state esterification of starch with magnesium hydrogen sulfate³² opened a path to a synthesis of new generation metal containing esters of starch. It has also been demonstrated that convectional heating produced different products than the microwave heating. Monoesterification in one case and crosslinking esterification could explain these differences. The resulting esters disposed with a higher water binding capacity. Starch silicates were superior in that respect. The microwave irradiation at 180-800 W, and the convectional heating at 100°C usually increased the ability of potato starch to bind water. Short, lasting just a few minutes, microwave irradiation increased the water binding capacity of starch twice and the irradiation prolonged to 20 min might increase it even tenfold. Usually the water binding capacity and aqueous solubility of esters increased with the degree of esterification. Also treatment of the reaction mixtures with microwaves provided products of a higher aqueous solubility.

Except tetrachlorocuprate(II) esters which melted at higher temperature the esterification with other reagents usually decreased that temperature, most considerably in the case of the use of borax, sodium metasilicate and sodium tetrahydrozincate. Although the microwave irradiation reduced the degree of crystallinity of starch, microwave-assisted esterification with sodium selenite, selenate, and also with boric and silicic acids did not induce such changes.

The esters were mostly non-Newtonian and shear thinning fluids with the yield stress. In contrast to short microwave irradiation of potato starch, the prolonged radiation led to an increase in the value of the flow behavior index, and a significant reduction in the values of all other rheological parameters. This means that with increasing in the irradiation time, starch pastes became more resistant to thinning by shear forces, less viscous and more susceptible to deformation – their yield stress completely vanished. Such changes indicated that starch degraded. This was confirmed by decreasing values of the molecular weights of the polymer with increasing time of microwave irradiation.

In the case of starch modified with the reagents examined, differences in the chromatogram profiles obtained showed that the lower concentration of esterifying reagent, contrary to the higher one, retained both fractions, amylose and amylopectin, in the starch molecules. Differences between the chromatogram profiles of native starch and the starch modified with the use of reagents at higher concentration indicated that during the reactions simultaneous processes of substitution, cross-linking and degradation took place. Further, the analysis of the plots of the differential molar mass distribution versus molar mass for starch silicated with sodium metasilicate and zincated starch indicated that on esterification the number of starch molecules of the amylopectin fraction was reduced. Thus, it could be assumed that starch esterification with the reagents examined resulted in the products in which acidic moieties were more often arranged along the linear than along the branched chains.

Among a variety of starches of various botanical origin, potato starch distinguished for its unique anionic character.³³ Potato starch was in fact an ester of orthophosphoric acid. The phosphoric acid residue was principally bound to the hydroxyl groups of the CH₂OH moiety of the D-glucose mers. In native potato starch

that group was neutralized first of all with the sodium, potassium magnesium and calcium ions present in the soil. These ions could be substituted by metathesis with the hydrogen on treating native starch with diluted hydrochloric acid followed by rinsing the product with water.^{34,35} The proton of hydrogen starch could subsequently be substituted with metal ions such as Li, Na, K, Mg, Ca, Ba, Al, Zn, Cu(II), Tl(I) of corresponding hydroxides^{14,36-39} or chlorides of Ti(IV)¹⁵ and Fe(III).²¹ The saturation of hydrogen starch with univalent cations of the 1st non-transition group increased the viscosity of starch pastes whereas for instance, Tl⁺ the bi- and tri-valent cations decreased it. That observation could be applied in controlling the viscosity of starch pastes. Also a susceptibility of starch pastes to amylolysis could be controlled in such manner.²¹ Potentially, such starches can be carriers of bioelements.¹¹

There are several claimed as well as potential applications of the starch derivatives with covalently bound metal atoms. Lithiated⁴⁰ and thallated (I)¹⁴ starches were considered as synthons in chemical modifications of starch. Moreover, the thallated starch was proposed as a rodent poison. Starch seems to be carrier of bioelements and elements of certain therapeutic value. Such point of view rationalized syntheses of V(III), Cr(III), Mo(V), W(V),¹⁷ Bi(III) and Bi(V)^{18, 41-45} and Al²⁰ starch derivatives. Starch stannates attracted attention as potential bactericides and pesticides and As(III), Cu(II) and Ti(IV) derivatives were considered as antimoulding agents and additives for corrugated board and plywood, respectively.¹¹

STARCH WERNER COMPLEXES

Lone electron pairs at the oxygen atoms of starch can potentially be employed in the formation of the Werner complexes with metal ions, that is, in the formation of the –O–Metal ion coordination bonds.⁴⁶ Formerly, that problem was exhaustively reviewed by

Rendleman in 1978¹⁰ and Tomasik and Schilling in 1998.¹¹ It has been shown that the hydroxyl groups at C2 and C3 of the D-glucose units were mainly involved in the coordination. At low concentration of the salt added complexes of disordered structure were formed and the ordering progressed with increase in the concentration of the salt added.²¹ The involvement of the pyranose ring oxygen atom in the coordination of the metal ions was also suggested.⁴⁷

Pasting reduces several intra- and intermolecular hydrogen bonds in starch polysaccharides, thus it facilitated complexation. However, native amylose-amylopectin complex survived pasting⁴⁸ and also some starch granules remained intact in the gel.⁵⁰ Thus, usually, pasting was not completed.⁵¹

The behavior of salts in respect to starch depended on the position of the cation in the Periodical Chart. Thus, except lithium compounds, the compounds of remaining atoms of that group interacted with starch involving their counterions, that is, the anions formed the surface sorption complexes.⁵² For its colligative properties the lithium cation and not its counterion was coordinated by starch.^{53,54} Hydrolyzing salts coordinated and, simultaneously, hydrolyzed starch.

Due to differences in the solvation enthalpy, charge of the metal ion influenced stability and structure of the complexes, particularly in polar solvents. The oxygen atoms of the hydroxyl groups more readily affected the solvation sphere of bivalent metal ions than that of the trivalent metal ions.⁵⁵ The complexation depended on the orientation of ligating groups in respect to the metal central atom and the stability of such complexes was controlled by a dimension of the coordinating center of the ligand.⁵⁶

Numerical simulations⁵⁷ revealed that the stability of the hydrated cations accompanied by the chloride and nitrate counterions declined in the order



whereas in the presence of the acetate counterions that order turned into



These irregularities seemed to be a consequence of some differences in the structure of the inner coordination spheres of those aquacomplexes.

The central Co(II) ion in its complex with α -D-glucose was either anhydrous or it held 4 D-glucose ligands and 2 molecules of water in its inner coordination sphere. Exceptionally, in the presence of the nitrate counterion, when the simulations also pointed to coordination of 4 D-glucose ligands and 2 water molecules, remaining results presented about $20 \text{ kJ} \cdot \text{mole}^{-1}$ preference for the structures containing solely 6 D-glucose ligands in the inner coordination sphere free of water ligands (Table 1). The same simulations indicated free of water inner coordination sphere of the Mn(II) and Fe(III) complexes with D-glucose. Solely in the presence of the acetate counterion the complex containing 4 D-glucose and 2 water ligands was energetically favored. The Cu(II) central atom surrounded with 4 D-glucose ligands was favored when the acetate and chloride counterions were present whereas in the presence of the nitrate counterion apart from 2 water molecules two D-glucose ligands resided in the inner coordination sphere. Regardless the counterion, the Ni(II) central atom coordinated 4 D-glucose ligands. It may be seen in Table 1 that complexes of Mn(II) and Co(II) were the most stable.

Table 1

Data in Table 1 show that increase in the complex stability of the complexes is paralleled by an increase in the number of its D-glucose ligands. The water molecules

coordinated to the inner coordination sphere decline the stability of the complexes. Particularly unstable are complexes of Co(II) and Fe(III) bearing odd number of D-glucose and water molecules, 3 and 3, respectively.

Recently, corresponding studies on the starch salt complexes with the transition metal salts were performed for sago,⁵⁸ potato,⁵⁹ tapioca,⁶⁰ normal and waxy corn,⁶¹ and amaranthus⁶² starches. The metal cations of the transition groups were ligated by amylose as well as amylopectin. Starch in its native form complexed cations more efficiently than both polysaccharides separately.^{63,64} As proven by epr spectra, the structure of resulting polycenter complexes depended on the counter ions. Cu(II) and Co(II) acetates, Ni(II) chloride, nitrate and acetate, and Fe(III) chloride had tetrahedral inner coordination sphere, Cu(II) nitrate and chloride complexes were square planar and complexes with Co(II) chloride and nitrate were octahedral. Amount of cations bound by starch gels was only slightly depended on the starch origin. Average value reached 10 mg metal ions per 1 g starch.

Usually, the studies on the complexation of starch was performed in aqueous solutions. Recently the study was presented on the complexation of tapioca amylopectin preliminarily sonicated to reduce its molecular weight and size, performed in aqueous dimethylsulfoxide (1:9) solution.⁶⁵ The solvent appeared suitable for the syntheses of complexes of that polysaccharide with salts of Pb(II), Fe(III), Cu(II), Cr(III) and Ni(II). The highest yields of relevant complexes depended on reaction temperature, reaction time and concentration of the salt solution. Reactions performed at 25°C, within 5 h provided the highest complexation yield. The latter depended on the cation as well as its counterion. Generally, Cr(III) salt tested $[\text{Cr}(\text{NO}_3)_3]$ and $\text{Cr}_3(\text{CH}_3\text{COO})_7(\text{OH})_2$ complexed most readily. The yield of the level of 55% was counterion independent. The around 40% yield of complexation was achieved for the Fe(III) and Cu(II) cations

provided they were assisted by the NO_3 counterion. In case of the Cl counterion the yields were lower by 10 and 15%, respectively. The yield of complexation of the Ni(II) cation reached 32% and was counterion independent. The slightly counterion dependent complexation of the Pb(II) cation gave the yield on the level about 20%. According to Szymonska et al.,⁶⁶ the effects of counterions were associated with their role as the water structure breakers.

Ligating ability of starch has been employed for synthesis of quantum dots of ZnS and CdS within the gelatinized starch matrix.⁶⁷ ZnS and CdS quantum dots generated in maize amylopectin readily aggregated⁶⁸ whereas in tapioca starch gel they resided non-aggregated.⁶⁹ Generation of such quantum dots was based on converting zinc and cadmium acetates, respectively, with sodium sulfide. Likely, coordination of acetates to the starch polysaccharides took preliminarily place. The coordination to amylopectin component of starch was more essential than coordination to amylose. Contradicting results on application of maize amylopectin and tapioca starch pointed to the role of viscosity of the polysaccharide matrix. Also the anionic character of the polysaccharide is beneficial for the stability toward aggregation of the quantum dots formed. The character of the polysaccharide matrix made them unsuitable for generation of quantum dots from the hydrolyzing salts of the elements of the IInd and IIIrd non-transition groups. This limitation could be, to a certain extent, overcome when distarch phosphate was used as a matrix.⁷⁰

Quantum dots generated inside potato starch gels did not agglomerate on evaporation of the gels to dryness. On generation of CdS quantum dots in potato starch gels, formation of polysaccharide nanotubes was observed. Such nanotubes included CdS but not ZnS quantum dots. There were no recognizable interactions between quantum dots and polysaccharide matrix.

Potato starch gels provided a suitable matrix hindering nanosilver, nanogold particles^{71,72} and bimetallic nanoAg/Au particles⁷³ from agglomeration. Villanueva et al.⁷⁴ prepared nanocopper particles in cornstarch.

Frequently, amylose and amylopectin clathrated the water molecules and the mode of the coordination of the hydroxyl groups to the central metal atom controlled the clathrate formation. Potato amylopectin bound metal atoms to the phosphoric acid moiety and formed cage by coordination of the hydroxyl groups to them. The coordination to the metal central ions had an essential effect on the rheology of coordinated starch gels. Only potato starch gels appeared exceptional to a certain extent. Gels of other starches, e.g. amaranthus, corn, tapioca and waxy corn starches reacted similarly to the coordination to the given cation [Co(II), Cu(II), Fe(III), Ni(II)]. The coordination of the starch gel components to metal salts affected the gel viscosity. Mn(II) and Co(II) salts increased it.¹¹ All gels turned from pseudoplastic into these being on the borderline between pseudoplastic and Herschel-Bulkley fluids.⁶¹ Coordination of potato starch to the transition metal central atoms drastically decreased pseudoplasticity and thixotropic properties of the gel. In terms of the parameters of the Herschel-Bulkley model, except FeCl₃, the magnitude of the effects upon both properties was practically independent of the cation and counterion of the salt added (Table 2). Table 2. presents rheology of the potato starch gels coordinated to various salts.

Table 2

The formation of starch coordination complexes with metal salts found practical applications, for instance, in the textile industry. The complexes can be used in the

textile finishing and dyeing.¹¹ Soluble starch was used as a heavy metal trap on polymer-enhanced ultrafiltration of mixed heavy metal salt solutions.⁷⁵ Hydrogel of native cassava starch was suitable for collecting heavy metal ions from aqueous solutions.⁷⁶ Preparations from wheat and rice starches coordinated to Fe(III), Cu(II), Zn, Al, Sn(IV) and other ions were patented as screening agents against UV radiation and stimulating healing wounds and burns.⁷⁷ The application of neutral and anionic starch – metal complexes for stabilization of soil in embankments and slopes appeared promising.⁷⁸ There is also patent for starch – metal complexes for improvement of hair and skin appearance and healing wounds. In the latter case starch of various botanical origin was coordinated to Cu(II) and Sn(II) ions.⁷⁹

The ligation of the central metal atoms resulted in a variation of the thermal stability, pathway, and rate of the thermal decomposition of starch. Table 3 presents temperature of decomposition of potato amylose, potato amylopectin and corn amylopectin as well as amaranthus, tapioca and potato starches given as the position of the main DTG peaks in the thermograms of those species. In the same Table main DTG peaks of complexes of those polysaccharides with selected metal salts are also given.

Table 3.

Isolated amylose and amylopectin are slightly more thermally stable than starches as on the isolation various admixtures residing in starch granules were removed. The thermal stability of those isolated polysaccharides resembled one another. The thermal stability of particular starches was more variety dependent.

Table 4 presents yield of volatile fraction and carbonizate collected after thermolysis of complexes of potato starch (PS), potato amylose (PA), potato

amylopectin (PAP), corn amylopectin (CAP), amaranthus starch (AS) and tapioca starch (TS) to 500°C.

Table 4

Temperature of the beginning of the thermal decomposition, yield of the volatile fraction and carbonizate depended on botanical origin of starch, metal cation and its counteranion. There was no clear relationship between decomposition temperature and the yield of the volatiles and carbonizate. A high yield of carbonizate could be achieved from potato starch thermolyzed after its coordination to Cu(II) acetate as well as from corn amylopectin (waxy corn starch) coordinated to Mn(II) acetate and from tapioca starch coordinated to Cu(II) nitrate. Results collected for the thermolysis of potato amylopectin metal complexes showed that starches rich in amylopectin might be more beneficial for preparation of carbonizate. However, results collected in case of thermolysis of amaranthus starch which was purely waxy starch contradicted that point of view. Also the selection of salts beneficial for the highest yield of volatile products was specific for the particular starches. The content of CO in the total volatile products was also essential. Thus, amaranthus and potato starches provided the highest yield of CO.

The coordination to selected metal salts could control pathway and products of the polysaccharide ligand thermolysis. It might be interesting source for generation of syngas for production of, for example, liquid fuels (Table 1), metal ion collectors and components of drilling muds.^{80,81} Therapeutic significance of the formation of the polysaccharide – metal complexes in organisms was recently reviewed by Scott and Orvig.⁸²

STARCH SORPTION COMPLEXES

Starch readily absorbs water. In aqueous metal salt solutions contacting gelatinized starch a competition takes place between salt ions and starch for the water molecules. Water binding ability of starch, that is, the dehydration of ions depends on salts added. That ability decreases in the order⁸³: $\text{Ca} > \text{Mg} > \text{Al} = \text{K} > \text{Na} > \text{Li}$ and $\text{CNS} > \text{I} > \text{Br} > \text{NO}_3 > \text{Cl} > \text{SO}_4$. Dehydration of cations is more difficult than anions.⁸⁴

Salts of the metals of the non-transition groups, except lithium compounds, interact with starch involving their counterions, that is, the surface sorption complexes are formed in which chiefly salt counter anions are bound to the hydroxyl groups as seen in Fig. 1 and cations are held in these complexes electrostatically.⁵⁴

Metal hydroxides of the I_{st} and II_{nd} non-transition groups also form sorption complexes rather than Werner complexes.^{11,14}

Alternative way of the formation of the surface sorption compounds is employed when a non-ionized metal compound is held on starch involving Starch-O...H... non-ionized metal compound bonding (Fig. 1).

STARCH INCLUSION COMPLEXES

In the presence of sufficiently long hydrophobic structures amylose and amylopectin are capable formation of helical complexes with those molecules entrapped inside the helical channels. These guest molecules can be of the inorganic¹¹ as well as organic in their character.⁸⁵ Among inorganic guests these with KI_5 are most common. Their formation is significant for starch identification involving colorimetric methods.¹¹ In such complexes the I_5^- complex anion occupies the interior of the polysaccharide helices and the K^+ counterion resides outside the helix. Also complexes with I_5^- ion carrying other metal ions instead the K^+ cation are also known.¹¹ Ambident anions such as OCN^-

, SCN⁻ also form hydrophobic rods around of which amylose can coil into helical complexes carrying the counter cations outside the helices.¹¹ Among organic guests, fatty acids and their esters are commonly used for the formation of amylose and amylopectin complexes. The use of metal salts of fatty acids can be taken into account as a way of the formation of the corresponding starch metal inclusion complexes. Such complexes might play a role in a formation of a proper macrostructure of dough for bakery goods.

STARCH CAPILLARY COMPLEXES

Starch can be reacted either directly in the granular state or after its pasting (gelatinization). The size and shape of granules is specific for particular botanical origin of starch. The granules are composed of concentric polysaccharide spheres of higher degree of polymerization. They have a crystalline character. Between these layers entangled amylose and amylopectin molecules form amorphous regions of the granules.⁸⁶⁻⁸⁸

As shown by Huber and BeMiller,⁸⁹ granules of all starches but potato starch are penetrated by reagents whereas the granules of the latter starch react on their surface. However, water penetrates granules of all starch varieties causing their swelling. As shown by microscopy employing polarized light and red laser beam, granules uptake water already on the isolation of starch from tubers, grain, seeds or sago bark.⁹⁰ Maintaining granules in water results in exudation of the amorphous part of granules leaving empty space between particular spheres. In such manner starch granules can be employed as microcapsules.⁹¹⁻⁹³

When capillaries between starch granules are filled with aqueous salt solutions, the swelling of granules is retarded and the efficiency of that process depends on the

cations and anions of the applied salts. Empty domains formed inside granules by exudation of the amorphous fraction are populated solely by water molecules, and the exuded material interacts with salts in the manner described above for coordination complexes. In case of salts of the first non-transition group, only lithium cation coordinates to starch, and in case of other salts of that group their counteranions interact with starch.⁵⁴ In contrast to that behavior, saturated aqueous solutions of BaF_2 , MgBr_2 and BaBr_2 caused gelatinization of potato starch. A transparent gel was formed showing that starch won the competition for water with those salts. The same volume of saturated aqueous solutions of SrCl_2 , BaI_2 , $\text{Mg}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$ added to potato starch produced semi-solid blends. In that case salts dominated in the competition for the water molecules. Equivalent volume of aqueous solutions of the same concentration of MgCl_2 , CaCl_2 , BaCl_2 , CaBr_2 , CaI_2 , and Mg, Ca, Sr and Ba nitrates produced from potato starch shear-thinning semi-liquids. These salts were better water-soluble than the former salts and their aqueous solution remained non-saturated. The salts penetrated starch granules occupying cavities left by exuded amorphous material.⁹⁴

Prolonged contact of granular starch with aqueous solutions of the transition metal salts resulted in deterioration of granules. Coordination complexes such as described above were formed.⁶³ In specific cases the problem might be more complex, for instance, when the salt could modify starch chemically. Such circumstances took place when starch granules were contacted with dichromate ions in highly acidic aqueous solutions. The $\text{Cr}_2\text{O}_7^{2-}$ anions were reduced to Cr^{3+} ion accompanied by the formation of intermediate Cr^{5+} ions. Then the Cr^{3+} ions were at least partly accumulated in granules. The quantity of such ions taken by the granules from the solution was noticeably higher than that delivered by trivalent chromium suggesting that these ions were not only cumulated on the granule surface but also penetrated the granule interior.⁹⁵ It made

starch suitable in reducing environmental pollution with chromium, for instance, around tanneries.

Formation of the capillary complexes were involved in observed corrosion of metal vessels in which rice was cooked.⁹⁶ The ability of starch to form all types of complexes can be successfully utilized in trapping heavy metal salts [Zn(II), Pb(II), Cr(III) and Cr(VI)] from their aqueous solutions Permeation and retention parameters as well as rejection coefficient depend on pH of aqueous solutions and the concentration of the ion and the ion itself. Values of those parameters and coefficient for starch were comparable with those for polyethylene glycol as shown in Table 5.⁷⁵

Table 5

Bryce and Greenwood⁹⁷ reported that admixture of inorganic salts to starch influenced its thermal decomposition (pyrolysis) into water, carbon dioxide, and carbon monoxide. The experiments were performed on evaporated at 60°C aqueous slurries of amylo maize starch and certain amount of selected metal salts. All salts decreased the starch pyrolysis threshold temperature following the order: no additive (plain starch) > CuCl₂ > CaCl₂ > MgCl₂ > 2% NaH₂PO₄ > KCl > LiCl > NaCl > 8% NaH₂PO₄ > Na₂B₄O₇ > NaHCO₃. Also the stoichiometry of formed volatiles depended on the salt added. Based on collected results the authors claimed that since NaH₂PO₄, CuCl₂ and MgCl₂ had no effect on the stoichiometry of the volatiles evolved they acted as catalysts whereas the other salts acted chemically. Generally, the effect of anions prevailed over the effect of the cations upon both the pyrolysis threshold temperature and stoichiometry of generated volatiles.

These data seek reinterpretation in terms of the facts presented above, that is, the granule swelling and formation of corresponding salt complexes. The role of pH resulting from the hydrolysis of the salts in the slurries should also be taken into account. It is common that in acidic medium the proton catalyzed hydrolysis takes place whereas in alkaline media in contact with the air oxidation can be involved.³ Ciesielski et. al.⁹⁸ showed that effect of salts in terms of the count of generated C and O free radicals could be observed on the thermolysis of air dry starches at 300°C when starch contained 10% admixture of either sodium, potassium or magnesium chlorides and nitrates. Generally, the sodium and potassium salts performed poorly, and nitrates depending on the starch variety (cornstarch, waxy cornstarch, potato starch and amylopectin) provided a slightly higher free radical count. Magnesium salts offered significantly higher free radical count and Mg(NO₃)₂ usually appeared less successful than MgCl₂. The results could be obscured by the degree of pulverization of the salts. Likely, the reaction began from the formation of complexes of the magnesium cations with starch exudates⁹⁰ on the surface of granules.

These studies were then extended to thermolysis of cereal grains^{80,81,99} and straws^{80,81} treated with various aqueous salt solutions. Table 6 sheds light on the suitability of cereals for production of volatiles and the role of metal salts added.

Table 6

Particular cereals revealed individual susceptibility to particular cations but, generally, triticale seemed to be the best source for production of the volatiles.

CURRENT RESEARCH TRENDS AND DEVELOPMENTS

Currently, more attention is paid to metal complexes of cationic,¹⁰⁰⁻¹⁰³ neutral, for instance, starch dialdehyde^{104,105} and its derivatives as dioximes,¹⁰⁶ dihydrazones,¹⁰⁷ disemicarbazones,¹⁰⁸ o-phenylenediamine starch dialdehyde,¹⁰⁹ starch esters,^{102,103,110} aminostarch,¹¹¹ aminothiazolone¹¹² and anionic starch derivatives, such as carboxylated starches,^{113,114} soluble¹¹⁵ and insoluble¹¹⁶ starch xanthates, carboxymethyl starch¹¹⁷ and other chemically modified starches.^{101,118-125} Complexing zinc acetate with enzymatically modified starches involving α -amylase and glucoamylase was also studied.¹²⁶

These studies have been performed chiefly for checking these derivatives for their ability as collectors of heavy metal ions from aqueous solutions. Coordination to metal cations stabilized thermally starch – urea biodegradable copolymer and reduced its affinity to enzymatic degradation.¹²⁷ Starch alkyl triethanolammonium chloride derivatives metal complexes with Cu^{2+} , Co^{2+} and Fe^{3+} ions possess a potent effect on some bacteria and fungi.¹²⁸ Starch ethers complexes with Fe, Mg, Ca, Mn, Zn, Co, Ni, Cu, and other oxides can be used as x-ray contrasts. They are non-toxic and stable, thus they can be injected into blood.^{102,103}

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Table 1. Computed enthalpies of the formation of the inner coordination spheres populated with D-glucose and water ligands

Enthalpy of the formation, $-\Delta H$ (kJ \cdot mol $^{-1}$)*												
Structure of the coordination sphere (D-glucose units + H ₂ O)												
Ion	0+4	0+6	1+3	1+5	2+2	2+4	3+1	3+3	4+0	4+2	5+1	6+0
Cl ⁻												
Co	-786			-812		-895		-654		-978	-953	-998
Cu	-695		-564		-826		-783		-854			
Fe		-954		-645		-956		-715		-987	-910	-752
Mn		-964		-704		-684		-497		-990	-494	-1005
Ni	-731		-781		-625		-589		-873			
NO ₃ ⁻												
Co		-517		-512		-607		-507		-785	-545	-765
Cu	-412		-759		-796		-598		-701			
Fe		-695		-688		-852		-362		-764	-852	-906
Mn		-556		-604		-464		-549		-799	-694	-952
Ni	-459		-681		-525		-689		-947			
CH ₃ COO ⁻												
Co		-541		-792		-541		-575		-818	-459	-845
Cu	-542		-579		-617		-515		-791			
Fe		-695		-458		-552		-622		-684	-561	-596
Mn		-556		-484		-384		-699		-729	-342	-847
Ni	-654		-312		-421		-554		-561			

*Energetically favored structures are given in bold figures.

Table 2. Rheological and tixotropic properties of gelatinized potato starch and its complexes with metals of the transition groups (10 mL 0.2M aq. solutions per 1g starch gel)

Salt added	Herschel-Bulkley model				R^2	η_{100} (Pa·s)	Surface of the hysteresis loop (W·m ⁻³)
	K (Pa·s ⁿ)	n (-)	τ_0 (Pa)				
None	1.93±0.13	0.66±0.01	0.01±0.00	0.9966±0.0000	0.41±0.01	1980.50±14920	
Cu(NO ₃) ₂	0.08±0.01	0.84±0.01	0.00±0.00	0.9999±0.0001	0.04±0.00	154.00±13.01	
CuCl ₂	0.06±0.00	0.87±0.01	0.02±0.01	0.9999±0.0000	0.03±0.00	111.70±10.61	
Cu(CH ₃ COO) ₂	0.06±0.00	0.88±0.01	0.10±0.03	0.9997±0.0001	0.03±0.00	158.00±5.37	
Ni(NO ₃) ₂	0.08±0.00	0.83±0.01	0.05±0.03	0.9998±0.0001	0.04±0.00	138.00±16.97	
NiCl ₂	0.04±0.00	0.96±0.02	0.13±0.04	0.9999±0.0001	0.03±0.00	112.90±4.81	
Ni(CH ₃ COO) ₂	0.07±0.01	0.85±0.02	0.00±0.00	0.9997±0.0000	0.04±0.00	178.80±2.55	
Co(NO ₃) ₂	0.06±0.01	0.86±0.02	0.01±0.00	0.9997±0.0002	0.03±0.00	147.40±3.68	
CoCl ₂	0.05±0.01	0.92±0.03	0.08±0.01	0.9995±0.0006	0.03±0.00	147.30±37.62	
Co(CH ₃ COO) ₂	0.04±0.01	0.94±0.03	0.09±0.02	0.9993±0.0006	0.03±0.00	137.50±47.38	
FeCl ₃	0.13±0.02	0.66±0.02	0.39±0.12	0.9994±0.0003	0.03±0.00	61.71±18.02	
MnCl ₂	0.08±0.00	0.84±0.00	0.01±0.00	0.9997±0.0000	0.04±0.00	182.10±19.52	
Mn(CH ₃ COO) ₂	0.06±0.01	0.88±0.01	0.06±0.01	0.9997±0.0001	0.04±0.00	170.75±3.32	

Table 3. Decomposition temperature (°C) in terms of the position of the main DTG peak in the thermograms of potato amylose, potato amylopectin, corn amylopectin, as well as amaranthus, tapioca and potato starches

Complexing salt		Position of the main DTG peak (°C) in thermograms					
Cation	Anion	Amylose	Amylopectin			Starch	
			Corn	Potato	Amaranthus	Tapioca	Potato
None		287	293	285	267	284	275
Co(II)	Cl	292	243	196	259	276	351
	NO ₃	289	248	291	207	299	248
	Ac*	332	208	290	287	283	295
Cu(II)	Cl	285	247	130	250	257	182
	NO ₃	286	247	265	274	249	248
	Ac*	144	269	282	298	280	274
Fe(III)	Cl	294	298	302	243	245	140
Mn(II)	Cl	281	291	134	240	293	236
	Ac*	314	242	288	307	212	280
Ni(II)	Cl	289	298	294	227	297	175
	NO ₃	294	271	233	302	264	250
	Ac*	131	262	237	289	115	140

*Ac = CH₃COO

Table 4. Yield (%) of volatile fraction and carbonizate after the thermolysis of complexes of potato starch (PS), potato amylose (PA), potato amylopectin (PAP), corn amylopectin (CAP), amaranthus starch (AS) and tapioca starch (TS) thermolyzed to 500°C

Coordinating salt	Yield (%)											
	Volatile fraction						Carbonizate*					
	PS	PA	PAP	CAP	AS	TS	PS	PA	PAP	CAP	AS	TS
CoCl ₂	28.9	35.7	25.1	39.3	40.3	41.9	-10.9	-13.7	+3.8	-0.8	-12.6	-4.6
Co(NO ₃) ₂	36.2	36.3	33.9	39.8	41.7	38.2	-8.2	-18.8	+2.6	+1.5	-7.6	+1.7
Co(CH ₃ COO) ₂	41.2	34.2	45.3	46.7	44.5	48.6	-14.2	-12.7	-4.8	-2.2	-20.2	-2.5
CuCl ₂	43.8	62.2	30.3	70.2	58.2	53.5	-6.3	-18.7	+0.3	-13.2	-19.2	-4.5
Cu(NO ₃) ₂	40.2	56.6	56.9	47.6	63.2	46.8	-14.2	-18.0	-7.9	+3.9	-20.2	+7.5
Cu(CH ₃ COO) ₂	35.7	37.3	59.4	49.8	58.9	62.2	+11.5	-6.3	-4.7	-0.8	-21.3	-10.5
FeCl ₃	21.8	31.2	40.4	40.9	41.7	46.8	+5.5	-17.8	-7.4	-5.9	-18.8	-10.1
MnCl ₂	47.7	54.1	40.3	54.1	56.7	58.6	-6.2	-16.6	+32.2	-7.1	-14.2	-10.1
Mn(CH ₃ COO) ₂	65.7	54.7	32.8	48.2	57.5	62.1	-5.9	-16.2	-4.8	+7.8	-21.3	-5.1
NiCl ₂	22.4	40.3	24.2	34.1	34.9	44.2	-3.4	-18.3	-8.0	+1.9	-16.3	-7.2
Ni(NO ₃) ₂	35.7	40.8	31.5	41.3	29.6	31.9	-6.9	-17.8	+25.0	-0.8	-14.5	-9.4
Ni(CH ₃ COO) ₂	30.8	26.5	40.6	43.8	34.4	28.6	-2.7	+3.0	+1.4	-8.5	-15.3	-1.8

*Compared to the yield from native, non-coordinated source.

Table 5. Permeate and retentate parameters and rejection coefficient of aqueous solution containing Zn(II), Pb(II), Cr(III) and Cr(VI) ions in mixtures solution (pH 5.7, transmembrane pressure 1.5 bar, t 2 hours, linear velocity 0.134 cm · min⁻¹)⁷⁵

Polymer		Unmodified starch (0.05 g · L ⁻¹)				Polyethylene glycol (1g · L ⁻¹)		
Metal ion	Metal	Permeate conc.	R	Retente	Permeate conc.	R	Retente	
conc.(mg·L ⁻¹)		(mg·L ⁻¹)	(%)	(mg · L ⁻¹)	(mg·L ⁻¹)	(%)	(mg · L ⁻¹)	
10	Zn	0.8956	91.044	20.353	1.0216	89.764	12.829	
	Pb(II)	1.6139	83.869	11.62	1.4115	85.865	19.29	
	Cr(III)	1.2261	87.739	24.79	0.8675	91.125	9.641	
	Cr(VI)	0.7936	92.064	24.65	0.8464	91.536	9.557	
30	Zn	8.8854	70.382	19.303	4.8345	83.885	13.678	
	Pb(II)	7.7271	74.243	18.01	5.1609	82.297	5.664	
	Cr(III)	4.4691	85.101	20.06	5.7948	80.684	17.03	
	Cr(VI)	5.8842	80.386	19.84	3.2601	89.133	17.74	
50	Zn	14.9245	70.151	19.527	9.158	81.684	21.77	
	Pb(II)	14.9955	70.009	27.75	11.3235	77.353	19.09	
	Cr(III)	10.1355	79.729	15.39	10.7525	78.495	22.71	
	Cr(VI)	14.5095	70.981	15.44	9.158	81.684	22.61	

Table 6. Yield of metal free carbonizate and volatile products from thermolysed cereals⁹⁷

Metal ion	Solid residue*	Volatiles
	(%)	(%)
Barley		
Ni(II)	12.4	46.1
Zn(II)	3.8	94.1
Cu(II)	5.8	61.1
Co(II)	54.3	39.6
Fe(III)	27.8	49.7
Cr(III)	21.4	37.7
Cr(VI)	10.5	24.8
Mn(II)	3.5	51.7
Oat		
Ni(II)	38.2	16.4
Zn(II)	11.2	65.8
Cu(II)	7.6	32.7
Co(II)	0.5	65.5
Fe(III)	12.7	86.1
Cr(III)	4.2	38.4
Cr(VI)	13.5	21.9

Mn(II)	7.5	69.6

Wheat		

Ni(II)	55.3	21.1
Zn(II)	3.1	31.6
Cu(II)	11.2	61.4
Co(II)	39.3	13.2
Fe(III)	33.1	51.3
Cr(III)	9.4	66.1
Cr(VI)	7.4	50.3
Mn(II)	7.4	81.4

Rye		

Ni(II)	3.9	44.2
Zn(II)	34.7	45.7
Cu(II)	3.6	68.1
Co(II)	23.7	28.6
Fe(III)	28.5	26.6
Cr(III)	12.4	52.4
Cr(VI)	51.4	12.5
Mn(II)	3.7	68.1

Triticale		

Ni(II)	2.3	82.7
Zn(II)	3.2	72.4
Cu(II)	2.1	84.2
Co(II)	4.3	58.7
Fe(III)	12.7	72.2
Cr(III)	80.2	5.4
Cr(VI)	1.8	34.2
Mn(II)	2.9	64.1

*After subtracting the mass of metal oxides.

FIGURE CAPTIONS

Figure 1. Starch complexes: a – inclusion complex of amylose, b – sorption complex of amylose, c – capillary complex of granular starch (black areas represent guest molecules).

Figure 2. Numbering atoms in D-glucose mer.

Figure 3. Starch lanthanum derivatives.

Fig. 1

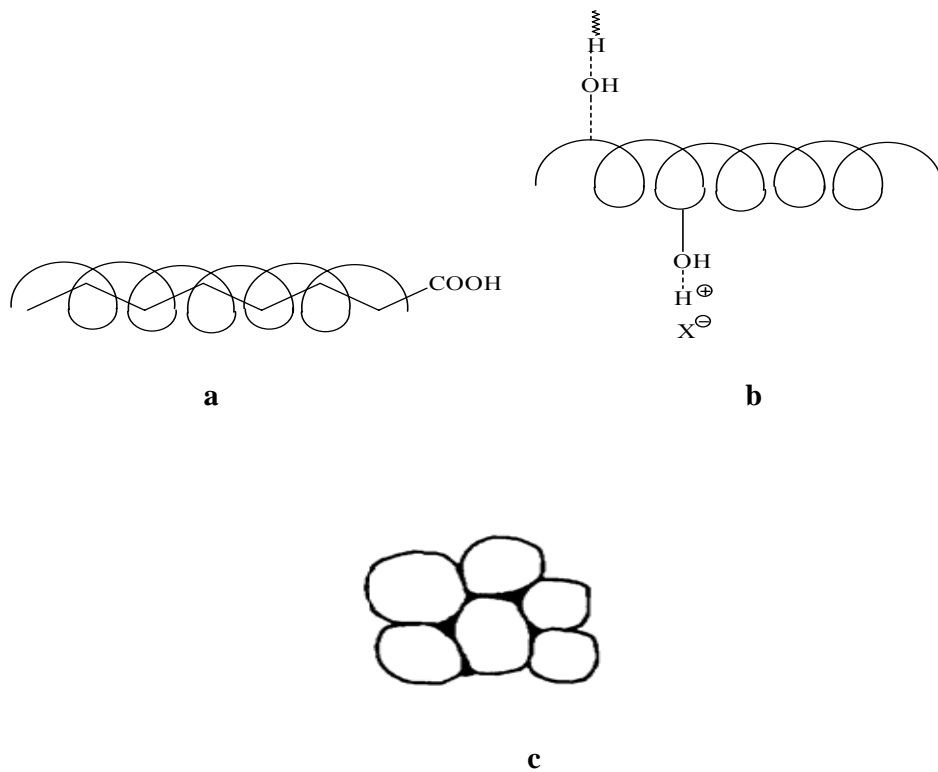


Fig. 2

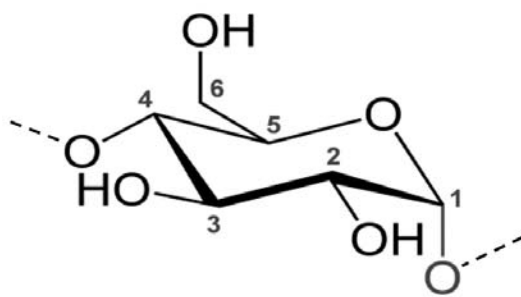


Fig. 3

