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Starch complexes with bismuth (III) and (V)

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Abstract

Studies are presented on bismuth (III) and bismuth (V) derivatives of starch. Bismuth (III) derivatives of starch were prepared by reaction of either bismuth trichloride or bismuth tri-*tert*-pentoxide with either granular or activated potato starch. Bismuth (V) starch derivatives were prepared by heating a solid blend of activated starch and $NaBiO_3$ in a microwave oven. Thermal analysis (thermogravimetry—TGA, differential thermogravimetry—DTGA, and differential thermal analysis—DTA) as well as IR- and X-ray photoelectron spectroscopies showed that starch reacted with bismuth (III) alkoxide by substitution of its one alkoxide group with one hydroxyl group of the D-glucose unit. D-Glucose units bound no more than two $Bi(O\text{-akyl})_2$ groups. D-Glucose units reacted with $BiCl_3$ in benzene with the evolution of hydrochloride which hydrolysed starch to dextrins. Starch was crosslinked on heating with sodium bismuthate. Bismuthated starches were slightly less thermally stable than original starches.

Keywords: Bismuth; Potato starch; Starch–metal complexes; Thermogravimetric analysis

1. Introduction

Primary and secondary hydroxyl groups of glucose units of starch react similarly as primary and secondary alcohols. Among others, with the involvement of these groups, starch readily esterifies inorganic and organic acids, forms ethers and metal derivatives, in which metal atoms are bound via valence bonds to the hydroxyl oxygen atoms (Tomasik & Schilling, 2002.) Heavy metal atoms might additionally be coordinated to other oxygen atoms residing closely to one another within the starch matrix as proven in iron (III) (Tomasik, Jane, Spence, & Anderegg, 1995), titanium (IV) (Tyrlik, Tomasik, & Anderegg, 1997), and lanthanum (Tomasik, Schilling, Anderegg, & Refvik, 2000) derivatives of starch. Such coordination considerably stabilises the carbon–oxygen–metal bond system against hydrolysis. Also, chlorine atoms in starch chloroaluminate are less sensitive to hydrolysis (Marusza & Tomasik, 1995).

Several potential applications of metal derivatives of starch have resulted from research in this field. For example, lithiated (Kratzl, Bertl, & Kaufmann, 1961) and thallated (I) (Baran, Sikora, Tomasik, & Anderegg, 1997) starches were considered as synthons in starch chemistry. The latter derivatives were also suggested as poison for rodents. Generally, starch can be a convenient carrier of bioelements. This point of view stimulated synthesis of V(III), Cr(III), Mo(V), and W(V) derivatives of starch (Tomasik, Anderegg, Jane, & Baczkowicz, 2001). Starch stannates were synthesised as bactericides and pesticides (Carraher et al., 1987, Patel & Pyle, 1964). Aluminum (Marusza & Tomasik, 1995) derivatives of starch could be potentially useful in the treatment of gastric ulcers and dermatological diseases. Other reported applications of metal derivatives of starch are antimoulding agents [As(III) (Gaver, Lasure, & Tieszen, 1951)], molding binders [Cu(II) (Gaver et al., 1951)], and additives for corrugated paperboard and plywood [Ti(IV) (Signaigo, 1951)]. Some bismuth (V) derivatives of starch were already reported previously (Jones, 1974).

Bismuth (III) derivatives have been used in therapy as antacids, astringents, antiseptics, antiprotozoals, and

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radiocontrasts (Budavari, O'Neil, Smith, & Heckleman, 1989; Doull, Klassen, & Amdur, 1980; Korolkovas & Burckhalter, 1976; Korzybski & Formanski, 1978; Pawełczyk, 1978). There are also examples of the medicinal use of pentavalent bismuth derivatives (Doull et al., 1980). In this study bismuth (III) and bismuth (V) derivatives of starch were prepared for biological tests as an aid in curing skin diseases and radiocontrasts.

2. Materials and methods

Materials. Potato starch was isolated by Potato Enterprise in Łomża (Poland) following Polish Standards PN-93/A-74710. This starch was dried for 2 h at 130 °C prior to experimentation. Chromatography grade thiophene-free benzene (Hopkin and Williams, Essex, England), analytical grade bismuth trichloride (Chemische Fabrik, Goerlitz, Germany), analytical grade sodium bismuthate (Merck, Dortmund, Germany), and bismuth tri(*tert*-pentoxide) (Gelest Inc., Tullytown, PA., USA) were used in the preparations.

Methods. Starch was activated by 1 h agitation of a 7% aqueous starch slurry at 96 °C followed by cooling to room temperature and precipitation of starch with ethanol. After 24 h the suspension was centrifuged and dried by exposure to air at room temperature.

Synthesis of Bi(III)–starch complexes.

(a) Oven-dried starch (8.13 g) and $BiCl_3$ (17.6 g) were refluxed for 6 h in benzene (50 cm^3) with protection from moisture (a $CaCl_2$-drying tube). The solid was filtered off and stored in vacuum desiccator.
(b) Activated starch (1.71 g) was blended with either 2.61, 5.21, or 7.83 g of Bi (*tert*-$OC_5H_{11})_3$ and heated for 15 min at 50% power in a microwave oven (Whirlpool AKL 535, 800W, Benton Harbor, Missouri, USA) operating at 2450 MHz. Heating below this energy and for less than 15 min resulted in incomplete reaction. The product was stored in a tightly closed container.

Synthesis of Bi(V)–starch complex. Activated starch (16.2 g) was thoroughly blended with either 28, 54, or 82 g of $NaBiO_3$ and heated in the microwave oven (Whirlpool AKL 535, 800W) for either 5, 10, or 15 min. Reaction products were stored in tightly closed containers.

Thermal analysis (thermogravimetry—TGA, differential thermogravimetry—DTGA, and differential thermal analysis—DTA). Individual samples (~100 mg) were placed in a corundum crucible and heated in air from room temperature to 500 °C at a rate of 10 °C/min. A computer-controlled instrument Paulik-Paulik-Erdey Derivatograph D-1500Q (Budapest, Hungary) was used.

IR-spectra. Spectra were recorded in KBr discs (1:100) using the FTIR instrument Matson 3000 (Madison, WI, USA)

X-ray photoelectron spectroscopy. Spectra were recorded with a Physical Electronics Model 5000 Multitechnique Surface Analysis System. The pass energy was 29.350 eV using a Mg source at 300 eV. Samples were mounted on double-sided adhesive tape. The positions of the peaks were normalised to the position of the main component of the C1s band at 285.0 eV.

3. Results and discussion

Five minutes of heating activated starch with sodium bismuthate in the microwave oven at 40% power resulted in carbonisation of the sample, whereas samples of granular starch appeared more stable and carbonised after 10–15 min heating at the same energy level. The addition of sodium bismuthate inhibited starch from carbonisation. Granular starch with the highest dose (1:3) of bismuthate survived heating for 15 min. but samples with the lower dose of the bismuthate carbonised. Reaction of activated starch with bismuth trialkoxylate required 15 min heating at the 50% energy level to be completed.

Evidence for the reaction between the components of the blends came from the results of TGA as well as IR and XPS spectra. Table 1 reports thermogravimetric data.

Thermogravimetric studies revealed that bismuth (III) alkoxide required more drastic conditions than sodium bismuthate (V) to react completely. Reaction of the Bi(III) reagent admixed to starch in the proportion of 3:1 could not be fully completed. Thermal analysis of the product obtained from the 1:1 reaction mixture exhibited two-steps, 13 and 22%, of weight loss, consecutively. The first weight loss follows the assumption that one Bi(III) alkoxide reacted with one hydroxyl group of the D-glucose unit to form starch dialkoxybismuthate (**3**) and the evolution of one molecule of *tert*-pentanol (**4**). On heating to 95 °C the product (**3**) decomposed with the loss of 2-methyl-1-butene (**6**) turning into starch hydroxyalkoxy bismuthate (**5**). In the subsequent step one molecule of *tert*-pentanol (**4**) was lost (calculated weight loss was 18.7%) and starch bismuth oxide (**7**) was formed

$$\underset{(1)}{\text{Unit of D-glucose}}\text{–OH} + \underset{(2)}{\text{Bi}(OC_5H_{11}\text{-}t)_3}$$

$$\rightarrow \underset{(3)}{\text{Unit of D-glucose}}\text{–O–Bi}(OC_5H_{11}\text{-}t)_2 + \underset{(4)}{t\text{-}C_5H_{11}OH}$$

$$(3) \rightarrow \underset{(5)}{\text{Unit of D-glucose}}\text{–O–Bi}(OC_5H_{11}\text{-}t) + \underset{(6)}{CH_2{=}C(CH)_3\text{–}CH_2\text{–}CH_3}$$

$$(5) \rightarrow \underset{(7)}{\text{Unit of D-glucose}}\text{–O–Bi=O} + (4)$$

Table 1
TGA and DTGA analysis of the reaction products of bismuth compounds with granular (GS) and activated (PS) starches

Bismuth reagent and starch/reagent proportion	TGA				DTGA, peak (°C)	
	Temperature range (°C)		Total accompanying weight loss[a] (%)			
	GS	PS	GS	PS	GS	PS
Experiments with Bi(III) (15 min at 50% energy)						
None	RT–280	RT–268	25	10	280	268
	280–400	268–310	45	18		
		310–400		20		
$Bi(O\text{-}tert\text{-}C_5H_{11})_3$						
1:1		RT–115		13(12.8)		95
		115–310		35(33.7)		280
2:1		RT–105		7.5(7.4)		
		105–248		28		246
		246–306		46(39.7)		
Experiments with $BiCl_3$ in benzene (6 h reflux)						
:$BiCl_3$ 1:1	RT–115		2.0			
	115–185		9.3		154	
	185–500		26.2			
Experiments with Bi(V) (15 min at 30% energy)						
None	RT–160	RT–160	2.0	3.3		
	160–300	160–330	24.0	33.9	286	280
	300–500	330–500	47.3	48.3		
$NaBiO_3$[b]						
1:1	RT–160	RT–160	1.5	2.4		
	160–345	160–275	19.4(11.7)	11.6(16.0)	266	270
	345–500	275–330	23.3	14.9		
1:2	RT–160	RT–160	1.4	1.4		
	160–274	260–280	10.2(9.8)	8.5(9.7)	269	271
1:3	RT–160	RT–160	2.5	2.2		
	160–280		14.8(8.6)	9.2(14.5)	277	275

[a] The weight loss calculated from experiments with individual components is given in parentheses.
[b] $NaBiO_3$ thermolysed without starch decomposed in the following stages: from RT to 160, 160–200, 200–400, and 400–500 °C losing 2.8, 5.7, 8.3, and 14.2% of its weight, respectively. The DTGA maxima peaks were at 126, 145, and 368 °C, respectively.

A similar reaction resulted from the mixture composed of a 2:1 proportion of the same reagents. One D-glucose unit (**1**) was substituted with two $Bi\text{-}(OC_5H_{11}\text{-}tert)_2$ groups. The first decomposition step, resulting in approximately 7.5% weight loss, could be distinguished. It corresponded to the loss of one molecule of 2-methyl-1-butene (**6**). Further thermal effects were attributed to the subsequent loss of another 2-methyl-1-butene (**6**) and two molecules of *tert*-pentanol (**4**). These thermal effects overlapped with one another and with the decomposition of the polysaccharide. The overall weight loss reached 46% whereas the weight loss due to decomposition of only the bismuth alkoxide moieties should lead to a weight loss of 39.7%. As a result of the sequence of thermal decompositions, bismuthated starch (**7**) was prepared.

Determination of the structure of complexes of Bi(V) with starch from corresponding thermograms was practically impossible. After losing residual water the complexes decomposed up to 400 °C in one step, which is common also for decomposition of non-reacted polysaccharide. Complexes from granular and activated starch decomposed at lower temperatures than the original starches. The decrease in the decomposition temperature was practically independent of whether granular or activated starch was reacted. An increased proportion of Bi reagent: starch provided products of a higher decomposition point. This effect could result from crosslinking of starch. However, the distribution of the reaction products was evidently dependent on the reacted starch. Granular starch reacted preferably on the surface utilising exudations from the granule interior developed on the surface (Starzyk, Tomasik, & Lii, 2001). Thus, the non-reacted portion of polysaccharide in the granule interior decomposed freely. The actual weight loss exceeded that calculated from the thermograms of particular components of the complexes.

Table 2
IR-characteristics of potato starch and its Bi-complexes

GS[a]	PS[a]	PS/Bi(III), 1:1[b]	GS/Bi(V)		PG/Bi(V)			Band assignment
			1:1	1:3	1:1	1:2	1:3	
3447vs	3437vs		3435s	3434s	3410s	3418s	3435s	ν OH
2942w	2922w	2949m	2947w	2920w	2957w	2931vw		ν CH
		2889m,b						ν CH
1653w	1638w	1574m	1667m	1667m	1667m	1667m	1667m	ν C=O
		1509m						δ OH
		1453 m						δ OH
1373w	1375w		1387w	1389w	1391w	1389w	1390w	δ CH
1161s	1157m		1161m	1128w				δ OH
1082s	1082s		1082m					δ C–O–C
983s	1018m	1009w	985m	984w				δ C–O
			861m					
			685m					
			630s					
			463vs	500vs	500vs	500vs	500vs	ν Bi–O

The notation for the band intensity is as follows: vs—very strong, s—strong, m—medium, w—weak, vw—very weak, b—broad.
[a] GS—granular starch, PS—activated starch. The data relate to starches after microwave heating.
[b] The spectral pattern for the 2:1 complex was similar.

Activated starch reacted with bismuthate more uniformly and crosslinking could take place in the whole volume of complexes. Complexes from activated starch decomposed less readily. The weight loss was in every case lower than the loss calculated. Obviously, the reaction products were alkaline. The pH of their aqueous solutions was around 10.5, which was similar to the pH of the sodium bismuthate solutions.

Thermograms of the reaction product of starch with $BiCl_3$ in benzene indicated that starch dextrinised. The product decomposed between 148 and 156 °C.

Infrared spectroscopy provided further evidence for the reaction of starch with sodium bismuthate (Table 2).

Spectral bands, particularly that around 1650 cm^{-1} moved up to 1667 cm^{-1} as the result of the reaction with bismuthate. The bands typical for O–H modes (1600–1000 cm^{-1}) ceased to an extent that was dependent on the extension of substitution of these groups with bismuth containing moieties (Fig. 1).

Comparison of the spectra of original granular starch and the product of its reaction with $BiCl_3$ in benzene (Fig. 2) showed significant dehydration of granular starch and, simultaneously, substitution of a large number of hydrogen atoms (within hydroxyl groups) with bismuth atoms. Taking into account the corresponding thermogram in Table 1, bismuthated starches were formed.

Table 3 presents results of XPS investigations of starch Bi(III) complexes. Comparison of the XPS spectra of both Bi (III) starch complexes in the 159–165 eV region confirmed that they were different compounds. Also, comparison of all XPS spectra in the C 2s region of 283–291 and O 2s region of 530–533 eV led to the same conclusion. Particular peaks resulting from the fitting of resulting spectra could not be attributed to unchanged carbon and oxygen atoms in the D-glucose units of starch. The different steric situation of individual D-glucose units of the starch macromolecule resulted in selective involvement of many particular atoms in

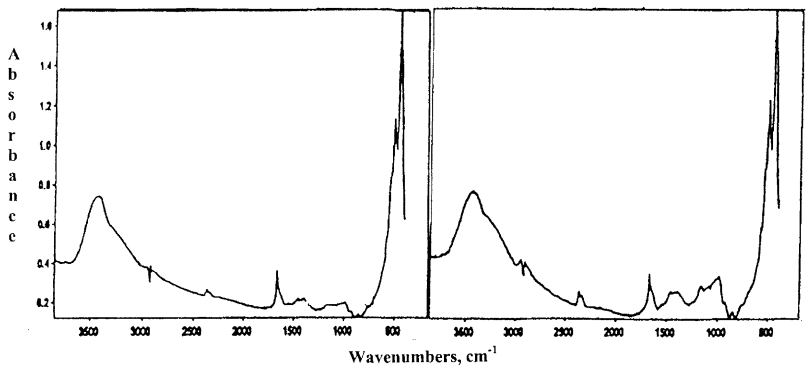

Fig. 1. Infrared spectra (in KBr) of the 1:1 complex of granular starch with sodium bismuthate (left) and the 3:1 complex from the same components (right).

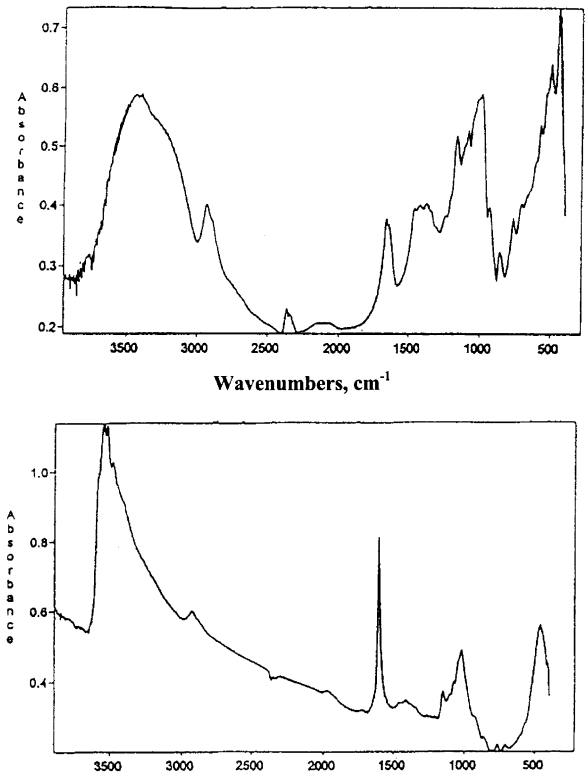

Fig. 2. Infrared spectrum (in KBr) of granular starch (top) and the complex resulting from reaction of that starch with $BiCl_3$ (proportion of reagents was 1:1, reflux in benzene) (bottom).

the formation of inter- and intra-molecular hydrogen bonds.

The 530–533 eV region of the spectrum seemed to be the most beneficial for the interpretation of the position of attachment of Bi atoms to starch because the oxygen atoms carried potential centres of ligation. The peak at 531.17 eV might result from the ionisation of the oxygen atom of the 6-CH_2OH group. This atom as a component of the primary hydroxyl group has the highest electron density among all oxygen atoms. Moreover, the area under that peak roughly showed that this signal should be attributed to the least abundant group of oxygen atoms in the starch macrostructure. As a consequence of the bismuth ion, this peak suffered essential changes which could be evidence for involvement of this oxygen atom in the bonding of the Bi atom. One could assume that other oxygen atoms also participated in the ligation of the Bi atom, because the other peaks also showed changes.

Table 3
Positions of the maximum ionisation energy of Bi, C, and O atoms [eV] in the XPS spectra of potato starch (control) and its Bi (III) complexes prepared from Bi(*tert*-$OC_5H_{11})_3$

Ionisation energy (eV) (samples with Bi:starch ratio)		
Control	1:1	2:1
	160.09(58.02)	169.89(54.08)
	166.15(41.98)	166.20(45.92)
285.17(6.21)	285.10(1.86)	
286.70(46.99)	286.70(52.61)	286.70(45.10)
288.22(33.70)	288.43(6.79)	288.06(10.63)
289.69(13.10)	290.61(5.44)	289.91(4.34)
	291.88(33.30)	291.89(39.94)
532.69(7.24)	531.23(6.13)	
	532.79(66.34)	532.84(37.56)
534.49(92.76)	533.92(27.53)	533.84(62.44)

4. Conclusions

1. Starch reacted with bismuth (III) alkoxide by the substitution of one alkoxide group with one hydroxyl group of the D-glucose unit. D-Glucose units bound no more than two Bi(O-akyl)$_2$ groups.
2. D-Glucose units reacted with $BiCl_3$ in benzene with the evolution of hydrochloride which causes hydrolysis of starch to dextrins.
3. Starch reacted with sodium bismuthate by crosslinking of the polysaccharide structure.

References

Baran, W., Sikora, M., Tomasik, P., & Anderegg, J. W. (1997). Thallium(I) starchate. *Carbohydrate Polymers*, *32*, 209–212.

Budavari, S., O'Neil, M. J., Smith, A., & Heckelman, P. E. (1989). *The Merck index* (11th ed). Rahway, NJ: Merck, pp. 195–198.

Carraher, C. E., Jr., Naoshima, Y., Butler, C., Foster, V. R., Gill, D., Williams, M., Giron, D., & Mykytiuk, P. D. (1987). Biological activities of tin-containing saccharides and polysaccharides. *Polymeric Materials Science and Engineering*, *57*, 186–190.

Doull, J., Klassen, C. D., & Amdur, M. O. (1980). *Casarett and Doull's toxicology* (2nd ed). New York: Macmillan, pp. 439–440.

Gaver, K. M., Lasure, E. P., & Tieszen, D. V (1951). Uniformly substituted glucopyranose polymers. US Patent 2,572,923; (1952), *Chemical Abstracts*, 46, 1786.

Jones, K. W (1974). Spanish white filler for paper manufacture. French Patent 2,220,623; (1975) *Chemical Abstracts*, 82, 172884a.

Korolkovas, A., & Burckhalter, J. H. (1976). *Essentials of medicinal chemistry*. New York: Wiley, pp. 381–382.

Korzybski, R., & Formański, T. (1978). *Pharmaceutical chemistry (in Polish)*. Warsaw: PZWL, pp. 268–270.

Kratzl, K., Bertl, H., & Kaufmann, E. (1961). Preparation of high-molecular-weight pharmaceuticals. Part III. Synthesis and labelling of vanillic acid diethylamide starch carbonate and related compounds. *Monatshefte fuer Chemie*, *92*, 384–392.

Marusza, K., & Tomasik, P. (1995). Aluminium and arsenic(III) starchates. *Starch/Staerke*, *46*, 13–17.

Patel, C. & Pyle, R. E (1964). High-viscosity starches. US Patent 3,117,892; (1964). *Chemical Abstracts*, 60, 8218.

Pawełczyk, E. (1978). *Chemistry of medicines (in Polish)*. Warsaw: PZWL, pp. 435–437.

Signaigo, F. K., (1951). Starch titanium reaction product. US Patent 2,570, 499; (1952). *Chemical Abstracts*, 46, 3782.

Starzyk, F., Tomasik, P., & Lii, C. Y. (2001). Optical properties of starch granules. Visible light absorption, transmission, and scattering by

potato starch granules. *Polish Journal of Food and Nutrition Sciences*, *10*(4), 27–34.

Tomasik, P., Anderegg, J. W., Jane, J., & Baczkowicz, M. (2001). Potato starch derivatives with some chemically bound bioelements. *Acta Poloniae Pharmaceutica, Drug Research*, *58*, 447–452.

Tomasik, P., Jane, J., Spence, K., & Anderegg, J. W. (1995). Starch ferrates. *Starch/Staerke*, *47*, 68–72.

Tomasik, P., & Schilling, C. H. (2002). Chemical modification of starch. *Advances in Carbohydrate Chemistry and Biochemistry*, in press.

Tomasik, P., Schilling, C. H., Anderegg, J. W., & Refvik, M. (2000). Starch–lanthanum complexes. *Carbohydrate Polymers*, *41*, 61–68.

Tyrlik, S. K., Tomasik, P., & Anderegg, J. W. (1997). Starch–titanium(IV) complexes. *Carbohydrate Polymers*, *34*, 1–7.