JOURNAL OF APPLIED POLYMER SCIENCE VOL. 8, PP. 1343–1355 (1964)

Water-Soluble Amylose: Preparation and Properties

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Synopsis

A dry form of amylose has been prepared that is easily soluble in water at all temperatures. It can go into solution even at high concentrations (up to 10%), forming very viscous liquids that are indistinguishable in appearance and properties from those prepared by autoclaving of retrograded amyloses. The solutions gel spontaneously upon standing. Two criteria were found to be important in the preparation of water-soluble amyloses: first, their molecular weight has to exceed 200,000; secondly, they must be dried from solution in a rapid manner, such as by drum- or spray-drying. Data from x-ray diffraction, infrared absorption, and iodine and water vapor absorption indicate the material to be an amorphous, substantially unbonded form of amylose, free of significant amounts of helical configuration. Data from β-amylase digestion limits and intrinsic viscosities on the water solutions of these amyloses indicate that they form true solutions in water and not merely dispersions.

INTRODUCTION

The best known property of amylose is its rapid and spontaneous retrogradation. For this reason the usual form of amylose is characterized by its insolubility in water. As the molecule is theoretically hydrophilic—in view of its many hydroxyl groups—one could speculate that if these groups were prevented from hydrogen bonding, a water-soluble form of amylose could be prepared. Such an amylose would not only be of interest from a theoretical point of view, but it might also be of value in industrial applications.

Consequently, a study was undertaken in this laboratory to determine the effects of a number of parameters on the water solubility of amylose. Of prime importance was the effect of molecular weight, followed by the effects exerted by different processing steps normally employed in the preparation of amylose. Partial impetus for studying the processing conditions was provided by the knowledge that the so-called V form of amylose (a helical configuration) is partially water-soluble, and that a report in the literature disclosed the preparation of an amorphous amylose that was soluble in hot water.[1]

No attempts were made to impart water solubility to amylose by chemical modifications.

The amyloses prepared by different means were to be characterized by procedures yielding maximum information on the nature of the material both as a solid and in solution, such as x-ray diffraction, infrared absorption, iodine and water vapor absorption, cold and hot water solubility, β-amylase digestibility, and intrinsic viscosity. The latter also served as a measure of molecular weight.

EXPERIMENTAL

Commercial starches—potato, corn, tapioca, and wheat—were used throughout the studies, as well as a commercially available form of amylose, Superlose (manufactured by Stein Hall & Co., New York, N.Y.).

Fractionation of Amylose from Starch

Two methods were generally employed, both yielding comparable results. The first method was due to Greenwood et al.,[2] who used thymol as the complexing-precipitating agent for amylose, followed by a butanol recrystallization step. The whole procedure was carefully carried out in an atmosphere of nitrogen gas to avoid the degradative effects of atmospheric oxygen, as recommended by Bottle et al.[3] As this method was somewhat time-consuming, a similar procedure was worked out involving the use of cyclohexanol as the precipitating agent, based on a suggestion by Hiemstra et al.[4] This compound produced dense and easily separable amylose precipitates in a shorter time. The details of the procedure were as follows.

A 440-g. portion of starch was slurried in a minimal amount of cold water and the slurry was dispersed in 20–25 l. of boiling, deaereated (with nitrogen) water. Boiling was continued with stirring for 30 min., passing nitrogen gas continually through the solution. 130 ml. of cyclohexanol was then added and boiling was continued for an additional 30 min., after which time the solution was allowed to cool to room temperature overnight. The precipitated amylose–cyclohexanol complex was removed by continuous centrifugation (either in a Sharples supercentrifuge or a Westphalia separator), reslurried in water, and purified by the repetition of the whole procedure. With this method 95% purity was easily obtained; a third repetition insured 100% purity.

Solubilization of Retrograded Amylose

Solubilization of dry amyloses could be effected in two ways: either by autoclaving[4,5] or by solubilizing in alkali. In the autoclaving method a 5% suspension of amylose in hot water was heated in a Parr reaction apparatus to 160°C., then cooled rapidly to below the boiling point. Such a solution had to be held above 45°C. to prevent gelling. When the amylose had been obtained from a fractionation procedure and was as yet undried, autoclaving temperatures were not necessary as the amylose was readily soluble in boiling water.

In the alkali-solubilization procedure, 1*N* aqueous NaOH solution was

chilled to 0°C., and the atmosphere in the reaction vessel was replaced with nitrogen gas. The low temperature, as shown by Whistler and Johnson,[6] prevented the degradation of amylose due to alkaline hydrolysis. Amylose was sifted slowly into the vessel with rapid stirring to a final concentration of 1%. The suspension was stirred under nitrogen and at 0°C. as long as needed for complete solubilization ($2^1/_2$–3 hr.). The solution was then neutralized by the addition of either concentrated HCl acid or glacial acetic acid. This procedure was used whenever the amylose was precipitated from the solution or used in applications not requiring immediate drying.

Drying of Amylose Solutions of Precipitates

Generally five methods of drying were employed: heat-drying under vacuum, freeze-drying, solvent-drying, drum-drying, and spray-drying.

Heat- and freeze-drying were done in the conventional manner. In solvent-drying, the amylose was precipitated from the solution (either autoclaved or alkali-solubilized) by the addition of ethanol, washed several times with absolute ethanol and ether, and dried in vacuum at room temperature.

Drum-drying was done with an atmospheric Buflovak drier with 18 in. stainless steel drums, using 50 psi steam pressure (drum surface temperature 165°C.), the closest possible spacing of drums, very sharp doctor blades, and a contact time of amylose with the drums of less than 60 sec.

Spray-drying was done with a small laboratory spray-drier (Niro Atomizer, Copenhagen, Denmark).

Intrinsic Viscosity

A Cannon-Ubbelohde dilution viscometer, size 100, capacity 40 ml., kept in a thermostatically controlled water bath at 30.10 ± 0.01°C., was used. Solutions of amylose were prepared at 1% concentration in the appropriate solvent (usually 0.5*N* NaOH, by dissolving in 2*N* NaOH at 0°C. with shaking, then diluting to 0.5*N*). The flow times were determined to 0.1 sec. in triplicate at concentrations of 1%, 0.8%, 0.615% 0.4%, and 0.2% by progressive dilution of the 1% solution. All solutions and solvents were filtered through glass wool prior to introduction in the viscometer. The value of intrinsic viscosity was arrived at by plotting $t - t_0/t_0C$ versus C and extrapolating to zero concentration, where t is flow time of amylose solutions in seconds, t_0 is flow time of the solvent, and C is concentration of amylose in grams per cent.

Purity of Amylose

The purity of amylose was determined by measuring its uptake of iodine, using the standard potentiometric titration procedure of Bates et al.[7] as modified by Lansky et al.[8]

X-Ray Diffraction

X-ray powder diagrams were obtained either with a direct-recording diffractometer or with a flat film camera with a film-to-sample distance of 5 cm. In both cases Cu $K\alpha$ radiation was used.

Infrared Absorption

The infrared absorption spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer, equipped with a NaCl prism, over a range of 2–14μ. The sample was usually in the form of a Nujol mull, or sometimes as a KBr disk.

Water and Iodine Vapor Absorption

In both tests accurately weighed samples of amylose were placed in desiccators containing, respectively, a saturated solution of $(NH_4)H_2PO_4$ and iodine crystals. The ammonium phosphate solution maintained a relative humidity of 93% at 25°C. The samples were weighed periodically to obtain the amount of water or iodine absorbed.

Solubility of Amylose in Water

The solubility of amylose was determined by dispersing a known quantity of it in water, with a Waring Blendor, then centrifuging the solution for 10 min. in a Servall angle centrifuge at 18,000 times the gravity to remove any unsolubilized material. The amount of amylose in solution was determined by hydrolyzing an aliquot of the solution in 1.5N H_2SO_4 for 2 hr. at 100°C., neutralizing the acid with 0.5N NaOH, and determining the amount of glucose in solution with the Glucostat reagent (Worthington Biochemical Corp.). The quantity of amylose in solution was calculated by multiplying the amount of glucose found by a factor of 0.9. Frequently, the solubility was merely estimated qualitatively, especially when no residue was left after centrifugation.

β-Amylase Digestion of Amylose

A volume of amylose solution containing exactly 15 mg. of amylose (the volume not exceeding 5.5 ml.) was added to a flask containing 25 ml. of 0.018N NaCl solution, 5 ml. of 0.375N acetate buffer of pH 4.8, and a quantity of water bringing the total volume to 30.5 ml. The flask was continually shaken in a water bath thermostatted at 38°C. A 2-ml. portion of a 0.375% solution of a known activity β-amylase was added, and the reaction was allowed to proceed for the desired length of time. A control solution containing all the ingredients except the active enzyme (a heat-killed enzyme solution was substituted) was carried through the same procedure. At definite intervals, aliquots of 1 ml. were removed from both solutions and analyzed for maltose content using a standard copper–arsenomolybdate colorimetric procedure. To obtain the amount of amylose hydrolyzed by

the enzyme, the quantity of maltose found was multiplied by a factor of 0.95.

RESULTS

Initially, an investigation was made of the effects of different processing steps on the chain-length of a standard amylose. In addition, amyloses of different starches were obtained by fractionation and their chain lengths determined. The results, in terms of intrinsic viscosity numbers, are shown in Table I.

TABLE I

Effects of Various Processing Steps on the Intrinsic Viscosity of Amylose. Intrinsic Viscosities of Amyloses from Different Starches

Amylose	Processing	Intrinsic viscosity in 0.5 *N* NaOH
Superlose	None	1.70
"	NaOH solubilization, neutralization without increase in temperature, EtOH precipitation and drying	1.55
"	As above, neutralization with increase in temperature	1.36
"	Autoclaving to 160°C., total processing time 35 min.	1.39
"	As above, followed by drum-drying	1.32
"	Autoclaving to 175°C., total processing time 40 min.	0.74
"	Autoclaving to 160°C., total processing time 40–60 min.	0.88–0.24
Corn starch	Thymol fractionation	1.21
Wheat "	" "	1.27
Tapioca "	" "	1.74
Potato "	" "	2.11
" "	Cyclohexanol "	2.32–3.45

As can be seen from these data, all processing steps introduce some degradation of the molecule, the steps utilizing heat being the more drastic. Different starches yield amyloses of different molecular weights, potato amylose being by far the largest molecule. For this reason all subsequent experiments were conducted with either amylose obtained by fractionation of potato starch, or when lower molecular weight materials were needed, with Superlose which is also a potato amylose. (It may be mentioned here that the relationship between the intrinsic viscosity number and the molecular weight is a linear one, as shown in Fig. 6.) All processing steps utilizing heat were also kept as short as possible in order to minimize degradation.

In the next series of experiments the effects of different drying procedures on the water solubility of the resulting amylose were investigated. In all

TABLE II

Solubilities and X-Ray Diffraction Patterns of Differently Dried Amyloses (Superlose)

Drying method	Appearance of dried product	Solubility in water	X-ray diffraction pattern
Spontaneous precipitation followed by vacuum-drying at 70°C.	Hard, off-white, semicrystalline material	Soluble only by autoclaving to 160°C.	Crystalline B pattern
Alcohol-precipitation followed by vacuum-drying at room temp.	Fine white powder	Soluble at 100°C., insoluble at 25°C.	Crystalline V pattern
Freeze-drying	Fluffy white powder	Soluble at 100°C., insoluble at 25°C.	Weak and diffuse B pattern
Drum-drying	Thin, flaky, gauzelike sheet	Soluble at 100°C., some samples soluble at 25°C.	Amorphous
Spray-drying	Extremely fine white powder	Soluble at 100°C., some samples soluble at 25°C.	Amorphous

cases the starting material was Superlose, solubilized by autoclaving. The results are shown in Table II.

As these data show, four of the five methods of drying yielded some measure of water solubility, only vacuum-drying at 70°C. producing a totally retrograded material. Many of the drum- and spray-dried amyloses were soluble both in cold and boiling water, although some samples were not fully soluble in cold water. The alcohol- and freeze-dried samples were insoluble in cold water, but soluble in boiling water.

In the following experiments the relationship between the molecular weight and the water solubility of amylose was investigated. Only drum- and freeze-dried samples were used, partly because these methods had previously shown most promise in yielding water soluble materials, and partly because such samples were the easiest to prepare. A number of different molecular weight amyloses was prepared, both by fractionation of potato starch and by degrading Superlose. Each fraction was characterized by determining its intrinsic viscosity, purity, and solubility. A typical solubility versus concentration plot for a cold water soluble amylose is shown in Figure 1; in this case up to 98% of the theoretical solubility

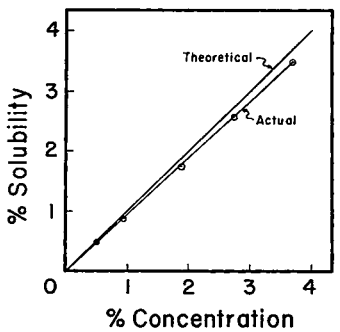

Fig. 1. Solubility of a drum-dried potato amylose in water at 25°C.

was achieved. At high concentrations the true solubility becomes somewhat obscured due to the rapid gelling of the solution.

Table III shows the solubility results of four freeze-dried amyloses, both at 25 and 100°C. It can be seen that the amylose with an intrinsic viscosity number of 1.36 is 100% soluble in hot water and that amyloses with lower intrinsic viscosities are progressively less soluble. Below the intrinsic viscosity of 0.66 the solubility seems to increase again; this is no doubt due to the degradation of some of the molecules to oligosaccharide size. None of the freeze-dried amyloses was significantly soluble in cold water.

TABLE III

Solubilities and Intrinsic Viscosities of Various Freeze-Dried Amyloses (Superlose)

Amylose	Intrinsic viscosity in 0.5*N* NaOH	Purity, %	Solubility, %	
			25°C.	100°C.
Degraded Superlose	0.24	100	1.4	28
"	0.66	100	0	6
"	1.02	100	6	57
Superlose	1.36	100	15.5	100

An analogous series of drum-dried amyloses is shown in Table IV, where cold water solubility is shown only. Again a fall-off in the solubility was observed below a certain intrinsic viscosity number, this time 1.26. It is obvious that above this value the chain length of the molecule exerts no restricting influence on the solubility.

TABLE IV

Solubilities and Intrinsic Viscosities of Various Drum-Dried Amyloses

Amylose	Intrinsic viscosity in 0.5*N* NaOH (before drying)	Purity, %	Solubility at 25°C., %
Superlose	0.74	100	Very slight
"	0.88	100	Slight
"	1.26	100	100
"	1.32	100	100
Potato amylose	1.95	96	100
" "	2.32	88	100
" "	2.65	100	100
" "	3.45	100	100

The results of the characterization of cold water soluble amyloses by means of x-ray diffraction, infrared absorption, water and iodine vapor absorption, and the limit β-amylase digestion are shown in Table II and Figures 2–5.

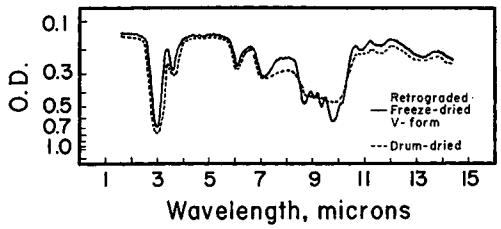

Fig. 2. Infrared absorption spectra of different amyloses.

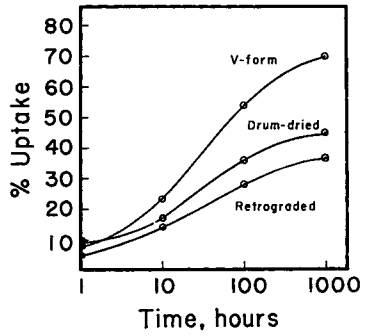

Fig. 3. Water vapor absorption by different amyloses.

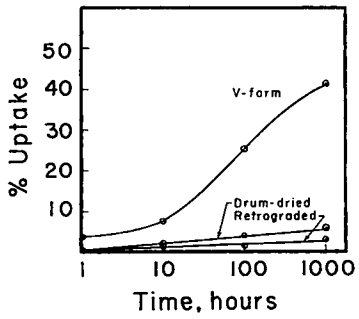

Fig. 4. Iodine vapor absorption by different amyloses.

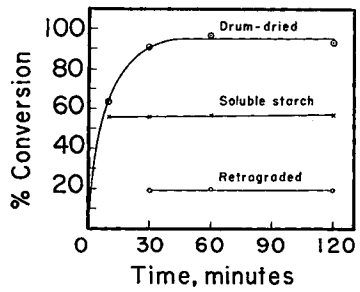

Fig. 5. β-Amylase digestion limits of two different amyloses and a "soluble starch."

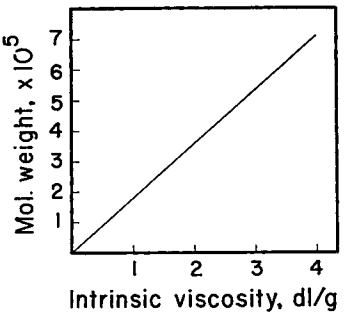

Fig. 6. Relationship between intrinsic viscosity in 0.5 N NaOH and the weight-average molecular weight of amylose.

As can be seen from the x-ray data in Table II, the cold water-soluble, spray-dried amylose is entirely amorphous, in contrast to the crystalline B pattern of the retrograded amylose and the crystalline V pattern of the ethanol-precipitated amylose. The freeze-dried sample shows a weak and diffuse B-type pattern. (The B and V patterns are well described by Rundle, Bear and co-workers.[9–13])

In Figure 2, the infrared spectra of four samples of amylose—a retrograded insoluble, a drum-dried cold water-soluble, a freeze-dried hot water soluble, and an ethanol-precipitated hot water-soluble—are reproduced. The only noticeable differences between the four spectra appear in the 8–11 μ region, where clearcut absorption peaks are evident in all but the drum-dried amylose. Absorption peaks in this region are ascribed to hydrogen bonding in linear polysaccharide polymers.[14–18] The peak at 3 μ, also due to hydroxyl groups, shows no differences between the four samples.

Water and iodine vapor absorption of three amyloses—cold water-soluble, V-form, and fully retrograded—are shown in Figures 3 and 4. As expected, the V-form absorbs large quantities of both water and iodine, whereas the retrograded amylose absorbs practically no iodine and a much smaller quantity of water. The drum-dried amylose absorbs only slightly larger amounts of both water and iodine than the retrograded amylose.

The limit of β-amylase digestion for two amyloses and a Baker soluble starch are shown in Figure 5. The starch is included for the purpose of comparison. As can be seen, the water-soluble amylose is digested almost to the theoretical limit of 100%, whereas the retrograded amylose is digested only to the extent of approximately 20%. The Baker soluble starch, for which the theoretical limit should be near 60%, is actually seen to reach this limit.

In order to provide a better visualization of the molecular weight range of amyloses encountered in this study, their weight-average molecular weights were calculated from the following form of the Staudinger equation:

$$[\eta] = 1.44 \times 10^{-5} \bar{M}_w^{0.93} \quad (1)$$

A number of investigators have determined the constants of the Staudinger equation for amylose from simultaneous viscosity and molecular weight determinations.[19–21] A good discussion of these results is given by Husemann et al.,[22] who recommend the above form of the equation for viscosities in 0.5*N* NaOH at 25°C. Cowie[23] has shown that the temperature dependence of the intrinsic viscosity of amylose in alkali is quite small; consequently, our measurements at 30°C. can be considered to be covered by this equation.

The molecular weights thus calculated were plotted against the intrinsic viscosity numbers, and the resulting plot is shown in Figure 6.

DISCUSSION

Although amylose tends to retrograde spontaneously, resulting in its insolubility, it can be prepared in a substantially unretrograded and water-soluble form. When in this form, it is easily and completely soluble in water at any temperature, and is capable of forming solutions at even high concentrations (up to 10%). The concentrated solutions are very viscous and in time form gels of very hard and rigid nature; the higher the concentration, the more rapid is the gelling. The solutions prepared with the soluble amylose are indistinguishable in appearance and properties from the solutions of retrograded amyloses prepared by autoclaving.

There are two important factors governing the solubility of such a dry amylose: first, the molecular weight has to exceed ~200,000; secondly, the conditions of preparation must be rigidly controlled. As regards the molecular weight, it seems that relatively small molecules of amylose are able to aggregate and retrograde quite rapidly, no doubt because of many interchain hydrogens bonds they are able to form. As the chain length increases, the molecules become too unwieldy for parallel aggregation and the amylose retrogrades at a far smaller rate. With very small molecules the solubility again increases, due to the presence of a relatively small number of hydrogen-bonding groups. At some point, there should be a minimum in solubility and a maximum in the rate of retrogradation. As our data show, there is a minimum in solubility near the intrinsic viscosity number of 0.66, corresponding well with the value of approximately 0.5 at which Whistler and Johnson[6] reported a maximum rate of retrogradation. Above this minimum solubility point the solubility increases steadily until complete solubility is attained in the range of 1.2–1.3 in terms of intrinsic viscosity numbers. This explains why in initial experiments some drum- and spray-dried amyloses were cold water-soluble whereas others were not; the starting amylose used then produced materials that were just in this intrinsic viscosity range.

It seems that there is no upper limit of solubility of amylose in terms of its molecular weight, at least not in the range encountered by us.

Aside of molecular weight considerations, the crucial steps in preparing water soluble amyloses consist of, first, solubilizing the amylose completely,

followed by drying it in the manner which removes water without permitting the establishment of inter- or intrachain hydrogen bonds. Drum-drying and spray-drying can fulfill these drying conditions completely, as they permit an almost instantaneous removal of water. When the drum-drying is done correctly, the final material appears as a very thin and airy, gauzelike sheet, easily crumbled into small particles. The correctly spray-dried amylose appears as an extremely fine powder.

In contrast, freeze-drying is not such an instantaneous process, resulting in a less soluble form of amylose, although the process is still sufficiently fast not to produce a completely retrograded amylose. At the other end of the scale, vacuum-drying of an amylose solution consists of a process of slowly increasing concentration gradients, accompanied by much chance for optimal rearrangement of amylose molecules for hydrogen bonding. The resulting dry amylose is completely retrograded. A special form of amylose—the V-form—can be prepared, as is well known, by precipitating the amylose from its solution with a suitable organic chemical, such as alcohol. This form of amylose exists in the form of a helical configuration with much less interchain hydrogen bonding than in the retrograded amylose; consequently, it is soluble in hot water.

The data from x-ray diffraction and infrared absorption suggest that the water-soluble amylose is truly an amorphous and substantially unbonded form of amylose. As it absorbs no iodine vapor, it contains no significant amounts of helical configuration. In view of these results it seems that this amylose exists in a completely random solid configuration, a state that can perhaps be described best as a "frozen solution." This is not an unreasonable assumption since it has been shown that amylose in solution exists as a random coil.[19,24]

When the water-soluble amylose is dissolved in water it seems to form a true solution and not merely a dispersion, as evidenced by the almost 100% β-amylase digestion limit. It is well known that β-amylase does not attack amylose unless the latter is completely unretrograded.[25,26] Further proof for the completely disaggregated solution was obtained by determining the intrinsic viscosity of a water-soluble amylose in water and comparing it to the intrinsic viscosity for the same amylose after dissolving it in alkali and neutralizing the alkali. The resulting intrinsic viscosity numbers were, respectively, 1.22 and 1.33. As it has been postulated that both water and aqueous salt solutions are theta-solvents for amylose,[19] the good agreement between the two values can be considered as proof that this amylose really formed a true solution in water.

The water-soluble amylose, as prepared by us, is quite likely a metastable form of amylose, in that it can revert spontaneously into a thermodynamically more stable retrograded form. How fast this will occur is another question, since many metastable materials are known to be stable for an indefinite period. The stability of the water-soluble amylose was not investigated; however, samples kept on hand were not observed to retrograde at a noticeable rate.

It is conceivable that if the water-soluble amylose were complexed with some agent so as to form preferential hydrogen bonding between the amylose and the complexing agent, an another preferred amylose configuration might be achieved. This matter might be of sufficient interest for further study.

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Résumé

On a préparé de l'amylose sec aisément soluble dans l'eau à toutes températures. Il peut passer en solution même à des concentrations élevées (jusqu'à 10%) en formant des liquides très visqueux qui ne se distinguent pas à première vue en ce qui concerne l'apparence et les propriétés de ceux préparés en traitant en autoclave des amyloses rétrogradées. Les solutions se gélifient spontanément en laissant reposer. Deux critères sont importants pour la préparation d'amyloses solubles dans l'eau; premièrement, leur poids moléculaire doit dépasser 200.000; deuxièmenent, elles doivent être assèchées de leur solutions de manière rapide, soit au moyen d'un séchoir tournant, soit au moyen d'un vaporisateur. Des résultats de diffraction par les rayons-X, d'absorption infra-rouge ainsi que d'absorption d'iode et de vapeur d'eau, indiquent que le matériel est une forme d'amylose amorphe, réellement non-liée, libre de quantités notoires d'amylose de configuration hélioïdale. Des résultats des limites dans la digestion des bèta-amyloses et des viscoités intrinsèques des solutions aqueuses de ces amyloses

montrent qu'elles forment des solutions vraies dans l'eau et non pas simplement des dispersions.

Zusammenfassung

Eine bei allen Temperaturen in Wasser leicht lösliche Trockenform von Amylose wurde hergestellt. Sie löst sich auch in hoher Konzentration (bis zu 10%) unter Bildung sehr viskoser Lösungen, die sich in Aussehen und Eigenschaften nicht von den durch Autoklavenbehandlung retrogradierter Amylose hergestellten Lösungen unterscheiden. Beim Stehenlassen der Lösungen erfolgt spontane Gelbildung. Für die Herstellung wasserlöslicher Amylose sind zwei Kriterien von Bedeutung: Erstens muss ihr Molekulargewicht höher als 200.000 sein und zweitens muss sie rasch, etwa durch Trommel- oder Sprühtrocknung, aus der Lösung getrocknet werden. Wie aus Röntgenbeugungs-, Infrarotabsorptions- sowie Jod- und Wasserdampfabsorptionsdaten hervorgeht, liegt in diesem Material eine amorphe, im wesentlichen ungebundene Amyloseform ohne grössere Anteile an Helixkonfiguration vor. Aus Daten über β-Amylase-Verdauungsgrenzen und Viskositätszahlen der wässrigen Lösung schliesst man, dass diese Amylose echte Lösungen und nicht nur Dispersionen bildet.

Received June 10, 1963