acid was obtained. After decarboxylation of the substituted malonic acid at 150–170°, the β-(5,6,7,8-tetrahydro-2-naphthoyl)-propionic acid was recrystallized from benzene using Norite; yield, 94.5 g. (85%); m. p. 120.5–121.5° (reported,[11] 121–122°). The methyl ester, prepared from 23 g. of the acid by means of diazomethane, solidified after distillation (b. p. 168–173° at 0.1 mm.) to a colorless solid; yield, 22 g.; m. p. 31–32° (reported,[15] 31°).

A Reformatsky reaction was carried out on 7.38 g. of the methyl ester as described. The product was an oil which was purified by evaporative distillation at 180° (0.05 mm.) and heated with 50 cc. of *N* sodium hydroxide in 50 cc. of methanol for three hours. The **3-(5′,6′,7′,8′-tetrahydro-2′-naphthyl)-2-hexendioic acid** (4.9 g., m. p. 183–185°) was sufficiently pure for the next step. A sample twice recrystallized from acetone–ligroin formed colorless prisms which melted at 185–186°.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.1; H, 6.6. Found: C, 70.0; H, 6.7.

The liquid dimethyl ester, prepared by means of diazomethane was evaporatively distilled at 180° (0.05 mm.); and 2.8 g. of it was cyclized as described. The cyclic keto ester was hydrolyzed and decarboxylated by heating with hydrochloric and acetic acids,[8] and the **3-(5′,6′,7′,8′-tetrahydro-2′-naphthyl)-cyclopenten-2-one-1** (VII) was evaporatively distilled at 150° (0.05 mm.) and recrystallized twice from methanol from which it crystallized in small colorless prisms; yield, 1.64 g. (77%); m. p. 82–82.5°.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.8; H, 7.6. Found: C, 84.6; H, 7.5.

The **semicarbazone** melted at 235–236°.

Anal. Calcd. for $C_{16}H_{19}ON_3$: N, 15.6. Found: N, 15.8.

A mixture of 50 mg. of VII and 10 mg. of palladium–charcoal catalyst was heated for fifteen minutes at 320° in an atmosphere of nitrogen. The 3-(2′-naphthyl)-cyclopenten-2-one-1 was evaporatively distilled at 150° (0.05 mm.); yield, 30 mg. (61%); m. p. 125–126°, alone and when mixed with a sample of VIa.

3-(5′,6′,7′,8′-Tetrahydro-2′-naphthyl)-cyclopentanone.—Reduction of 2.0 g. of the tetralylhexendioic acid by 2% sodium amalgam gave 2.0 g. (98%) of **β-(5,6,7,8-tetrahydro-2-naphthyl)-adipic acid** sufficiently pure for the next step; m. p. 159–160°. After two recrystallizations from acetone–ligroin a sample formed small colorless prisms which melted at 159.5–160°.

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.5; H, 7.2. Found: C, 69.8; H, 7.2.

The liquid dimethyl ester, prepared by means of diazomethane, was evaporatively distilled at 160° (0.05 mm.), 1.06 g. of it was cyclized (eight hours of refluxing), and the cyclic keto ester was hydrolyzed and decarboxylated as described.[8] The ketone was evaporatively distilled at 170° (0.05 mm.) and recrystallized twice from methanol; yield, 0.63 g. (83%) of colorless prisms; m. p. 73–74°. The same compound was formed in 74% yield when VII was hydrogenated in acetic acid in the presence of palladium–charcoal.

Anal. Calcd. for $C_{15}H_{18}O$: C, 84.1; H, 8.4. Found: C, 83.6; H, 8.5.

The **semicarbazone** crystallized in colorless prisms; m. p. 207–208°.

Anal. Calcd. for $C_{16}H_{21}ON_3$: N, 15.5. Found: N, 15.3.

Summary

The *cis* and *trans* forms of 1,2,3,4-tetrahydro-17-equilenone, an isomer of desoxyestrone, have been synthesized from 1-keto-*sym*-octahydrophenanthrene. The compounds were dehydrogenated by sulfur to the *cis* and *trans* forms of 17-equilenone (desoxyequilenin).

Three 3-arylcyclopentenones and the corresponding 3-arylcyclopentanones were prepared in which the aryl groups were 2′-naphthyl-, 2′-tetralyl- and 6′-methoxy-2′-naphthyl.

ANN ARBOR, MICHIGAN RECEIVED DECEMBER 31, 1943

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(15) Newman and Zahm, THIS JOURNAL, 65, 1099 (1943).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

Relationship between Solution Viscosity and Molecular Weight in the Amylose Series[1]

BY JOSEPH F. FOSTER[2] AND R. M. HIXON

Data on the solution viscosities of a series of amyloses prepared from various starch sources have recently been given.[3] Investigations of the osmotic behavior of some of these materials have been carried out with a view to establishing a relationship between molecular weight and viscosity for this series of glucose polymers. Unfortunately, it has been necessary to discontinue these investigations, temporarily, in the present rather preliminary stage.

Attempts to relate the solution viscosities of high polymers with their molecular weights through simple equations, of which that of Staudinger is best known, have been complicated by several factors. In the first place it is essential that the polymers be either linear or, if branched, have a constant degree of branching, so that the length or axial ratio may be expressed as a simple function of molecular weight. Much confusion has been caused in attempting to apply the Staudinger equation to starch and its degradation products, due to the fact that this polymer apparently consists of two types of molecules,[3,4,5] the one highly branched and the other linear. Obviously the same equations could not be expected to apply to both types of polymer.

In the second place it is now recognized that viscosity measurements on high polymers yield not a simple number average molecular weight as in the case of osmotic studies but one which is weighted in some manner.[6] Therefore it is essen-

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(3) Foster and Hixon, THIS JOURNAL, 65, 618 (1943).

(4) K. H. Meyer, "Natural and Synthetic High Polymers," Interscience Publishers, Inc., New York, N. Y., 1942, pp. 387–417.

(5) Bates, French and Rundle, THIS JOURNAL, 65, 142 (1943).

(6) Kraemer and Lansing, *J. Phys. Chem.*, 39, 153 (1935); Flory, THIS JOURNAL, 65, 372 (1943).

tial that the material used be well fractionated if a comparison of values from the two methods is to be made.

A third point of very great importance which must also be considered is the degree of flexibility (randomness of kinking) of the polymer chains. Theoretical derivations of Kuhn[7] and more recently Huggins[8] predict, for the case of rigid rods, a linear relationship between the intrinsic viscosity and the square of the molecular weight (or length). However, if the chain is kinked in a random manner the result is compatible, according to Huggins, with the Staudinger equation

$$\eta_i = KM \qquad (I)$$

Kuhn,[9] in fact, predicts for such molecules a dependence of η_i on a power of M even lower than 1.0, the lower limit being 0.5. Most actual long-chain molecules would be expected to behave in a manner intermediate between these extremes and a general form for the equation relating these quantities would be[10] where α takes on values be-

$$\eta_i = KM^{\alpha} \qquad (II)$$

tween the limits 0.5 and 2.0 depending on the flexibility of the chains. Values for α of 0.64 for the polyisobutylene series[11a] and 0.67 for cellulose acetates[11b] have been found.

The evidence is quite conclusive that the amyloses are linear polymers,[3,4,5] and there is some evidence that they are fairly homogeneous with respect to molecular size.[5] With regard to the third point mentioned above, the amyloses are of peculiar interest. Inspection of molecular models[12] emphasizes in a striking manner the difference between this polymer and a polymer such as a simple hydrocarbon or rubber, or even cellulose. The amylose molecule is remarkably rigid due to restricted rotation about the glucosidic linkages. Thus in this case it might be expected that the value of the exponent in Equation (II) would be considerably greater than unity, perhaps approaching the maximum value of 2.0. The present paper presents evidence that this is the case.

Osmotic Pressure Measurements

Apparatus.—The osmotic cell used for this investigation was of the dynamic type working on the counter-pressure principle, patterned after a cell previously described by Hepp.[13] Peters and Saslow[14] have found this type of cell satisfactory for aqueous solutions. The design was considerably simplified in the present cell through the use of all-brass construction. A flat, circular brass block was drilled vertically and then horizontally to meet the glass capillary which was platinized and set in Wood's metal to provide a tight seal. The membrane was placed on top of this block over a disk of bolting silk and clamped in place by means of a brass ring. To prevent upward motion of the membrane, it was weighted with a grooved brass block which fitted inside the brass ring. Evaporation of solvent was minimized by covering the cell with an inverted glass funnel, open to the atmosphere through a fine capillary.

Suitable pressures (positive and negative) were obtained by means of leveling bulbs containing water and were measured with a water manometer.

Membranes.—Cellophane[15] was found to be the most satisfactory membrane material for this work in spite of its low permeability to organic solvents. Three grades of cellophane were tried, numbers 300, 450 and 600. In general the thinner grades, 300 and 450, were somewhat more satisfactory. Swelling in water–alcohol as recommended by McBain and Stuewer,[16] was found to increase the permeability temporarily but this decreased again after a few hours contact with the organic solvent. Ordinary parchment was also fairly satisfactory, being much more permeable than cellophane and hence giving more rapid attainment of equilibrium (about one hour as compared to four to eight hours with cellophane). In a few cases parchment disks were found permeable to the solute molecules. This was in no case observed with cellophane.

Materials.—Inasmuch as there is no solvent for amylose suitable for osmotic pressure work it was necessary to render the material soluble in organic solvents. This was done by acetylating, using pyridine and acetic anhydride which have been shown to produce no degradation.[17] The amyloses were the same preparations used in the viscosity work.[3] Chloroform was the solvent for all measurements reported here.

Procedure.—It is necessary to correct the equilibrium pressure in the cell for head of solvent and capillarity. This zero point was ascertained experimentally prior to each run by filling the cell with solvent and permitting it to come to equilibrium. The value varied somewhat from run to run, apparently due to slight leakage around the membrane which affects the rate of flow. This variation constitutes the chief uncertainty of the measurements.

Following the determination of the zero point the solvent was withdrawn from the chamber above the membrane and the top of the membrane pressed dry with filter paper. The cell was now filled with solution and permitted to come to equilibrium. The rate of flow of the meniscus was ascertained at various pressures using a low power microscope mounted on a micrometer, and the equilibrium point obtained by interpolating to zero flow rate.

Results and Calculations

The osmotic pressure results are given in Table I, and in Fig. 1 the quantity π/C is given as a function of concentration.

Substituting the limiting values of π/C in the van't Hoff equation the molecular weights of corn and tapioca amylose are found to be 42,000 and 75,000, respectively, corresponding to 260 and 460 glucose units.

Viscosity of Amylose Acetates in Chloroform.—The viscosities of the acetates of corn, tapioca and potato amyloses (butanol method) were determined. An Ostwald viscometer (capillary dimensions 15 by 0.04 cm., capacity 10 ml., flow time with chloroform about 21 sec.) equipped with ground-glass joints to cut down solvent evaporation was used. All measurements were at 25 ± 0.01° and all the usual precautions were observed. Results are shown graphically in Fig. 2.

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[7] Kuhn, *Z. physik. Chem.*, **A161**, 1 (1932).

[8] Huggins, *J. Phys. Chem.*, **42**, 911 (1938); **43**, 439 (1939).

[9] Kuhn, *Kolloid-Z.*, **68**, 2 (1934); *Angew. Chem.*, **49**, 858 (1936).

[10] In this connection see Simha, *J. Applied Phys.*, **13**, 147 (1942).

[11] (a) Flory, THIS JOURNAL, **65**, 372 (1943); (b) Bartovics and Mark, *ibid.*, **65**, 1901 (1943).

[12] Photographs of such models of amylose have been published by Caesar and Cushing, *J. Phys. Chem.*, **45**, 776 (1941).

[13] Hepp, *Z. ges. expl. Med.*, **99**, 709 (1936).

[14] Peters and Saslow, *J. Gen. Physiol.*, **23**, 177 (1939).

[15] Supplied through the courtesy of E. I. du Pont de Nemours and Company, Inc., Wilmington, Delaware.

[16] McBain and Stuewer, *J. Phys. Chem.*, **40**, 1157 (1936).

[17] Staudinger and Husemann, *Ann.*, **527**, 195 (1937).

TABLE I

SUMMARY OF RESULTS

Material	Concn., g./100 ml.	Pressure π, mm. of H_2O	π/C	Membrane
Corn amylose acetate	0.237	9.0	38	Parchment
	.474	2.10	44	Parchment
	.860	46.0	53	Cellophane
	.860	49.0	57	Cellophane
	1.440	92.0	64	Cellophane
	2.400	214.0	89	Cellophane
	2.480	234.0	94	Cellophane
Tapioca amylose acetate	0.197	4.0	20	Cellophane
	.197	4.0	20	Parchment
	.197	5.5	28	Parchment
	.396	10.5	26	Parchment
	.596	17.5	29	Parchment
	.996	33.0	33	Parchment
	.996	33.5	34	Parchment

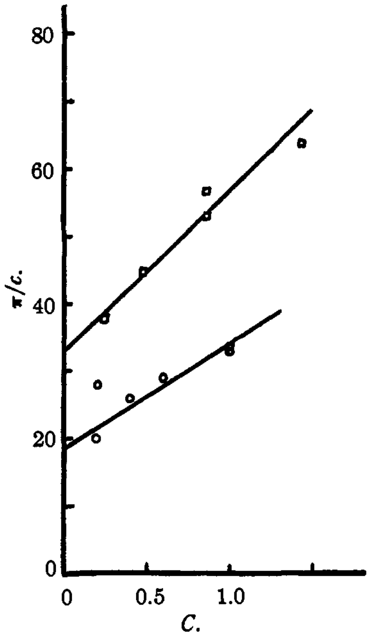

Fig. 1.—Concentration dependence of the function π/c. Concentration is given in g. per 100 ml., π in mm. of water. Squares are experimental points for corn amylose, circles for tapioca amylose.

Discussion

Unfortunately, of the materials whose viscosity behavior was studied earlier,[3] only three were available in large enough quantities for acetylation and osmometric study, namely, corn, tapioca and potato butanol precipitates. Discordant results were obtained with the latter, at least in part due to a strong tendency of even 1% solutions in chloroform to gel. Nevertheless, other evidence is available as to molecular weight of some of these preparations. Schoch[18] has recently reported "alkali numbers" for the potato and corn amyloses. The method is admittedly empirical but it is apparently a measure of the number of reducing groups present. It does not seem unlikely that for molecules of this size, where any inconsistencies should enter equally in the two cases, the ratio of the molecular weights would be approximately inversely proportional to the ratio of the alkali numbers which are about 25 for corn and 11 for potato amylose. This would correspond to a value of about 600 glucose units for potato amylose based on the osmometric value for corn.

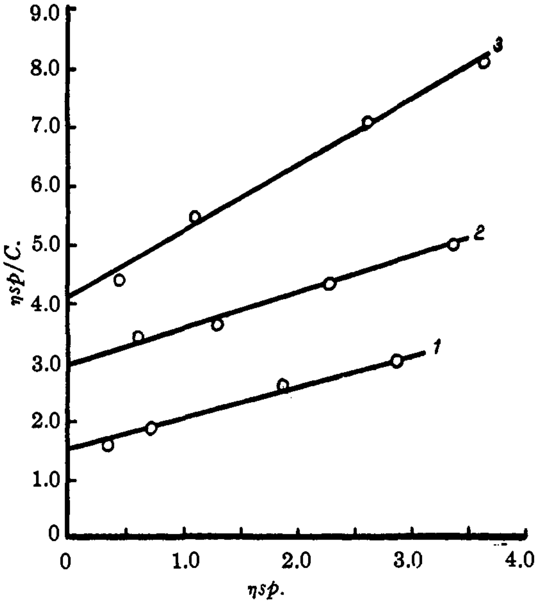

Fig. 2.—Calculation of the intrinsic viscosities of: 1, corn; 2, tapioca and 3, potato amylose acetates.

Haworth, *et al.*,[19] have determined the chain length of a synthetic starch preparation, prepared in identically the same manner as the one used here, by means of analysis for end-groups (tetramethyl glucose analysis). They report a value of 80–90 glucose units.

Reducing value measurements,[20] both by hypoiodite and ferricyanide, on the amylodextrin fraction number 4 give values of the order of 50 glucose units for the molecular size.

In Fig. 3 these various values are plotted as log N *versus* log η_i where N is the number of glucose units in the molecule. The slope of this curve, 1.5, corresponds to α in Equation II.

All of the molecular weight calculations made above yield number average molecular weights. Too much emphasis cannot be placed on the value of 1.5 for α in view of uncertainty as to the homogeneity of these materials. Fraction 4 of amylodextrin was prepared by careful fractionation and should be reasonably homogeneous. The other materials have not been fractionated except in that the preparation itself probably gives fractionation, the longer amylose molecules precipitating preferentially. However, in view of the fact

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[18] Schoch, THIS JOURNAL, 64, 2957 (1942).

[19] Haworth, Heath and Peat, *J. Chem. Soc.*, 55 (1942).

[20] Bates, unpublished data in this Laboratory.

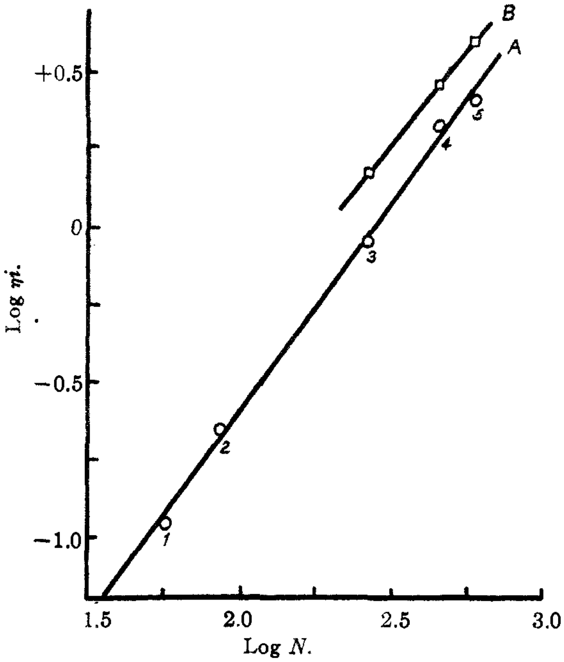

Fig. 3.—Relation between intrinsic viscosity and degree of polymerization for amyloses in ethylenediamine (A) and amylose acetates in chloroform (B): 1, amylodextrin 4; 2, synthetic starch; 3, corn; 4, tapioca and 5, potato amylose.

that most of these materials are prepared from natural sources with little if any degradation it does not seem unlikely that their homogeneity approaches that of materials prepared by fractional precipitation of originally highly polydisperse materials such as synthetic polymers (or even such natural polymers as cellulose where considerable degradation is involved in the preparation). Also the fact that these different materials can be titrated quantitatively with iodine in mixtures[5,21] would seem to indicate that the molecular weight distributions are fairly small relative to the magnitude of the differences between them. For the present, however, it is perhaps best to consider the value 1.5 as an upper limit for α in this series. There would seem to be little doubt that the value is greater than unity confirming the expectations from the rigidity of Fischer-Hirschfelder models of amylose.

The fact that α for the acetates in chloroform is the same, within the experimental error, as for the amyloses in ethylenediamine (as shown by the similar slopes in Fig. 3) is somewhat surprising. This would seem to indicate the molecules to be equally rigid in the two cases.

Summary

1. Osmotic pressure values for corn and tapioca amylose are given and molecular weights of other members of this series estimated from other considerations.

2. A dependence of intrinsic viscosity on a power of molecular weight greater than unity is indicated, confirming expectations from the comparative rigidity of Fischer–Hirschfelder models of amylose.

3. The rigidity of acetylated amylose molecules in chloroform appears to be the same as that of amylose in ethylenediamine.

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[21] The implications of this observation are being further investigated. It does not seem unlikely that the iodine titration method may provide a means for the direct determination of molecular weight distribution in amylose preparations.

Ames, Iowa Received August 20, 1943

[Contribution from the Division of Plant Nutrition, College of Agriculture, University of California]

The Preparation and Purification of Glucose 1-Phosphate by the Aid of Ion Exchange Adsorbents

By R. M. McCready[1] and W. Z. Hassid

The establishment of glucose-1-phosphate (Cori ester) as an important intermediary product in the synthesis and breakdown of glycogen and starch[2,3] contributed much toward the stimulation of further study of the mechanism of carbohydrate formation in general. Since studies along these lines require an available supply of glucose-1-phosphate, it is important to have a satisfactory method whereby this ester can readily be prepared. Although Hanes' method[3] of preparing the ester from starch in fairly large quantities is satisfactory, the product is usually contaminated with small amounts of dextrins, which are very difficult to remove, and which are objectionable in certain types of experiments. Green and Stumpf[4] for example, in studying the influence of different carbohydrates on the synthesis of starch from glucose-1-phosphate *in vitro*, were obliged to use synthetic glucose-1-phosphate, which is laborious to prepare. Hanes' procedure can be very much shortened and improved by using ion exchange adsorbents,[5,6] whereby the following steps are eliminated: concentration of large volumes of

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[1] Present address, Western Regional Research Laboratory, U. S. Department of Agriculture, Albany, Calif.

[2] C. F. Cori, *Endocrinology*, **26**, 285 (1940).

[3] C. S. Hanes, *Proc. Roy. Soc.* (London), **B129**, 174 (1940).

[4] D. E. Green and P. K. Stumpf, *J. Biol. Chem.*, **142**, 355 (1942).

[5] The synthetic resins IR-100 and IR-4 were obtained from the Resinous Products and Chemical Company, Inc., Philadelphia, Penna.

[6] For a review on the use of ion exchange adsorbents see: R. J. Myers, *Ind. Eng. Chem.*, **35**, 858 (1943).