[Contribution from the Department of Chemistry of The Ohio State University]

Condensation Polymers from Tetra-*O*-acetylgalactaroyl Dichloride and Diamines[1,2]

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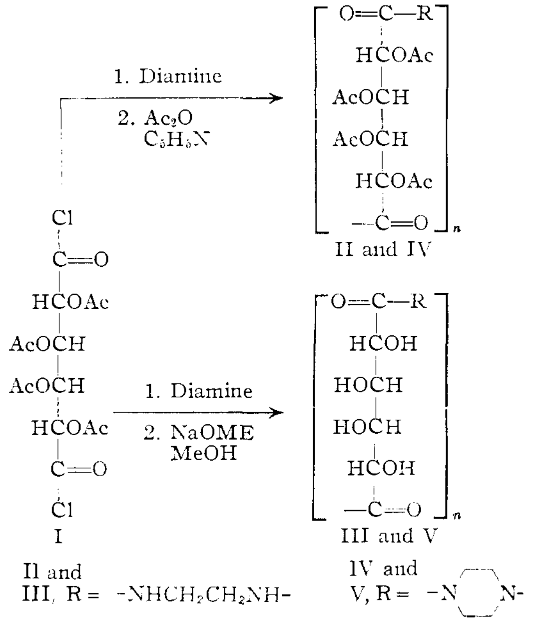
Polymers were obtained from the condensation of tetra-*O*-acetylgalactaroyl dichloride with ethylenediamine or piperazine with subsequent reacetylation. Deacetylation was effected with probable hydrolytic degradation to yield polymers containing 30–40 repeating units. These hydroxy polyamides were unstable to both acid and basic media. Certain monomolecular amides and an ester were synthesized for comparative purposes.

The preparation of polymers containing carbohydrate repeating units has been of considerable interest in recent years. Haworth, Heath and Wiggins[3] reported the condensation of 1,6-diamino-1,6-dideoxy-di-*O*-methylene-D-mannitol with di-*O*-methylene-D-glucaric acid to afford a brittle polymer which could not be drawn. Somewhat later, Wiggins[4] reported the condensation of 1,2:5,6-dianhydro-3,4-*O*-isopropylidene-D-mannitol with 1,6-diamino-1,6-dideoxy-di-*O*-methylene-D-mannitol to produce a polymer which exhibited fiber-forming characteristics. Mehltretter and Mellies[5] have reported the condensation polymerization of 2,4:3,5-di-*O*-methylene-D-gluconic acid upon heating in pyridine containing benzoyl chloride. The acrylate and methacrylate esters[6] and the allyl ethers[7] of a number of carbohydrates have been prepared and polymerized. The preparation of carbohydrate derivatives of polyvinyl alcohol and polyvinylamine have been studied.[8] The thermal condensation of methyl 2-deoxy-β-D-galactofuranoside has been shown to afford low molecular weight polymers.[9] Mora and Wood[10] have furnished details of the synthesis of high molecular weight polysaccharides arising from the thermal polycondensation of α-D-glucose under acid conditions.

The ease of synthesis of tetra-*O*-acetyl-galactaroyl (mucyl) dichloride (I) suggested that its reaction with diamines or diols should be examined. This difunctional acyl halide should provide polymers which could be deacetylated to the parent hydroxylic substance which should then be convertible to other derivatives.

The diamines, ethylenediamine and piperazine (2 moles), were added at 0° to stirred suspensions of I (1 mole) in benzene. The second mole of amine was employed to combine with the hydrogen chloride liberated in the condensation and could be replaced by tertiary amines. High yields were obtained of polymeric products which had been partially deacetylated under the final basic conditions of the reaction. Reacetylation of these products afforded the fully substituted derivatives II and IV. The acetylated polymers were insoluble in the common organic solvents. They dissolved in 50 to 80% sulfuric acid with degradation.

The action of methanolic sodium methoxide on the originally prepared polymers caused deacetylation, polymers III and V being isolated in 30–40% yields. These hydroxy polyamides dissolved with degradation in anhydrous ethylenediamine and 50–80% sulfuric acid and without chemical change in 50% lithium chloride. Intrinsic viscosities, [η] = 0.13 deciliter per gram for III and 0.11 for V, were obtained in this latter solvent. Light scattering investigations on III afforded a minimum molecular weight of 8,500 or about 36 repeating units. Experimental difficulties in obtaining exact stoichiometry of the reacting species were probably responsible, in part, for the low molecular weights achieved. For example, a 1% deviation from stoichiometry would result in a maximum theoretical chain length of about 100 repeating units.[11] Deviations of this order could easily have arisen in the current work.



The polymers were degraded in ethylenediamine solution as shown by viscosity changes (Fig. 1). The differences in the limiting viscosities obtained are probably the result of fractionation during

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[1] This work was performed under contract, DA-33-019-ord-2025, between the U. S. Army Ordnance Corps (technical supervising agency, Ballistic Research Laboratories of Aberdeen Proving Ground) and The Ohio State University Research Foundation (Project 675).

[2] From the M.Sc. Thesis submitted by Madeline S. Toy, The Ohio State University, 1957; complete infrared spectra of all new compounds are therein presented.

[3] W. N. Haworth, R. L. Heath and L. F. Wiggins, *J. Chem. Soc.*, 155 (1944).

[4] L. F. Wiggins, *ibid.*, 384 (1946).

[5] C. L. Mehltretter and R. L. Mellies, This Journal, **77**, 427 (1955).

[6] W. N. Haworth, R. L. Heath and L. F. Wiggins, *J. Chem. Soc.*, 448 (1946).

[7] P. L. Nichols and E. Yanovsky, This Journal, **66**, 1625 (1944).

[8] F. Micheel and W. Himmelmann, *Naturwiss.*, **42**, 297 (1955).

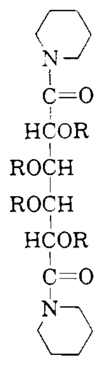
[9] W. G. Overend, F. Shafizadeh and M. Stacey, *J. Chem. Soc.*, 384 (1949).

[10] P. T. Mora and J. W. Wood, This Journal, **80**, 685 (1958).

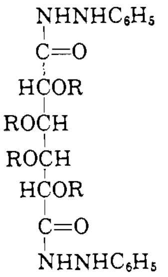
[11] F. W. Billmeyer, Jr., "Textbook of Polymer Chemistry," Interscience Publishers, Inc., New York, N. Y., 1957, p. 181.

preparation of the various derivatives from the original polymers. The low yields of the deacetylated polymers, III and V, prepared in strongly basic media, are probably due to degradation effected by amide hydrolysis. Furthermore, the molecular weight of these materials, as determined by the light scattering method, is undoubtedly considerably lower than that of the polymers originally prepared. It recently has been shown[12] that the aldonamides are hydrolyzed more easily than are the unsubstituted amides. Therefore, in the present case, the degradation of the hydroxy polyamides might be expected to occur with greater ease than with the simple aliphatic polyamides.

The infrared spectra[2] of the polymers and the various model compounds prepared (VI to IX) fully confirmed the assignment of the polyamide structures, II to V. The model compounds are new substances: 1,1′-(tetra-*O*-acetylgalactaroyl)-dipiperidine (VI), 1,1′-(galactaroyl)-dipiperidine (VII), tetra-*O*-acetylgalactaric bis-(phenylhydrazide) (VIII), galactaric bis-(phenylhydrazide) (IX) and bis-(2-hydroxyethyl) tetra-*O*-acetylgalactarate. The analytical data obtained further substantiated the structures (II to IX) assigned.



VI, R = CH_3CO
VII, R = H



VIII, R = CH_3CO
IX, R = H

Nitration of the deacetylated polymers by various techniques[13] failed to give well defined products and very low yields of unstable materials were obtained. It appears that acid media cause severe degradative hydrolysis of the polymers.

Experimental

Preparation of Tetra-*O*-acetylgalactaroyl (Mucyl) Dichloride (I).—Galactaric (mucic) acid, 100 g., was refluxed for 2 hr. with 625 ml. of acetic anhydride containing 2.5 ml. of concd. sulfuric acid. The mixture was filtered hot and the filtrate cooled. The precipitate of tetra-*O*-acetylgalactaric acid which formed was collected by filtration, washed with anhydrous acetic acid and cold abs. ethanol, and recrystallized from boiling ethanol; yield 89 g., m.p. 242–243°, identical with the recorded value.[14]

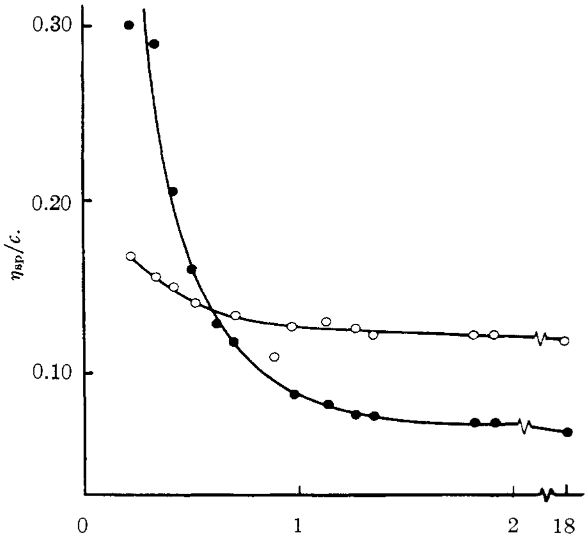


Fig. 1.—Change of viscosity with time at 25.0° in ethylenediamine: ○, polymer V, *c* 0.5; ●, polymer IV (not fully acetylated), *c* 1.0.

A mixture of 45 g. of this acetate, 60 g. of phosphorus pentachloride and 450 g. of acetyl chloride was stirred at room temperature. After 15 min., a clear solution resulted from which silky white crystals began to separate. After 1 hr., the separation was completed by the addition of petroleum ether (b.p. 30–60°). The solid tetra-*O*-acetylgalactaroyl dichloride was recovered by rapid filtration and washed with petroleum ether; yield 44 g., m.p. 177°, in agreement with that recorded.[15]

Condensation of Tetra-*O*-acetylgalactaroyl Dichloride with Diamines. 1. Ethylenediamine.—A solution or suspension of 41.4 g. (100 mmol.) of tetra-*O*-acetylgalactaroyl dichloride in 400 ml. of chloroform or benzene, respectively, was stirred under anhydrous conditions at 0° during the slow addition of 12.2 g. (200 mmol.) of anhydrous ethylenediamine dissolved in 50 ml. of the same solvent. One-half of the diamine may be replaced by an equimolar amount of anhydrous triethylamine added following the addition of the diamine. The mixture was then permitted to warm to room temperature and the stirring was continued for 24 hr. The yellow mixture was filtered and the solid washed with benzene and methanol. Drying afforded nearly quantitative yields of white polymeric material which was shown by analysis to be partially deacetylated.

An amount of 10 g. of this polymer was acetylated at room temperature for 100 hr. with a mixture of 100 ml. of dry pyridine and 200 ml. of acetic anhydride. The solid product was filtered, washed with anhydrous acetic acid and methanol, and dried under reduced pressure over phosphoric anhydride; yield 10.9 g. (83%, basis I). A sample was prepared for analysis and other studies by suspension of this polymer in water and dialysis against water employing a cellophane membrane. The purified polymer II was recovered by ice-sublimation of the frozen dialyzed suspension.

Anal. Calcd. for $[C_8H_{10}N_2O_6(CH_3CO)_4]_n$: C, 47.76; H, 5.51; N, 6.96; CH_3CO, 42.8. Found: C, 47.10; H, 5.54; N, 6.48; CH_3CO, 41.5.

The polymer II decomposed on heating above 250° with no evidence of melting. No unreactive solvent was found for the polymer.

A portion (6 g.) of the crude polymer was suspended in 280 ml. of 0.2 *N* sodium methoxide in methanol at room temperature. After stirring for 24 hr., the solid was collected by centrifugation and extracted with methanol in a Soxhlet apparatus. The deacetylated polymer III was further purified by dialysis in water suspension and dried by ice-sublimation; yield 1.5 g.

Anal. Calcd. for $[C_8H_{14}N_2O_6]_n$: C, 41.02; H, 6.02; N, 11.96. Found: C, 41.09; H, 5.94; N, 11.98.

The deacetylated polymer decomposed at temperatures above 250° with no evidence of melting. Comparison of the infrared spectra[2] of the polymers II and III showed loss of acetate function (5.8 and 8.2 μ) in the deacetylation process. Both spectra were consistent with the proposed polyamide structures II or III. Although polymer III was soluble in anhydrous ethylenediamine and 50 to 80% sulfuric acid,

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(12) M. L. Wolfrom, R. B. Bennett and J. D. Crum, THIS JOURNAL, **80**, 944 (1958).

(13) J. Honeyman and J. W. W. Morgan, *Advances in Carbohydrate Chem.*, **12**, **117** (1957).

(14) Z. H. Skraup, *Monatsh.*, **14**, 488 (1893).

(15) O. Diels and F. Löflund, *Ber.*, **47**, 2351 (1914).

the viscosity of the solutions decreased rapidly with time to a limiting value.

A 50% aqueous solution of lithium chloride was found to be an unreactive solvent for the polymer III. Solutions of the polymer were studied in Fenske viscometers. A plot of the reduced viscosity (η_{sp}/c) against the specific viscosity (η_{sp}) was linear and had negligible slope. Extrapolation to zero specific viscosity gave an intrinsic viscosity, $[\eta]$, of 0.13 deciliter/g. Solutions of the polymer were also subjected to a light scattering molecular weight determination following the techniques and instrumentation employed by Heilweil and Van Winkle.[16] Calculations were made as outlined by Flory.[17] In this manner the minimum molecular weight for polymer III was found to be 8,500 or about 36 repeating units.

2. **Piperazine.**—Piperazine (300 mmol.), dissolved in 400 ml. of benzene, was added slowly under anhydrous conditions to a stirred suspension of 43.3 g. (105 mmol.) of I in 300 ml. of benzene at 0°. The stirring was continued while the mixture warmed to room temperature. Centrifugation afforded a white solid which was washed with benzene and ethanol. A portion of this polymer was acetylated to yield product IV, as described for the ethylenediamine polymer; yield 81% (basis I).

Anal. Calcd. for $[C_{10}H_{12}N_2O_6(CH_3CO)_4]_n$: C, 50.46; H, 5.61; N, 6.54; CH_3CO, 40.1. Found: C, 50.10; H, 5.67; N, 6.55; CH_3CO, 39.2.

No solvent was available that did not degrade the polymer and no melting point was found; decomposition began on heating above 250°.

Another portion of the polymer, before acetylation, was treated with sodium in methanol as described above. The deacetylated polymer V was again obtained in poor yield.

Anal. Calcd. for $[C_{10}H_{16}N_2O_6]_n$: C, 46.15; H, 6.15; N, 10.77. Found: C, 46.35; H, 6.19; N, 10.81.

The infrared spectra,[2] thermal behavior and solubility properties of V were similar in all respects to the ethylenediamine analog III. From viscosity studies in 50% aqueous lithium chloride an intrinsic viscosity, $[\eta]$, of 0.11 deciliter/g. was derived.

Attempted Nitration of Polymers.—A variety of nitration techniques[13] were applied to various preparations of the deacetylated polymers. In no case was a satisfactory yield obtained; the products appeared to be mainly water-soluble or were decomposed by water.

Synthesis of Model Compounds. 1. **1,1′-(Tetra-*O*-acetylgalactaroyl)-dipiperidine (VI).**—Piperidine (16.2 ml., 164 mmol.) was added slowly to a stirred suspension of 16.3 g. (39 mmol.) of tetra-*O*-acetylgalactaroyl dichloride (I) in 550 ml. of benzene at 0°. The heterogeneous mixture was stirred at room temperature for 24 hr. The solid recovered by filtration was washed with benzene, ethanol and water. The dried crude product was crystallized from hot chloroform–ethanol; yield 15.4 g. (76%), m.p. 255–256°.

Anal. Calcd. for $C_{24}H_{36}N_2O_{10}$: C, 56.25; H, 7.03; N, 5.47. Found. C, 56.26; H, 7.20; N, 5.37.

2. **1,1′-(Galactaroyl)-dipiperidine (VII).**—Deacetylation of VI by stirring 12.9 g. overnight at room temperature with 200 ml. of 0.6 *N* sodium methoxide in methanol afforded a yellow solid that was recovered by filtration. After washing the solid with methanol, a suspension in methanol was neutralized by the addition of 2 *N* hydrochloric acid. The insoluble material was recovered by filtration and washed with water. Pure 1,1′-(galactaroyl)-dipiperidine was obtained on crystallization from hot N,N-dimethylformamide; yield 2.5 g. (29%), m.p. 238–239° dec.

Anal. Calcd. for $C_{16}H_{28}N_2O_6$: C, 55.81; H, 8.14; N, 8.14. Found: C, 55.66; H, 8.39; N, 8.34.

3. **Tetra-*O*-acetylgalactaric Bis-(phenylhydrazide) (VIII).**—Phenylhydrazine (38.0 ml., 386 mmol. was added slowly to a stirred suspension of 29.0 g. (70 mmol.) of tetra-*O*-galactaroyl dichloride (I) in 550 ml. of benzene at 0°. The mixture was stirred overnight at room temperature and the solid was filtered, washed with benzene, ethanol, dilute aqueous alkali and water. The crude product was extracted with boiling acetone. The insoluble tetra-*O*-acetylgalactaroyl bis-(phenylhydrazide) (VIII) was crystallized twice from N,N-dimethylformamide solution by adding ethanol and cooling; yield 16.6 g. (42%), m.p. 257–258°.

Anal. Calcd. for $C_{26}H_{30}N_4O_{10}$: C, 55.91; H, 5.37; N, 10.03. Found: C, 55.99; H, 5.55; N, 9.88.

4. **Galactaric Bis-(phenylhydrazide) (IX).**—Deacetylation of VIII, 7.1 g., was accomplished by stirring with 140 ml. of 0.6 *N* sodium methoxide in methanol for 24 hr. at room temperature. The heterogeneous reaction mixture was filtered. The solid, suspended in methanol, was treated with 2 *N* hydrochloric acid until neutral, filtered, washed with methanol and water, and twice recrystallized from hot N,N-dimethylformamide–acetone to give pure crystalline galactaric bis-(phenylhydrazide); yield 2.9 g. (73%), m.p. 242–244°.

Anal. Calcd. for $C_{18}H_{22}N_4O_6$: C, 55.38; H, 5.64; N, 14.36. Found: C, 54.90; H, 5.64; N, 13.79.

5. **Bis-(2-hydroxyethyl) Tetra-*O*-acetylgalactarate.**—During the course of an unsuccessful attempt to prepare a polyester by the condensation of tetra-*O*-acetylgalactaroyl dichloride with ethylene glycol a small amount of crystalline material was isolated. Thus, I, 11.9 g., was dissolved in 60 ml. of ethylene glycol with heating. The solution was concentrated at 2 mm. pressure and 145–155°. Methanol was added to the resulting sirup and the white solid which formed was separated and washed with methanol and water. Crystallization from acetone afforded bis-(2-hydroxyethyl) tetra-*O*-acetylgalactarate; yield 80 mg., m.p. 209°.

Anal. Calcd. for $C_{18}H_{26}O_{14}$: C. 46.42; H, 5.57; mol. wt., 468. Found: C, 46.47; H, 5.23; mol. wt., 457 (Rast).

Acknowledgment.—We appreciate the coöperation of Dr. Quentin Van Winkle in carrying out the light scattering molecular weight studies.

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[16] I. J. Heilweil and Q. Van Winkle, *J. Phys. Chem.*, **59**, 944 (1955).

[17] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 291–303.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, STANFORD UNIVERSITY]

Sabinene Hydrate: a Constituent of American Peppermint Oil[1]

BY JOHN W. DALY, F. CHARLOTTE GREEN AND RICHARD H. EASTMAN

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The methyl Grignard reaction with sabina ketone forms two isomeric sabinene hydrates, one of which is identical with an alcohol isolated from American peppermint oil. This isomer is assigned the *trans* (methyl/isopropyl) configuration on the basis of the yields of the isomers in the Grignard reaction, on the Von Auwer–Skita rule, and on differences in the chemical properties of the two isomers.

A new terpene alcohol, which melted at 62°, was isolated from American peppermint oil by fractional distillation. The compound was very unstable under acid conditions, which suggested that it was a tertiary alcohol. A Zerewitinoff determination[2] showed one active hydrogen per molec-

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[1] From the Doctoral Dissertations of J. W. Daly and F. C. Green, in the Department of Chemistry at Stanford University, reported in part at the 133rd A.C.S. Meeting, San Francisco, Calif., April 16, 1958.

[2] T. Zerewitinoff, *Ber.*, **40**, 2027 (1907).