platinum crucible. The ash was dissolved in an excess of 0.02 *N* hydrochloric acid and titrated back with 0.02 *N* sodium hydroxide. No blank analysis of the urea was carried out. A small amount of an impurity in the urea may produce the apparent increase in solubility found by Medes.

I wish to thank the head of the laboratory, Professor Niels Bjerrum, for his kind interest in my work.

Summary

The solubility of calcium oxalate at 25.0° in aqueous solutions of urea, from 0 to 2 *M*, may be expressed by the equation

$$s = 4.84 \times 10^{-5} [1 + 0.19 (\text{urea})]$$

where the concentrations are given in moles per liter of solution.

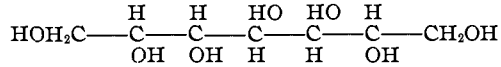
COPENHAGEN, DENMARK RECEIVED OCTOBER 19, 1938

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Proof of the Structure and Configuration of Perseulose (L-Galaheptulose)[1]

BY RAYMOND M. HANN AND C. S. HUDSON

The polyhydric alcohol perseitol[2] was discovered in the avocado by Avequin[3] and was long regarded as a hexahydric alcohol, isomeric with mannitol. Maquenne[4] first proved that it belonged in the seven carbon series, and shortly thereafter Fischer and Passmore[5] synthesized it by reduction of *d*-α-mannoheptose (D-manno-D-gala-heptose)[6] with sodium amalgam; this synthesis established the configurations of four of the asymmetric carbon atoms (those derived from D-mannose) of perseitol, but that of the fifth remained unknown, because the configuration of carbon 2 of D-manno-D-gala-heptose had not been established. Bertrand[7] discovered that perseitol is oxidized by *Bacterium xylinum* (syn. *Acetobacter xylinum*) to a ketoheptose, which he crystallized and named perseulose; its ketose character was shown by the observations[8] that (1) it was not oxidized by bromine water and (2) its reduction by sodium amalgam generated two alcohols, namely, perseitol and a new alcohol which he named "perséulite" and characterized as having a relatively high levorotatory power of "more than 8° to the left." It was not possible to establish the structure or configuration of perseulose from these data because the configuration of "perséulite" was quite unknown and that of perseitol was known only in part. The next step was made by Peirce[9] when he proved that D-α-galaheptitol (D-gala-L-manno-heptitol) is the enantiomorph of perseitol, from which it follows that the full configuration of perseitol must be (I). The structure and configuration of perseulose remained unknown, however, because the position of its ketone group was still undisclosed. Bertrand's[10] study of the action of *B. xylinum*. on numerous polyatomic alcohols led him to the generalization that the oxidation to a ketose, if it occurs, always takes place at a penultimate carbon atom. When La Forge[11] discovered D-mannoheptulose (II) in the avocado and proved its configuration (2-ketoperseitol, if the carbon atoms of (I) are numbered from right to left) and its non-identity with perseulose, he was led by Bertrand's generalization to regard perseulose as probably 6-ketoperseitol (III). If such were the case, perseulose



(I) Perseitol
(D-Manno-D-gala-heptitol or L-Gala-D-manno-heptitol)

(1) Publication authorized by the Surgeon General, U. S. Public Health Service. Presented in part before the Divisions of Organic Chemistry and of Sugar Chemistry and Technology, at the Milwaukee meeting of the American Chemical Society, Sept. 5–9, 1938.

(2) The alcohol was named perséite (from the name of the avocado genus, *Persea*) by Muntz and Marcano [*Ann. chim. phys.*, [3] **6**, 280 (1884)], and no advantage is seen in changing the established English equivalent, perseitol, to persitol (Armstrong and Armstrong, "The Carbohydrates," 5th ed., 1934, p. 146). We also advocate retention of the original name perseulose (assigned by Bertrand, discoverer of the sugar) rather than its replacement by perselose [Isbell, *J. Research Natl. Bur. Standards*, **18**, 513 (1937)].

(3) J. B. Avequin, *Journal de chimie médicale, de pharmacie et de toxicologie*, [1] **7**, 467 (1831); available in the Library of the Surgeon General of the Army, Washington, D. C. Avequin was a pharmacist of Port-au-Prince, Santo Domingo, in 1831; his discovery of perseitol appears to be the first isolation in the Western Hemisphere of a new naturally occurring pure organic substance. A bibliography of Avequin's publications appears in the "Catalogue of Scientific Papers," 1800–1863, published by the Royal Society of London.

(4) Maquenne, *Ann. chim. phys.*, [6] **19**, 5 (1890).

(5) Fischer and Passmore, *Ber.*, **23**, 2231 (1890).

(6) Hudson, THIS JOURNAL, **60**, 1537 (1938).

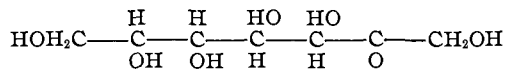
(7) Bertrand, *Compt. rend.*, **147**, 201 (1908).

(8) Bertrand, *ibid.*, **149**, 225 (1909).

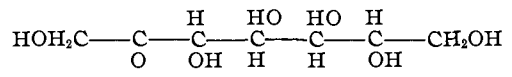
(9) Peirce, *J. Biol. Chem.*, **23**, 327 (1915).

(10) Bertrand, *Compt. rend.*, **126**, 762 (1898).

(11) La Forge, *J. Biol. Chem.*, **28**, 511 (1917).



(II) Mannoketoheptose
(D-Mannoheptulose)



(III) Perseulose
(L-Galaheptulose)

osazone (m. p. 233°, Bertrand) must be the enantiomorph of the common osazone (m. p. 224°, Fischer; 222°, La Forge) of the two D-galaheptoses (D-gala-L-manno- and D-gala-L-gluco-heptoses); the existing meager data, from melting points solely, seemed not incompatible with this viewpoint. No further study of the subject has been made during the subsequent twenty-one years.

Through the coöperation of Messrs. H. T. Herrick and P. A. Wells, of the Industrial Farm Products Research Division of the Bureau of Chemistry and Soils, U. S. Department of Agriculture, we have been able to prepare perseulose readily and in considerable quantity by the action of *Acetobacter suboxydans* on perseitol. We also had available good supplies of the two D-galaheptoses in pure condition; thus an opportunity came to make a decisive test of La Forge's surmise that perseulose is 6-keto-perseitol. The results prove conclusively that his surmise is correct; the configuration of perseulose is that of L-galaheptulose (III).

1. Proof from the Study of the Phenylosazones.—The phenylosazone of perseulose and that of either of the D-galaheptoses should be enantiomorphic substances. It was found that the osazones from all three sources melted in capillary tubes simultaneously with decomposition, but that this decomposition point varied (190–202°) with the rate of heating, rendering the test inexact. A more satisfactory criterion of their enantiomorphic character was found upon measuring the specific rotation[12] of the osazones in pyridine–alcohol solution; perseulose osazone rotated, at equilibrium, −50.1°, and D-galaheptose osazone rotated +49.6°; in absolute pyridine solution the former showed slow mutarotation from −114 to −35° in the course of several days, and the latter changed at approximately the same rate from +114 to +36°. The most satisfactory results were obtained by a study of the acetylated phenylosazones; after thorough purification through recrystallization, the perseulose phenylosazone pentaacetate melted sharply at 117–118° without decomposition and rotated −86.8° in chloroform (no mutarotation) and the D-galaheptose osazone pentaacetate melted at the same temperature and rotated +86.9°. These results prove that the osazones are enantiomorphic substances, from which it follows that perseulose is L-galaheptulose.

2. Proof from the Reduction of Perseulose to Two Alcohols.—The reduction of an aqueous solution of perseulose with hydrogen under a pressure of 167 atm. at 100°, using Raney nickel catalyst, yielded two heptahydric alcohols, which were separated by recrystallization from aqueous alcohol. The less soluble one was identified as perseitol by its melting point, mixed melting point with authentic D-manno-D-galaheptitol, and its conversion to D-manno-D-gala-heptitol heptaacetate of correct melting point and rotation. The more soluble alcohol, named "perséulite" by Bertrand and stated by him to have a rotation greater than −8°, was purified carefully and found to rotate −2.4° in water and to melt at 141°. This melting point agrees with the 141–144° value reported by Peirce for D-β-galaheptitol (D-gala-L-gluco-heptitol) and with that of 138–141° given by La Forge[13] for D-α-guloheptitol (D-gulo-L-gala-heptitol), which has the same configuration as Peirce's heptitol. The reductions which Peirce and La Forge conducted were made with sodium amalgam; a slight epimerization of the aldoses in alkaline solution would not be unexpected and would result in a contamination of the main product with small amounts of the epimeric heptitol. Accordingly, we have reduced pure D-gala-L-gluco-heptose with hydrogen and Raney nickel and obtained pure D-gala-L-gluco-heptitol of melting point 141° and specific rotation +2.4° in water. This heptitol upon acetylation yielded a heptaacetate melting at 118° and rotating +11.4° in chloroform, while the heptitol from perseulose upon acetylation gave a heptaacetate melting at the same temperature, and of equal but opposite rotation, namely, −11.4°. The data show that the second alcohol from perseulose is the enantiomorphic form of D-gala-L-gluco-heptitol, namely, L-gala-D-gluco-heptitol; perseulose is therefore L-galaheptulose.

3. Proof through the Alkaline Oxidation of Perseulose.—A third independent proof of the

(12) All rotations are constant specific rotations at 20° for sodium light, c is concentration in grams in 100 cc. of solution, and l is the tube length in decimeters.

(13) La Forge, *J. Biol. Chem.*, **41**, 251 (1920).

configuration of perseulose, through its oxidative degradation to L-galactonic acid, is described in the accompanying paper.[14]

We express our appreciation to Drs. E. B. Tilden, W. D. Maclay and W. T. Haskins for assistance in various parts of this study, and to Dr. A. E. Knauf, who prepared the perseitol from avocados.

Experimental

Perseulose (-Galaheptulose) from Perseitol (D-Manno-D-galaheptitol).[15]—One liter of a sterile aqueous 3% solution of perseitol containing 0.05% glucose, 0.3% potassium acid phosphate, and 0.5% of Difco yeast extract as nutrients, was inoculated with *Acetobacter suboxydans*, and sterile air passed through the solution at a rate of 200 cc. per minute. In one week the copper reduction value of the solution indicated complete conversion of the alcohol to reducing sugar. The fermented solution was clarified by filtration and successive treatments with lead acetate and hydrogen sulfide, and the final filtrate was concentrated *in vacuo* to a sirup of about 60 cc. volume; the sirup was then dissolved in three volumes of warm glacial acetic acid and upon cooling the solution became filled with the separated crystalline ketose. After several days in the ice box the crystals were filtered, washed with a mixture of acetic acid and absolute alcohol to remove the sirup, and then with absolute alcohol and ether and dried: yield 28.4 g. (91.6%). The filtrate, heated with phenylhydrazine on the steam-bath for four hours, yielded 3.4 g. of perseulose phenylosazone, equivalent to a further 2.1 g. of ketose hemihydrate, bringing the crude yield from the oxidation to 98.4%.

Perseulose hemihydrate crystallizes from 15 parts of 95% alcohol in small colorless prisms. Because of its solubility in its water of hydration, the melting point varies with the rate of heating. Samples held in an Abderhalden apparatus at 78° melt slowly. However, on rapid heating the hemihydrate shows a characteristic and reproducible melting point of 102–103° (corr.). The aqueous solutions of the hemihydrate show a rapid downward mutarotation, which is not unimolecular in its early stages, but becomes so after about four minutes (see Table I). The rate of mutarotation is a rapid one, resembling that of D-fructose in speed and in the sign and magnitude of the initial and final rotations; this similarity is doubtless to be attributed to the possession by the two ketoses of identical configurations for their carbon atoms 3, 4 and 5. It is noteworthy in this connection that fructose, which customarily crystallizes in the anhydrous form, is also known to form a crystalline hemihydrate,[16] an unusual type of hydration in the carbohydrate series. The crystalline form of D-fructose (initial $[\alpha]_D$ about −133°, equilibrium about −92°) is designated β-D-fructose; since perseulose belongs in the L series of Fischer, its crystalline hemihydrate, of initial $[\alpha]_D$ about −102° and equilibrium −86° (on the anhydrous basis), should be designated α-L-galaheptulose.

(14) Richtmyer, Hann and Hudson, THIS JOURNAL, **61**, 340 (1939).

(15) E. B. Tilden, forthcoming publication.

(16) Hönig and Jesser, *Monatsh.*, **9**, 563 (1888).

Anal. Calcd. for $C_7H_{14}O_7 \cdot {}^1/_2H_2O$: C, 38.34; H, 6.90. Found: C, 38.33; H, 6.97.

TABLE I

MUTAROTATION OF PERSEULOSE HEMIHYDRATE IN WATER

Concentration 0.6315 g. in 25 cc. of solution; tube length 4 dm.; temp., 20 ± 0.5°

Time after making soln., min.	$[\alpha]^{20}D$ (hemihydrate)	$[\alpha]^{20}D$ (anhydrous)	Time, min.	$k_1 + k_2$
1.1	−96.4	−100.5	0	...
1.9	94.8	98.9	0.8	0.065
3.1	93.0	97.0	2.0	.060
4.1	91.4	95.3	3.0	.063
6.1	89.5	93.3	5.0	.058
8.1	87.9	91.7	7	.059
11.1	86.0	89.7	10	.058
13.1	85.2	88.9	12	.057
14.1	85.0	88.6	13	.055
16.1	84.4	88.0	15	.055
18.1	83.8	87.4	17	.057
19.1	83.6	87.2	18	.058
21.1	83.3	86.9	20	.057
26.1	82.6	86.2	25	.062
31.1	82.4	85.9	30	...
36.1	82.3 (equilibrium)	85.8	35	...
24 hrs. (final)	82.3		..	...
			Average	.059

Perseulose Phenylosazone.—The 3.4 g. of phenylosazone was recrystallized in nearly quantitative yield from 100 parts of boiling 95% alcohol. For comparison, samples of D-galaheptose phenylosazone were prepared from D-α- and D-β-galaheptose. The osazones from all three sources were similar in appearance and solubility and gave the same melting point when simultaneous determinations were made. When the rise in temperature was 5° in eight minutes the decomposition occurred at 190°, when 5° in 2.25 minutes at 197°, and when 5° in 1.25 minutes at 202°. The decomposition point on the Dennis melting point bar was 240 ± 1°. Measurement of the final specific rotation in Neuberg's[17] pyridine–absolute alcohol mixture gave values of −50.1° (*c*, 1.15; *l*, 1) for perseulose phenylosazone and +49.6° (*c*, 0.98; *l*, 1) for D-galaheptose phenylosazone. As indicated by

TABLE II

MUTAROTATION OF THE PHENYLOSAZONES OF PERSEULOSE AND D-GALAHEPTOSE IN PYRIDINE

Concentration 1 g. in 100 cc.; tube length, 1 dm.; temp., 20 ± 0.5°.

Time, hrs.	Specific rotation of perseulose osazone	Specific rotation of D-galaheptose osazone
0.1	−114	+114
1	104	...
2	100	99
21	52	50
43	36	39
72 (final)	35	36

Anal. Calcd. for $C_{19}H_{24}O_5N_4$: C, 58.73; H, 6.23. Found: (perseulose phenylosazone): C, 58.86; H, 6.26. (D-galaheptose phenylosazone): C, 58.84; H, 6.11.

(17) Neuberg, *Ber.*, **32**, 3384 (1900).

Table II the mutarotations of the two osazones in absolute pyridine are alike in velocity and opposite in sign.

Perseulose Phenylosazone Pentaacetate.—The solution of 3.0 g. of osazone in a mixture of 36 cc. of pyridine and 12 cc. of acetic anhydride at room temperature was completed in forty-eight hours; the osazone acetate was then precipitated by pipetting the solution into rapidly stirred ice water, yield 4.7 g. (quantitative). The acetate separated from its solution in 5 parts of 75% alcohol in clusters of light yellow needles, which melted at 117–118° (corr.) and had a specific rotation of −86.8° in chloroform (*c*, 1.18; *l*, 4).

Anal. Calcd. for $C_{29}H_{34}O_{10}N_4$: C, 58.16; H, 5.73. Found: C, 57.96; H, 5.77.

D-Galaheptose Phenylosazone Pentaacetate.—This compound was prepared from D-galaheptose osazone by the same method as its enantiomorph. It was obtained in quantitative yield and showed the same solubility and melting point as the perseulose osazone acetate, but its specific rotation was +86.9° (*c*, 1.25; *l*, 4) in chloroform.

Anal. Calcd. for $C_{29}H_{34}O_{10}N_4$: C, 58.16; H, 5.73. Found: C, 58.25; H, 5.84.

Racemic Galaheptose Phenylosazone.—A mixture of 1 g. of perseulose phenylosazone and 1 g. of D-galaheptose phenylosazone required 1000 parts of boiling alcohol to effect complete solution, indicating that the solubility of the racemate was approximately only one-fifth of that of either component. The substance crystallizes in fine yellow needles melting at 222° (corr.) in a capillary tube, and at 259° on the Dennis melting point bar. Its solution in pyridine is optically inactive.

Anal. Calcd. for $C_{19}H_{24}O_5N_4$: C, 58.72; H, 6.23. Found: C, 58.53; H, 6.08.

Racemic Galaheptose Phenylosazone Pentaacetate.—Upon acetylation the racemate yielded readily a crystalline pentaacetate. In spite of repeated recrystallizations the substance did not melt sharply; however, it exhibited a characteristic behavior in beginning to shrink at 116–117° and gradually softening to a sticky gum which was completely fluid at 125–126° (corr.). Its chloroform solution was optically inactive.

Anal. Calcd. for $C_{29}H_{34}O_{10}N_4$: C, 58.16; H, 5.73. Found: C, 58.25; H, 5.64.

Reduction of Perseulose Hemihydrate.—A solution of 12.2 g. of perseulose hemihydrate in 70 cc. of water was reduced for four hours at 100° under a pressure of 2500 pounds (167 atm.) of hydrogen in the presence of Raney nickel. The catalyst was removed and the solution concentrated to a volume of 25 cc. and allowed to crystallize. Following removal of the first fraction (3.7 g.; m. p. 185°), the solution was reconcentrated to 10 cc. and a second fraction crystallized (1.6 g.; m. p. 181°). The melting points and crystalline appearance of these two fractions indicated that they were nearly pure perseitol (m. p. 187°), and the yield of 5.3 g. was 45% of the total mixed alcohols theoretically obtainable by the reduction. To the filtrate 10 cc. of 95% alcohol was added, causing crystallization of a third fraction (3.2 g.; m. p. 135°), consisting mainly of well-formed prisms with a small amount of perseitol crystallized in needles. Upon addition of 10 cc. of absolute alcohol to this filtrate a fourth fraction (0.7 g.; m. p. 138°) was isolated and upon further concentration an end fraction (1.9 g.; m. p. 122°) was obtained, bringing the total recovered yield of reduction products to 11.1 g. (94%).

Identification of D-Manno-D-gala-heptitol (Perseitol).—The combined first and second fractions were recrystallized twice from 4 parts of water, yielding 4.3 g. of needles melting at 187°, unchanged in melting point upon admixture with an equal part of pure perseitol, and having a specific rotation of −1.2° (*c*, 5.5; *l*, 4) in water. A portion of the substance was acetylated, yielding an acetate melting at 119° (corr.) and rotating −13.3° (*c*, 2.08; *l*, 4) in chloroform. Pure perseitol melts at 187–188° and rotates −1.04° in water and its acetate melts at 119° and rotates −13.4° in chloroform.

Anal. Calcd. for $C_7H_{16}O_7$: C, 39.60; H, 7.60. Found: C, 39.81; H, 7.75.

Identification of L-Gala-D-gluco-heptitol.—The combined third and fourth fractions were repeatedly recrystallized from 6 parts of 50% alcohol yielding 1.6 g. of pure L-gala-D-gluco-heptitol melting at 141° (corr.) and having a specific rotation of −2.4° (*c*, 3.92; *l*, 4) in water. For comparison, a sample of D-gala-L-gluco-heptose was reduced catalytically and the resulting alcohol (D-gala-L-gluco-heptitol) was found to melt at 141–142° and to have a specific rotation in water of +2.4° (*c*, 4.03; *l*, 4).

Anal. Calcd. for $C_7H_{16}O_7$: C, 39.60; H, 7.60. Found: C, 39.48; H, 7.55.

L-Gala-D-gluco-heptitol Heptaacetate.—A mixture of 0.5 g. of L-gala-D-gluco-heptitol, which was obtained from the reduction of perseulose, 0.5 g. of fused sodium acetate and 8 cc. of acetic anhydride was refluxed for fifteen minutes, cooled and poured upon crushed ice, whereupon the desired acetate crystallized readily in a yield of 1.1 g. (92%). Upon recrystallization from 6 parts of 50% alcohol it was obtained in prismatic crystals melting at 118° (corr.) and rotating −11.4° (*c*, 2.15; *l*, 4) in chloroform. The heptaacetate of D-gala-L-gluco-heptitol melts at 118° and has a rotation of +11.4° (*c*, 2.62; *l*, 4) in chloroform.

Anal. Calcd. for $C_{21}H_{30}O_{14}$: C, 49.29; H, 5.97. Found: C, 49.67; H, 5.88.

Racemic Gala-gluco-heptitol Heptaacetate.—(1) A mixture of 0.5 g. of each of the D-gala-L-gluco- and L-gala-D-gluco-heptitol heptaacetates (m. p. 118°) was dissolved in 6 cc. of 50% alcohol and overnight the racemate crystallized in prisms melting at 127° (corr.). Upon recrystallization the melting point remained unchanged, but upon admixture with either component it was lowered, indicating the true racemic nature of the substance.

(2) Upon acetylation of 0.3 g. of racemic gala-gluco-heptitol a quantitative yield of heptaacetate (0.7 g.) was obtained. Recrystallized from 10 parts of 50% alcohol the substance separated in prisms melting at 127° (corr.) in agreement with the racemic acetate prepared from the active components.

Anal. Calcd. for $C_{21}H_{30}O_{14}$: C, 49.79; H, 5.97. Found: C, 49.93; H, 6.15.

Racemic Gala-gluco-heptitol.—(1) A mixture of 0.25 g. of each of the D- and L-forms (m. p. 141°) was dissolved in 2.5 cc. of hot 50% alcohol and upon cooling the solution 0.4 g. of racemate separated. The substance was re-

peatedly recrystallized from 50% alcohol, finally being obtained in fine needles melting at 138° (corr.).

(2) An ice cold solution of 1.0 g. of pure racemic gala-gluco-heptitol heptaacetate in 70 cc. of methyl alcohol was deacetylated by addition of 2 cc. of 1.35 *N* barium methylate. The next morning the barium was precipitated by addition of 27 cc. of 0.1 *N* sulfuric acid, and the filtered solution concentrated to a dry sirup. The sirup was dissolved in 10 cc. of hot alcohol and the solution when cooled deposited the racemate in rosets of very fine needles, differing greatly in crystalline appearance from the active forms. One recrystallization from 5 parts of 90% alcohol gave a pure product melting at 138° (corr.): yield 0.4 g. (quantitative). Because of the difficulty of removing small amounts of active component, the deacetylation of the pure racemic alcohol heptaacetate is definitely superior as a preparative method for this substance.

Anal. Calcd. for $C_7H_{16}O_7$: C, 39.60; H, 7.60. Found: C, 39.46; H, 7.77.

Summary

Perseulose phenylosazone and the phenylosazone that is common to D-gala-L-gluco- and D-gala-L-manno-heptose are found to be enantiomorphic forms, and the same is true of the pentaacetates of these osazones. The reduction of perseulose by hydrogen and Raney nickel yields D-manno-D-gala- and L-gala-D-gluco-heptitol. These data supply two independent conclusive proofs that perseulose is L-galaheptulose, as was surmised some years ago by La Forge.

WASHINGTON, D. C. RECEIVED DECEMBER 8, 1938

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Oxidative Degradation of Perseulose to L-Galactonic Acid[1]

BY NELSON K. RICHTMYER, RAYMOND M. HANN AND C. S. HUDSON

Kiliani and Sanda[2] observed that the oxygen of the air reacted with alkaline solutions of reducing sugars, and suggested that many interesting compounds would be found among the products of such reactions. The classical researches of Nef confirmed this prediction. Nef and his collaborators[3] studied the effect of passing very rapid streams of air through alkaline solutions of D-glucose, D-fructose and D-galactose. Among the numerous products isolated were D-arabonolactone from glucose and fructose, and D-lyxonolactone in 22% yield from galactose. These substances had been formed by cleavage of the hexose molecule between the first and second carbon atoms, the fragments appearing as formic acid and a pentonic acid which could be identified through its crystalline derivatives. Since D-glucose and D-fructose each yielded D-arabonic acid, it was apparent that the oxidation and cleavage involved the 1,2-enediol common to those sugars and formed readily from them under the influence of the caustic alkali. Nef, Hedenburg and Glattfeld,[4] applying this reaction in a study of the alkaline oxidation of pentoses with air, obtained D-threonic acid phenylhydrazide from D-xylose, and L-erythronolactone in 36% yield from L-arabinose. Hudson and Chernoff[5] oxidized rhamnose to L-rhamnotetronolactone, and Clark[6] oxidized fucose to L-fucotetronolactone, both reactions being of importance in studies of the configurations of the respective methylpentoses.

In 1935, Spengler and Pfannenstiel[7] oxidized a number of reducing sugars under conditions similar to those of Nef, but instead of air they used pure oxygen. The results were startling in that the yields of aldonic acid having one less carbon atom than the original aldehyde or ketone sugar rose to 60–75% of the theoretical. The further application of this oxidation with pure oxygen in alkaline solution furnished Neuberg and Collatz[8] with a 90% yield of D-arabonic acid-5-phosphoric acid from D-fructose-6-phosphoric acid.

Having available a considerable quantity of perseulose from previous researches in this Laboratory[9] we decided to seek still further confirmation of its formulation as L-galaheptulose[10] by applying to it the procedure of Spengler and

(1) Publication authorized by the Surgeon General, U. S. Public Health Service. Presented in part before the Divisions of Organic Chemistry and of Sugar Chemistry and Technology, at the Milwaukee meeting of the American Chemical Society, Sept. 5–9, 1938.

(2) Kiliani and Sanda, *Ber.*, **26**, 1650, 1654 (1893).

(3) Nef (and Lucas), *Ann.*, **376**, 55 Note (1910); Spoehr (and Rosario), *Am. Chem. J.*, **43**, 240 (1910); Glattfeld, *ibid.*, **50**, 152 (1913); Nef, *Ann.*, **403**, 204 (1914). *Cf.* also Framm, *Arch. ges. Physiol.* (Pflügers), **64**, 575 (1896); Schade, *Z. physik. Chem.*, **57**, 1 (1906); Buchner, Meisenheimer and Schade, *Ber.*, **39**, 4217 (1906).

(4) Nef, Hedenburg and Glattfeld, THIS JOURNAL, **39**, 1638 (1917).

(5) Hudson and Chernoff, *ibid.*, **40**, 1005 (1918).

(6) E. P. Clark, *J. Biol. Chem.*, **54**, 70 (1922).

(7) Spengler and Pfannenstiel, *Z. Wirtschaftsgruppe Zuckerind.*, **85**, Tech. Tl. 547 (1935).

(8) Neuberg and Collatz, *Cellulosechem.*, **17**, 125 (1936).

(9) Hann, Tilden and Hudson, THIS JOURNAL, **60**, 1201 (1938); Tilden, forthcoming publication.

(10) La Forge, *J. Biol. Chem.*, **28**, 511 (1917); Hann and Hudson, THIS JOURNAL, **61**, 336 (1939).