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L-Guloheptulose and 2,7-Anhydro-β-L-guloheptulopyranose[1,2]

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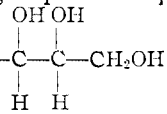
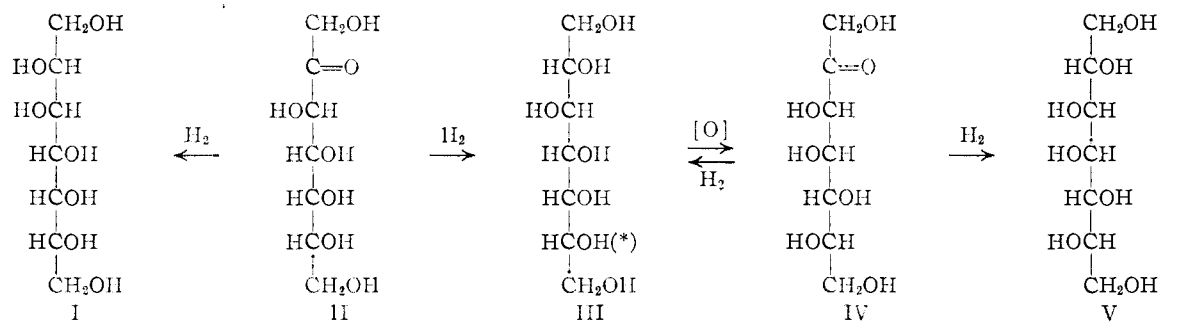
The oxidation of β-sedoheptitol (synonyms, D-altro-D-*gluco*-heptitol and L-gulo-D-*talo*-heptitol) by *Acetobacter suboxydans* has yielded, in accord with the specificity rule for that organism, the expected new L-guloheptulose. The sirupy sugar was identified by comparison of its phenylosazone and phenylosotriazole with the corresponding enantiomorphs prepared from authentic D-guloheptose. The structure was confirmed by catalytic hydrogenation of the heptulose to two known heptitols. L-Guloheptulose is converted by acids, readily and in 80% yield, to a crystalline L-guloheptulosan whose structure was proved by periodate oxidation methods to be 2,7-anhydro-β-L-guloheptulopyranose.

Other communications from this Laboratory on the behavior of *Acetobacter suboxydans* toward heptitols have described the biochemical oxidation of perseitol to perseulose (= L-galaheptulose),[3] of gluco-*gulo*-heptitol to L-glucoheptulose,[4] of volemitol (I) to both sedoheptulose (= D-altroheptulose) (II) and D-mannoheptulose,[5] and of D-gluco-D-*ido*-heptitol to D-idoheptulose.[6] In every case the oxidation was shown to involve the penultimate hydroxyl group of the polyol that contained the favorable  configuration.

We now wish to add that β-sedoheptitol (synonyms, D-altro-D-*gluco*-heptitol and L-gulo-D-*talo*-heptitol) (III), which is obtained, together with volemitol (I), by the reduction of sedoheptulose (II),[7] is oxidized readily by *A. suboxydans* with the probably quantitative formation of a new ketoheptose. The strongly reducing sirup had a rotation estimated to be $[\alpha]^{20}D$ −28°. Although the sugar has not yet crystallized, it was first identified tentatively as L-guloheptulose (IV) through its crystalline phenylosazone and phenylosotriazole because these, by their melting points and rotations, were shown to be the enantiomorphs of the corresponding derivatives prepared from the two D-guloheptoses. Conclusive proof of its L-guloheptulose formulation was secured by its catalytic hydrogenation to two heptitols. One of these was the original β-sedoheptitol (III) while the other was recognized as L-β-galaheptitol (synonyms, L-gulo-D-*gala*-heptitol and L-gala-D-*gluco*-heptitol) (V). The formation of these two heptitols could be accounted for only if the ketose were L-guloheptulose (IV). The production of L-guloheptulose from β-sedoheptitol confirms once more the specificity rule of Bertrand[8] for the action of *Acetobacter xylinum* on polyhydric alcohols as extended by Hann, Tilden and Hudson[3] to the similar action of *A. suboxydans*.



(*) Indicates point of attack by *Acetobacter suboxydans*.

It had previously been known that sugars with the altrose or idose configuration, namely, D-altroheptulose (= sedoheptulose),[7] D- and L-altrose,[9] D-idose,[10] D-idoheptulose[6] and D-gluco-D-*ido*-heptose,[11] form non-reducing anhydrides readily under the influence of aqueous acids. Sugars with other configurations were not believed to be affected. We were greatly surprised, therefore, to discover that L-guloheptulose, when heated in 0.2 *N* hydrochloric acid at 98°, was converted within one hour to an equilibrium mixture containing about 80% of a non-reducing anhydride. The resulting L-guloheptulosan was obtained crystalline first as an

(1) A portion of this material has been taken from the thesis submitted by Laura C. Stewart to the Department of Chemistry of the Graduate School of Georgetown University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1951.

(2) Presented in part before the Division of Sugar Chemistry at the Boston Meeting of the American Chemical Society, April 3, 1951.

(3) R. M. Hann, E. B. Tilden and C. S. Hudson, THIS JOURNAL, **60**, 1201 (1938); E. B. Tilden, *J. Bact.*, **37**, 629 (1939).

(4) W. D. Maclay, R. M. Hann and C. S. Hudson, THIS JOURNAL, **64**, 1606 (1942).

(5) L. C. Stewart, N. K. Richtmyer and C. S. Hudson, *ibid.*, **71**, 3532 (1949); see also V. Ettel and J. Liebster, *Collection Czechoslov. Chem. Communs.*, **14**, 80 (1949).

(6) J. W. Pratt, N. K. Richtmyer and C. S. Hudson, THIS JOURNAL, **74**, 2210 (1952).

(7) F. B. LaForge and C. S. Hudson, *J. Biol. Chem.*, **30**, 61 (1917).

(8) G. Bertrand, *Ann. chim. phys.*, [8] **3**, 202 (1904).

(9) N. K. Richtmyer and C. S. Hudson, THIS JOURNAL, **57**, 1716 (1935).

(10) E. Sorkin and T. Reichstein, *Helv. Chim. Acta*, **28**, 1 (1945).

(11) J. W. Pratt, N. K. Richtmyer and C. S. Hudson, Abstracts of Papers, Chicago Meeting of the American Chemical Society, Sept. 3–8, 1950, page 10R.

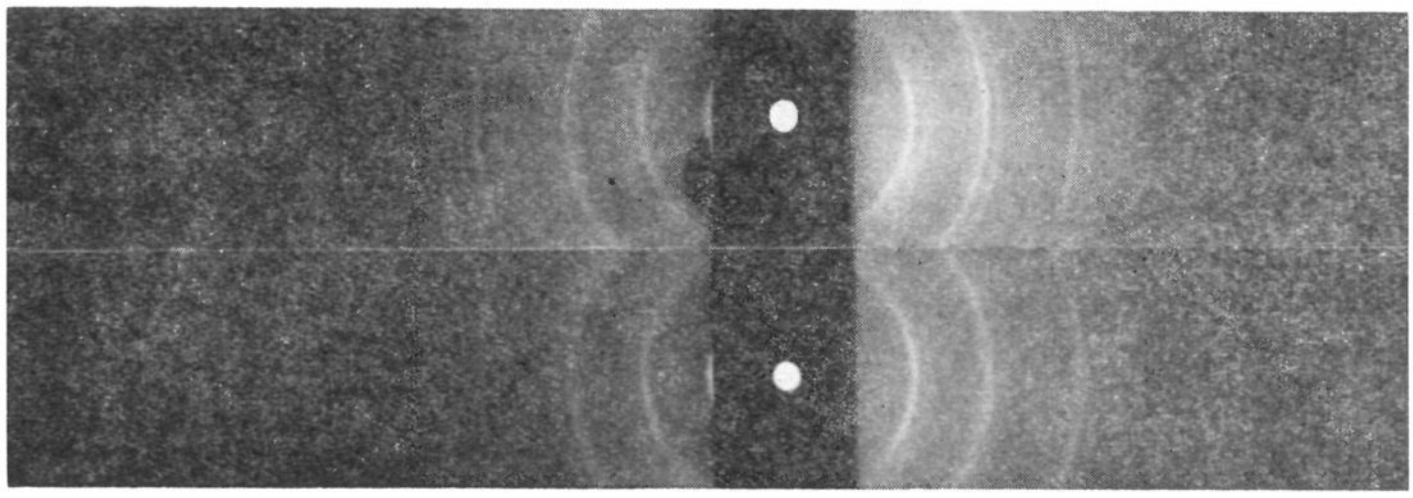
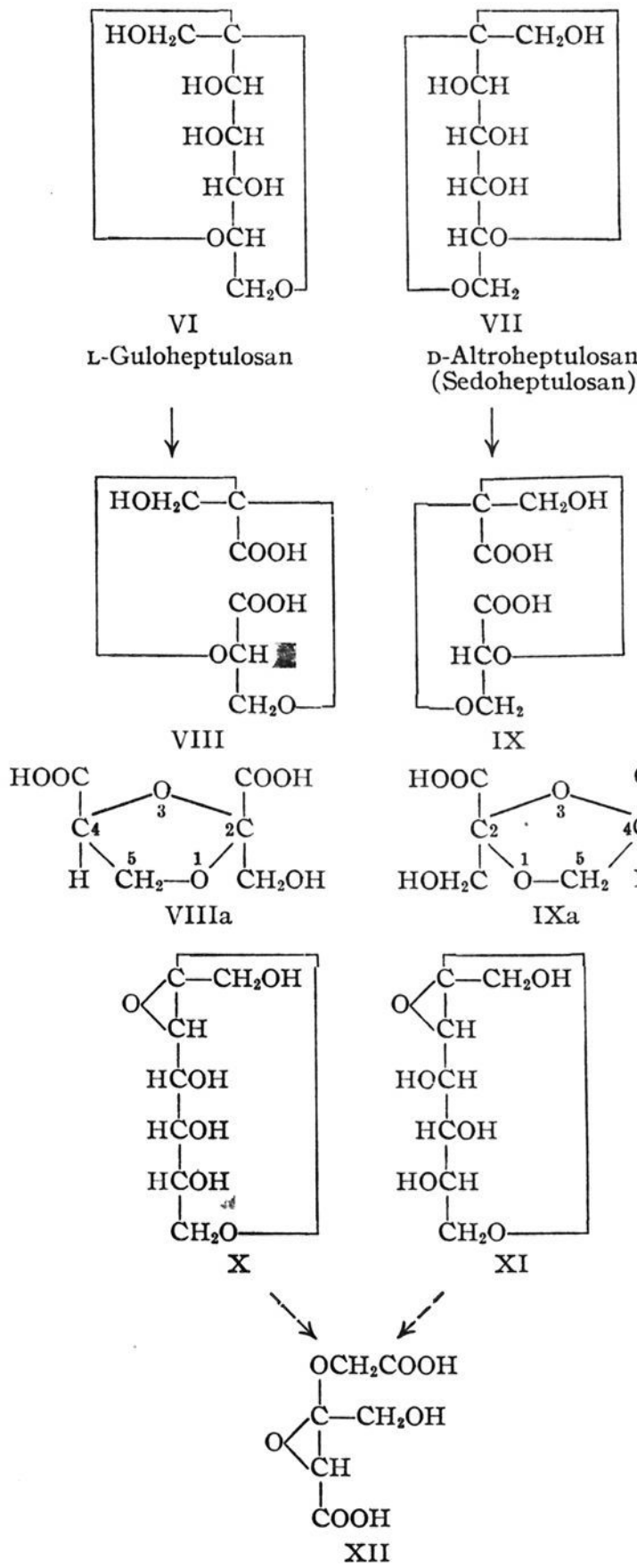


Fig. 1.—X-Ray powder diffraction patterns of the dibenzimidazole hydrates derived from D-altroheptulosan (upper) and L-guloheptulosan (lower).

anhydrous modification and later as a hemihydrate.

The ring structure of L-guloheptulosan was established by periodate oxidation methods. The reaction consumed two molar equivalents of oxidant and liberated one molar equivalent of formic acid but no formaldehyde, thus indicating the presence of three contiguous secondary hydroxyl groups. The resulting solution had a rotation, calculated as the expected dialdehyde, of $[\alpha]^{20}D$ +17.2°, a value that is of the same magnitude but opposite in sign to the $[\alpha]^{20}D$ −16.9° observed in the similar oxidations of both D-altroheptulosan (= sedoheptulosan)[12] and D-idoheptulosan.[6] Subsequent hypobromite oxidation of the dialdehyde to a dibasic acid and condensation of the latter with *o*-phenylenediamine yielded a dibenzimidazole that was shown by comparison of melting points, rotations and X-ray powder diffraction patterns (Fig. 1) to be the enantiomorph of the dibenzimidazole derived from sedoheptulosan. Further proof was obtained by comparison of the respective dibenzimidazole dihydrochlorides. Since the structure of sedoheptulosan has been established as 2,7-anhydro-β-D-altroheptulopyranose (VII)[12] and that of its dibasic acid as IX, the enantiomorphous dibasic acid must be VIII, which would be named L′-hydroxymethyl-D′-oxy-L-methylenediglycolic acid according to Jackson and Hudson[13] or 4-L-*glycero*-2-hydroxymethyl-1,3-dioxolane-2,4-*cis*-dicarboxylic acid when written as the dioxolane derivative VIIIa. It follows, then, that L-guloheptulosan must be 2,7-anhydro-β-L-guloheptulopyranose (VI). Thus, all the monomeric anhydrides known so far that have been formed by the action of acids on reducing sugars have either the combination of 1,5 and 1,6 rings found in the aldosans or the similar combination of 2,6 and 2,7 rings found in the ketosans. A study of the formation under acidic conditions of non-reducing anhydrides from aldose sugars with the gulose configuration is now in progress.

In a recent communication[12] from this Laboratory in which sedoheptulosan was proved to have the structure VII it was necessary also to eliminate the possible formula X that had been proposed on the basis of some experimental work reported earlier



(12) J. W. Pratt, N. K. Richtmyer and C. S. Hudson, THIS JOURNAL, **74**, 2200 (1952).

(13) E. L. Jackson and C. S. Hudson, *ibid.*, **59**, 994 (1937); **62**, 958 (1940).

from another laboratory. As the result of our present studies on L-guloheptulosan (VI), an additional argument can now be advanced to dispose of X as a possible formula for sedoheptulosan. We have noted above that the combination of periodate and hypobromite oxidations of L-guloheptulosan (VI) and D-altroheptulosan (VII) led to the antipodal dibasic acids VIII and IX, respectively. If sedoheptulosan did have the unusual combination of 2,3 and 2,7 rings shown in formula X and L-guloheptulosan formed an analogous anhydride, the 2,3 ring in the latter compound could only be written on the left in the Fischer projection formula because of the orientation of the participating hydroxyl group at C_3 in L-guloheptulose, and L-guloheptulosan would have the formula XI. Periodate and hypobromite oxidations of the glycosans X and XI would then yield the same dibasic acid XII. Since our experimental results have shown that antipodal rather than identical acids are produced by the oxidations, it must be concluded that although sedoheptulosan and L-guloheptulosan possess the same ring systems the glycosans cannot have the 2,3 and 2,7 combinations represented in formulas X and XI, respectively. On the other hand, as has just been shown, the 2,6:2,7 ring structures for D-altroheptulosan and L-guloheptulosan lead unequivocally to the enantiomorphous dibasic acid structures IX and VIII, respectively.

Experimental

Preparation of β-Sedoheptitol (III) from Sedoheptulosan (VII).—β-Sedoheptitol (D-altro-D-*gluco*-heptitol, L-gulo-D-*talo*-heptitol) was obtained orginally by the sodium amalgam reduction of purified, sirupy sedoheptulose (II) from *Sedum spectabile* Bor., followed by separation of the volemitol (I) and subsequent isolation of the β-sedoheptitol through its tribenzylidene derivative.[7,14] It has recently been obtained also by the catalytic hydrogenation of D-altro-D-*gluco*-heptose.[15] Having available a considerable amount of crystalline sedoheptulosan hydrate,[12] we decided to utilize it as a starting material. A 250-g. portion of the hydrate ($[\alpha]^{20}D$ −134°) in 1500 ml. of 0.5 *N* sulfuric acid was heated on the steam-bath for 8 hours; the rotation became constant at $[\alpha]^{20}D$ −108°, indicating that the expected equilibrium mixture containing 80% sedoheptulosan and 20% sedoheptulose had been formed. The solution was freed from acid by passage through the anion-exchange resin Duolite A-4, concentrated *in vacuo* to 1 liter, and the sedoheptulose therein hydrogenated by shaking the mixture with 15 g. of Raney nickel catalyst and hydrogen at 3000 p.s.i. (about 200 atmospheres) for 4 hours at 125°. The solution, no longer reducing toward Fehling solution, was filtered, concentrated and heated again with 0.5 *N* sulfuric acid. In this way 20% of the remaining sedoheptulosan was converted to sedoheptulose, which was then freed from acid, concentrated and hydrogenated as before. The combination of three such experiments should theoretically produce 270 g. of mixed heptitols and leave 480 g. of unchanged sedoheptulosan hydrate. In actual practice, by concentration of the solutions and crystallization of the residues from aqueous ethanol, we recovered 385 g. of sedoheptulosan hydrate, 65 g. of volemitol (I) and 50 g. of β-sedoheptitol (III). The separation of the heptitols by fractional crystallization was so tedious that further isolation of the several components from the mother liquor was postponed.

Oxidation of β-Sedoheptitol (III) by *Acetobacter suboxydans* to L-Guloheptulose (IV).—A solution of 24 g. of the carefully purified heptitol (m.p. 127–129°) in 1200 ml. of water containing 0.5% of Difco yeast extract, 0.3% of potassium dihydrogen phosphate and 0.05% of D-glucose was distributed evenly among six 2-liter erlenmeyer flasks, sterilized by autoclaving, and inoculated with 1 ml. per flask of a 48-hour culture of *A. suboxydans*.[16] Incubated at 30°, the mixture attained maximal reducing power (95%, calculated as D-mannoheptulose) in about one week, as estimated by Hanes' modification of Hagedorn and Jensen's ferricyanide method,[17] and did not change during an additional week. At that time the combined solutions were deproteinized by the addition of 150 ml. of a 20% aqueous solution of zinc sulfate heptahydrate followed by sufficient saturated aqueous barium hydroxide to bring the solution to *p*H 7 (brom thymol blue as indicator). About 20 g. of activated carbon was added and the mixture filtered through a buchner funnel precoated with Filter-Cel. The rotation of the L-guloheptulose in the filtrate (*c* 0.8) was estimated as $[\alpha]^{20}D$ −28°, based on the assumption of its quantitative formation from the β-sedoheptitol. The solution was deionized by passage through Amberlite IR-120 and Duolite A-4 ion-exchange resins, then concentrated *in vacuo* to 25.7 g. of a thick sirup that did not crystallize.

L-Guloheptulose Phenylosazone.—To 4 g. of sirupy L-guloheptulose in 30 ml. of water were added 6 ml. of phenylhydrazine and 4 ml. of glacial acetic acid, and the mixture was heated on the steam-bath. Yellow needles appeared within 10 minutes. Heating was continued for 2 hours, then the mixture was cooled and the product filtered and washed with 5% aqueous acetic acid followed by cold 50% ethanol. The air-dried phenylosazone weighed 4.2 g. It was recrystallized twice as yellow needles from 50 parts of hot 95% ethanol. The m.p. 197–200° (dec.) was in good agreement with the m.p. 195–198° (dec.) of the D-enantiomorph described below. Mutarotation data are reported in Table I.

Anal. Calcd. for $C_{19}H_{24}N_4O_5$: C, 58.75; H, 6.23; N, 14.43. Found: C, 58.93; H, 6.31; N, 14.06.

D-Guloheptose Phenylosazone.[18]—The notebook of Dr. Alice T. Merrill records that she prepared D-guloheptose phenylosazone in the usual manner from both D-gulo-L-*talo*-heptose and D-gulo-L-*gala*-heptose. The recrystallized product melted at 195–198° (dec.); mutarotation data are given in Table I.

Anal. Calcd. for $C_{19}H_{24}N_4O_5$: C, 58.75; H, 6.23; N, 14.43. Found: C, 58.83; H, 6.28; N, 14.54.

The L- and D-Guloheptose Phenylosotriazoles.—Because a comparison of phenylosazones is seldom completely satisfactory either by melting points or mutarotations, confirmation of the enantiomorphous character of the L- and D-guloheptose phenylosazones was sought through a comparison of their respective phenylosotriazoles. A suspension of 4.2 g. of L-guloheptulose phenylosazone in 350 ml. of water containing 4.2 g. of cupric sulfate pentahydrate was boiled under a reflux condenser for 2 hours according to the procedure of Hann and Hudson.[19] The resulting phenylosotriazole appeared to be readily soluble in water and it was necessary to remove the copper ions with hydrogen sulfide and the sulfate ions with barium hydroxide,[20] then evaporate the filtered solution to dryness, and add methanol before crystals could be obtained. The dark-colored product was recrystallized from 4 or 5 parts of methanol, using a minimum of activated carbon, until after several crystallizations the **L-guloheptose phenylosotriazole** consisted of small, colorless needles weighing 1.0 g., with m.p. 122–123° and $[\alpha]^{20}D$ −18.3 ± 0.5° in water (*c* 0.8) and −15.9 ± 0.5° in pyridine (*c* 0.8).

A small amount of **D-guloheptose phenylosotriazole**, prepared similarly, melted at 122–123°, and showed $[\alpha]^{20}D$ +17.6 ± 2.1° in pyridine (*c* 0.2).

Anal. Calcd. for $C_{13}H_{17}N_3O_5$: C, 52.87; H, 5.80. Found (L-isomer): C, 52.98; H, 5.87. (D-isomer): C, 53.14; H, 5.71.

Hydrogenation of L-Guloheptulose (IV) to β-Sedoheptitol (III) and L-β-Galaheptitol (V).—Five grams of sirupy L-

(14) A. T. Merrill, W. T. Haskins, R. M. Hann and C. S. Hudson, THIS JOURNAL, **69**, 70 (1947).

(15) D. A. Rosenfeld, N. K. Richtmyer and C. S. Hudson, *ibid.*, **73**, 4907 (1951).

(16) American Type Culture Collection No. 621.

(17) H. C. Hagedorn and B. N. Jensen, *Biochem. Z.*, **135**, 46 (1923); C. S. Hanes, *Biochem. J.*, **23**, 99 (1929).

(18) From the unpublished researches of A. T. Merrill, R. M. Hann and C. S. Hudson in this Laboratory. See also reference 14.

(19) R. M. Hann and C. S. Hudson, THIS JOURNAL, **66**, 735 (1944).

(20) *Cf.* L-fucose phenylosotriazole [W. T. Haskins, R. M. Hann and C. S. Hudson, *ibid.*, **69**, 1461 (1947)].

TABLE I

MUTAROTATION OF GULOHEPTOSE PHENYLOSAZONES

From L-guloheptulose				From D-gulo-L-*talo*-heptose[18]		From D-gulo-L-*gala*-heptose[18]	
In methyl cellosolve *c* 0.40, *l* 2		In pyridine *c* 0.40, *l* 2		In pyridine *c* 0.41, *l* 1		In pyridine *c* 0.41, *l* 2	
Time	$[\alpha]^{20}D$	Time	$[\alpha]^{20}D$	Time	$[\alpha]^{20}D$	Time	$[\alpha]^{20}D$
11 min.	+27.0°	6 min.	+111°	55 min.	−102°	11 min.	−97.4°
20 hr.	+8.9	24 hr.	+75.7	3 days	−63.7	4 days	−65.7
44 hr.	+0.9	47 hr.	+65.8	10 days	−63.7	6 days	−63.6
3 days	+0.4	5 days	+56.7			11 days	−61.5
8 days	−0.4	9 days	+47.6				
17 days	−2.2	15 days	+46.7				
25 days	−1.3	23 days	+41.1				
36 days	+0.6	34 days	+42.0				
3 mo.	+9.0	92 days	+40.7				
4 mo.	+15.0						
10 mo.	+30.0						
16 mo.	+42.0						
22 mo.	+46.7						

guloheptulose in 100 ml. of water was shaken with 9 g. of Raney nickel catalyst and hydrogen at 2500 p.s.i. for 24 hours at 100°. The non-reducing solution was deionized, concentrated *in vacuo* to a sirup, and the latter dissolved in hot 95% ethanol. As the solution cooled, the first material to separate came out as a gel that soon became crystalline. One recrystallization from ethanol yielded 1.2 g. of elongated prisms melting at 141–142°; this value was not depressed when the compound was mixed with authentic L-β-galaheptitol (L-gala-D-*gluco*-heptitol; L-gulo-D-*gala*-heptitol) (V) prepared by the reduction of perseulose (L-gala-heptulose).[21] Additional proof of the identity of the two samples was secured through a comparison of their rotations in 5% aqueous ammonium molybdate and in the acidified molybdate solutions.[22] In the former (*c* 0.40), our product showed $[\alpha]^{20}D$ +26.2° and that from perseulose +26.1°; in the latter (*c* 0.32), identical values of $[\alpha]^{20}D$ +9.6° were found.

The mother liquor, on standing, deposited a second substance that, after one recrystallization from aqueous ethanol, weighed 0.8 g. and was readily recognized as β-sedoheptitol (D-altro-D-*gluco*-heptitol, L-gulo-D-*talo*-heptitol) (III) by its melting point and mixed melting point of 127–129°. A rotation in 5% aqueous ammonium molybdate (*c* 0.40) of $[\alpha]^{20}D$ +49.5° was found both for our compound and for the same heptitol recently prepared by catalytic hydrogenation of D-altro-D-*gluco*-heptose[15]; the closely agreeing value of $[\alpha]^{20}D$ +49.6° had been reported earlier from this Laboratory[14] for β-sedoheptitol (at *c* 0.42) from sedoheptulose. In acidified molybdate solutions (*c* 0.32), $[\alpha]^{20}D$ values of +29.2° and +29.1° were obtained for our product and that from D-altro-D-*gluco*-heptose, respectively.

L-Guloheptulosan (= 2,7-Anhydro-β-L-guloheptulopyranose) (VI).—A mixture of 11.6 g. of sirupy L-guloheptulose and 40 ml. of *N* hydrochloric acid was diluted to 200 ml. with water. The rotation of the sugar in the 0.2 *N* hydrochloric acid solution was $[\alpha]^{20}D$ −22.4° and its reducing value, estimated by the ferricyanide method[17] and calculated as D-mannoheptulose, was 53 mg. per ml. When this mixture was heated for 1 hour in a boiling water-bath the rotation changed to $[\alpha]^{20}D$ −27.0° while the reducing value dropped to 9.6 mg. per ml., a loss of about 80%; a second-hour heating caused no appreciable change in these figures. The somewhat discolored solution was then clarified with activated carbon, deionized, and concentrated *in vacuo* to a clear, colorless sirup. Upon solution of this sirup in hot ethanol and inoculation with seed crystals obtained in a preliminary experiment, in which the 20% of unchanged ketose was destroyed by heating the equilibrium mixture with an excess of barium hydroxide prior to its deionization, about 5 g. of the desired anhydride was isolated. The product was recrystallized several times by dissolving it in water, concentrating the solution to a sirup, and adding absolute ethanol. At first an **anhydrous L-guloheptulosan** separated as small prisms melting at 113–115° to a viscous liquid. Several months later a melting point determination of the original analytical sample showed a marked softening at 82–85° with final liquefaction occurring at 95–105°. At the same time a new batch of crystals from a mother liquor was observed as elongated prisms that melted completely at 82–85° to a viscous sirup, and analyses confirmed that **L-guloheptulosan hemihydrate** as well as the anhydrous modification can separate from aqueous ethanol depending apparently upon the conditions used in the crystallization. From methanol by the addition of acetone the anhydrous modification usually separates as clusters of stout, irregular, radiating prisms with rounded, wedge-like ends. From aqueous ethanol the hemihydrate crystallizes as columns with characteristically squared ends. Like sedoheptulosan,[12] the anhydrous L-guloheptulosan also becomes hydrated upon exposure to moist air. The rotation $[\alpha]^{20}D$ −39.7° in water (*c* 5) observed for the anhydrous L-guloheptulosan would be equivalent to $[\alpha]^{20}D$ −37.9° for the hemihydrate.

Anal. Calcd. for $C_7H_{12}O_6$: C, 43.75; H, 6.30. Found (anhydrous modification): C, 43.78; H, 6.43. Calcd. for $C_7H_{12}O_6 \cdot {}^1/_2H_2O$: C, 41.79; H, 6.51; H_2O, 4.48. Found (hydrated in air): C, 41.95, 41.58; H, 6.50, 6.34. (crystallized from aqueous ethanol): C, 41.89, 41.88; H, 6.59, 6.64; H_2O (dried 27 hours, to constant weight, *in vacuo* at 77°; at 100° *in vacuo* the product slowly sublimes), 4.47.

Oxidation of L-Guloheptulosan (VI) with Sodium Metaperiodate Followed by Hypobromite.—To 1.023 g. of L-guloheptulosan in 40 ml. of water was added 50 ml. of an approximately 0.45 *M* aqueous solution of sodium metaperiodate. An appreciable amount of heat was generated by the reaction, so the mixture was left at 20° for 3 hours before being diluted exactly to 100 ml. with water. At that time the specific rotation, calculated for the glycosan, had changed from its original $[\alpha]^{20}D$ −39.7° (estimated) to +15.4°; after 11 hours a value of +14.3° was reached and this remained unchanged at the end of 23 hours. The final value corresponds to +17.2° when calculated as the expected dialdehyde and is in good accord with the value −16.9° reported for the enantiomorphous dialdehyde produced from both D-altroheptulosan[12] and D-idoheptulosan.[8] Titration of 2-ml. samples at the end of 11 and 23 hours indicated the consumption of 2.06 and 2.11 molar equivalents of periodate and the liberation of 0.99 and 1.01 molar equivalents of formic acid, respectively. A test for formaldehyde with the dimedon reagent was negative.

To oxidize the dialdehyde thus obtained to the dibasic acid (VIII), the iodate and periodate ions were first removed through precipitation with 10 ml. of a 30% aqueous solution of barium chloride. To the filtered solution were then added 4 g. of barium carbonate and 0.8 ml. of bromine, and the reaction mixture was kept in the dark, with occasional shaking, for 15 hours. The solution was aerated to remove any excess bromine, shaken with silver carbonate to remove halide ions, freed from cations by passage through a column of Amberlite IR-120, and concentrated *in vacuo* to a thick sirup of the dibasic acid (VIII).

4-L-*glycero*-2-Hydroxymethyl-2,4-*cis*-di-(2-benzimidazolyl)-1,3-dioxolane and Its Hydrate.—The sirupy dibasic acid (VIII) just described was mixed in a test-tube with 2 g. of *o*-phenylenediamine and 6 ml. of 4 *N* hydrochloric acid and heated in an oil-bath for 3 hours at 130 ± 5°. The

(21) R. M. Hann and C. S. Hudson, *ibid.*, **61**, 336 (1939).

(22) N. K. Richtmyer and C. S. Hudson, *ibid.*, **73**, 2249 (1951).

product was dissolved in a small amount of water and made alkaline with aqueous ammonia. The dark brown crystalline material that deposited was filtered and recrystallized several times from ethanol by the addition of water with sufficient activated carbon being used so that the final flaky crystalline product was practically colorless; the yield was 130 mg. Analyses showed the dibenzimidazole to be a monohydrate, thus confirming the earlier statement[12] that the enantiomorphous product derived from D-altroheptulosan (sedoheptulosan) was probably a monohydrate. Desiccation of the hydrate by heating for 5 hours at 100° *in vacuo* produced an anhydrous benzimidazole that melted at about 137° to a stiff sirup with subsequent characteristic liquefaction at about 160°. Identical values had been observed previously with specimens of the enantiomorphous dibenzimidazole derived from both D-altroheptulosan[12] and D-idoheptulosan.[6] Identical X-ray powder diffraction patterns (Table II and Fig. 1) also confirmed the enantiomorphous character of the dibenzimidazole hydrate derived from the D-series (D-altroheptulosan) and that from the new L-series (L-guloheptulosan). A comparison of their rotations will be discussed below.

Anal. Calcd. for $C_{18}H_{16}N_4O_3 \cdot H_2O$: N, 15.81; H_2O, 5.09. Found: N, 15.77; H_2O, 5.15. Calcd. for $C_{18}H_{16}N_4O_3$: C, 64.27; H, 4.80; N, 16.66. Found (dried 5 hours *in vacuo* at 100°): C, 64.49; H, 4.84; N, 16.59.

4-L-*glycero*-2-Hydroxymethyl-2,4-*cis*-di-(2-benzimidazolyl)-1,3-dioxolane Dihydrochloride Dihydrate and Its Enantiomorph.—When an attempt was made to measure the rotation in *N* hydrochloric acid of the dibenzimidazole derived from L-guloheptulosan, a crystalline hydrochloride separated almost immediately from the solution. The product, therefore, was filtered, and recrystallized from 80% ethanol by the addition of ether. The long needles melted at 237–245° (dec.). In *N* hydrochloric acid (*c* 1.1) the rotation $[\alpha]^{20}D$ +9.9° was equivalent to +13.1° when calculated as the anhydrous dibenzimidazole, and the latter is thus of the same magnitude but opposite in sign to the value −12.9° reported for the anhydrous dibenzimidazole derived from sedoheptulosan.[12]

For an additional comparison, about 50 mg. of the dibenzimidazole from the sedoheptulosan experiments[12] was converted similarly to its hydrochloride. The appearance of the product as long needles upon recrystallization from aqueous ethanol and ether, its m.p. of 239–247° (dec.), and its composition as a dihydrochloride dihydrate were in agreement with those expected for the enantiomorphous D-*glycero* form.

Anal. Calcd. for $C_{18}H_{16}N_4O_3 \cdot 2HCl \cdot 2H_2O$: C, 48.55; H, 4.98; N, 12.58; Cl, 15.92; H_2O, 8.09. Found (L-*glycero* form): C, 48.55; H, 5.05; N, 12.57; Cl, 16.07, (D-*glycero* form): C, 48.53; H, 5.16; N, 12.86; Cl, 15.95; H_2O (5 hours at 100° *in vacuo*), 8.59.

TABLE II

X-RAY POWDER DIFFRACTION PATTERN[a] OBTAINED FROM BOTH THE 4-D- AND THE 4-L-*glycero*-2-HYDROXYMETHYL-2,4-*cis*-DI-(2-BENZIMIDAZOLYL)-1,3-DIOXOLANE HYDRATES

Interplanar spacings, Å.	Relative intensities	Interplanar spacings, Å.	Relative intensities
17.1	5	4.38	2
8.45	4	4.24	2
7.7	3	4.02	2
7.0	1	3.83	4
6.15	2	3.66	3
5.75	3	3.49	2
5.45	4	3.36	3
5.1	3	3.22	1
4.80	2	2.83(B)	1
4.56	2		

[a] These data were obtained by the powder-wedge technique in a cylindrical camera with 7.16-cm. radius exposed to radiation from a copper anode X-ray tube with a nickel-foil filter giving essentially Cu Kα radiation. The relative intensities were estimated visually; 5 represents the strongest band, 1 the weakest band, and B a broad band.

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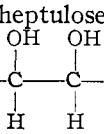
D-Idoheptulose and 2,7-Anhydro-β-D-idoheptulopyranose[1]

BY JAMES W. PRATT, NELSON K. RICHTMYER AND C. S. HUDSON

The oxidation of D-gluco-D-*ido*-heptitol (synonym, D-ido-L-*gulo*-heptitol) to D-idoheptulose by *Acetobacter suboxydans* is in accord with the rule of specificity for that organism. The sirupy D-idoheptulose was characterized through its crystalline phenylosazone and phenylosotriazole, and its structure was proved through its catalytic hydrogenation to a mixture of D-gluco-D-*ido*-heptitol and the new ido-*ido*-heptitol. The action of acid on D-idoheptulose yielded a crystalline D-idoheptulosan whose structure was established, by periodate oxidation methods, as 2,7-anhydro-β-D-idoheptulopyranose.

Researches on the oxidation of heptitols by *Acetobacter suboxydans* in this Laboratory have shown the method to be very effective for the preparation of heptuloses when the heptitol has the favorable  configuration. Thus, perseitol (synonyms, D-manno-D-*gala*-heptitol and L-gala-D-*manno*-heptitol) was converted to crystalline L-galaheptulose (= perseulose)[2] and gluco-*gulo*-heptitol (II) (a *meso* form) was converted to crystalline L-glucoheptulose (I),[3] both sugars being produced in nearly quantitative yields. A third heptitol, volemitol (synonyms, D-manno-D-*talo*-heptitol and D-altro-D-*manno*-heptitol), has the favorable grouping at each end of its molecule and was found to be oxidizable by *A. suboxydans* to two ketoses, with crystalline D-mannoheptulose and sirupy D-altroheptulose (= sedoheptulose) being obtained

(1) A portion of this material has been taken from the thesis submitted by James W. Pratt to the Department of Chemistry of the Graduate School of Georgetown University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1951.

(2) R. M. Hann, E. B. Tilden and C. S. Hudson, THIS JOURNAL, **60**, 1201 (1938); E. B. Tilden, *J. Bact.*, **37**, 629 (1939).

(3) W. D. Maclay, R. M. Hann and C. S. Hudson, THIS JOURNAL, **64**, 1606 (1942).