tilled methanolysis sirup (2.0 g.) was dissolved in 15 ml. of *N* sulfuric acid and heated for 10 hours on a boiling water-bath. The solution was then neutralized with barium carbonate, filtered, evaporated under reduced pressure to a sirup, and extracted with acetone. The components of the latter solution were separated by paper partition chromatography using the strip technique with ethyl acetate, acetic acid and water (9:2:2) as the developer. The appropriate sections cut from three separate chromatograms were combined, eluted, and the solution analyzed by the alkaline iodine method.[17] The average values from five determinations, calculated on the basis of six molar parts, were as follows: 2,3,4-trimethyl-D-xylose (1.06 parts), 3,4-dimethyl-D-xylose (1.07 parts), 2,3,4,6-tetramethyl-D-galactose (1.02 parts), 2,3,6-trimethyl-D-glucose (0.86 part) and 2,3-dimethyl-D-glucose (1.96 parts).

Acknowledgment.—One of us (P. S. R.) wishes to express his thanks to The Institute of Paper Chemistry for a Research Fellowship and to the Government of the United States for a Fulbright Travel Grant.

APPLETON, WIS.

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[17] A. E. Flood, E. L. Hirst and J. K. N. Jones, *J. Chem. Soc.*, 1679 (1948).

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH, PUBLIC HEALTH SERVICE, FEDERAL SECURITY AGENCY]

Crystalline Tetrabenzoyl-β-D-fructopyranosyl Bromide and its Reduction by Lithium Aluminum Hydride to 1,5-Anhydro-D-mannitol and 1,5-Anhydro-L-gulitol

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RECEIVED JANUARY 23, 1953

Treatment of the known 1,3,4,5-tetrabenzoyl-β-D-fructose with hydrogen bromide in glacial acetic acid has led to the isolation of tetrabenzoyl-β-D-fructopyranosyl bromide in a crystalline form containing one quarter mole of acetic acid. The behavior of this substance in dioxane–methanol and in aqueous dioxane has been studied and supports the configuration assigned. Reduction of the halide with lithium aluminum hydride afforded a very small yield of 1,5-anhydro-D-mannitol and demonstrated that the bromine was at least in part replaced without inversion of configuration at carbon 2. The major product of the reduction, however, was a new hexitan, 1,5-anhydro-L-gulitol, which was produced by Walden inversion at carbon 2 upon replacement of the bromine by hydrogen. This new anhydride was characterized through its 4,6-benzylidene and 2,3-dibenzoyl-4,6-benzylidene derivatives. Its identity was confirmed by the synthesis of authentic corresponding derivatives of the D-series *via* the reduction of tetraacetyl-D-gulopyranosyl bromide with lithium aluminum hydride.

The relative instability of tetraacetyl-β-D-fructopyranosyl bromide and chloride[1] suggests that, as in the D-ribose series,[2,3] a more stable benzoyl analog might offer advantages for synthetic and other purposes. For the preparation of such an analog, the crystalline 1,3,4,5-tetrabenzoyl-β-D-fructopyranose (I), which Brigl and Schinle[4] prepared through the direct benzoylation of D-fructose, was employed. When this substance was treated with hydrogen bromide in glacial acetic acid there was obtained in 89% yield a crystalline tetrabenzoylhexosyl bromide containing one quarter mole of acetic acid of crystallization. Attempts to obtain the product in crystalline, solvent-free form were unsuccessful. By analogy with the known tetraacetyl-β-D-fructopyranosyl halides[1,5] the new bromide may be assigned structure III, tetrabenzoyl-β-D-fructopyranosyl bromide. Evidence adduced below confirms this assignment.

As with other benzoylated glycosyl halides previously studied in this Laboratory,[6] it was of interest to examine the behavior of this new bromide with methanol in the absence of an acid acceptor. Polarimetric observations of a solution of the halide in 1:9 (v./v.) dioxane–methanol disclosed the reaction to be of an approximately pseudo-unimolecular nature and yielded an average rate constant (minutes, decadic logs) of 0.057. Comparison of this rate with values previously obtained in a similar manner for other series may be made through examination of Table I where such constants are arranged in the order of decreasing magnitude. Consider first the benzoylated aldopyranosyl bromides. Both of those which possess a benzoyloxy group on carbon 2 *trans* to the halogen (β-D-ribose and α-L-rhamnose) and may thus react by a neighboring group mechanism[3] are more rapid than any of those halides which have a *cis* relationship on carbon 2 and presumably react by simple inversion only. While there is not a sharply defined gap between the two groups, the β-D-fructosyl halide clearly belongs in the more rapid one. Inspection of formula III shows that while the benzoyloxy group attached to carbon 3 is *cis* to the bromine and therefore would

TABLE I

RATES OF REACTION OF BENZOYLATED GLYCOPYRANOSYL BROMIDES WITH 1:9 DIOXANE–METHANOL AT 20° IN THE ABSENCE OF AN ACID ACCEPTOR

Series	*k* (min., decadic logs)	Benzoyloxy group available for participation in mechanism?
β-D-Ribose	0.076[a]	Yes
β-D-Fructose	.057	Yes
α-L-Rhamnose	.016[b]	Yes
α-D-Xylose	.013[c]	No
β-D-Arabinose	.011[c]	No
α-D-Ribose	.004[a]	No
α-D-Glucose	.00031[d]	No

[a] Ref. 3. [b] Ref. 8. [c] H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, 72, 4173 (1950). [d] Ref. 6.

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[1] D. H. Brauns, THIS JOURNAL, 45, 2381 (1923).

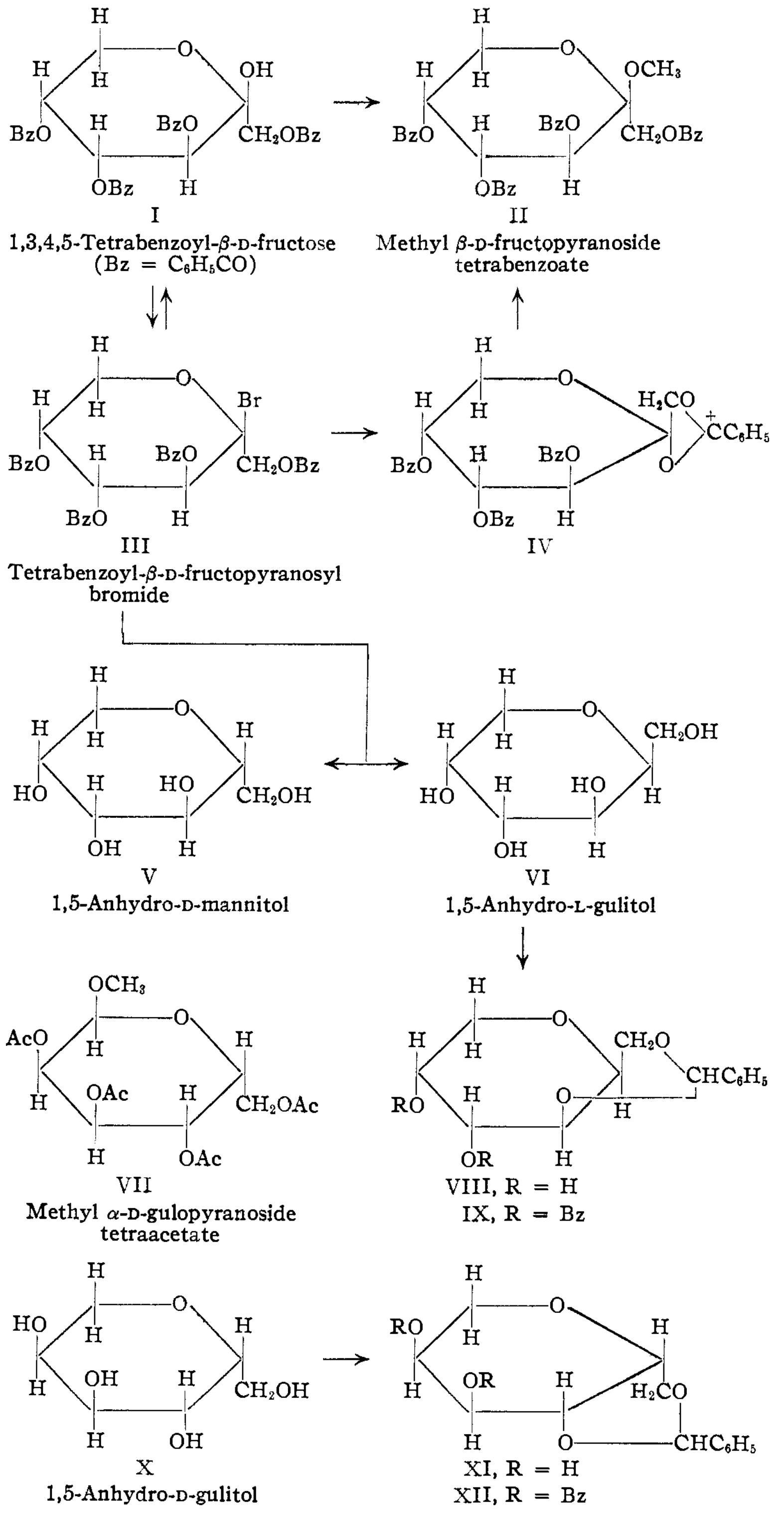
[2] R. Jeanloz, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, 70, 4055 (1948).

[3] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, 73, 959 (1951).

[4] P. Brigl and R. Schinle, *Ber.*, 66, 325 (1933). These authors assigned the structure given (I) since the substance gave methyl β-D-fructopyranoside tetrabenzoate (II) when methylated and showed a high negative rotation (−164.9°) similar to that of the previously known 1,3,4,5-tetraacetyl-β-D-fructose (−92.3°).

[5] C. S. Hudson, THIS JOURNAL, 46, 477 (1924).

[6] See R. K. Ness and H. G. Fletcher, Jr., *ibid.*, 74, 5344 (1952) and the references cited therein.



I
1,3,4,5-Tetrabenzoyl-β-D-fructose (Bz = C_6H_5CO)

II
Methyl β-D-fructopyranoside tetrabenzoate

III
Tetrabenzoyl-β-D-fructopyranosyl bromide

IV

V
1,5-Anhydro-D-mannitol

VI
1,5-Anhydro-L-gulitol

VII
Methyl α-D-gulopyranoside tetraacetate

VIII, R = H
IX, R = Bz

X
1,5-Anhydro-D-gulitol

XI, R = H
XII, R = Bz

not be expected to participate in methanolysis, the benzoyloxy group attached to carbon 1 is favorably situated with respect to the bromine and would be expected to participate in the mechanism of its removal. Such a postulated path through the ionic intermediate IV involves two inversions at carbon 2 and requires the formation of methyl β-D-fructopyranoside tetrabenzoate (II) as the final product. Actually, when tetrabenzoyl-β-D-fructopyranosyl bromide reacted with anhydrous methanol in the absence of an acid acceptor methyl β-D-fructopyranoside tetrabenzoate was isolated in 63% yield.[7] Attempts to isolate a methyl 1,2-orthobenzoate by the use of an acid acceptor failed to give a crystalline product although the amorphous material obtained mutarotated when subjected to methanolic hydrogen chloride.[8]

The rate of reaction of tetrabenzoyl-β-D-fructopyranosyl bromide with *ca.* 18:7 dioxane–water was also studied; the change of rotation with time is plotted in Fig. 1. The rapid initial dextromutarotation is typical of β-D-halides under these circumstances; the subsequent levomutarotation may be interpreted as the conversion of an ortho-type intermediate to 1,3,4,5-tetrabenzoyl-β-D-fructose or, more simply, the mutarotation of the α-form of that substance to an equilibrium mixture of the two anomers. That the equilibrium lies almost wholly on the side of the β-anomer appears from the fact that the end-point here (corresponding to $[\alpha]^{20}D$ $-114°$) is very close to the specific rotation of 1,3,4,5-tetrabenzoyl-β-D-fructose in 18:7 dioxane–water ($[\alpha]^{20}D$ $-113°$) and is confirmed by the fact that mutarotation of 1,3,4,5-tetrabenzoyl-β-D-fructose in 18:7 dioxane–water could not be detected even upon the addition of ammonia.[9]

The reduction of acylaldopyranosyl halides with lithium aluminum hydride has been shown[10] to afford a practicable means for the synthesis of 1,5-anhydroglycitols. Similarly an acylaldofuranosyl halide has been reduced to a 1,4-anhydroglycitol.[11] However, in none of these cases has the carbon to which the halogen was attached retained its asymmetry upon reduction and an anomeric pair of acylaldosyl halides would be expected to give the

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[7] The final value in the determination of the rate of reaction of tetrabenzoyl-β-D-fructopyranosyl bromide with 1:9 dioxane–methanol was somewhat more dextrorotatory ($-135°$) than the rotation of methyl β-D-fructopyranoside in that solvent ($-168.7°$). This fact may indicate that a part of the bromide reacts by direct inversion and that the anomer of the main product (which would be more dextrorotatory) is also formed.

[8] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **73**, 296 (1951).

[9] Brigl and Schinle (ref. 4) observed that the substance did not appear to mutarotate in chloroform. 1,3,4,5-Tetraacetyl-β-D-fructose was found by E. Pacsu and F. V. Rich [*ibid.*, **55**, 3018 (1933)] to mutarotate in pyridine only from $[\alpha]^{20}D$ -101.6 to $-99.9°$ in several days.

[10] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **72**, 4547 (1950).

[11] R. K. Ness, H. G. Fletcher, Jr., and C. S. Hudson, *ibid.*, **73**, 3742 (1951).

same anhydroglycitol. An acylketosyl halide, however, would not lose asymmetry on reduction and could give two products according to whether inversion did or did not take place at carbon 2 when the halogen was replaced by hydrogen. Thus, reduction of tetrabenzoyl-β-D-fructopyranosyl bromide (III) without inversion would lead to the formation of 1,5-anhydro-D-mannitol (V) (synonyms: styracitol, 2,6-anhydro-D-mannitol) while reduction with inversion would give 1,5-anhydro-L gulitol (VI) (synonym: 2,6-anhydro-D-glucitol). While the former anhydride is a relatively well-known substance[12] the latter has not hitherto been reported.

Experimentally it was found that the reduction of tetrabenzoyl-β-D-fructopyranosyl bromide with lithium aluminum hydride gave a sirup from which 1,5-anhydro-D-mannitol was isolated (as its tetrabenzoate) in 0.54% yield. Benzalation of the sirup gave crystalline material, the monobenzylidene derivative of a new anhydroglycitol, in 60% yield. This substance consumed one mole of periodate and therefore possessed two adjacent hydroxyl groups. Hydrolysis of the acetal converted it to an amorphous anhydroglycitol which consumed two moles of periodate and produced one mole of formic acid, the end rotation of the solution being equal in magnitude (within experimental error) but opposite in sign to that obtained when 1,5-anhydro-D-mannitol is so oxidized. These facts indicated that the substances in hand were 1,5-anhydro-L-gulitol (VI) and its 4,6-benzylidene derivative (VIII). To confirm the configuration of the anhydride its enantiomorph was synthesized from methyl α-D-gulopyranoside tetraacetate (VII). Acetolysis of this substance to D-gulopyranose tetraacetate[13] was followed by conversion to tetraacetyl-D-gulopyranosyl bromide which, without isolation, was reduced with lithium aluminum hydride to sirupy 1,5-anhydro-D-gulitol. This anhydride of the D-series was characterized through its 4,6-benzylidene derivative (XI) and 2,3-dibenzoyl-4,6-benzylidene derivative (XII), Comparison of the physical properties listed in Table II clearly shows the derivatives from the reduction of the bromide to be the enantiomorphs of the authentic derivatives of the D-series.

TABLE II

THE ENANTIOMORPHIC 1,5-ANHYDROGULITOLS AND THEIR DERIVATIVES

Gulitols	M.p., °C.	$[\alpha]^{20}D$
1,5-Anhydro-D	Amorph.	-7.9 ± 0.2 (H_2O)
1,5-Anhydro-L	Amorph.	$+7.8 \pm 0.2°$ (H_2O)
1,5-Anhydro-4,6-benzylidene-D	168–169; 176–178	$+5.8 \pm 0.4°$ (EtOH)
1,5-Anhydro-4,6-benzylidene-L	164–167; 173–176	$-6.8 \pm 0.3°$ (EtOH)
1,5-Anhydro-4,6-benzylidene-D,L	136–141	$\pm 0.0°$ (EtOH)
1,5-Anhydro-2,3-dibenzoyl-4,6-benzylidene-D	177–180	$-3.1 \pm 0.2°$ ($CHCl_3$)
1,5-Anhydro-2,3-dibenzoyl-4,6-benzylidene-L	177–180	$+3.6 \pm 0.2°$ ($CHCl_3$)
1,5-Anhydro-2,3-dibenzoyl-4,6-benzylidene-D,L	164–165	$\pm 0.0°$ ($CHCl_3$)

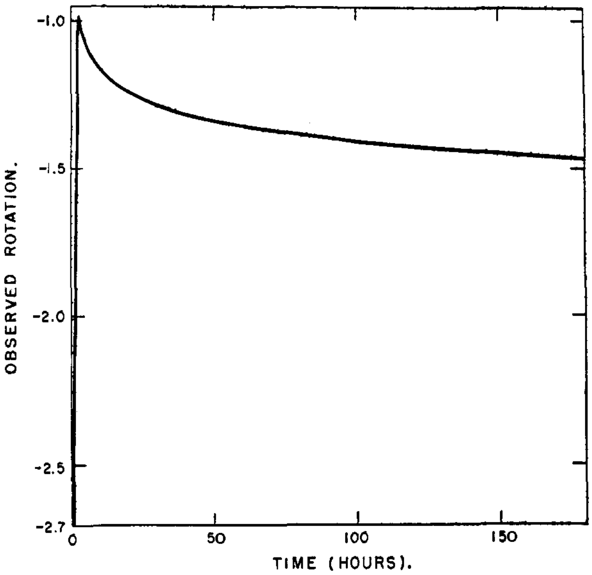

Fig. 1.—Reaction of tetrabenzoyl-β-D-fructopyranosyl bromide with 18:7 dioxane–water (v./v.) at 20°.

Careful hydrolysis of a weighed sample of pure 1,5-anhydro-4,6-benzylidene-L-gulitol afforded amorphous 1,5-anhydro-L-gulitol[14] which showed a rotation in water of $[\alpha]^{20}D$ +7.8 ± 0.2°. From this rotational value and the known rotation of 1,5-anhydro-D-mannitol in water we may calculate that the sirup obtained from the reduction of tetrabenzoyl-β-D-fructopyranosyl bromide is approximately 14% 1,5-anhydro-D-mannitol and 86% 1,5-anhydro-L-gulitol if we assume that the sirup consists of these two substances only. In any case it is established that 1,5-anhydro-L-gulitol is the chief product and that most of the bromide underwent Walden inversion at carbon 2 when reduced with lithium aluminum hydride. As far as the authors are aware, this is the first conclusive test of the stereochemistry of the reduction of a tertiary halide by lithium aluminum hydride.

Experimental[15]

1,3,4,5-Tetrabenzoyl-β-D-fructose (I).—The direct benzoylation of D-fructose according to the procedure of Brigl and Schinle[4] gave a crude product melting at 165–177°. Two recrystallizations from absolute ethanol raised the melting point to 179–182°. In chloroform the substance rotates −172.4° (*c* 4.2) and in 18:7 dioxane–water (v./v.) −113° (*c* 2.0). Mutarotation was not observed in either solvent nor did addition of two drops of concentrated aqueous ammonia to the latter solvent mixture produce a detectable change in the rotation of the substance. Brigl and

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[12] H. G. Fletcher, Jr., and H. W. Diehl, THIS JOURNAL, **74**, 3175 (1952).

[13] R. M. Hann and C. S. Hudson, *ibid.*, **56**, 2465 (1934).

[14] It may be noted here that the molecular rotation of 1,5-anhydro-L-gulitol (−1300) lies not far from the mathematical mean (−3515) of the molecular rotations for methyl α-L-gulopyranoside (−23,210) and methyl β-L-gulopyranoside (+16,180). This fact is expected on the basis of the generalization regarding such interrelations which was published several years ago [H. G. Fletcher, Jr., and C. S. Hudson, THIS JOURNAL, **71**, 3682 (1949)].

[15] Melting points are corrected. Rotations are specific rotations for the D-line of sodium at 20°, concentration being expressed in g. of substance per 100 ml. of solution.

Schinle[4] reported a melting point of 174–175° and a rotation of −164.9° ($CHCl_3$) for 1,3,4,5-tetrabenzoyl-β-D-fructose.

Anal. Calcd. for $C_{34}H_{28}O_{10}$: C, 68.45; H, 4.73. Found: C, 68.35; H, 4.72.

Tetrabenzoyl-β-D-fructopyranosyl Bromide (III).—A solution of 20 g. of 1,3,4,5-tetrabenzoyl-β-D-fructose in 50 ml. of glacial acetic acid was treated with 50 ml. of a 32% solution of hydrogen bromide in the same solvent. After a few minutes at room temperature the reaction mixture was seeded,[16] left at room temperature for 8 hours and then cooled at +5° overnight. Washed successively with glacial acetic acid, glacial acetic acid–pentane and pentane, the product (20.06 g., 89%) melted at 105–110°. The stout prisms were dissolved in ether, the solution concentrated *in vacuo* to a sirup and dissolved in 2 parts of glacial acetic acid; under these conditions crystallization was spontaneous and rapid. One part of pentane was finally added and the product removed after storage overnight at +5°. A second recrystallization from glacial acetic acid–pentane yielded material melting at 106–110° and rotating in chloroform −179.5° (*c* 4.57).

Anal. Calcd. for $C_{34}H_{27}O_9Br \cdot {}^1/_4C_2H_4O_2$: C, 61.43; H, 4.18; Br, 11.85; $C_2H_4O_2$, 2.23. Found: C, 61.33; H, 4.10; Br, 11.87.

A sample recrystallized from ether–pentane and then from carbon tetrachloride–pentane[17] melted at 101–104°, rotated −181° in chloroform (*c* 3.59) and gave the following analysis: C, 61.33; H, 4.17; loss of wt. *in vacuo* at 110° for 15 min., 2.12. The amorphous residue remaining from the determination of weight loss gave the following.

Anal. Calcd. for $C_{34}H_{27}O_9Br$: C, 61.92; H, 4.13. Found: C, 61.81; H, 4.15.

A powdered sample (0.5 g.) of the crystalline product was heated *in vacuo* at 100–105° and the gases evolved condensed in a Dry Ice–acetone trap. Acetic acid was isolated from the distillate as its *p*-bromophenacyl ester[18] which melted at 85–86° either alone or in admixture with authentic *p*-bromophenacyl acetate.

Reaction of Tetrabenzoyl-β-D-fructopyranosyl Bromide (III) with Methanol in the Absence of an Acid Acceptor.—A solution of 239.5 mg. of crystalline tetrabenzoyl-β-D-fructopyranosyl bromide (containing ${}^1/_4$ mole of acetic acid) in 2.5 ml. of pure dioxane was diluted with absolute methanol to 25.0 ml. and the rotation of the resulting solution observed in a 2-dm. tube at 20°. The following data and the first-order reaction constants calculated therefrom were obtained.

Time, (min.)	Obsd. rotation, α_D (2 dm., circular degrees)	*k*, min., decadic logs.
0	−3.19° (extrapolated)	...
1.5	−3.14	0.050
3.5	−2.91	.063
5.3	−2.75	.069
8.7	−2.61	.063
15.1	−2.50	.051
38.4	−2.36	.044
128	−2.34	...

The final rotation corresponds to a specific rotation of −135° based on the assumption of complete conversion to methyl fructopyranoside tetrabenzoate. In 1:9 dioxane–methanol (v./v.) methyl β-D-fructopyranoside tetrabenzoate shows −168.7° (*c* 0.65).

Crystalline tetrabenzoyl-β-D-fructopyranosyl bromide (5.26 g.) was added to 50 ml. of methanol and left overnight at room temperature. The reaction mixture was then warmed at 50° for 30 minutes to dissolve unreacted halide and finally left at +5° for 24 hours. The crystals which deposited (3.04 g., 63%) melted at 78–81° either alone or in admixture with methyl β-D-fructopyranoside tetrabenzoate (II) containing ${}^1/_4$ mole of methanol of crystallization (see below). After recrystallization from absolute ethanol (seeding with anhydrous form) the product melted at 109–112°.

Methyl β-D-Fructopyranoside Tetrabenzoate (II) from 1,3,4,5-Tetrabenzoyl-β-D-fructose (I).—1,3,4,5-Tetrabenzoyl-β-D-fructose was methylated with methyl iodide and silver oxide as was done by Brigl and Schinle.[4] The product, recrystallized to constant melting point from methanol, melted at 77–79° and showed in chloroform a rotation of −166.0° (*c* 4.17).

Anal. Calcd. for $C_{35}H_{30}O_{10} \cdot {}^1/_4CH_3OH$: C, 68.44; H, 5.05; CH_3O, 6.27; CH_3OH, 1.29. Found: C, 68.47; H, 5.06; CH_3O, 7.50; wt. loss *in vacuo*, 1.36.

Recrystallization of the methanol-containing product from absolute ethanol gave crystals melting at 67–69°.

Anal. Calcd. for $C_{35}H_{30}O_{10} \cdot {}^1/_2C_2H_5OH$: C, 68.24; H, 5.25. Found: C, 68.14; H, 5.04.

After a period this latter form turned spontaneously into an anhydrous one which could, thereafter, be obtained by recrystallization from absolute alcohol. It melted at 109–112° and showed in chloroform a rotation of −171° (*c* 1.26). Brigl and Schinle[4] reported a melting point of 113° and a rotation in chloroform of −171.3° for methyl D-fructopyranoside tetrabenzoate.

Anal. Calcd. for $C_{35}H_{30}O_{10}$: C, 68.84; H, 4.95; CH_3O, 5.08. Found: C, 68.73; H, 4.74; CH_3O, 5.14.

The Rate of Reaction of Tetrabenzoyl-β-D-fructopyranosyl Bromide (III) with Aqueous Dioxane at 20°.—A solution of 250.9 mg. of crystalline tetrabenzoyl-β-D-fructopyranosyl bromide (containing ${}^1/_4$ mole of acetic acid) dissolved in 18 ml. of dioxane was diluted to 25.0 ml. with water and the mutarotation of the resulting solution observed at 20° in a 1.5-dm. tube. The data obtained are plotted in Fig. 1. The final observed rotation (36 days) was −1.52°, corresponding to a specific rotation of −114° for the theoretical yield of tetrabenzoylhexose. The rotation of pure 1,3,4,5-tetrabenzoyl-β-D-fructose in 18:7 dioxane–water is −113° (*c* 1.0), a value unaltered by the addition of an equimolar amount of hydrogen bromide even after 32 days.

A curve identical with that obtained above was found when a solution of 1.0018 g. of the crystalline bromide in 72 ml. of dioxane was diluted to 100.0 ml. with water and treated with 1 g. of dry Duolite A-4.[19]

Reduction of Tetrabenzoyl-β-D-fructopyranosyl Bromide (III) with Lithium Aluminum Hydride.—A solution of 20.95 g. of the crystalline bromide described above in 110 ml. of dry ether was added over the course of 35 min. to 100 ml. of *ca.* 1 *M* lithium aluminum hydride in ether. The reaction mixture was boiled under reflux for 25 min., cooled, and treated cautiously with 200 ml. of water. After filtration with the aid of Filter-Cel the aqueous layer was extracted with ether (to remove benzyl alcohol) and deionized by successive passage through columns of Amberlite IR-120[20] and Duolite A-4.[19] Water was removed *in vacuo* and the sirup dried by the evaporation therefrom of 100 ml. of absolute alcohol *in vacuo*. The amorphous residue showed in water a rotation of −0.18° (*c* 1.96) corresponding to a mixture of 14% 1,5-anhydro-D-mannitol ($[\alpha]^{20}D$ −50.9°) and 86% 1,5-anhydro-L-gulitol ($[\alpha]^{20}D$ +7.8°). Attempts to obtain crystalline material directly from it were, however, unsuccessful. Benzoylation of 0.95 g. of a similar amorphous reduction product followed by chromatography on alumina gave 0.018 g. (0.54% based on the amorphous mixture of anhydrides) of crude 1,5-anhydro-D-mannitol tetrabenzoate. After one recrystallization from alcohol the compound rotated −148.4° in chloroform (*c* 0.88) and melted at 145–146° either alone or in admixture with authentic 1,5-anhydro-D-mannitol tetrabenzoate. Asahina[21] reported a melting point of 142° and a specific rotation in chloroform of −150.4° for styracitol tetrabenzoate.

1,5-Anhydro-4,6-benzylidene-L-gulitol (VIII).—The entire reduction product above, dissolved in 20 ml. of absolute ethanol containing 1% of hydrogen chloride, was treated with 3.5 ml. of freshly distilled benzaldehyde and left at +5° for 2 days to give 4.67 g. (60%, based on the original bromide) of crude product. After two recrystallizations from 5–10 parts of absolute alcohol the material melted at

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[16] Crystals were initially obtained when a solution of 1 g. of 1,3,4,5-tetrabenzoyl-β-D-fructose in 15 ml. of 32% hydrogen bromide-glacial acetic acid was held at +5° for 16 days.

[17] Crystallization was very slow in these solvent mixtures.

[18] F. Schneider, "Organic Qualitative Microanalysis," John Wiley and Sons, Inc., New York, N. Y., 1946, p. 153.

[19] A product of the Chemical Process Co., 901 Spring St., Redwood City, Calif.

[20] A product of the Resinous Products and Chemical Co., Washington Square, Philadelphia, Pa.

[21] Y. Asahina, *Arch. Pharm.*, **247**, 157 (1909).

161–175° and rotated −0.5 ± 0.5° in chloroform (c 1.00).

Anal. Calcd. for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.94; H, 6.39.

Further recrystallization from 20–25 parts of water afforded long, flat prisms melting at 165–175° and rotating in chloroform ±0.0° (c 0.76); recrystallization from 25 parts of chloroform gave m.p. 168–176° and $[\alpha]^{20}D$ ±0.0° ($CHCl_3$, c 0.75). A sample prepared *via* the catalytic debenzoylation of the dibenzoate described below melted at 164–167°, resolidified and melted again at 173–176°. It showed rotations of +0.3 ± 0.3° in chloroform (c 0.85) and −6.8 ± 0.3° in absolute ethanol (c 0.81).

Following the technique developed by Jackson and Hudson[22] the purified benzylidene derivative (100 mg.) was dissolved in a few ml. of water, the solution treated with 5.0 ml. of 0.48 M sodium metaperiodate and diluted to 25.0 ml. with water. After 27 hours titration of an aliquot showed the consumption of 1.07 moles of oxidant per mole of compound.

1,5-Anhydro-2,3-dibenzoyl-4,6-benzylidene-L-gulitol (IX).—Crude 1,5-anhydro-4,6-benzylidene-L-gulitol (4.1 g.) was benzoylated in the usual manner to give, from 25 ml. of absolute alcohol, 4.49 g. (60%) of product melting at 177–180°. Recrystallizations from 2:1 ether–pentane and from absolute ethanol failed to change this value. The pure substance rotated +3.6 ± 0.2° in chloroform (c 1.26).

Anal. Calcd. for $C_{27}H_{24}O_7$: C, 70.42; H, 5.25. Found: C, 70.66; H, 5.39.

Amorphous 1,5-Anhydro-L-gulitol (VI) from 1,5-Anhydro-4,6-benzylidene-L-gulitol (VIII).—1,5-Anhydro-4,6-benzylidene-L-gulitol (1.1826 g.) was added to 25 ml. of 0.2 N sulfuric acid and the solution steam distilled until the benzaldehyde was removed. Diluted to 50.00 ml., the solution rotated +0.48° in a 4-dm. tube, corresponding to a specific rotation of +7.8 ± 0.2° for 1,5-anhydro-L-gulitol in water (c 1.54).

Acid was removed from the above solution with Duolite A-4[19] and solvent removed *in vacuo*. The residual sirup was dried by the repeated evaporation *in vacuo* of batches of absolute alcohol, the sirup finally being held *in vacuo* (*ca.* 1 mm.) at 50° for 10 minutes. A sample (0.2541 g.) of this sirup was dissolved in water and the solution treated with 10 ml. of 0.48 M sodium metaperiodate and diluted to a volume of 50.00 ml. After 18 days at 20° analysis showed the consumption of 1.98 molar equivalents of oxidant and the formation of 0.94 mole of formic acid. In a 4-dm. tube the solution showed an observed rotation of +0.15 ± 0.01° corresponding to a specific rotation for the dialdehyde of +9.2 ± 0.6°. In a parallel experiment 0.2531 g. of 1,5-anhydro-D-mannitol consumed 2.11 moles of periodate, produced 1.01 moles of formic acid and gave an observed rotation in a 2-dm. tube of −0.07 ± 0.01°. This observed rotation corresponds to a specific rotation of −8.6 ± 1.2° for the dialdehyde formed. Richtmyer and Hudson[23] reported that the rotation of a styracitol–sodium metaperiodate oxidation mixture became constant after 10 days at 20° and then corresponded to a specific rotation for the dialdehyde of −9.7°.

1,5-Anhydro-4,6-benzylidene-D-gulitol (XI) from Methyl α-D-Gulopyranoside Tetraacetate (VII).—Twenty grams of methyl α-D-gulopyranoside tetraacetate[24] was added to a cold mixture of 70 ml. of acetic anhydride and 1.4 ml. of concentrated sulfuric acid. After 30 minutes at 0°, the reaction mixture was left at room temperature overnight and then poured on ice. The product was extracted with methylene chloride, the extract washed with cold, saturated sodium bicarbonate and dried over sodium sulfate. After filtration through decolorizing carbon the solution was concentrated *in vacuo* (45°) to a sirup which was dissolved in 200 ml. of glacial acetic acid and the solution treated with 130 ml. of 32% hydrogen bromide in glacial acetic acid. Polarimetric observations showed that mutarotation had substantially ceased after 64 minutes at 20° and the reaction mixture was then poured into a mixture of ice, water and methylene chloride. The organic layer, kept cold, was washed twice with sodium bicarbonate, dried over sodium sulfate and finally concentrated *in vacuo* at 40°. The residual sirup thus obtained was dissolved in 100 ml. of absolute ether and the solution added over the course of 18 minutes to 100 ml. of *ca.* 1 M lithium aluminum hydride in ether. The reaction mixture was boiled under reflux for 55 minutes, left at room temperature 16 hours, and then treated with 300 ml. of water. The precipitate thus formed was filtered off and washed thoroughly with hot water; the resulting aqueous solution, after deionization with Amberlite IR-120[20] and Duolite A-4,[19] was concentrated *in vacuo* (90° bath). Moisture was removed from the resulting sirup of crude 1,5-anhydro-D-gulitol by repeated evaporation therefrom of absolute ethanol. The dry, nearly solvent-free sirup was then dissolved in 5 ml. of absolute ethanol and the solution treated with 4 ml. of 1% ethanolic hydrogen chloride and 4.0 ml. of freshly distilled benzaldehyde. After 16 hours at +5° the solution was concentrated slightly *in vacuo* and crystallization induced by scratching: 0.99 g., m.p. 153–159°. A second crop of 0.42 g. (m.p. 165–167°) was obtained from the mother liquor by the addition of pentane (total yield from methyl α-D-gulopyranoside tetraacetate, 10%). The product was recrystallized successively from 5 parts of absolute ethanol, 25 parts of chloroform, 15 parts of water and, finally, twice from chloroform. The pure 1,5-anhydro-4,6-benzylidene-D-gulitol thus obtained showed, like its enantiomorph described above, a double melting point: 168–169° and then 176–178°. In alcohol the substance showed a rotation of +5.8 ± 0.4° (c 0.81).

Anal. Calcd. for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.84; H, 6.39.

Hydrolysis of 130.3 mg. of 1,5-anhydro-4,6-benzylidene-D-gulitol with 2.5 ml. of 0.2 N sulfuric acid as was done earlier with the enantiomorph led to a rotation of −7.9 ± 0.2° in water (c 3.25) for 1,5-anhydro-D-gulitol.

1,5-Anhydro-4,6-benzylidene-D,L-gulitol.—Equal quantities (32.5 mg.) of the two enantiomorphs were dissolved in 0.5 ml. of absolute ethanol. The addition of pentane gave 55.4 mg. of flat, elongated prisms which, recrystallized from absolute ethanol–pentane, melted at 136–141° and in ethanol showed no rotation in a 4-dm. tube at a concentration of 0.68.

Anal. Calcd. for $C_{13}H_{16}O_5$: C, 61.89; H, 6.39. Found: C, 61.59; H, 6.37.

The 1,5-Anhydro-2,3-dibenzoyl-4,6-benzylidene-D-gulitol (XII).—The 1,5-anhydro-4,6-benzylidene-D-gulitol (320 mg.) was benzoylated in the usual fashion to yield from 10 ml. of absolute alcohol 410 mg. (55%) of prismatic needles melting at 177–180°. Recrystallization from 12 ml. of absolute alcohol did not alter the melting point; the pure material showed a rotation of −3.1 ± 0.2° in chloroform (c 1.29).

Anal. Calcd. for $C_{27}H_{24}O_7$: C, 70.42; H, 5.25. Found: C, 70.12; H, 5.18.

The infrared spectrum of this substance proved to be identical with that of its enantiomorph prepared earlier.

1,5-Anhydro-2,3-dibenzoyl-4,6-benzylidene-D,L-gulitol.—Equal amounts (101.3 mg.) of the pure enantiomorphs were combined in methylene chloride solution and the solvent then removed *in vacuo*. From 5 ml. of ether the sirup thus obtained afforded 160.4 mg. of crystals melting at 164–166°. Recrystallization from *ca.* 5 ml. of absolute ethanol yielded clear prisms melting at 164–165°.

Anal. Calcd. for $C_{27}H_{24}O_7$: C, 70.42; H, 5.25. Found: C, 70.85; H, 5.43.

Acknowledgment.—The authors wish to thank Mr. Harry W. Diehl for technical assistance. The analytical data were obtained by the Institute's Microanalytical Laboratory under the direction of Dr. William C. Alford.

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