hemin-containing protein cytochrome c. The catalase experiment was run in triplicates. All parts of the pattern showed catalase activity.

Pattern C shows the chromatogram obtained with human plasma "gamma globulins" fraction prepared according to method 10 of Cohn and associates.[9] Trisodium citrate buffer (0.02 *M*) of *p*H 6.0 containing 9.25 ml. (2 *N*) of hydrochloric acid and 50 g. of sodium chloride per 5 l. was used in the first dimension and 2% tartaric acid in the second dimension.

It has been shown by Franklin, *et al.*,[7] that normal human serum gives a typical pattern when subjected to two dimensional filter paper chromatography and in various disorders specific patterns are found. Pattern D shows the pattern which we obtained with normal human serum (total application 0.02 ml.) using 0.1 *M* sucrose solution in the first dimension and 0.1 *M* sodium potassium tartrate solution in the second dimension. Our staining procedure was then applied. This pattern of course cannot be similar to the normal pattern obtained by Franklin, *et al.*,[7] since in their method some proteins do not combine with hemin.

Discussion

It is generally assumed (with low molecular compounds) that multiplicity of spots indicates a multiplicity of molecular species. Franklin and associates speak of "patterns" when serum or snake venum is concerned and of "separations" when less complex protein mixtures are considered.

Recently Hall and Wewalka[10] subjected the procedure of Franklin and co-workers to serious criticism but concluded that the separation of proteins of quite dissimilar nature by this method is perfectly practicable but not of complex mixtures such as serum.

The proteins which we studied consist probably of more than one molecular species. In view of this, at present, we cannot support the claim of Franklin, *et al.*, that separation of proteins takes place at any time under the conditions of two dimensional paper chromatography. It has been shown by Tauber,[11] however, in a paper entitled "The Selective Adsorption of Enzymes by Cellulose," long before filter paper chromatography was introduced, that enzymes may be separated from other proteins by adsorption on filter paper. The enzymes were eluted with salt solutions.

It is apparent that definite developing solutions must be found for each type of protein. An important question that is still unanswered: Why do most proteins leave on the filter paper, at the application spot, a firmly bound concentric ring? This occurs even when the protein is dried at low temperatures.

While it is safer, at the present, to speak of patterns rather than separation of proteins, it is hoped that our simple procedure, as described in this report, will contribute toward further development of the technique of paper chromatography of proteins.

(9) E. J. Cohn, *et al.*, THIS JOURNAL, **72**, 465 (1950).

(10) D. A. Hall and F. Wewalka, *Nature*, **168**, 685 (1951).

(11) H. Tauber, *J. Biol. Chem.*, **113**, 753 (1936).

CHAPEL HILL, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

A New Di-D-fructose Dianhydride

BY M. L. WOLFROM, H. W. HILTON[1,2] AND W. W. BINKLEY[1]

Concentrated hydrochloric acid at −5° dehydrates D-fructose to yield, in addition to the previously reported di-D-fructopyranose 1,2′:2,1′-dianhydride and D-fructopyranose-D-fructofuranose 1,2′:2,1′-dianhydride, the difructose anhydrides I (di-D-fructofuranose 1,2′:2,1′-dianhydride) and II of Jackson and co-workers as well as a new crystalline dianhydride characterized as a hexaacetate and designated diheterolevulosan III. Periodate oxidation of the latter compound indicates that it is either di-D-fructopyranose 1,2′:2,3′-dianhydride or an anomeric form of D-fructopyranose D-fructofuranose 1,2′:2,1′-dianhydride (diheterolevulosan II). Analysis of the optical rotatory data in the light of the Hudson isorotation rules makes it probable that diheterolevulosans II and III and difructose anhydrides II and III contain the dioxane ring and differ only in the anomerism of one of the two asymmetric centers in such a ring.

Pictet and Chavan[3] studied the dehydrating action of concentrated hydrochloric acid solutions upon D-fructose and isolated a crystalline substance designated by them diheterolevulosan (herein termed diheterolevulosan I) later[4−6] shown to be di-D-fructopyranose 1,2′:2,1′-dianhydride. An isomer of this, isolated from such a reaction mixture by chromatographic methods,[6] was designated diheteroleuvulosan II, and was proved to be D-fructopyranose-D-fructofuranose 1,2′:2,1′-dianhydride.[7] The relative quantities of these two compounds so formed was studied[7] by chromatographic methods and there remained a sirupy mother liquor product. We report herein a further and rather exhaustive chromatographic fractionation of this residual material (Fraction D) upon clay[8] with the results shown diagrammatically in Fig. 1. The characterization of Fractions A, B and C has been detailed previously.[7] Further quantities of diheterolevulosans I and II were found in zones 1b and 3a (Fig. 1), respectively. Zone 2b yielded a new difructose dianhydride (m.p. 255–258°, $[\alpha]^{26}D$ −179° in water) further characterized as a crystalline hexaacetate. This substance, designated diheterolevulosan III, consumes three moles (per mole of reductant) of periodate with the formation of one mole of formic acid and no formaldehyde, this behavior being identical with that of D-fructopyranose-D-fructofuranose 1,2′:2,1′-dianhydride (diheterolevulosan II).

(1) Sugar Research Foundation Fellow (to July 1, 1951) and Research Associate (W. W. B.) of The Ohio State University Research Foundation (Project 190).

(2) The Visking Corporation Fellow (from July 1, 1951).

(3) A. Pictet and J. Chavan, *Helv. Chim. Acta*, **9**, 809 (1926).

(4) H. H. Schlubach and C. Behre, *Ann.*, **508**, 16 (1934).

(5) Emma J. McDonald and R. F. Jackson, *J. Research Natl. Bur. Standards*, **35**, 497 (1945).

(6) M. L. Wolfrom and M. Grace Blair, THIS JOURNAL, **70**, 2406 (1948).

(7) M. L. Wolfrom, W. W. Binkley, W. L. Shilling and H. W. Hilton, *ibid.*, **73**, 3553 (1951).

(8) B. W. Lew, M. L. Wolfrom and R. M. Goepp, Jr., *ibid.*, **67**, 1865 (1945); **68**, 1449 (1946).

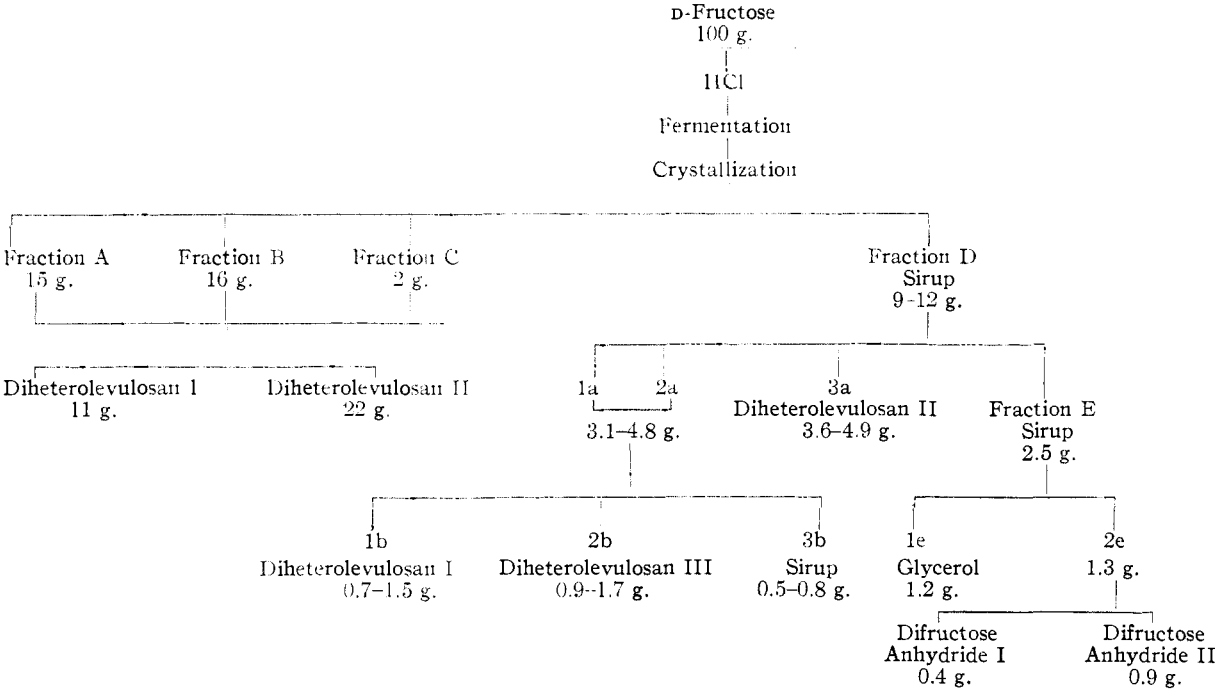
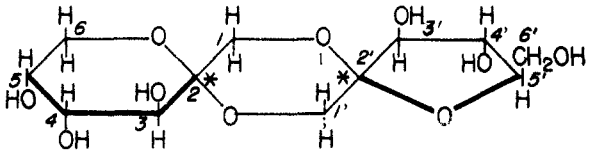


Fig. 1.—Chromatographic analysis of the products formed by the action of concentrated hydrochloric acid (4 parts) upon D-fructose for 72 hr. at −5°; top zones to the left.



Diheterolevulosan II (D-fructopyranose-D-fructofuranose 1.2′:2,1′-dianhydride).

The new compound is therefore either an anomer of D-fructopyranose-D-fructofuranose 1,2′:2,1′-dianhydride or is one of the possible anomeric forms of di-D-fructopyranose 1,2′:2,3′-dianhydride. Optical rotatory data can be marshalled to favor the former view.

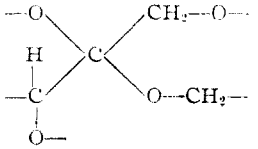
Applying the Hudson isorotation rules[9]

$[M]^{25}D$ of diheterolevulosan II, $(-39° \times 324)$	=	−12,600
$[M]^{25}D$ of diheterolevulosan III, $(-179° \times 324)$	=	−58,000
subtracting	$2A$ =	45,400
	A =	22,700

This value compares favorably with that calculable from the known pair of methyl D-fructopyranosides,[10,11] wherein

$[M]^{20}D$ of α-D-form, $(+45°)(194)$	=	8,700
$[M]^{20}D$ of β-D-form, $(-172°)(194)$	=	−33,400
subtracting	$2A$ =	42,100
	A =	21,000

Each of the two anomeric carbons in the substituted dioxane rings of these di-D-fructose dianhydrides



compares closely in structure to that of the C-2 in a methyl fructoside, all having the following unit in common.

In their studies on inulin hydrolysis, Jackson and co-workers isolated three isomeric di-D-fructose dianhydrides designated by them difructose anhydrides I, II and III (Table I). For difructose anhydride II McDonald and Turcotte[12] preferred the structure di-D-fructofuranose 2,1′:4,2′-dianhydride but actually their data do not exclude the simpler structure of an anomer of di-D-fructofuranose 1,2′:2,3′-dianhydride. That difructose anhydrides II and III are very probably structural units differing only in the configuration of one of the asymmetric centers on the substituted dioxane ring, is shown by the calculation below resulting in a value for A in close agreement with those cited above.

$[M]^{20}D$ of difructose anhydride III, $(+136°)(324)$	=	44,100
$[M]^{20}D$ of difructose anhydride II, $(+14°)(324)$	=	4,500
subtracting	$2A$ =	39,600
	A =	19,800

A very rapidly moving zone (2e of Fig. 1) was found even below the glycerol arising from the fermentative removal of unchanged D-fructose. This was shown to be a mixture of the difructose anhydrides I (di-D-fructofuranose 1,2′:2,1′-dianhydride)[13–16] and II[12,16,17] isolated by Jackson and co-

(9) C. S. Hudson, THIS JOURNAL, **31**, 66 (1909).
(10) C. S. Hudson and D. H. Brauns, *ibid.*, **38**, 1216 (1916).
(11) H. H. Schlubach and G. A. Schröter, *Ber.*, **61**, 1216 (1928).
(12) Emma J. McDonald and Anne L. Turcotte, *J. Research Natl. Bur. Standards*, **38**, 423 (1947).
(13) R. F. Jackson and Sylvia M. Goergen, *Bur. Standards J. Research*, **3**, 27 (1929).
(14) J. C. Irvine and J. W. Stevenson, THIS JOURNAL, **51**, 2197 (1929).
(15) E. W. Bodycote, W. N. Haworth and C. S. Woolvin, *J. Chem. Soc.*, 2389 (1932).
(16) Emma J. McDonald, *Advances in Carbohydrate Chem.*, **2**, 253 (1946).
(17) R. F. Jackson and Emma McDonald, *Bur. Standards J. Research*, **6**, 709 (1931).

TABLE I

DIFRUCTOSE DIANHYDRIDES

Trivial name	Structure	M.p., °C.	Principal lines, X-ray powder diffraction, Å.	$[\alpha]^a$	First isolation
Diheterolevulosan I	Di-D-fructopyranose 1,2′:2,1′-dianhydride	270–272 dec.[b]	5.32(1)[c,23,24] 4.65(2) 4.02(3)	− 46°	Pictet and Chavan[3]
		278–282 dec.	5.42(1)[23,24] 4.24(2) 3.88(3)		
Diheterolevulosan II	D-Fructopyranose-D-fructofuranose 1,2′:2,1′-dianhydride	256–259 dec.[b]	6.24(3)[23,24] 5.54(1) 4.33(2)	− 39	Wolfrom and Blair[6]
		265–267 dec.	5.40(2)[23,24] 4.76(1) 2.93(3)		
Diheterolevulosan III	Anomer of diheterolevulosan II or di-D-fructopyranose 1,2′:2,3′-dianhydride	255–258	5.02(1) 4.69(2) 4.26(3)	−179	This work
Difructose anhydride I	Di-D-fructofuranose 1,2′:2,1′-dianhydride	164[d]	5.36(3)[23] 4.81(1) 4.04(2)	+ 27	Jackson and Goergen[13]
Difructose anhydride II	Anomer of difructose anhydride III or di-D-fructofuranose 2,1′:4,2′-dianhydride[12]	198[d]	7.02(3)[23] 6.63(1) 4.96(2)	+ 14	Jackson and McDonald[17]
Difructose anhydride III	Di-D-fructofuranose 1,2′:2,3′-dianhydride	162[d]	5.98(3)[23] 5.07(1) 3.84(2)	+136	Jackson and McDonald[17]

[a] 5892.5 Å., 25 ± 5°, $c < 5$, water. [b] Dimorphous; metastable form is the lower melting; melting points taken in this work on Fisher–Johns apparatus and are corrected values. [c] Strongest line. [d] Uncorrected.

workers by the action of dilute sulfuric acid solutions upon D-fructose. Our method of separation of these two substances was essentially that of Jackson and Goergen[13] and we also find that di-D-fructofuranose 1,2′:2,1′-dianhydride hexaacetate is dimorphous[15] (m.p. 125–127° and 138–139°). X-Ray powder diffraction diagrams are recorded for this hexaacetate (lower melting form) and for the new difructose dianhydride and its hexaacetate. This technique has been employed advantageously for identification.

In Table I are summarized the main properties of the six known di-D-fructose dianhydrides. The frequent occurrence of dimorphism in this series is notable.

Experimental

First Chromatography of Fraction D; Isolation of Further Amounts of Diheterolevulosan II.—As described previously,[7] D-fructose (100 g.) was treated for 72 hr. at −5° with 4 parts of concd. HCl and the unchanged D-fructose was largely removed by yeast fermentation. After removal of Fractions A, B and C (Fig. 1) and their separation into diheterolevulosans I and II,[7] Fraction D (9–12 g.) remained as a sirup. An amount of 2.5 g. of this fraction dissolved in 70 ml. of abs. methanol was brought to 250 ml. with methanol–water (90:10[18]) and this solution was added to the top of a tapered[19] glass column containing a 23 × 7.5 (i.d.)[20] cm. admixture (500 g.) of Florex XXX[8]–Celite[8] (5:1 by wt.) prewet with *ca.* 5000 ml. of ethanol–water (90:10) and conditioned further with 50 ml. of methanol–water (90:10). The chromatogram was developed with 1400 ml. of ethanol–water (90:10) and the effluent yielded the sirupy Fraction E (0.7–0.8 g., see below) on solvent removal under reduced pressure. The extruded column was partially wrapped with aluminum foil, dried and streaked with the alkaline permanganate indicator as described previously.[21] Three zones were detected: 1a (Fig. 1) at 10–36 mm. from the column top, 2a at 50–80 mm. and 3a at 104–200 mm. Zones 1a and 2a were eluted simultaneously with 1600 ml. of ethanol–water (70:30) to yield on solvent removal, under reduced pressure, 0.6–0.8 g. of partially crystalline material (see below). Crystalline material was obtained, after solvent removal under reduced pressure, when zone 3a was eluted with 2000 ml. of the same solvent; yield 0.9–1.2 g., m.p. 240–245° (dec.). Seven such chromatograms were run.

The material in zone 3a was dissolved in water, treated with decolorizing carbon and filtered under suction through a bed of acid-washed asbestos and finally by gravity through hardened filter paper. Concentration under reduced pressure and addition of ethanol yielded crystalline material identified as the metastable form of diheterolevulosan II; yield 0.9–1.0 g., m.p. 258–261° (dec., cor.), $[\alpha]^{28}D$ −35.4° (c 3.8, water), recorded[6,7] values 250–252° (dec., uncor.) and −39°. The X-ray diffraction pattern was identical with that recorded[7] for the metastable form of diheterolevulosan II. The crystalline hexaacetate was identical in melting point, mixed melting point and rotation with an authentic specimen and both exhibited the same X-ray powder diffraction diagram, as follows: 5.11, 4.32 (1, strongest), 3.74 (2), 3.64 (4), 3.20 (3), 2.79, 2.58, 2.30, 2.07 (5), 1.84, 1.71.

Chromatography of Fraction E; Isolation of the Di-D-fructose Dianhydrides I and II of Jackson and Co-workers.—An amount of 5.0 g. of Fraction E combined sirups was dissolved in abs. ethanol and chromatographed on a 23 × 7.7 (i.d.) cm. column of Florex XXX–Celite (5:1 by wt., 600 g.) held in a tapered glass column and prewet with 1320 ml. of abs. ethanol. Development was effected with 640 ml. of abs. ethanol. The permanganate streak on the ex-

(18) All solvent ratios indicate volumes before mixing.

(19) Tapered glass tubes can be purchased from the Scientific Glass Co., Bloomfield, N. J.

(20) Adsorbent dimensions.

(21) Reference 7, p. 3555.

truded column indicated two principal zones: 1e at 18–40 mm. from the top and 2e at 84–136 mm. Elution of each zone was effected with 1500 ml. of ethanol–water (80:20).

The principal adsorbate in zone 1e was identified as glycerol; yield 2.3 g., m.p. 190–192° (cor.) for *p*-nitrobenzoate unchanged on admixture with an authentic specimen of glycerol tri-*p*-nitrobenzoate.

The adsorbate mixture in zone 2e was isolated as a sirup; yield 1.6 g., $[\alpha]^{29}D$ +24° (*c* 4.6, water).

Anal. Moles periodate consumed per mole $C_{12}H_{20}O_{10}$,[22] 1.6. No formic acid or formaldehyde detected.

Crystallization of the sirup from abs. ethanol yielded crystals as a first crop that were identified as the difructose anhydride II of Jackson and McDonald[12,16,17]; yield 1.0 g., m.p. 204.5–208° (cor.), $[\alpha]^{30}D$ +13.1° (*c* 1.8, water), reported[17] values 198° and +13.9°. X-Ray powder diffraction data: 8.07, 6.62 (3), 5.64, 4.97 (1, most intense), 4.50, 4.18, 3.72 (2), 3.48, 3.31, 3.17, 2.98, 2.73, 2.58, 2.48, 2.40 (4), 2.30, 2.20, 2.11, 2.01 (5), 1.93, 1.86, 1.79, 1.72, 1.66, 1.60, 1.57, 1.53, 1.49, 1.45, 1.43, 1.37, 1.32, 1.29, 1.26, 1.25, 1.20, 1.17, 1.15, 1.12, 1.09, 1.07, 1.05, 0.927. These data are in agreement with those reported by Chu.[23-24]

A crop of crystals separated from the ethanol mother liquor on seeding and these were identified as the di-D-fructofuranose 1,2′:2,1′-dianhydride or difructose anhydride I of Jackson and co-workers[13,16]; yield 0.5 g., m.p. 158–160° on acetylation (see below) and deacetylation (barium methoxide at 70°), $[\alpha]^{30}D$ +26° (*c* 1.6, water), reported[13,17] 164° and +27°. X-Ray powder diffraction data: 7.92, 6.47, 5.80 (5), 5.32 (4), 4.82 (2), 4.40, 4.01 (1, strongest), 3.66 (3), 3.38, 3.18, 2.98, 2.86, 2.75, 2.63, 2.52, 2.40, 2.26, 2.10, 2.01, 1.94, 1.87, 1.81, 1.72, 1.64, 1.57, 1.52, 1.47, 1.40, 1.38, 1.32, 1.24, 1.22, 1.18, 1.15, 1.12, 1.10, 1.09, 1.07, 1.05, 1.03. These data are identical with those obtained on an authentic specimen[25] of di-D-fructofuranose 1,2′:2,1′-dianhydride (m.p. 163.5–165°) and are in agreement with the data of Chu.[23-24]

Acetylation of 500 mg. of zone 2e material with 10 ml. of dry pyridine and 10 ml. of acetic anhydride for 36 hr. at 0° yielded a crystalline acetate as a fibrous mass from ether; yield 313 mg., m.p. 138.5–139° (cor.) with sintering at 125.5–127° (cor.). After five recrystallizations from benzene–ether the substance melted at 125.5–127°, resolidified and remelted at 138.5–139° in agreement with Haworth and co-workers[15]; $[\alpha]^{26}D$ +1.6°, $[\alpha]^{26}$ 5160 +1.8°, $[\alpha]^{26}$ 4960 +2.1° (*c* 3.6, U.S.P. chloroform). Jackson and Goergen[13] report for the hexaacetate of difructose anhydride I: m.p. 137° with sintering at 125°, $[\alpha]^{20}D$ +0.54° and $[\alpha]^{20}$ 5780 +0.65° (*c* 10, chloroform). X-Ray powder diffraction data for the lower melting dimorph (identical with that of an authentic sample received from Dr. McDonald[25]): 8.76, 7.91 (6), 6.89 (5), 5.55 (2), 4.70 (3), 4.28 (1, strongest), 3.87 (4), 3.37 (7), 3.12 (8), 2.93 (9), 2.74, 2.66, 2.50, 2.32, 2.17, 2.08 (10), 2.00, 1.94, 1.90, 1.81, 1.74, 1.70, 1.56, 1.49, 1.46, 1.14, 1.09.

Anal. Calcd. for $C_{24}H_{32}O_{16}$: C, 49.99; H, 5.60; mol. wt., 577. Found: C, 50.06; H, 5.64; mol. wt. (Rast), 501.

(22) See below under diheterolevulosan III for method.

(23) Chia-Chen Chu, Ph.D. Dissertation, University of Illinois, 1951.

(24) L. Sattler, F. W. Zerban, G. L. Clark, Chia-Chen Chu, N. Albion, D. Gross and H. C. S. deWhalley, *Ind. Eng. Chem.*, in press (1952).

(25) Kindly furnished by Dr. Emma McDonald of the National Bureau of Standards, Washington, D. C.

Rechromatography of Zones 1a and 2a; Isolation of Further Amounts of Diheterolevulosan I.—The combined zone material from zones 1a and 2a above was rechromatographed in the same manner but increasing the volume of ethanol–water (90:10) developer to 2400 ml. The alkaline permanganate indicator located three zones on the extruded column: 1b at 28–52 mm. from the column top, 2b at 76–128 mm. and 3b at 162–194 mm. Each zone was eluted with 1500–2000 ml. of ethanol–water (70:30). Solvent removal under reduced pressure yielded crystalline material from the two top zones and a non-reducing sirup (0.77 g.) from the bottom zone.

The combined material from three 1b zones was purified and crystallized as described above for the zone 3a material. It was identified as di-D-fructopyranose 1,2′:2,1′-dianhydride (diheterolevulosan I) of fair purity by its X-ray powder diffraction diagram; yield 1.10 g. This diagram was that of the stable dimorph to which the previously reported[7] or metastable form is convertible by recrystallization (nucleation) from aqueous ethanol[26]; 6.36 (4), 5.42 (1, strongest), 4.24 (2), 3.88 (3), 3.62, 3.37, 3.21, 3.06 (10), 2.94, 2.78 (6), 2.60 (5), 2.46, 2.34, 2.25, 2.19, 2.13 (8), 2.00, 1.90, 1.84, 1.78, 1.70, 1.61, 1.51, 1.46, 1.41, 1.37, 1.30, 1.26, 1.23, 1.20, 1.18. Acetylation of this stable form of diheterolevulosan I yielded the previously reported[7] crystalline hexaacetate identified by melting point, mixed melting point and rotation and by the fact that it and an authentic specimen exhibited the same X-ray powder diffraction data, as follows: 7.98 (2), 6.94 (4), 5.90 (6), 4.86 (1, strongest), 4.45 (5), 4.05 (3), 3.74, 3.42, 3.20, 2.98, 2.71, 2.57, 2.46, 2.34, 2.20, 2.13, 1.95.

Isolation of a New Difructose Dianhydride (Diheterolevulosan III) from Zone 2b.—The crystalline material from five zones 2b was purified as described above for zone 3a and was recrystallized repeatedly from water–ethanol; yield 1.52 g., m.p. 255–258° (cor., no dec.), $[\alpha]^{29}D$ −179° (*c* 3.6, water) unchanged on acetylation and deacetylation (see below). X-Ray powder diffraction data: 6.64 (4), 5.70, 5.02 (1, strongest), 4.69 (2), 4.26 (3), 3.90, 3.68, 3.51, 3.29, 3.16, 3.04, 2.82 (5), 2.73, 2.62, 2.46, 2.36, 2.29, 2.16, 2.09, 2.03, 1.98, 1.93, 1.86, 1.81, 1.69, 1.64, 1.61, 1.58, 1.56, 1.53, 1.48, 1.32, 1.25, 1.22, 1.18, 1.16. The substance exhibited positive Molisch and Seliwanoff tests and was reducing only after acid hydrolysis.

Anal. Calcd. for $C_{12}H_{20}O_{10}$: C, 44.44; H, 6.22. Found: C, 44.16, H, 6.62. Periodate assay (0.0490 *M* sodium metaperiodate, 0.037 *M* reductant, 25° in the dark, time curves run with reactions being complete in *ca.* 5 days) in moles per mole of substance: oxidant consumed, 3.06; formic acid (brom cresol purple indicator[27]), 1.06; formaldehyde (dimedon), absent.

Diheterolevulosan III Hexaacetate.—Acetylation of 102 mg. of diheterolevulosan III with acetic anhydride (5 ml.) and anhydrous sodium acetate (0.1 g.) at 130–150° yielded a crystalline product; yield 168 mg., m.p. 131.5–132°. Pure material (plates) was obtained on recrystallization from benzene–ether; m.p. 135.5–136.5° (cor.), $[\alpha]^{25}D$ −169° (*c* 1, U.S.P. chloroform). X-Ray powder diffraction data: 6.64 (2), 6.14, 5.62, 5.32, 4.40 (1, strongest), 4.09 (3), 3.84 (5), 3.63, 3.38 (4), 3.13, 2.93, 2.76, 2.67, 2.52, 2.45, 2.35, 2.27, 2.07, 2.00, 1.95, 1.80, 1.76, 1.70, 1.65.

Anal. Calcd. for $C_{24}H_{32}O_{16}$: C, 49.99; H, 5.60; mol. wt., 576.5. Found: C, 50.06; H, 5.75; mol. wt. (Rast), 545.

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(26) The dimorphism of diheterolevulosan I was first demonstrated by G. L. Clark and Chia-Chen Chu, ref. 23–24.

(27) K. Meyer and P. Rathgeb, *Helv. Chim. Acta*, **32**, 1102 (1949).