presence of only two radioactive reducing substances, which corresponded in mobility to glucose and galactose.

The two carbohydrates were separated by large scale paper chromatography. The areas containing each of the carbohydrates were located with radioautograms, and the sugars were eluted with water and concentrated to sirups under reduced pressure at 35°. The sirup containing glucose-U-C^{14},4-T was stored at −20°.

The sirup containing galactose-U-C^{14},4-T (45 mg.) was dissolved in methanol and a methanol solution containing 40 mg. of unlabeled galactose was added in order to reduce rapid decomposition attributed to a high tritium content. After refrigeration of the methanolic solution a crystalline precipitate formed which was recrystallied twice from methanol, yielding 38 mg. of galactose, m.p. 166–168°, $[\alpha]^{18}D$ +79.4° (*c*, 1, water, equilibrium), having a specific activity of 3.97×10^4 disintegrations per minute of C^{14} per mg. and 4.18×10^6 disintegrations per minute of H^3 per mg.[31] Further amounts of galactose can be obtained from the mother liquors.

(31) Assays for radioisotopes were carried out by New England Nuclear Assay Corporation, Boston, Mass.

1,6-Anhydro-2,3-di-*O*-methyl-β-L-idopyranose and 1,6-Anhydro-2,3,4-tri-*O*-methyl-β-L-idopyranose[1]

NEIL BAGGETT,[2] PIERRE J. STOFFYN,[3] AND ROGER W. JEANLOZ

Laboratory for Carbohydrate Research, Departments of Biological Chemistry and Medicine, Harvard Medical School and the Massachusetts General Hospital, Boston, Massachusetts

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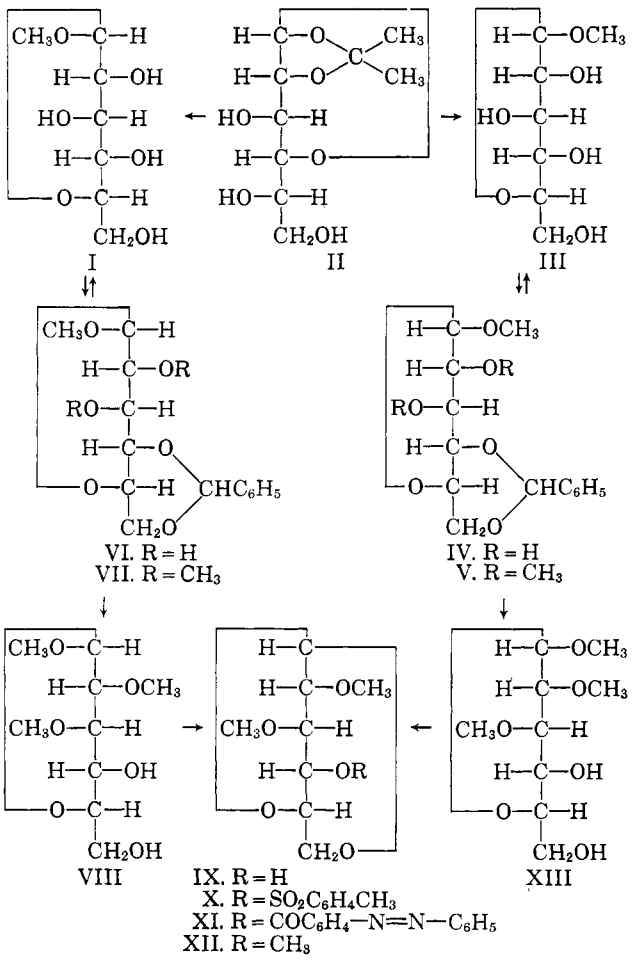
The syntheses of 1,6-anhydro-2,3-di-*O*-methyl-β-L-idopyranose, a reference substance used in the elucidation of the structure of dermatan sulfate, and of 1,6-anhydro-2,3,4-tri-*O*-methyl-β-L-idopyranose are described.

Recently, it has been shown that the uronic acid component of dermatan sulfate (also named β-heparin or chondroitin sulfate B), a polysaccharide isolated from various connective tissues, is L-iduronic acid.[4] Investigation of the structure of this polysaccharide by the methylation procedure resulted in the isolation of a dimethyl ether of 1,6-anhydro-β-L-idopyranose, which was found to be identical to the 2,3-di-*O*-methyl ether described in the present publication.[5]

In order to obtain the methyl ether derivatives of L-idose to be used as reference substances, the synthesis of methyl α-L-idopyranoside (I) and methyl β-L-idopyranoside (III) was undertaken, starting from 1,2-*O*-isopropylidene-L-idofuranose (II).[6] Reaction with methanolic hydrochloric acid gave a sirupy mix ture, and a partial separation of the two anomers could be achieved by partition chromatography on cellulose powder. A more convenient separation was obtained by condensing the sirupy mixture of glycosides with benzaldehyde in the presence of zinc chloride. The resulting mixture was chromatographed on silicic acid and gave two crystalline products: one (VI) melting at 148–149° and having an optical rotation $[\alpha]^{22}D$ −47° in chloroform; the other (IV) melting at 159–161° and having an optical rotation $[\alpha]^{22}D$ +87° in the same solvent.

The corresponding compounds in the D-series have been prepared and their structures firmly established: methyl 4,6-*O*-benzylidene-α-D-idopyranoside melts a 148–149° and has $[\alpha]^{14}D$ +49°, whereas the β-anomer melts at 163–164° with $[\alpha]^{20}D$ −88°, both rotations



measured in chloroform.[7] Consequently, on this basis, the α-L-configuration was allocated to the anomer VI, and the β-L-configuration to the anomer IV. Further substantiation of these allocated structures was obtained by study of the periodate oxidation of both methyl α-L-idopyranoside (I) and β-L-idopyranoside (III), obtained from VI and IV by reductive debenzyli-

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(2) Department of Chemistry, University of Birmingham, Birmingham, England.

(3) Advanced Research Fellow of the American Heart Association. Present address: Research Laboratory, McLean Hospital, Belmont, Mass.

(4) P. J. Stoffyn and R. W. Jeanloz, *J. Biol. Chem.*, **235**, 2507 (1960).

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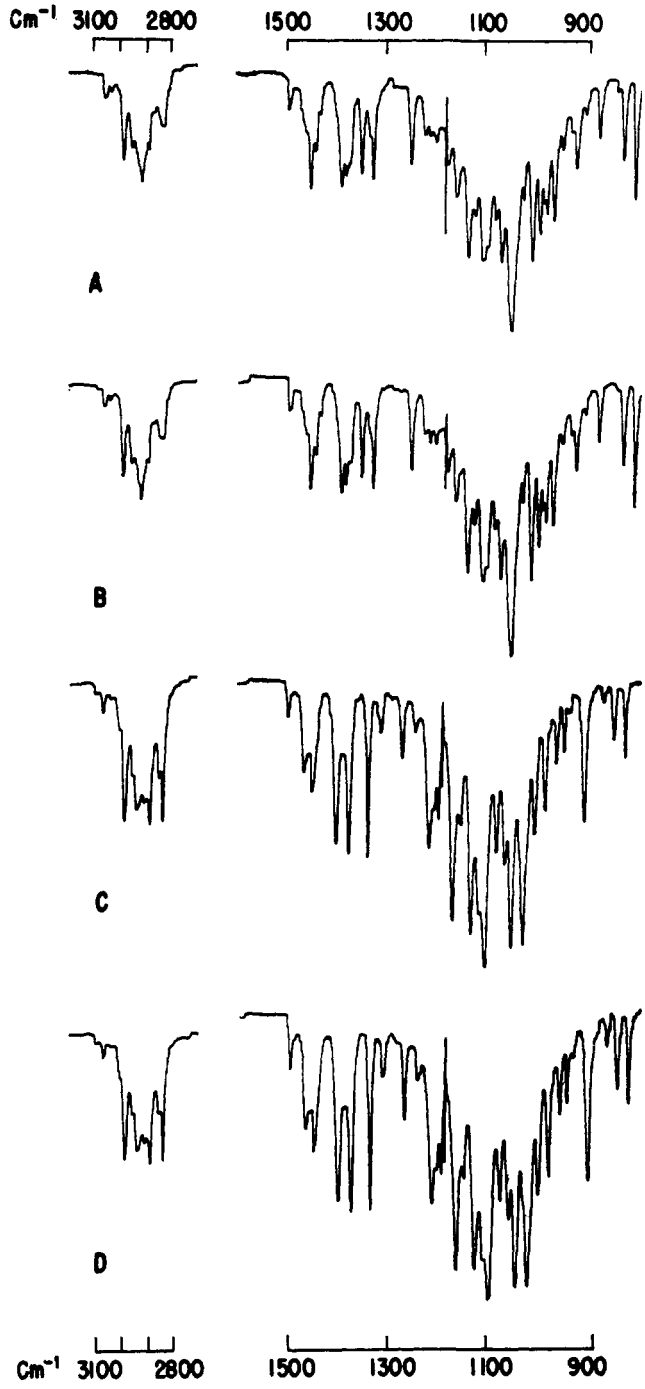

Fig. 1.—Infrared spectra of methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-α-L-idopyranoside (A); methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-α-D-idopyranoside (B); methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-β-L-idopyranoside (C); and methyl 4,6-*O*-benzylidene-2,3-di-*O*-methyl-β-D-idopyranoside (D).

denation. The observed consumption of two molar equivalents of periodate, and liberation of the molar equivalent of formic acid are indicative of the pyranoside nature of the ring in each case, and the optical rotations of the final products were consistent with the expected values. The formation of the benzylidene ring at positions 4 and 6 follows numerous other examples in the hexopyranoside series.

Methylation of both benzylidene derivatives VI and IV gave the crystalline dimethyl ethers VII and V, respectively. The infrared spectra of these compounds were identical to those of the corresponding D-compounds,[7-9] which were kindly provided by Professor T. Reichstein (see Fig. 1). Removal of the benzylidene group afforded a crystalline α-anomer VIII, whereas the β-anomer XIII failed to crystallize. The physical properties of the above described compounds, and the corresponding derivatives of D-idose, are reported in Table I. Both compounds were hydrolyzed to the sirupy 1,6-anhydro-2,3-di-*O*-methyl-β-L-idopyranose (IX), which was characterized by two crystalline derivatives, the 4-*O*-*p*-toluenesulfonate X and the 4-*O*-*p*-phenylazobenzoate XI.

Methylation of the previously described 1,6-anhydro-β-L-idopyranose[4] gave the crystalline 2,3,4-tri-*O*-methyl ether (XII).

Experimental

Melting points were taken on a hot stage, equipped with a microscope, and correspond to "corrected melting point." Rotations were determined in semimicro or micro (for amounts smaller than 3 mg.) tubes with lengths of 100 or 200 mm., using a polarimeter equipped with a Rudolph photoelectric attachment, Model 220; the chloroform used was A.R. grade and contained approximately 0.75% of ethanol. Infrared spectra were determined on a Perkin–Elmer spectrophotometer, Model 237. Chromatograms were made with the flowing method on "Silica Gel Davison," from the Davison Co., Baltimore 3, Md. (grade 950; 60–200 mesh) used without pretreatment. When deactivation by contact with moist air occurred, reactivation was obtained by heating to 170–200° (manufacturer's instructions). The sequence of eluents was hexane, benzene or dry chloroform, ether, ethyl acetate, acetone, and methanol individually or in binary mixtures. The proportion of weight of substance to be adsorbed to weight of adsorbent was 1 to 50–100; the proportion of weight of substance in grams to volume of fraction of eluent in milliliters was 1 to 100. The ratio of diameter to length of the column was 1 to 20. Evaporations were carried out *in vacuo*, with an outside bath temperature kept below 45°. Amounts of volatile solvent smaller than 20 ml. were evaporated by blowing dry nitrogen. The microanalyses were carried out by Dr. M. Manser, Zurich, Switzerland.

Mixture of Methyl L-Idosides.—A solution of 4.0 g. of 1,2-*O*-isopropylidene-L-idofuranose[6] (II) in 400 ml. of 2.3% dry hydrogen chloride in methanol was stored at room temperature for 4 days, the acid was neutralized with silver carbonate, the silver salts were removed by filtration through Celite, and the solution concentrated. The thin sirup was decolorized with Norit A and evaporated to dryness to yield 3.69 g. of pale yellow sirup.

Methyl 4,6-*O*-benzylidene-α-L-idopyranoside (VI) and Methyl 4,6-*O*-benzylidene-β-L-idopyranoside (IV).—A mixture of 20 ml. of benzaldehyde, 7 g. of freshly fused and powdered zinc chloride, and 3.44 g. of the above described mixture of methyl L-idosides was shaken at room temperature for 24 hr. The homogeneous solution was stored at room temperature for 2 days, then poured with vigorous stirring into 300 ml. of 2% sodium carbonate solution. After filtration, the filtrate was extracted two times with 100 ml. of hexane, then three times with 100 ml. of chloroform. The chloroform solution was dried with sodium sulfate and evaporated to yield 3.69 g. of sirupy product. The aqueous solution was evaporated and the residue extracted with chloroform to give a further crop of 0.75 g. of sirup. The two fractions were combined and thoroughly dried, affording 4.14 g. (83%) of product. After dissolution in benzene, it was fractionated by chromatography on 100 g. of silica gel.

A mixture of chloroform and ether (2:1) eluted 0.97 g. of a waxy solid and 1.43 g. of crystalline material. The latter was recrystallized from a mixture of ethyl acetate and pentane, to give 1.31 g. (26%) of **methyl 4,6-*O*-benzylidene-α-L-idopyranoside (VI)**, as prisms, m.p. 148–149°, $[\alpha]^{22}D$ −47° (in chloroform, *c* 1.07).

Anal. Calcd. for $C_{14}H_{18}O_6$: C, 59.56; H, 6.43. Found: C, 59.65; H, 6.43.

Elution with a mixture of chloroform and ether (1:1), then with pure ether, gave 0.67 g. of crystalline material, which was recrystallized from a mixture of ethyl acetate and pentane to give

(8) M. Gyr and T. Reichstein, *Helv. Chim. Acta*, **28**, 226 (1945).
(9) L. F. Wiggins, *J. Chem. Soc.*, 522 (1944).

TABLE I

PHYSICAL PROPERTIES OF D- AND L-IDOSE DERIVATIVES

Derivatives	D-Series		L-Series[a]	
	$[\alpha]_D$[b]	M.p., °C.	$[\alpha]_D$[b]	M.p., °C.
Methyl α-idopyranoside	+100 (22, W)	67–68[c]	−98 (25, M)	sirup
β-	−95 (20, M)	sirup[c]	+61 (27, M)	sirup
Methyl 4,6-O-benzylidene-α-idopyranoside	+49 (14, C)	148–149[c]	−47 (22, C)	148–149
-β-	−88 (20, C)	163–164[c]	+87 (22, C)	159–161
Methyl 4,6-O-benzylidene-2,3-di-O-methyl-	+73 (24, C)	155–156[d]	−69 (22, C)	151–153
α-idopyranoside	+69 (15, C)	152[e]		
-β-	−53 (19, C)	124–125[c]	+51 (21, C)	129–130
	−53 (21, C)	127[e]		

[a] In experimental part of this paper. [b] Temperature and solvents are reported in parenthesis, after value: C = chloroform; M = methanol; and W = water. [c] Ref. 7. [d] Ref. 8. [e] Ref. 9.

0.34 g. (7%) of **methyl 4,6-O-benzylidene-β-L-idopyranoside (IV)** as prisms, m.p. 159–161°, $[\alpha]^{22}D$ +87° (in chloroform, *c* 1.48).

Anal. Calcd. for $C_{14}H_{18}O_6$: C, 59.56; H, 6.43. Found: C, 59.52; H, 6.33.

A second crop of 0.22 g. (total yield 11%) of this material m.p. 151–154° was obtained from the mother liquor. Further elution with more polar solvents gave a total of 0.67 g. of sirup, presumably unchanged L-idoside, which was not further investigated.

Methyl α-L-Idopyranoside (I).—A suspension of 100 mg. of 2% palladized charcoal in 50 ml. of methanol was saturated with hydrogen, and then 52 mg. of VI was added and the mixture stirred under a slight overpressure of hydrogen. After 1 hr. the uptake of hydrogen ceased, the mixture was filtered through a charcoal pad, and the solution evaporated to give 37 mg. (100%) of I as a sirup, $[\alpha]^{25}D$ −98° (in methanol, *c* 1.10). Descending chromatography on paper Schleicher and Schuell no. 589 green in the mixture *t*-amyl alcohol, *n*-propyl alcohol, and water 3:1:1 showed a R_f of 0.57.

Anal. Calcd. for $C_7H_{14}O_6$: C, 43.29; H, 7.27. Found: C, 43.11; H, 7.25.

A study of the periodate oxidation of I in 0.05 *M* sodium metaperiodate solution at room temperature gave the following results.

Time (hr.)	0.33	0.5	1.0	24.0
Periodate consumed (moles)	1.3	1.7	1.7	2.1
Acid released (moles)	0.8			1.0

No formaldehyde could be detected with dimedone. The molecular rotation of the final solution was $[M]^{20}D$ −20,600.[10]

Methyl β-L-Idopyranoside (III).—Hydrogenation of 71 mg. of IV was carried out as above and gave 54 mg. (100%) of III as sirup, $[\alpha]^{27}D$ +61° (in methanol, *c* 1.50). Descending chromatography on paper Schleicher and Schuell No. 589 Green in the mixture *t*-amyl alcohol, *n*-propyl alcohol, and water 3:1:1 showed a R_f of 0.63.

A study of the periodate oxidation of III in 0.04 *M* sodium metaperiodate solution at room temperature gave the following results.

Time (hr.)	0.2	1.0	2.5	19
Periodate consumed (moles)	0.5	1.4	1.6	2.0
Acid released (moles)	0.2	0.6		1.0

The molecular rotation of the final product was $[M]^{27}D$ +23,300.[12]

Methyl 4,6-O-Benzylidene-2,3-di-O-methyl-α-L-idopyranoside (VII).—A suspension of 0.47 g. of VI and 0.50 g. of freshly prepared silver oxide in 10 ml. of methyl iodide was stirred and heated under reflux. After 5 hr., a further addition of 0.50 g. of silver oxide and 3 ml. of methyl iodide was made. Seven hours later 0.50 g. of silver oxide was added, and the mixture was stirred overnight. The mixture was filtered through Celite, the silver salts were washed with hot chloroform, and the solution evaporated. The crystalline product (0.52 g.) was dissolved in benzene and chromatographed on 25 g. of silica gel. The major portion of the material was eluted with a mixture of chloroform and ether (4:1). It was recrystallized from ethyl acetate, to give 0.44 g. (86%) of needles, m.p. 151–153°, $[\alpha][^{22}D$ −69° (in chloroform, *c* 1.0).

Anal. Calcd. for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15; OCH_3, 30.00. Found: C, 61.82; H, 7.10; OCH_3, 30.02.

Methyl 4,6-O-Benzylidene-2,3-di-O-methyl-β-D-idopyranoside (V).—A mixture of 65 mg. of IV, 200 mg. of fresh silver oxide, and 5 ml. of methyl iodide was stirred and heated under reflux. Further portions of 200 mg. of silver oxide were added after 1 hr. and 4 hr. and the mixture stirred overnight. It was then filtered, the residue was washed with chloroform, the solution evaporated, and the resulting 80 mg. of crystalline product was recrystallized from a mixture of acetone and pentane, giving 63 mg. (87%) of small plates, m.p. 129–130° $[\alpha]^{21}D$ +51° (in chloroform, *c* 1.14).

Anal. Calcd. for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15; OCH_3, 30.00. Found: C, 61.99; H, 7.19; OCH_3, 30.05.

Methyl 2,3-Di-O-methyl-α-L-idopyranoside (VIII).—A suspension of 5% palladized charcoal in methanol was saturated with hydrogen, then stirred overnight with 625 mg. of VII under a slight overpressure of hydrogen. The mixture was filtered through Celite, the filtrate evaporated, and the residue, dissolved in a mixture of benzene and ether 1:1, was chromatographed on 25 g. of silica gel. The main peak was eluted with ethyl acetate. It was recrystallized from a mixture of ether and pentane, yielding 286 mg. (64%) of fine needles, m.p. 50–52°, $[\alpha]^{24}D$ −78° (in chloroform, *c* 0.85).

Anal. Calcd. for $C_9H_{18}O_6$: C, 48.64; H, 8.16; OCH_3, 41.89. Found: C, 48.51; H, 8.31; OCH_3, 42.06.

Methyl 2,3-Di-O-methyl-β-L-idopyranoside (XIII).—A solution of 63 mg. of V in 50 ml. of methanol was stirred overnight with 10% palladized charcoal under a slight overpressure of hydrogen and treated as described for VIII. The main peak of the chromatogram gave 41 mg. (92%) of a colorless sirup, $[\alpha]^{22}D$ +77° (in chloroform, *c* 1.0). It was hygroscopic and could not be satisfactorily dried for elemental analysis.

Anal. Calcd. for $C_9H_{18}O_6$: C, 48.64; H, 8.16; OCH_3, 41.89. Found: C, 49.89; H, 8.33; OCH_3, 39.15.

1,6-Anhydro-2,3-di-o-methyl-β-L-idopyranose (IX). From VIII.—A solution of 200 mg. of VIII in 40 ml. of *N* sulfuric acid was heated at 100° for 14 hr. in a sealed tube. A 10-ml. aliquot of the acid hydrolysate was extracted continuously overnight with chloroform, after addition of lead carbonate to the boiling solution of chloroform. The chloroform extract was filtered through Celite, evaporated, and the product distilled in a sublimator with a bath temperature below 130° at 0.06 mm. The distillate was transferred to a flask, the solvent was evaporated, and the product was dried for 3 hr. at *ca.* 0.1 mm. at room temperature, to give 41.5 mg. (97%) of colorless sirup, $[\alpha]^{21}D$ +84° (in chloroform, *c* 2.07).

Anal. Calcd. for $C_8H_{14}O_5$: C, 50.52; H, 7.42. Found: C, 50.60; H, 7.55.

Another aliquot of 10 ml. of the hydrolysis solution was passed through a column (4.5 cm. × 1 cm. diameter) filled with a mixture of Norit A (1 g.) and Celite 535 (0.5 g.). The column was washed with water (35 ml.) until the effluent was sulfate-free, then with 15 ml. of acetone. The acetone fractions were evaporated, and the sirup was distilled to give 34 mg. (79%) of product, $[\alpha]^{27}D$ +86° (in chloroform, *c* 0.84).

From XIII.—A solution of 17 mg. of XIII in 1 ml. of 2 *N* sulfuric acid was heated at 100° for 7 hr. in a sealed tube. The

(10) Jackson and Hudson[11] found $[M]D$ +19,520 for D'-methoxy-D-hydroxymethyl diglycolic aldehyde.

(11) E. L. Jackson and C. S. Hudson, *J. Am. Chem. Soc.*, **59**, 994 (1937).

(12) Jackson and Hudson[11] found $[M]D$ −24,200 for L'-methoxy-D-hydroxymethyl diglycolic aldehyde.

hydrolysate was extracted continuously overnight with chloroform, with the addition of lead carbonate to the chloroform solution. The chloroform extract was filtered, evaporated, and the sirup distilled, to yield 13.2 mg. (90%), $[\alpha]^{24}D$ +83° (in chloroform, *c* 0.66).

1,6-Anhydro-2,3-di-*o*-methyl-4-*o*-*p*-tolylsulfonyl-β-L-idopyranose (X).—A solution of 30 mg. of IX and 72 mg. of *p*-toluenesulfonyl chloride in 0.3 ml. of dry pyridine and 0.1 ml. of alcohol-free chloroform was stored at room temperature for 3 days. The excess acid chloride was decomposed with water, and the product was taken up in 5 ml. of chloroform. The solution was washed successively with ice-cold *N* sulfuric acid, water, sodium bicarbonate solution, and water, then dried over potassium carbonate. Evaporation of the filtered solution gave a sirup, which was dissolved in benzene and chromatographed on 2.5 g. of silica gel. Crystalline material (40 mg.) was obtained as a single peak eluted with a mixture of benzene and ether (1:1). Recrystallization from a mixture of ether and pentane gave 25 mg. (45%) of rectangular plates, m.p. 69–69.5°, $[\alpha]^{21}D$ +27° (in chloroform, *c* 2.23).

Anal. Calcd. for $C_{15}H_{20}O_7S$: C, 52.32; H, 5.86; S, 9.30. Found: C, 52.31; H, 5.76; S, 9.33.

1,6-Anhydro-2,3-di-*o*-methyl-4-*o*-*p*-phenylazobenzoyl-β-L-idopyranose (XI).—A solution of 28 mg. of sirupy IX and 56 mg. of *p*-phenylazobenzoyl chloride in 1 ml. of dry pyridine was heated at 100° for 14 hr. in a sealed tube. After cooling at 0°, the excess of acid chloride was decomposed by addition of one drop of water and the mixture was kept for 0.5 hr. at room temperature. It was evaporated to dryness by codistillation with toluene, and the crystalline residue was dissolved in ethanol-free chloroform and passed through a column (7 cm. × 2 cm. diameter) of neutral alumina, activity Brockman III. Elution with 100 ml. of chloroform gave 32 mg. (55%) of orange sirup which was recrystallized from a mixture of benzene and pentane as clusters of plates, m.p. 108–109°, $[\alpha]^{21}D$ −76° (in chloroform, *c* 0.65).

Anal. Calcd. for $C_{21}H_{22}N_2O_6$: C, 63.31; H, 5.57; N, 7.03; OCH_3, 15.58. Found: C, 63.20; H, 5.60; N, 7.00; OCH_3, 15.74.

1,6-Anhydro-2,3,4-tri-*o*-methyl-β-L-idopyranose (XII).—A solution of 200 mg. of 1,6-anhydro-β-L-idopyranose[4] in 1 ml. of water at 70° was vigorously stirred and, at 10-min. intervals, ten additions of 1 ml. of 30% aqueous sodium hydroxide and 0.35 ml. of dimethyl sulfate were made. Then the temperature of the stirred suspension was maintained at 100° for 1 hr. The cooled mixture was diluted with an equal volume of water and passed through a column (7 cm. × 1.7 cm. diameter) containing a mixture of Norit A and Celite (2:1). The column was washed with 350 ml. of water when the effluent was sulfate-free. The column was then washed with 80 ml. of acetone. The acetone solution was evaporated to dryness and the residue, dissolved in a mixture of hexane and benzene 4:1, was chromatographed on 10 g. of silicic acid. Elution with a mixture of benzene and ether 1:1 gave crystalline fractions which were recrystallized from a mixture of ether and pentane to give 114 mg. (42%) of stout prisms, m.p. 39–40°, $[\alpha]^{19}D$ +88° (in chloroform, *c* 1.0).

Anal. Calcd. for $C_9H_{17}O_5$: C, 52.93; H, 7.90; OCH_3, 45.60. Found: C, 52.85; H, 7.85; OCH_3, 45.68.

Elution with acetone gave an additional 49 mg. of sirup, which was not further investigated.

Thiocarbonyls. IX. The Use of Thin Layer Chromatography in the Separation of the Isomeric Trithiofluorobenzaldehydes[1]

E. CAMPAIGNE AND M. GEORGIADIS[2]

Contribution No. 1103 from the Chemistry Laboratories of Indiana University, Bloomington, Indiana

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Thin layer chromatography was found to be very successful in the separation and purification of the α- and β-isomers of trimers of *o*-, *m*-, and *p*-fluorothiobenzaldehydes. By the use of this method pure samples of each isomer may be obtained from small quantities of crude mixture, and purity of samples may be checked. The conformation of the isomers was established by nuclear magnetic resonance, and it was possible to determine the ratio of isomers in crude product by n.m.r. spectra of samples dissolved in the minimum required solvent. Contrary to previous claims, it was found that the α-(*cis–trans*) isomer is always formed to a higher degree than the β-(all *cis* equatorial) isomer, which is consistent with a reasonable mechanism proposed for trimer formation.

The products usually obtained by treating aldehydes with hydrogen sulfide in the presence of an acid catalyst, usually hydrogen chloride, are trimers of the thioaldehydes. This general area has been the subject of several reviews.[3,4] Some forty or more different aromatic aldehydes have been converted to trithianes, but never more than two isomers have been obtained and for some only one trithiane could be prepared.[3,5,6] Studies based on dipole moments of substituted (and unsubstituted) trithiobenzaldehydes indicate that the α-isomer has the *cis,trans*-2,4-6-triaryl-1,3,5-trithiane structure, having one axial and two equatorial phenyl groups on a chair trithiane ring, while the β form has the all equatorial *cis,cis*-2,4,6-triaryl-1,3,5-trithiane orientation.[7]

Traditionally, the higher melting, less soluble product was assigned the β-configuration.[3] Consequently repeated recrystallizations gave product rich in the β-isomer, and the mother liquor was enriched in this way in the α-isomer. This repeated recrystallization or selective extraction of one isomer was the reported technique of separation of trithianes.[3,8] Although the above seems reasonable, in practice the separation was a tedious task. The α- and β-isomers form eutectics,[8] which may confuse the structure assignment on the basis of melting point. During the procedure of recrystallization, there is a danger that the more soluble isomer will be lost, and even if tedious work or luck yields the α-isomer this may not be 100% pure. The assignment of the structure on the basis of melting points may be erroneous in cases where the melting points are close together or, as in tri-(*m*-fluorothio-

(1) This work was supported by a grant, no. G-9855, from the National Science Foundation to Indiana University. For paper no. VIII of this series see E. Campaigne and B. E. Edwards, *J. Org. Chem.*, **27**, 3760 (1962).

(2) Taken from a thesis to be submitted by M. G. in partial fulfillment of the requirements for the degree, Doctor of Philosophy.

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