Fritzsche were incorrect in their characterization of Baeyer's product as 6-nitro-oxindole. Accordingly the nitration of oxindole by Baeyer's procedure was repeated. Instead of decomposing at about 175° as reported by Baeyer the product was found to melt at 240–241°. The same product was obtained when oxindole was nitrated through the agency of fuming nitric acid rather than potassium nitrate. Treatment of a solution of this compound in ethyl alcohol with nitrous acid in accordance with the procedure of Borsche, Weussmann and Fritzsche failed to yield an isatin oxime but resulted only in the recovery of unchanged nitro-oxindole; m. p. 240–241°.

On the other hand, treatment of a solution of the nitro-oxindole in glacial acetic acid with sodium nitrite yielded 5-nitroisatin-β-oxime, identical with an authentic sample prepared from 5-nitroisatin of known structure.[5,6] It follows from this fact that Baeyer's nitro-oxindole is 5-nitro-oxindole and not 6-nitro-oxindole[7] as stated by Borsche and his co-workers.

To further support the conclusion that the compound in question was 5-nitro-oxindole a sample was coupled with benzenediazonium chloride. The β-phenylhydrazone of 5-nitroisatin which resulted was identified by comparison with an authentic sample.[5]

5-Nitro-oxindole (II).—A. The nitration was accomplished as directed by Baeyer.[1] The crude product was purified by crystallization from 50% acetic acid from which it separated as nearly colorless needles; m. p. 240–241°.

B. Oxindole (0.05 mole) was dissolved in 25 ml. of concentrated sulfuric acid and the mixture maintained at 0° while 2.1 ml. of fuming nitric acid (sp. gr. 1.5) was added dropwise. After the addition of the nitric acid the reaction mixture was allowed to stand at 0° for thirty minutes and poured over cracked ice. The precipitate was collected, washed with water and crystallized from 50% acetic acid from which it separated as nearly colorless needles; m. p. 240–241°. The yield was 7.35 g. or 82% of the theoretical. The identity of the product with that obtained by Baeyer's procedure was established by melting point methods.

Anal. Calcd. for $C_8H_6N_2O_3$: N, 15.73. Found: N, 15.57.

5-Nitroisatin-β-oxime.—Nitro-oxindole (0.01 mole) was dissolved in 100 ml. of glacial acetic acid and 1.73 g. (0.025 moles) of sodium nitrite added in small portions. The yellow precipitate which soon separated was collected and purified by crystallization from ethyl alcohol from which it separated as light yellow needles; m. p. 228–229°. The melting point was unchanged when the substance was mixed with a sample of 5-nitroisatin-β-oxime (m. p. 228–229°) prepared from 5-nitroisatin.[5,6]

5-Nitroisatin-β-phenylhydrazone.—Nitro-oxindole (1.34 g.) was dissolved in 75 ml. of ethyl alcohol and a solution of 10 g. of sodium acetate in 25 ml. of water added. The mixture was cooled to 0° and a solution of benzenediazonium chloride (from 0.75 g. aniline) added. The reddish yellow precipitate which soon formed was collected and purified by crystallization from glacial acetic acid. The melting point of the substance was 295° both alone and when mixed with an authentic sample of 5-nitroisatin-β-phenylhydrazone.[5]

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(6) Calvery, Noller and Adams, THIS JOURNAL, **47**, 3059 (1925).

(7) A compound designated as 6-nitro-oxindole was employed by Parks and Aldis (*J. Chem. Soc.*, 1845 (1938)). Due to the fact that these authors gave erroneous literature references it is impossible to determine from an examination of their paper the origin of the substance they designated as 6-nitro-oxindole.

The Identification of Aldose Sugars by their Mercaptal Acetates

BY M. L. WOLFROM AND J. V. KARABINOS[1]

E. Fischer[2] has stated that the ease of crystallization of most aldose thioacetals (mercaptals) should lend itself to the preparative isolation of sugars from their solutions. Application of this principle has been made in the case of a number of aldoses, as for example, with 6-bromo-D-glucose,[3] 5-desoxy-L-arabinose,[4] D-altrose[5] and 2,3,6-O-trimethyl-D-glucose.[6]

The mercaptals of the aldoses have occasionally been employed for identification purposes.[7] It is our purpose herein to describe a general procedure of wide applicability for the identification of aldomonosaccharides as their acetylated diethyl mercaptals. The ease of isolation of these substances and their high yield of formation make them excellent characterizing derivatives. They are optically active and their rotations in chloroform solution can readily be ascertained. Furthermore, these derivatives are characteristic of one particular sugar and not of three, as is the case with the osazones. The presently known acetylated diethyl mercaptals of the aldomonosaccharides are listed in Table I. If desired, the acetylated mercaptal can readily be deacetylated to the parent mercaptal and the latter used as a confirmatory derivative.

Since concentrated acid is employed in their formation, the acetylated diethyl mercaptals of the aldoses are best limited to the characterization of the aldomonosaccharides, although the low temperature employed does keep the hydrolysis at a minimum and the acetylated diethyl mercaptal of maltose has indeed been isolated in crystalline form.[8] Ketoses[2] and 2-desoxyaldoses[9] are very sensitive to acidity and are destroyed by the high acidity employed in the mercaptalation

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(1) Hoffmann-La Roche Fellow of The Ohio State University Research Foundation.

(2) E. Fischer, *Ber.*, **27**, 673 (1894).

(3) E. Fischer, B. Helferich and P. Ostmann, *ibid.*, **53**, 873 (1920).

(4) D. R. Swan and W. L. Evans, THIS JOURNAL, **57**, 200 (1935).

(5) N. K. Richtmyer and C. S. Hudson, *ibid.*, **57**, 1716 (1935). R. C. Hockett and L. B. Chandler, *ibid.*, **66**, 627 (1944).

(6) M. L. Wolfrom and L. W. Georges, *ibid.*, **59**, 601 (1937).

(7) C. Neuberg, *Ber.*, **33**, 2243 (1900); M. L. Wolfrom, W. J. Burke, K. R. Brown and R. S. Rose, Jr., THIS JOURNAL, **60**, 571 (1938); M. L. Wolfrom and T. S. Gardner, *ibid.*, **62**, 2553 (1940); *ibid.*, **65**, 750 (1943); M. L. Wolfrom and D. E. Pletcher, *ibid.*, **63**, 1050 (1941).

(8) M. L. Wolfrom, Mildred R. Newlin and E. E. Stahly, *ibid.*, **53**, 4379 (1931).

(9) Private communication from Dr. J. Compton

reaction. D-Fructose diethyl mercaptal exists and has been made by an indirect method.[10] The hexosamines are essentially insoluble in concentrated hydrochloric acid and the procedure is not applicable to them. The acetylated diethyl mercaptals of the ethyl[11] and methyl[11,12] esters of D-galacturonic acid have been recorded.

An obvious disadvantage of the method is the odor of the ethyl mercaptan but this can be minimized by the employment of small quantities of material and by the use of good fume cupboards. The purified substances are odorless.

TABLE I

CHARACTERIZING PROPERTIES OF THE KNOWN FULLY ACETYLATED DIETHYL MERCAPTALS OF ALDOMONOSACCHARIDES

Fully acetylated diethyl mercaptal of	M. p., °C.	$[\alpha]^{20-25}D$ ($c < 5$, $CHCl_3$)
D-Arabinose[a]	80	+30°
L-Arabinose[b]	79–80	−30
D-Xylose[c]	46–48	+13
D-Lyxose[d]	36–37	+40.5
D-Glucose[e]	45–47	+11
D-Galactose (trimorphous)[f]	76.5–77	+11
	80.5–81[g]	+11
	90.5–91	+11
6-Desoxy-L-galactose (L-fucose)[h]	99–100	+ 5
D-Mannose[i]	52–53	+32
6-Desoxy-L-mannose (L-rhamnose)[i]	59–61	−42
D-Gluco-D-*gulo*-heptose[j]	99–100	−12
D-Gala-L-*gluco*-heptose[k]	105	+27
D-Gala-L-*manno*-heptose[l]	145–146	+56
D-Manno-D-*gala*-heptose[m]	77	− 2.2
D-Gala-L-*gala*-octose[n]	106	+30
Methyl D-galacturonate[o,p]	112.5–113.5	+20.5
Ethyl D-galacturonate[p]	80–81	+11

[a] M. L. Wolfrom, D. I. Weisblat, W. H. Zophy and S. W. Waisbrot, THIS JOURNAL, **63,** 201 (1941). [b] M. L. Wolfrom and Mildred R. Newlin, *ibid.*, **52,** 3619 (1930). [c] Ref. 8. [d] M. L. Wolfrom and F. B. Moody, *ibid.*, **62,** 3465 (1940). [e] W. Schneider and Johanna Sepp, *Ber.*, **51,** 220 (1918); M. L. Wolfrom, THIS JOURNAL, **51,** 2188 (1929); first nuclei difficult to obtain but the deacetylated form crystallizes with ease. [f] M. L. Wolfrom, *ibid.*, **52,** 2464 (1930); L. H. Welsh and G. L. Keenan, *ibid.*, **64,** 183 (1942). [g] Stable form. [h] M. L. Wolfrom and J. A. Orsino, *ibid.*, **56,** 985 (1934). [i] N. W. Pirie, *Biochem. J.*, **30,** 374 (1936); Mildred R. Newlin, Ph.D. dissertation, The Ohio State University (1932); in the publication of Pirie, L-rhamnose diethyl mercaptal tetraacetate is recorded incorrectly as being dextrorotatory. [j] M. L. Wolfrom, M. Konigsberg, F. B. Moody (and Mildred R. Newlin), THIS JOURNAL, **62,** 2348 (1940); higher sugar nomenclature of C. S. Hudson, *ibid.*, **60,** 1537 (1938). [k] R. M. Hann and C. S. Hudson, *ibid.*, **56,** 2080 (1934). [l] R. M. Hann and C. S. Hudson, *ibid.*, **59,** 1898 (1937). [m] Edna Montgomery and C. S. Hudson, *ibid.*, **56,** 2463 (1934). [n] R. M. Hann, W. D. Maclay and C. S. Hudson, *ibid.*, **61,** 1270 (1939). [o] Ref. 12. [p] Ref. 11.

Experimental

Identification of D-Mannose as D-Mannose Diethyl Mercaptal Pentaacetate.—The general procedure employed was an adaptation of that reported previously[8] from this Laboratory. D-Mannose (50 mg.) was dissolved in 0.5 cc. of concentrated hydrochloric acid (*ca.* 12 *N*) in an ice-bath and 0.5 cc. of ethyl mercaptan added. The mixture was stirred or shaken mechanically for one hour and was then neutralized in the cold with concentrated ammonium hydroxide (*ca.* 15 *N*) and concentrated to dryness at 40° under reduced pressure. The salt residue was dried by adding absolute ethanol and removing this by distillation under reduced pressure at 40°, the process being repeated several times. The dried residue was treated with 3 cc. of a 2:1 (by volume) mixture of acetic anhydride and dry pyridine. After standing overnight at room temperature, the solution was poured into 10 cc. of water and extracted twice with 10-cc. portions of chloroform. The chloroform extract was washed four times with 10 cc. of a saturated aqueous sodium bicarbonate solution and finally with water. The sirup obtained on solvent removal from the dried chloroform extract was crystallized from methanol solution by the gradual addition of water; yield of D-mannose diethyl mercaptal pentaacetate practically quantitative, m. p. 51–52°.

Identification of D-Galactose in a Crude Hydrolyzate.—A fraction of solid material (50 mg.) obtained by the acid hydrolysis of a galactose-containing polysaccharide and containing *ca.* 25% of D-galactose (as determined by the mucic acid assay) was treated as described above and the product isolated in the same manner; yield of D-galactose diethyl mercaptal pentaacetate 15 mg., m. p. 78–79°.

As a confirmatory derivative, the above acetate was deacetylated to D-galactose diethyl mercaptal. To 9 mg. of the D-galactose diethyl mercaptal pentaacetate dissolved in 2 cc. of anhydrous methanol was added 0.5 cc. (*ca.* 10% excess) of 0.2 *N* barium methoxide in methanol (prepared by refluxing barium oxide with anhydrous methanol) and the solution refluxed for one hour. Carbon dioxide gas was then introduced until precipitation was complete and the precipitated barium carbonate was removed by centrifugation. The residue obtained on solvent removal from the centrifugate was extracted with 2 cc. of warm ethanol (acetone is likewise useful as a solvent in which the sugar mercaptals have some solubility) and crystallized from aqueous ethanol; yield of D-galactose diethyl mercaptal 3 mg., m. p. 138–139° (micro stage).

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NEW COMPOUNDS

Esters of Mesitoic Acid

2-Mesitoyl-4-methylphenyl Mesitoate.—A mixture of 22 g. of 2-mesitoyl-4-methylphenol[1] and 20 g. of mesitoyl chloride was warmed until hydrogen chloride ceased to be evolved. The reaction mixture was dissolved in ether, and the resulting solution washed successively with water, dilute sodium hydroxide solution and water. Evaporation of the ether left the ester as a solid which, after being recrystallized from ethanol, melted at 135–136°; yield 32%.

Anal. Calcd. for $C_{27}H_{28}O_3$: C, 80.97; H, 7.05. Found: C, 81.31; H, 7.09.

Phenyl Mesitoate.—The phenyl ester was prepared in 83% yield from phenol and mesitoyl chloride. It formed colorless needles; m. p. 37–38° (cor.).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.28; H, 6.75.

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