Dye Adsorption.—The dyes prepared from both stereoisomers and the racemic modification of 2,2′-diamino-1,1′-binaphthyl were used in a series of dyeing experiments to attempt to detect an optically selective adsorption according to the methods of Brode.[3]

Samples of 7.000 g. of purified, desulfurized viscose rayon were dyed in 200 ml. (the volume of the bath in ml. was "29 times" the weight of the fiber sample in g.) dye-baths containing about 0.18 g. of the dye (the weight of the dye was "2.7%" of the weight of the fiber sample) and 0.03 g. of sodium acetate. The dyeings were commenced at 49°, taken to 100° in forty-five minutes and maintained at that temperature for one and one-half hours. The samples were then removed, thoroughly washed and freed of the dye liquors. The dye liquors were next analyzed by titrating with excess titanous chloride and back-titrating with standard ferric alum solution. Portions of the dye liquors were also diluted to equal strengths, about 0.043 g. per liter, and examined polarimetrically and spectrophotometrically. In a similar manner, 4.000 g. samples of purified, unbleached and unspun wool were dyed in dye-baths of the same strength (equivalent to 50 times and 4.7% of the weight of the fiber sample), but maintained at 100° for only forty-five minutes. The results were compared to blank experiments, the per cent. of dye taken up by the fibers calculated and the results set forth in the table.

Solution	Dye in liquors, g.	Dye taken up, g.	Dyeing, %	$[\alpha]^{25°C.}_{6600\text{ Å.}}$ (±500)
l-blank	0.1776			+1044
d & *l*-blank	.1888			+ 464
d-blank	.1964			−1177
l-rayon	.1641	0.0135	7.64±0.6	+1508
d & *l*-rayon	.1743	.0145	7.53±1.0	− 116
d-rayon	.1816	.0148	7.56±1.1	−1177
l-wool	.1091	.0685	38.6±1.5	+ 928
d & *l*-wool	.1107	.0781	41.3±0.8	+ 232
d-wool	.1187	.0777	37.4±1.1	−1161

Within the experimental error, the spectrophotometric observations confirmed the titanous chloride analyses. Together, they show that under the conditions of the experiments no optically selective adsorption of the stereoisomeric forms of 2,2′-di-(1-hydroxy-2-azo-3-sulfonic acid-6-anilino-naphthalene)-1,1′-binaphthyl occurred. This is substantiated by the polarimetric observations.

Summary

Optically active and racemic dyes have been prepared through the tetrazotization of the active and racemic forms of 2,2′-diamino-1,1′-binaphthyl and coupling to phenyl-J-acid. Dyeing tests with these active and racemic dyes failed to show any selective absorption by wool or rayon fibers and thus confirm previous experimental work. The data support a physical rather than a chemical combination between fiber and dyestuff.

COLUMBUS, OHIO RECEIVED DECEMBER 7, 1940

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Acetone Derivatives of the Mercaptals of Some Monosaccharides. VI. Crystalline 2-Monomethyl *d*-Mannose and its *alpha*-Methylglycofuranoside, Dimethyl Acetal and Dibenzyl Mercaptal

BY EUGENE PACSU AND S. M. TRISTER[1]

In 1931 Levene and co-workers[2] definitely established that Pacsu's supposed 4-methyl glucose[3] was identical with the true 2-methyl glucose,[4] the structure of which was proved by Brigl and Schinle.[5] Subsequently, Levene's conclusion was confirmed by Pacsu,[6] who also pointed out that in all probability the 4-methyl mannose of Pacsu and v. Kary[7] likewise represented a 2-methyl derivative, since the osazones derived from the two methyl hexoses were identical. Brigl and Schinle[5d] had previously found that under the standard conditions of osazone formation 2-methyl glucose gave rise to phenylglucosazone with the loss of the methyl group. In 1936 Munro and Percival[8] undertook "A Revision of the Constitution of the Supposed 4-Methyl Galactose and 4-Methyl Mannose of Pacsu. . . " and found that close agreement exists between the physical constants of the supposed 4-methyl galactose[9] as well as its osazone and phenylhy-

(1) Research Assistant on Special Funds from the Rockefeller Foundation.

(2) (a) Levene, Meyer and Raymond, *Science*, **73**, 291 (1931); *J. Biol. Chem.*, **91**, 497 (1931); *cf.* (b) Schinle, *Ber.*, **64**, 2361 (1931).

(3) (a) Pacsu, *ibid.*, **58**, 1455 (1925); *cf.* (b) Part I, *ibid.*, **57**, 849 (1924).

(4) The similarly named sirupy products described both by Pictet [Pictet and Castan, *Helv. Chim. Acta*, **3**, 645 (1920)] and by Irvine [Irvine, *J. Chem. Soc.*, **125**, 1 (1924)] cannot any longer be regarded as the true representatives of 2-methyl glucose.

(5) (a) Brigl and Schinle, *Ber.*, **63**, 2884 (1930); *cf.* (b) Hickinbottom, *J. Chem. Soc.*, 3140 (1928); (c) Lieser, *Ann.*, **470**, 110 (1929); (d) Brigl and Schinle, *Ber.*, **62**, 1716 (1929).

(6) Pacsu, *ibid.*, **65**, 51 (1932); (b) THIS JOURNAL, **58**, 2076 (1936).

(7) Part II, Pacsu and v. Kary, *Ber.*, **62**, 2811 (1929).

(8) Munro and Percival, *J. Chem. Soc.*, 640 (1936).

(9) Part III, Pacsu and Löb, *Ber.*, **62**, 3104 (1929).

drazone and those of the 6-methyl galactose[10] and its corresponding derivatives. This has been confirmed in our revisionary work[11] on the structures of the acetone derivatives and the methylated acetone derivatives of *d*-galactosedibenzylmercaptal. Regarding the constitution of the supposed 4-methyl mannose Munro and Percival interpreted their results as indicating a 2-methyl structure of this mannose derivative. In repeating the work of Pacsu and v. Kary, Munro and Percival first isolated what they subsequently found to be an impure monomethyl mannosedibenzylmercaptal with m. p. 118° and $[\alpha]^{20}D$ −48° in pyridine solution and stated that this compound "invariably showed a OCH_3 content of about one-third of the theoretical for a monomethyl mannosedibenzylmercaptal." By repeated acetone condensation, methylation and hydrolysis the same authors found it possible to increase the OCH_3 content of the crystals to 80% of the theoretical amount, but, according to them, "pure monomethyl mannosedibenzylmercaptal . . . could not be produced by this method." In our present revisionary work we have obtained after two methylations by a recently recommended[12] procedure and subsequent hydrolysis of the sirupy diacetone mannosedibenzylmercaptal a crystalline compound in 83% yield. Our substance[13] had m. p. 117° and $[\alpha]^{21}D$ −43.1° in pyridine solution and on analysis it showed a methoxyl content[14] in good agreement with the theoretical amount for a monomethyl mannosedibenzylmercaptal. For the preparation of their methyl mannose Pacsu and v. Kary have not isolated the monomethyl mannosedibenzylmercaptal but treated the methylated diacetone mannosedibenzylmercaptal with mercuric chloride in boiling alcohol, then hydrolyzed the resulting ethyl glycopyranoside of the monomethyl mannose with hydrochloric acid. The final product, the supposed 4-methyl mannose, was a sirup and it had a constant specific rotation of 7.38° in aqueous solution. In their revisionary work Munro and Percival likewise obtained a sirupy monomethyl mannose [$[\alpha]^{20}D$ 4.3° in aqueous solution; found: OMe, 11.7; calcd.: OMe, 16.0] from their impure monomethyl mannosedibenzylmercaptal. In our present reinvestigation we have succeeded in obtaining for the first time a crystalline monomethyl mannose. It had m. p. 136–137° and an initial specific rotation of 7.0° in aqueous solution, which value slowly changed to 4.5° in twenty-four hours. On treatment in the usual manner with a hot solution of phenylhydrazine in acetic acid the monomethyl mannose gave rise to phenylglucosazone with the loss of the methyl group. Such a behavior is now regarded as evidence for the presence of the methoxyl group in position 2, because only in such case would the methyl group be lost during the formation of an osazone. Confirmatory evidence for the presence of the methoxyl group on carbon atom 2 was obtained from the result of the Parnas–Klimek test[15] for adjacent, free, *cis*-hydroxyl groups with copper sulfate and alkali. This test was positive for mannose where such hydroxyl groups (2 and 3) occur and negative for the monomethyl mannose in question. Our crystalline material, therefore, must represent the 2-monomethyl mannose and the parent substance from which it originated must then be the 2-monomethyl mannosedibenzylmercaptal. The formation of the latter crystalline compound in a yield of 83% from the sirupy diacetone mannosedibenzylmercaptal by methylation and subsequent hydrolysis is considered as proof of the relative uniformity of the sirupy starting material, which, therefore, must mainly consist of 3,4–5,6-diisopropylidene mannosedibenzylmercaptal.

Beside the final product of crystalline 2-monomethyl mannose we have also succeeded in obtaining two other new crystalline mannose derivatives from the pure 2-monomethyl mannosedibenzylmercaptal by the employment of the general procedure of Pacsu and Green[16] for the preparation of furanosides. One of these sub-

(10) Freudenberg and Smeykal, *Ber.*, **59**, 100 (1926).

(11) (a) Part V, Pacsu and Trister, THIS JOURNAL, **62**, 2301 (1940); *cf.* (b) Part IV, Pacsu, Trister and Green, *ibid.*, **61**, 2444 (1939).

(12) Pacsu and Trister, *Ber.*, **61**, 2442 (1939).

(13) Although we have repeated these experiments several times in no instance could we obtain the product with m. p. 188° and $[\alpha]^{20}D$ −106.63° in pyridine solution described by Pacsu and v. Kary as the 4-methyl mannosedibenzylmercaptal. Similar failure was reported by Munro and Percival concerning the preparation of this high melting and strongly negatively rotating substance. Since the physical constants of the analogous glucose derivative[3b] (m. p. 190–191°, preceded by slight sintering; $[\alpha]^{15}D$ −109.02° in pyridine solution) are very close to the corresponding values recorded for the supposed 4-methyl mannosedibenzylmercaptal, it appears probable that, in consequence of an oversight, the data obtained on a sample of the glucose derivative have been given by Pacsu and v. Kary for the mannose derivative.—E. P.

(14) In these methoxyl estimations carried out by the method of Vieböck and Schwappach [*Ber.*, **63**, 2818 (1930)] as modified by Clark [*J. Assoc. Official Agr. Chem.*, **15**, 136 (1932)] we have found it necessary to place into the washer of the apparatus a concentrated solution of cadmium sulfate in order to eliminate the hydrogen sulfide formed during the reaction.

(15) Parnas and Klimek, *Z. physiol. Chem.*, **217**, 75 (1933).

(16) Pacsu and Green, THIS JOURNAL, **58**, 1823 (1936), *et seq.*

stances, the α-methyl 2-monomethylmannofuranoside with m. p. 82° and $[\alpha]^{25}D$ 129.5° in aqueous solution, represented the main product of the reaction and it served for the preparation of the crystalline 2-methyl mannose by acid hydrolysis. The second compound, the 2-monomethyl mannosedimethylacetal with m. p. 111–112° and $[\alpha]^{21}D$ −11.3° in aqueous solution, was isolated only in a small yield as a by-product and it also gave 2-methyl mannose on acid hydrolysis. The formation of this acetal is noteworthy since it furnishes another example that demonstrates the readiness of certain carbohydrates to yield open-chain derivatives even when all of the hydroxyl groups in the molecule are unoccupied, the other examples being the acetal formations under similar conditions from the mercaptals of *l*-rhamnose[17] and *d*-fructose.[18] It is also interesting to note that in contrast to the 2-monomethyl mannosedibenzylmercaptal the mannosediethylmercaptal does not seem to give an acetal, since Scattergood and Pacsu[19] reported that a careful search in the reaction mixture failed to reveal the presence of mannosedimethylacetal.

While the reaction between 2-methyl mannose and a hot solution of phenylhydrazine in acetic acid yielded the expected phenylglucosazone with the loss of the methyl group, the reaction between the same substances in the cold led to the phenylhydrazone of 2-methyl mannose. This product was also obtained on treatment of the 2-methyl mannose with phenylhydrazine in alcoholic solution in the absence of acetic acid according to the procedure employed by Butler and Cretcher[20] for the preparation of mannosephenylhydrazone from mannose.

The investigation is being continued.

Experimental

Preparation of Mannosedibenzylmercaptal from α-Methyl-*d*-mannopyranoside.—The mercaptal was prepared according to the procedure used by Scattergood and Pacsu[19] for the preparation of mannosediethylmercaptal from the easily available α-methylmannopyranoside.[21] Seventy grams of the crude glycoside was dissolved in 70 g. of concd. hydrochloric acid and to the solution 105 g. of benzyl mercaptan was added. The mixture was shaken for twenty-two hours at room temperature. The resulting clear solution solidified on cooling. The solid mass was triturated with benzene and filtered. The precipitate was shaken for one hour with 500 cc. of benzene, filtered, then dried under reduced pressure; yield practically quantitative. After two recrystallizations from ethyl alcohol the mercaptal had m. p. 126° in agreement with the value given by Pacsu and v. Kary.[7]

2 - Monomethyl Mannosedibenzylmercaptal.—Fifty grams of mannosedibenzylmercaptal was converted into the diacetone derivative by the procedure described in Part V[11a] for the preparation of the diacetone galactosedibenzylmercaptal. From the united petroleum ether extracts 43 g. of a light yellow sirup, representing the 3,4-5,6-diacetone mannosedibenzylmercaptal, was obtained. The substance had $[\alpha]^{21}D$ 59.3° in acetylene tetrachloride solution (*p*, 2.24; sp. gr. 1.58). Pacsu and v. Kary[7] recorded $[\alpha]^{20}D$ 66.26° for the same product. The diacetone derivative (40 g.) was then methylated[12] twice by conversion into the sodium alcoholate and subsequent treatment with methyl iodide; yield, 34 g. of sirupy monomethyl diacetone dibenzylmercaptal. For the removal of the isopropylidene groups 60 g. of the product was dissolved in 750 cc. of 80% ethyl alcohol containing 35 cc. of concd. hydrochloric acid and the solution was heated under reflux for twenty minutes. The solution was then cooled, neutralized with 6 *N* sodium hydroxide solution, diluted with an equal volume of water and kept at 0° overnight. The voluminous, light brown precipitate, the 2-monomethyl mannosedibenzylmercaptal, was filtered, dried, then purified by shaking with ether, which removed the coloring matter; yield, 33 g. From the ethereal filtrate, which had been kept at 0° for several days, 6 g. of the same material was isolated; total yield, 39 g. or 83% of the theoretical. After several recrystallizations from chloroform the colorless product had m. p. 117° and $[\alpha]^{21}D$ −43.1° in pyridine solution (*p*, 2.59; sp. gr. 0.985). Another preparation had $[\alpha]^{21}D$ +39.5° in chloroform solution (*c*, 0.92).

Anal.[14] Calcd. for $C_{21}H_{28}O_5S_2$: OCH_3, 7.3. Found: OCH_3, 7.1.

Pacsu and v. Kary[7,13] gave m. p. 188° and $[\alpha]^{20}D$ −106.63° in pyridine solution, whereas Munro and Percival[8] recorded m. p. 118° and 117°, $[\alpha]^{20}D$ −48° and −54° in pyridine solution, and OCH_3 2.8 and 5.8 for different preparations recrystallized from alcohol.

2-Monomethyl α-Methylmannofuranoside and 2-Monomethyl Mannosedimethylacetal.—Twenty-three grams of the 2-monomethyl mercaptal was dissolved in 200 cc. of absolute methyl alcohol and the solution was treated at 60° with 23 g. of yellow mercuric oxide and 30 g. of mercuric chloride according to the procedure of Pacsu and Green.[16] After six hours of continuous stirring the solution was worked up in the usual manner; yield, 10 g. of a colorless, non-reducing liquid with $[\alpha]^{18}D$ 67.4° in aqueous solution (*c*, 1.3). Five grams of this liquid was dissolved in 15 cc. of ethyl acetate and, on cooling of the solution at 0°, a crystalline precipitate (2.4 g.) was obtained. The crystals represented the 2-monomethyl α-methylmannofuranoside contaminated with a small quantity of the 2-monomethyl mannosedimethylacetal. For separation the product was crystallized from a mixture of two parts of ethyl alcohol and one part of ether, from which at 0° the glycoside separated out in long prismatic needles (2.2 g.). From the filtrate, on concentration and cooling, the acetal

(17) Green and Pacsu, THIS JOURNAL, **60**, 2288 (1938).
(18) Pacsu, *ibid.*, **60**, 2277 (1938); **61**, 1671 (1939).
(19) Scattergood and Pacsu, *ibid.*, **62**, 903 (1940).
(20) Butler and Cretcher, *ibid.*, **53**, 4358 (1931).
(21) Hudson, in Gilman, *et al.*, "Organic Syntheses," J. Wiley and Sons, Inc., New York, N. Y., Coll. Vol. I, 362 (1932).

crystallized out in small plates (0.025 g.). After recrystallization from a mixture of equal portions of alcohol and ether the 2-monomethyl α-methylmannofuranoside had m. p. 82° and $[\alpha]^{25}D$ 129.5° in aqueous solution (*c*, 2.625).

Anal. Calcd. for $C_8H_{16}O_6$: OCH_3, 29.8. Found: OCH_3, 29.5.

A somewhat larger sample of the acetal was recrystallized from *n*-propyl alcohol; m. p. 111–112° and $[\alpha]^{21}D$ −11.3° in aqueous solution (*c*, 2.65).

Anal. Calcd. for $C_9H_{20}O_7$: OCH_3, 38.7. Found: OCH_3, 38.0.

The acetal is non-reducing but is easily hydrolyzed by dilute acids. A study of the rate of hydrolysis was made and the data are reported in Table I.

TABLE I

HYDROLYSIS OF A SOLUTION OF 0.0359 G. OF 2-MONOMETHYL MANNOSEDIMETHYLACETAL IN 2 ML. OF 0.05 *N* HYDROCHLORIC ACID AT 21° IN A 2-DM. TUBE

Time, hours	Obsd. rotation	k (first order)
0.13	−0.50	.....
3	− .77	0.054
6	− .89	.044
24	−1.28	.043
31	−1.36	Mean .047
31	−1.36	.....
96	−1.12	.00100
144	−0.92	.00125
192	− .81	.00115
240	− .73	.00105
336	− .45	.00122
432	− .16	.00154
576	+ .02	.00164
696	+ .13	.00200
792	+ .15	.00170
840	+ .22	Mean .00140

The specific rotation of the acetal in dilute acid changed in thirty-one hours from the initial value of −14° to −38°. This change was probably due to the formation of a mixture of the 2-monomethyl α- and β-methylmannofuranoside from the dimethylacetal and the reaction followed a first order course with the velocity constant of $10^4 k = 470$. After the point of maximum levorotation had been reached, the rotation changed slowly to the final value of 7.6°. This second change apparently represented the hydrolysis of the furanosides to methyl alcohol and 2-methyl mannose and it proceeded about one-thirty-third as rapidly ($10^4 k = 14$) as the first stage of the hydrolysis reaction.

2-Monomethyl Mannose.—For the preparation of this compound the crystalline furanoside was dissolved in 0.05 *N* hydrochloric acid and the solution was heated under reflux for four hours in a boiling water-bath. The solution was then worked up in the usual manner. The resulting product was crystallized from 95% ethyl alcohol; yield, 80% of the theoretical. The substance had m. p. 136–137° and $[\alpha]^{20}D$ 7.0° in aqueous solution (*c*, 2.88), which value after twenty-four hours changed to the constant rotation of 4.5°.

Anal. Calcd. for $C_7H_{14}O_6$: OCH_3, 16.0. Found: OCH_3, 15.8.

Formation of Phenylglucosazone from 2-Monomethyl Mannose.—One-tenth of a gram of crystalline 2-monomethyl mannose was heated with 0.3 g. of phenylhydrazine in 2 cc. of 20% acetic acid. After thirty minutes the reaction mixture was cooled, the osazone filtered and washed with moist ethyl acetate; yield, 0.036 g. of light yellow crystals with m. p. 204–206° and $[\alpha]^{21}D$ −65.6° in a mixture of six parts of alcohol and four parts of pyridine (*c*, 0.581). After twenty-four hours the rotation became constant at −34.4°. A methoxyl estimation gave negative result. On the basis of these data the substance was identified as pure phenylglucosazone.

2-Monomethyl Mannosephenylhydrazone.—For the preparation of this substance according to a procedure of Butler and Cretcher[20] 0.1 g. of 2-methyl mannose was dissolved in 3 cc. of ethyl alcohol containing 0.1 g. of phenylhydrazine. The solution was heated on the water-bath for fifteen minutes, then it was kept at room temperature for two hours and finally at 0° for twenty-four hours. During this time a colorless crystalline material separated out; yield, 0.110 g., or 86% of the theoretical. After recrystallization from water the substance (0.072 g.) had m. p. 163° and an initial specific rotation of −49.1° in pyridine solution (*p*, 3.05; sp. gr. 0.985), which value after twenty-four hours changed to the constant rotation of −60.7°.

Anal. Calcd. for $C_{13}H_{20}O_5N_2$: OCH_3, 10.9. Found: OCH_3, 10.6, 10.7.

The same substance was obtained when a mixture of 2-monomethyl mannose and phenylhydrazine in dilute acetic acid was kept first at room temperature for one hour, then at 0° for twenty-four hours. Pacsu and v. Kary[7] reported m. p. 179° for the hydrazone of their supposed 4-methyl mannose, which value would seem to indicate that their product was mainly mannosephenylhydrazone. From their impure monomethyl mannose Munro and Percival[8] isolated only mannosephenylhydrazone, which was identified by its m. p. and the results of analysis.

Summary

1. The supposed 4-methyl mannose of Pacsu and v. Kary was obtained in the crystalline state and it was found that the methoxyl group was attached on carbon atom 2.

2. This conclusion was drawn from the results of a series of transformations involving the following steps: mannosedibenzylmercaptal → 3,4–5,6-diacetone mannosedibenzylmercaptal → 2-monomethyl 3,4–5,6-diacetone mannosedibenzylmercaptal → 2-monomethyl mannosedibenzylmercaptal → 2-monomethyl α-methylmannofuranoside → 2-monomethyl mannose → phenylglucosazone. With the exception of the acetone derivatives all of the products including the phenylhydrazone of the 2-monomethyl mannose were obtained in the crystalline state.

3. Crystalline 2-monomethyl mannosedimethylacetal was isolated and its hydrolysis in dilute hydrochloric acid was studied.

PRINCETON, NEW JERSEY RECEIVED NOVEMBER 26, 1940