nitrobenzene (25 cc.) with phosphorus pentachloride (steam-bath) and add a solution of aluminum chloride (1.85 g.) in nitrobenzene (30 cc.) to the solution of the acid chloride under stirring in a salt–ice bath. A mustard colored complex separated. After stirring for five hours in the freezing bath and standing overnight at room temperature the ketonic product was collected in the usual way and the components separated as in (b). The crude 8-ketotetrahydro-1,2-benzanthracene collected amounted to 0.95 g., and 0.1 g. of crude 4-ketotetrahydrochrysene was isolated and identified.

4-Methylchrysene (XXI).—Condensation of the ketone XIX (2.5 g.) with methylmagnesium chloride was conducted as in the examples described above, and vacuum distillation gave 2.23 g. (90%) of solid product suitable for dehydrogenation. This crystallized from alcohol in colorless plates, but the melting point rose steadily on repeating the process, probably as the result of disproportionation. The crude dihydride (1.2 g.) was heated with sulfur (0.16 g.) at 215–245° for thirty minutes, followed by vacuum distillation from a little zinc dust. The yellow solid was sublimed at 190–200° (1–2 mm.) and crystallized from benzene–alcohol (Norite), giving 0.6 g. of colorless plates, m. p. 140–146°. Three crystallizations from benzene–alcohol gave 0.38 g. of highly fluorescent hydrocarbon of the constant m. p. 151–151.5°.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 94.00; H, 5.94.

The material in the mother liquors was converted to the red picrate; 0.25 g., m. p. 132–136°. This substance sublimed nicely at 110–120° (1 mm.), and the sublimate on crystallization from benzene–ligroin separated in either of two forms. One of these appeared as bright red needles which melted at 135–135.5° and remelted at 137.5–138°; the other separated as light orange needles, m. p. 137.5–138°. The orange form changes to the red form on standing in contact with the mother liquor.

Anal.[19] Calcd. for $C_{19}H_{14}\cdot C_6H_3O_7N_3$: N, 8.91. Found: N, 8.88.

A sample of 4-methylchrysene recovered (alumina tower) from the purified picrate melted at 151–151.5° as before and differed from the above sample only in showing a more intense fluorescence, the colorless crystals appearing violet in daylight.

Summary

In extension of previous work 8-keto-3,4,5,6,7,8-hexahydro-1,2-benzanthracene has been employed as an intermediate for the synthesis of the 8-ethyl, 8-hydroxy, and 8-amino derivatives of 1,2-benzanthracene. The 5-methyl and 5,8-dimethyl derivatives of the hydrocarbon have been synthesized from β-(9,10-dihydro-2-phenanthroyl)-propionic acid through the unsaturated acid resulting from the condensation of the ester of the keto acid with methylmagnesium halide. It is shown that this reaction can be conducted in such a way as to yield the lactone as well as the unsaturated acid, and the α-hydroxy acid has also been isolated. Another hydrocarbon of interest for its possible carcinogenic activity has been prepared by conversion of 8-methyl-1,2-benzanthracene into the 10-aldehyde, followed by Wolff–Kishner reduction. 4-Methylchrysene has been synthesized starting with γ-(2-phenanthryl)-butyric acid, conveniently prepared from the product of the succinoylation of 9,10-dihydrophenanthrene. This acid can be cyclized exclusively either to the chrysene derivative, using zinc chloride in acetic acid–anhydride, or to the isomeric ketotetrahydro-1,2-benzanthracene, using liquid hydrogen fluoride. Cyclization with 85% sulfuric acid or by the Friedel and Crafts reaction gives mixtures of the isomers.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS RECEIVED APRIL 18, 1939

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

The Synthesis of D-Mannoheptulose, and the Preparation of Some of its Derivatives[1]

BY EDNA M. MONTGOMERY AND C. S. HUDSON

F. B. LaForge reported in 1917 that the avocado (the fruit of *Persea gratissima*, Gaertn.) contains a seven carbon atom ketone sugar in the free state. The ketose was isolated in crystalline form, characterized, and its structure and configuration established as those of D-mannoheptulose.[2] The present paper describes the synthesis of D-mannoheptulose from D-α-mannoheptose (D-manno-D-gala-heptose), a transformation which would be expected to occur because of the configuration assigned to the ketose by LaForge.

The Lobry de Bruyn rearrangement was applied to D-manno-D-gala-heptose under the mild conditions[3] used previously in the synthesis of lactulose from lactose.[4] After equilibrium had

(1) Publication authorized by the Surgeon General, U. S. Public Health Service. Presented in part before the Division of Organic Chemistry at the New York meeting of the American Chemical Society, April 22, 1935.

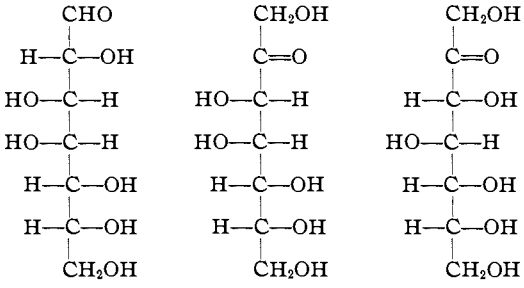
(2) LaForge, *J. Biol. Chem.*, **28**, 511 (1917); Wright, *ibid.*, **28**, 523 (1917).

(3) Wolfrom and Lewis, THIS JOURNAL, **50**, 837 (1928).

(4) Montgomery and Hudson, *ibid.*, **52**, 2101 (1930).

been established, as judged from the constancy of rotation, the aldose components were removed by oxidation with bromine water and subsequent precipitation of the barium aldonates. Crystallization of the ketose portion produced D-mannoheptulose in 25% yield, and D-glucoheptulose[5] in 13% yield. The formation of two ketone sugars from D-manno-D-gala-heptose is not unexpected if we compare this heptose with D-galactose with which it is identical in the configuration of the first four asymmetric carbon atoms, and which it resembles closely in physical and chemical properties. Thus, from the rearrangement of D-galactose with dilute potassium hydroxide, de Bruyn and van Ekenstein[6] were able to isolate not only D-tagatose but also the epimeric ketose, D-sorbose.

The less drastic rearrangement of D-manno-D-gala-heptose in pyridine solution,[7] followed by oxidation of the aldose components, resulted in the recovery of 72% as barium heptonates, and the separation of 21% of pure D-mannoheptulose. No D-glucoheptulose was detected in this case.



D-Manno-D-gala-heptose D-Mannoheptulose D-Glucoheptulose

Glycoside formation with the ketose occurred readily in 0.25 *N* methyl alcoholic hydrochloric acid at room temperature, and a constant rotation[8] of +71.3° was reached in three hours; practically the same rotation was attained when the reaction was carried out at the boiling point of the solution. The product was isolated in 68% yield. From its rotation of +69° in water it is to be designated as α-methyl-D-mannoheptuloside. From the similarity between its rotation and the rotation of the equilibrium solution from which it was obtained, it seems probable that the α-glycoside is formed almost exclusively. In this respect, D-mannoheptulose resembles the configurationally related aldoses, D-mannose and D-lyxose, each of which produces mainly the α-glycoside.

Acetylation of D-mannoheptulose with cold acetic anhydride and pyridine produced a crystalline hexaacetate in an 85% yield. The rotation, +39.0° in chloroform, indicates that it is the α-hexaacetate. Treatment of this acetate with glacial acetic acid saturated with gaseous hydrobromic acid resulted in a crystalline acetobromo-D-mannoheptulose, rotating +104° in chloroform; accordingly, it also is to be designated an α-form. Replacement of the bromine atom through the agency of silver oxide and methyl alcohol yielded a crystalline pentaacetyl-α-methyl-D-mannoheptuloside, rotating +49.5° in chloroform; the same compound is generated by the acetylation of α-methyl-D-mannoheptuloside; deacetylation regenerates the original glycoside. Thus, all the known derivatives of D-mannoheptulose appear as α-forms, and no evidence for a β-form has yet been discovered. The ketose itself shows no mutarotation, and presumably is the pure α-isomer. It is noteworthy that there is no Walden inversion in the passage from the acetobromo compound to the acetylated methylglycoside.

Although D-mannoheptulose is converted to its α-methylglycoside at 20° with the rapidity considered to be characteristic of furanoside formation in the aldose series, nevertheless it seems likely that methyl mannoheptuloside is a pyranoside. Evidence for this belief comes from the data in Table I, in which are compared the rotations of D-mannoheptulose and its derivatives with the rotations of D-mannose and its derivatives, both furanoside and pyranoside. Since the configurations of the asymmetric carbon atoms in the two sugars are identical, it would not be unreasonable to expect a certain similarity in rotations between compounds with the same ring systems. Although the α-mannoheptuloside is formed rapidly at room temperature with acidic methyl alcohol, it also is produced as the principal product when the solution is heated, showing that it is the stable end-product of the reaction and therefore, in all probability, a pyranoside.

Corresponding to the rapid glycoside formation from D-mannoheptulose in methyl alcoholic hydrochloric acid, there is a rapid hydrolysis of the

(5) Austin, THIS JOURNAL, **52**, 2106 (1930).

(6) De Bruyn and van Ekenstein, *Rec. trav. chim.*, **16**, 262 (1897); **19**, 5 (1900).

(7) The method of Danilow, Venus-Danilowa and Schantarovitsch, *Ber.*, **63**, 2269 (1930).

(8) Throughout the article the rotations are specific rotations at 20° for sodium light; *c* designates concentration in grams per 100 cc. of solution.

TABLE I

ROTATIONS[a] OF α-D-MANNOSE, α-D-MANNOHEPTULOSE, AND THEIR DERIVATIVES

	α-D-Mannose			α-D-Mannoheptulose		
	$[\alpha]^{20}D$	Mol. wt.	$[M]^{20}D$	$[\alpha]^{20}D$	Mol. wt.	$[M]^{20}D$
Free sugar	+ 30°[b]	180	5,400	+ 29.2°	210	6,100
Acetate	+ 55.0°[c]	390	21,400	+ 39.0	462	18,000
Acetobromo-	+131.6[d]	411	54,100	+104	483	50,200
Methylpyranoside	+ 78.6[e]	194	15,200	+ 69	224	15,400
Methylfuranoside	+113[f]	194	21,900			
Methylpyranoside acetate	+ 49.1[g]	362	17,800	+ 49.5	434	21,500
Methylfuranoside acetate	+107[h]	362	38,700			

[a] Rotations in chloroform, except of the free sugars and glycosides, which are in water. [b] Initial rotation: Levene, *J. Biol. Chem.*, **57**, 333 (1923). [c] Hudson and Dale, THIS JOURNAL, **37**, 1282 (1915). [d] Brauns, *Bur. Standards J. Research*, **7**, 582 (1931). [e] Harris, Hirst and Wood, *J. Chem. Soc.*, 2116 (1932). This value was obtained at 25°. [f] Haworth and Porter, *ibid.*, 650 (1930). [g] Dale, THIS JOURNAL, **46**, 1048 (1924). [h] Haworth, Hirst and Webb, *J. Chem. Soc.*, 656 (1930).

glycoside in dilute aqueous hydrochloric acid. In 0.005 *N* acid at 98°, the hydrolysis constant *k*, expressed in minutes and decimal logarithms, is 0.050. Although this value is very much larger than the constants obtained in the hydrolysis of aldopyranosides, and even for aldofuranosides,[9] yet the recent work of Purves and Hudson[10] has shown that the "glycosides of the keto sugar fructose differ from those of the aldoses in that both ring types possess very nearly the same slight stability toward aqueous acid." A similar conclusion has been reached by Schlubach and Graefe[11] in their study of the sorbosides. In conclusion it may be stated that, although α-methyl-D-mannoheptuloside is hydrolyzed about twice as rapidly as sucrose,[9] a fructofuranoside, no evidence for the size of the ring can be adduced from this behavior.

Experimental

D-Mannoheptulose from D-Manno-D-gala-heptose.—A solution containing 20 g. of D-manno-D-gala-heptose in 200 cc. of 0.05 *N* aqueous barium hydroxide was kept at 35° until the Lobry de Bruyn rearrangement was completed as judged from the changes in rotation. The values observed were +68.6° after fifteen minutes, +49.0° after twenty-four hours, +34.6° after forty-eight hours, and +25.4° (constant) after seventy-two hours. The solution remained clear, and developed only a slight yellow color during the course of five days. At the end of that period sufficient bromine and barium benzoate[12] were added to oxidize the aldehyde sugars to the corresponding aldonic acids; excess bromine, barium, and benzoic acid were removed, and the barium aldonates precipitated with alcohol in the usual way. The filtrate was concentrated *in vacuo* to a sirup which, upon solution in ten volumes of hot methyl alcohol and cooling, deposited 4.2 g. of ketose rotating +60.0° in water. One recrystallization produced 2.6 g. of sugar melting at 170–174° and rotating +66.9° in water (*c*, 2); these data are in accord with the melting point 171–174° and rotation +67.5° in water (*c*, 2.5) reported by Austin for D-glucoheptulose.[5] The combined mother liquors, concentrated in a desiccator over calcium chloride, furnished 6.3 g. of crude ketose, from which was separated 5.1 g. of D-mannoheptulose. The melting point 152° and rotation +29.2° in water (*c*, 2) are in agreement with the values recorded by LaForge.[2] A mixture of the synthetic and natural sugars melted at 152° also. The identification was completed by the "mixed solubility" method;[13] thus, 10 cc. of 80% alcohol at 3° was found to contain 0.3870, 0.3865, and 0.3868 g. from undersaturation, and 0.3860, 0.3862, and 0.3871 g. from supersaturation, of the synthetic, natural, and mixed D-mannoheptuloses, respectively.

The rearrangement of D-manno-D-gala-heptose according to Danilow's procedure was carried out by refluxing a solution of 25 g. of the dried sugar in 250 cc. of pyridine for four and one-half hours. The pyridine was removed by distillation *in vacuo*, and the residue, with rotation +54.5° in water (*c*, 25), treated with bromine and barium benzoate to remove aldehyde sugars as in the preceding experiment. The barium salts weighed 25.3 g., and represented about 72% of the original heptose. From the mother liquor was obtained 5.2 g. of pure, recrystallized D-mannoheptulose melting at 152° and rotating +29.2° in water (*c*, 2).

D-Mannoheptulose from the Avocado.—A number of varieties of avocado were examined but none was found to contain as much ketose as the Trapp variety recommended by LaForge. His procedure was modified somewhat, as follows. The crushed pulp was mixed thoroughly with sufficient 20% ethyl alcohol to make a thin soup, and left overnight. The mixture was heated on a steam-bath until the pulp was well coagulated and then filtered by gravity through folded filters or run through a fruit press. The following morning the filtrate was siphoned from any oil which had collected at the surface of the liquid. The solution was clarified and decolorized by heating to 95° with activated carbon, filtered through carbon, and concentrated *in vacuo* to a thin sirup which was poured into eight volumes of methyl alcohol. The precipitated gum separated in small flakes, showing only a slight reducing action toward Fehling solution. The filtered solution was concentrated *in vacuo* to a thick sirup, which was dissolved in four volumes of methyl alcohol and cooled to 5°. Crystalline perseitol separated first, and was filtered after three hours. The mother liquor, allowed to stand for several days in the ice-box, deposited mannoheptulose contaminated with perseitol. The latter was removed by dissolving each 50-g. portion of the powdered crude sugar in 200 cc. of hot 80% methyl alcohol, and allowing the perseitol to crystallize overnight in the ice-box. The filtered solution was concen-

(9) See for example Haworth and Hirst, *J. Chem. Soc.*, 2625 (1930).
(10) Purves and Hudson, THIS JOURNAL, **59**, 1174 (1937).
(11) Schlubach and Graefe, *Ann.*, **532**, 218 (1937).
(12) Hudson and Isbell, THIS JOURNAL, **51**, 2225 (1929).
(13) Montgomery and Hudson, *ibid.*, **52**, 2105 (1930).

trated *in vacuo;* the sirup, dissolved in methyl alcohol and cooled, deposited practically pure D-mannoheptulose, melting at 152°, and rotating +29.1° in water (*c*, 2). From 21 kg. of pulp, from 36 avocados, there was obtained 315 g. of pure D-mannoheptulose and 75 g. of perseitol, plus 400 g. of non-reducing gum and 310 g. of a final sirup containing 80% solids.

α-Methyl-D-mannoheptuloside.—Glycoside formation occurred readily when a 1% solution of the ketose in absolute methyl alcohol was made 0.25 *N* in hydrogen chloride (see Fig. 1). The rotation, +34.7° after one minute, changed rapidly to +47.5° at the end of four minutes, remained constant during the next three minutes,[14] and then increased slowly to a constant value +71.3° at the end of three hours.[15] The reducing power of the solution was negligible after thirty minutes. An equilibrated solution from 10 g. of ketose was neutralized with silver oxide, the excess silver removed with hydrogen sulfide, and the filtrate concentrated *in vacuo* to a sirup which crystallized after two weeks. The product weighed 7.2 g. It showed no reducing power toward Fehling solution. It is readily soluble in water, methyl alcohol, and ethyl alcohol, sparingly soluble in ethyl acetate, insoluble in ether. Recrystallized from methyl alcohol, as small prisms, it melted at 142°, and showed a constant rotation of +69.0° in water (*c*, 2).

Anal. Calcd. for $C_8H_{16}O_7$: C, 42.83; H, 7.19; OCH_3, 13.84. Found: C, 42.9; H, 7.17; OCH_3, 13.7.

Hydrolysis of α-Methyl-D-mannoheptuloside.—The hydrolysis of a 4.2% solution of the heptuloside in 0.005 *N* aqueous hydrochloric acid at 98° was followed polarimetrically, the samples being cooled rapidly to 20° for measurement. The observed readings, in circular degrees, were +2.82° at zero time, +2.35° after three minutes, +1.72° after ten minutes, +1.43° after fifteen minutes, and a final constant value of +1.17°. The average hydrolysis constant in terms of minutes and decimal logarithms, $k = \frac{1}{t} \log \frac{(r_0 - r_\infty)}{(r - r_\infty)}$, is 0.050. The final reading +1.17°, calculated on the basis of complete hydrolysis, corresponds to a specific rotation of +29.7° as compared with the value +29.2° for the pure mannoheptulose.

D-Mannoheptulose α-Hexaacetate.—The acetylation of 10 g. of pure D-mannoheptulose was accomplished by dissolving the sugar in a mixture of 50 cc. of acetic anhydride and 50 cc. of pyridine at 0°. The solution was kept at that temperature for forty-eight hours, then poured into ice water; the chloroform extract was washed, dried, and concentrated in the usual manner. The resulting sirup crystallized readily. By recrystallization from warm ether there was obtained 18.8 g. (85%) of large prisms, melting at 110°, and rotating +39.0° in chloroform (*c*, 2).

Anal. Calcd. for $C_{19}H_{26}O_{13}$: C, 49.35; H, 5.67; acetyl, 13.00 cc. of 0.1 *N* NaOH per 100 mg. Found: C, 49.26; H, 5.70; acetyl, 13.03 cc.

(14) This plateau may be an indication of extremely rapid furanoside formation, and the subsequent rearrangement to the pyranoside form.

(15) The final rotation for glycoside formation at the boiling point of the solution was +73.5°. Calculated as methylmannoheptuloside, the rotations become +66.9° and 68.9°, respectively.

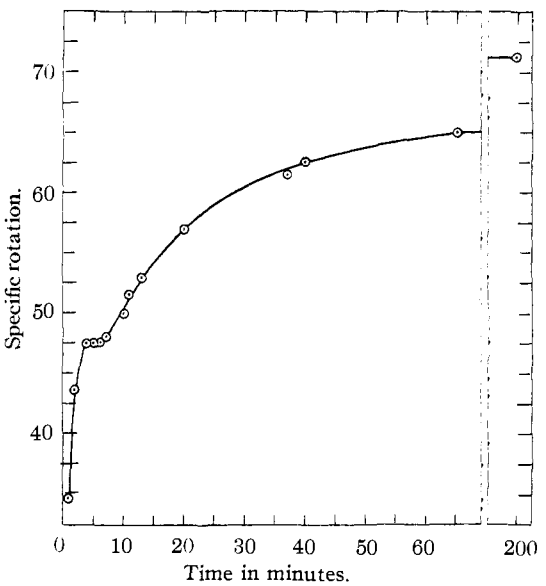


Fig. 1.—Change in rotation of a 1% solution of D-mannoheptulose in 0.25 *N* methyl alcoholic hydrochloric acid at 20°.

α-Acetobromo-D-mannoheptulose.—A paste of 10 g. of crystalline D-mannoheptulose α-hexaacetate and 5 cc. of glacial acetic acid, cooled to 0°, was dissolved at that temperature in 30 cc. of glacial acetic acid which had been saturated previously with gaseous hydrobromic acid. After two hours in an ice-bath the solution was poured into ice water and extracted with chloroform. The chloroform solution was washed, dried, and concentrated *in vacuo;* the resulting sirup, taken up in anhydrous ether, deposited 5.3 g. (50%) of rosets of prisms, melting at 92°. The recrystallized acetobromo-D-mannoheptulose rotated +104.0° in chloroform (*c*, 2).

Anal. Calcd. for $C_{17}H_{23}O_{11}Br$: Br, 16.55. Found: Br, 16.28.

Pentaacetyl-α-methyl-D-mannoheptuloside from α-Methyl-D-mannoheptuloside.—A 3-g. portion of the pure glycoside was acetylated at 0° with a mixture of 30 cc. each of acetic anhydride and pyridine. The product, isolated in the customary manner, weighed 5.3 g. Upon recrystallization from ether it separated in clusters of radiating needle-like prisms melting at 64° and rotating +49.5° in chloroform (*c*, 2). Deacetylation regenerated the original glycoside.

Anal. Calcd. for $C_{18}H_{26}O_{12}$: C, 49.74; H, 6.03; OCH_3, 7.14; acetyl, 11.51 cc. of 0.1 *N* NaOH per 100 mg. Found: C, 49.74; H, 5.90; OCH_3, 7.10; acetyl, 11.48 cc.

Pentaacetyl - α - methyl - D - mannoheptuloside from α-Acetobromo-D-mannoheptulose.—A solution of 4 g. of the pure acetobromo compound in 30 cc. of anhydrous methyl alcohol was shaken with 4 g. of silver oxide for five minutes. The halogen-free filtrate from the silver residues was concentrated *in vacuo* and the sirup dissolved in ether. The 1.5 g. of pentaacetyl-α-methyl-D-mannoheptuloside thus obtained had the same melting point, 64°, and the same rotation, +49.5°, as the sample prepared by acetylation of the α-methyl-D-mannoheptuloside

Summary

1. D-Mannoheptulose has been obtained by the rearrangement of D-α-mannoheptose (D-manno-D-gala-heptose) in dilute barium hydroxide solution, and also in pyridine solution.

2. D-Mannoheptulose α-hexaacetate, α-acetobromo-D-mannoheptulose, α-methyl-D-mannoheptuloside, and pentaacetyl-α-methyl-D-mannoheptuloside have been described.

3. A comparison of the rotations of these mannoheptulose derivatives with the rotations of the corresponding derivatives of D-mannose indicates a pyranoid ring in the mannoheptulose compounds.

4. α-Methyl-D-mannoheptuloside is very readily formed and very readily hydrolyzed; this behavior has been shown not to be inconsistent with the ketopyranoside formulation.

WASHINGTON, D. C. RECEIVED MARCH 27, 1939

[CONTRIBUTION FROM THE POLARIMETRY SECTION, NATIONAL BUREAU OF STANDARDS, AND THE NATIONAL INSTITUTE OF HEALTH, U. S. PUBLIC HEALTH SERVICE]

Relations between Rotatory Power and Structure in the Sugar Group. XXXIII. The Alpha and Beta Methyl Pyranosides of L-Fucose (L-Galactomethylose) and their Triacetates[1]

BY R. C. HOCKETT, F. P. PHELPS AND C. S. HUDSON

In 1925 one of us[2] reported two independent calculations of the specific rotation of α-methyl-L-fucoside, based upon its relationship to α-methyl-D-galactoside and to α-L-fucose, respectively; the values so predicted were −188 and −190. The deviation from the value (−122) that had been observed by Tadokoro and Nakamura[3] was so great that the purity of their product appeared doubtful; its rotation indicated that it might be a mixture of α- and β-forms. We undertook the preparation of the pure forms and soon found that the α-isomer is purified readily by recrystallization; its specific rotation was observed to be −196.9 as the average value of eleven preparations. It was then sought to obtain the pure β-form from the mother liquors of the other; the fractionation proved to be very slow and difficult because the isomers form mixed crystals over a wide range of composition, but it was learned that the β-form is certainly dextrorotatory. In 1930 Votoček and Valentin[4] reported the specific rotation of α-methyl-rhodeoside (α-methyl-D-fucoside) as +190. We then reinvestigated the purification of α-methyl-L-fucoside, confirmed our higher value and prepared the β-methyl-L-fucoside by fractional crystallization from the mother liquors of the α-form, obtaining a product of specific rotation +14, which was not changed by further recrystallization of the substance. In 1932 Minsaas[5] reported the values −197 and +16 for the specific rotations of the α- and β-methyl-L-fucosides, respectively, and Schlubach and Wagenitz[6] found the value −14 for β-methyl-D-fucoside (prepared by synthesis from D-galactose) and −5.9 for its triacetate. It was then discovered[7] that the β-L-fucoside forms a crystalline molecular compound with potassium acetate, but that the α-isomer does not, which enabled us to obtain the β-isomer readily in definite purity; its rotation confirmed the value +14. In 1937 Minsaas[8] reported the preparation of the triacetates of α- and β-methyl-L-fucosides (α-form, m. p. 74°, $[\alpha]^{20}D$ −151; β-form, m. p. 99°, $[\alpha]^{20}D$ +7.0). We have prepared both of these substances and find for the α-form, m. p. 67 and $[\alpha]^{20}D$ −149.7, and for the β-form, m. p. 96–97° and $[\alpha]^{20}D$ +7.1; by deacetylating them we have confirmed the purity of the original fucosides of rotations −197 and +14, respectively. It is evident that the value −197 which Minsaas found for the α-fucoside is substantially correct and that the α-methyl-D-fucoside (rhodeoside) of Votoček (+190) was an impure preparation containing some of the β-isomer. Our data con-

(1) Publication authorized by the Director of the National Bureau of Standards and by the Surgeon General, U. S. Public Health Service. The research was begun in 1926 at the National Bureau of Standards (F. P. P. and C. S. H.) and completed at the National Institute of Health (R.C.H. and C. S. H.). No. XXXII was published in THIS JOURNAL, **61**, 1525 (1939).

(2) Hudson, *ibid.*, **47**, 275 (1925).

(3) Tadokoro and Nakamura, *J. Biochem.* (Japan), **2**, 461 (1923).

(4) Votoček and Valentin, *Coll. Czechoslov. Chem. Commun.*, **2**, 36 (1930).

(5) Minsaas, *Rec. trav. chim.*, **51**, 475 (1932).

(6) Schlubach and Wagenitz, *Ber.*, **65**, 304 (1932).

(7) Watters, Hockett and Hudson, THIS JOURNAL, **56**, 2199 (1934).

(8) Minsaas, *Rec. trav. chim.*, **56**, 623 (1937). On p. 624 the rotations of β-methyl-L-fucoside and its triacetate are recorded as negative, obviously through a misprint because the context shows that the substances are dextrorotatory.