The mechanism of this catalyzed reaction follows from the addition of the reversible M–M reaction [A] and the reversible X–M reaction [B].

AMES, IOWA RECEIVED FEBRUARY 6, 1941

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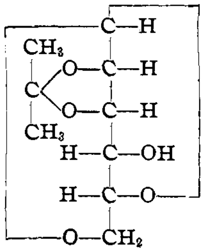
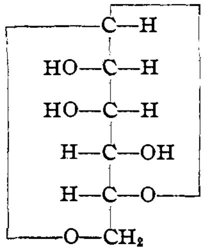
D-Mannosan<1,5>β<1,6> or Levomannosan[1]

BY A. E. KNAUF, RAYMOND M. HANN AND C. S. HUDSON

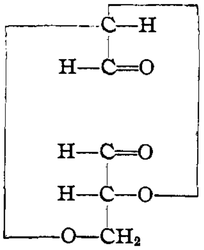
The polysaccharide (a D-mannan) which constitutes the greater part of the endosperm of palm seeds, seems to play a biological role which is similar to that of starch in many other seeds. Since the procedure using the pyrolysis of starch[1a] is the most convenient method of preparing D-glucosan<1,5>β<1,6> (levoglucosan) it seemed of interest to learn whether the pyrolysis of the so-called vegetable ivory, which is readily available as waste turnings, etc., in the manufacture of buttons from the large seeds of the ivory-nut palm (*Phytelephas macrocarpa*, Ruiz and Pav.), would yield some analogous simple anhydride of the D-mannose series. The first experiment verified this surmise. The pyrolysis under reduced pressure yielded a dark red-colored water-soluble sirup and some tar; treatment of this aqueous solution with decolorizing carbon, followed by removal of most of the water, left a light colored heavy sirup, which was then thinned somewhat with acetone. Overnight there crystallized in abundance a beautiful substance which was found to be a condensation product (I) of acetone with a non-reducing D-mannosan; since it seemed improbable that the required amount of acetone could have been produced in the pyrolysis it was



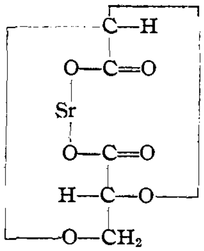
(I)[2]
2,3-Isopropylidene D-mannosan<1,5>β<1,6>



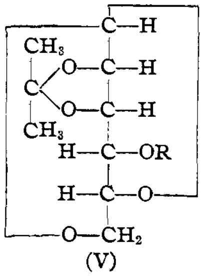
(II)
D-Mannosan<1,5>β<1,6> (levomannosan)



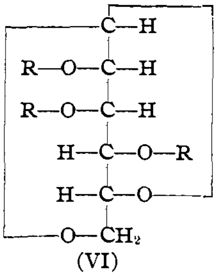
(III)
L′-Oxy-D-methylene diglycolic aldehyde



(IV)
Strontium L′-oxy-D-methylene diglycolate



(V)
(a) R = CH_3CO—
(b) R = $C_6H_5 \cdot CO$—
(c) R = p-$CH_3 \cdot C_6H_4 \cdot SO_2$—
(d) R = CH_3—



(VI)
(a) R = CH_3CO—
(b) R = $C_6H_5 \cdot CO$—
(c) R = p-$CH_3 \cdot C_6H_4 \cdot SO_2$—

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[1] Publication authorized by the Surgeon General, U. S. Public Health Service. The research was presented by one of us (C. S. H.) in a lecture before the Northeastern Section of the American Chemical Society in Cambridge, Mass., on May 9, 1940; publication at that time was limited to the statement ("The Nucleus," issue of May, 1940) that "the address on mannosan will set forth the properties and proof of structure of this new carbohydrate, as well as the method of obtaining it from vegetable ivory, a product of vegetable origin widely employed in the manufacture of buttons." The idea of seeking for a mannosan in the pyrolysis products from vegetable ivory had occurred independently to Zemplén, Gerecs and Valatin who have published (*Ber.*, **73B**, 575–580 (1940), issued June 4, manuscript received April 12), a description of two crystalline derivatives of the substance (its triacetate and its trimethyl ether). They prepared the mannosan itself in amorphous form by the deacetylation of its pure triacetate; fortunately it has crystallized readily in our studies. We do not find exact proof in their article for the definite structural and stereochemical formula (*i. e.*, the 1,5 and β-1,6 rings) that they ascribe to the mannosan; however our concurrent work proves conclusively through its new data that their formula, which is formula (II) of the present article, is the correct one. Zemplén, Gerecs and Valatin have named the mannosan *levomannosan* in suggestion of its similarity to the long known *levoglucosan* (C. Tanret, 1894); we are inclined to the view that the systematic naming D-mannosan<1,5>-β<1,6> and D-glucosan<1,5>β<1,6> of such anhydrides, which is now possible because of the convenient periodate method of correlating their structure and configurations (Jackson and Hudson, see ref. 5), has advantages which will in time be generally regarded as decisive. These considerations led Richtmyer and Hudson (see ref. 6) to name the corresponding anhydride of the D-altrose series D-altrosan<1,5>β-<1,6> rather than *levoaltrosan*. Since our colleagues have introduced the name *levomannosan* we include it in the title of the present article as synonymous with the systematic name D-mannosan<1,5>β<1,6>. An alternative systematic name would be D-mannopyranosanβ<1,6>.

[1a] Pictet and Sarasin, *Helv. chim. acta*, **1**, 87 (1918).

[2] In drawing these projection formulas we follow the conventions that are discussed with full clearness by K. Freudenberg in his "Stereochemie," edition of 1933, p 664.

assumed that the mannosan had condensed with the added acetone through the catalytic action of other products of the pyrolysis.[3]

Following this hypothesis, in the subsequent preparations the purified sirup from the pyrolysis was dissolved in much acetone and the solution was shaken with anhydrous copper sulfate for twenty-four hours to promote the condensation. The solution was then concentrated to a thin sirup which soon became a crystalline magma, from which pure acetone-D-mannosan (I) was obtained in a yield of 8.3% of the weight of the vegetable ivory.[4] Acetone-D-mannosan was fully hydrolyzed to acetone and D-mannosan (II) in 0.1 *N* sulfuric acid at 20° in twenty-four hours as shown by the attainment of a constant rotation without the production of any reducing sugar (negative Fehling test). Removal of the acid and the solvent left a solid substance which crystallized readily from ethyl acetate solution in a yield of 91%; pure D-mannosan$<1,5>\beta<1,6>$ melts at 210–211° (cor.) and shows $[\alpha]^{20}\mathrm{D}$ $-127.6°$ in water (concn. 1.5). Zemplén, Gerecs and Valatin found $-115°$ for the specific rotation of the amorphous D-mannosan that resulted from their deacetylation of its pure crystalline triacetate.

In contrast to the mild acid hydrolysis of acetone-D-mannosan (I) just described, to acetone and D-mannosan (II) without the generation of any reducing sugar, the heating of a solution of either (I) or (II) in *N* hydrochloric acid on the steam-bath for two hours to constant rotation generated D-mannose nearly quantitatively, as shown by the final rotation and by the isolation of crystalline D-mannose phenylhydrazone. The boiling of either (I) or (II) with methanol containing 5% of hydrochloric acid for eight hours gave pure crystalline α-methyl-D-mannopyranoside in high yield. These results prove that D-mannose is the parent hexose of (I) and (II).

The ring structure of D-mannosan was found through its oxidation by per-iodic acid or by sodium metaperiodate. One mole of it (II) reduced two moles of HIO_4 to HIO_3 and thereby generated one mole of formic acid and one mole of a non-crystalline dialdehyde (III), which has the same rotation as, and is apparently identical with, the amorphous dialdehyde from similar oxidations of D-glucosan$<1,5>\beta<1,6>$[5] and D-altrosan-$<1,5>\beta<1,6>$.[6] The oxidation of this dialdehyde from D-mannosan with bromine water and strontium carbonate gave the customary yield of pure crystalline strontium L′-oxy-D-methylene diglycolate (IV), the same salt that had previously been obtained from the D-glucosan[5] and D-altrosan.[6] This result proves that these three hexose anhydrides possess the same structure and the same α,β configuration of their rings; the D-mannosan from vegetable ivory is therefore D-mannosan$<1,5>\beta<1,6>$. The oxidation of D-mannosan with per-iodic acid follows quantitatively the equation $C_6H_{10}O_5$ (II) + $2HIO_4$ = H_2O + HCOOH + $C_5H_6O_4$ (III) + $2HIO_3$.

Acetone-D-mannosan (I) possesses only one free hyroxyl group; by customary reactions it readily yields a mono-acetate (Va), a mono-benzoate (Vb), a mono-tosylate (Vc), and a mono-methyl ether (Vd), all of them crystalline compounds. Hydrolysis of the last named substance (Vd) with hot *N* hydrochloric acid to consant rotation (four hours) generates a reducing sugar which yields the known 4-methyl-D-glucose phenylosazone of Shinle.[7] The free hydroxyl group of acetone-D-mannosan (I) is therefore on carbon atom four and consequently the acetone is attached to carbons two and three. The formulas of the monoacyl derivatives (Va, b, c) follow obviously.

The three hydroxyl groups of D-mannosan (II) can be acylated without difficulty; the triacetate (VIa), which Zemplén, Gerecs and Valatin[1] have described, the tribenzoate (VIb) and the tritosylate (VIc) are characteristic crystalline esters.

Acetone-D-mannosan (I), which is so readily available, is a useful new substance for various syntheses because its only free hydroxyl group is attached to carbon atom 4, a position of special importance on account of the 4-linkage that is present in many naturally occurring carbohydrates (maltose, lactose, starch, cellulose, etc.). It reacts, though rather slowly, with acetobromoglucose to give in fair yield the crystalline 4-[tetraacetyl-β-D-glucopyranosido]-2,3-isopropylidene-D-mannosan$<1,5>\beta<1,6>$ which will be described in a later article. Work is in progress in an effort to transform this substance by obvious customary reactions to the epimer of cellobiose, namely, 4-[β-D-glucopyranosido]-D-mannose.

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(3) It is known that acetaldehyde catalyzes the condensation of acetone with sugars (K. Freudenberg, Dürr and Hochstetter, *Ber.*, **61**, 174 (1928)); the pyrolysis distillate contains organic acids and doubtless also carbonyl compounds (furfural, etc.).

(4) Zemplén, Gerecs and Valatin (ref. 1) acetylated the purified sirup from their pyrolyses of vegetable ivory and crystallized the triacetate of D-mannosan (VIa) in a yield of about 2.5%.

(5) Jackson and Hudson, This Journal, **62**, 958 (1940).

(6) Richtmyer and Hudson, *ibid.*, **62**, 961 (1940).

(7) Shinle, *Ber.*, **65**, 317 (1932).

The 4-methyl-D-mannose, which has been mentioned previously as giving rise to 4-methyl-D-glucose phenylosazone, has been crystallized as an alpha form, doubtless a pyranose, showing large mutarotation in water. Other syntheses from acetone-D-mannosan, including that of the epimer of lactose, are also in view.

Experimental

Acetone-D-Mannosan (2,3-Isopropylidene-D-mannosan<1,5>β<1,6> (I)) from Vegetable Ivory.—One hundred grams of vegetable ivory meal in a one-liter round-bottom short-neck Pyrex flask was heated with the luminous flame of a Meker burner and the volatile products were led through an outlet tube of sufficient diameter to prevent its becoming plugged, into a two-liter round-bottom flask cooled in an ice-bath. The scale figure shows the apparatus accurately. The connection to the pyrolysis flask was made with a cork stopper which had been rendered nearly gas tight with sodium silicate solution; renewal of the stopper is required after a few runs. The outlet of the system was connected to a water pump, the pressure was 15–20 mm. and the distillation required about forty minutes. The combined dark colored distillate from six such runs was dissolved, except for some tar, in 300 cc. of water and the solution was filtered successively through 20 g. of filter cel and 90 g. of decolorizing carbon, using 13-cm. Büchner funnels. The straw colored filtrate was concentrated under reduced pressure to a thick sirup which was brought into solution by the gradual addition of 500 cc. of acetone, the last part of which caused clouding. After standing overnight the clear acetone solution was decanted from a small amount of a sirupy deposit and was shaken with 50 g. of anhydrous copper sulfate for twenty-four hours. The copper sulfate was removed and the solution concentrated to a magma of crystals, which was triturated with 25 cc. of absolute isopropyl alcohol and the crystals filtered off and washed with isopropyl alcohol until the washings were colorless; yield 50 g. (8.3% of the meal). The crude acetone-D-mannosan, which is nearly pure, was readily recrystallized from four parts of isopropyl or *n*-butyl alcohol as elongated prisms which melted at 161–162° (cor.) and showed a rotation[8] of −58.8° (*c*, 2.08) in water.

Anal. Calcd. for $C_9H_{14}O_5$: C, 53.46; H, 6.98; combined acetone,[9] 28.7. Found: C, 53.72; H, 6.97; combined acetone, 28.2.

The Hydrolysis of Acetone-D-mannosan to D-Mannosan (II).—A solution of 30 g. of acetone-D-mannosan in 500 cc. of 0.1 *N* sulfuric acid was allowed to stand for twenty-four hours at 20°, during which period it changed in rotation from −59° to a constant value of −101°, equivalent to a rotation of −126° for D-mannosan. The fact that the solution was free of reducing power indicated that the β<1,6> ring was not ruptured under these experimental conditions. After removal of the sulfuric acid as barium sulfate the solution was concentrated *in vacuo* to a dry sirup. Crystalline D-mannosan separated in a yield of 22 g. (91%) upon cooling a solution of the sirup in 450 cc. of hot ethyl acetate. Pure D-mannosan<1,5>β<1,6> melting at 210–211° (cor.) and rotating −127.6° in water (*c*, 1.5) was obtained by recrystallization from two parts of absolute alcohol or twenty parts of ethyl acetate. The mannosan is readily soluble in water, but insoluble in ether.

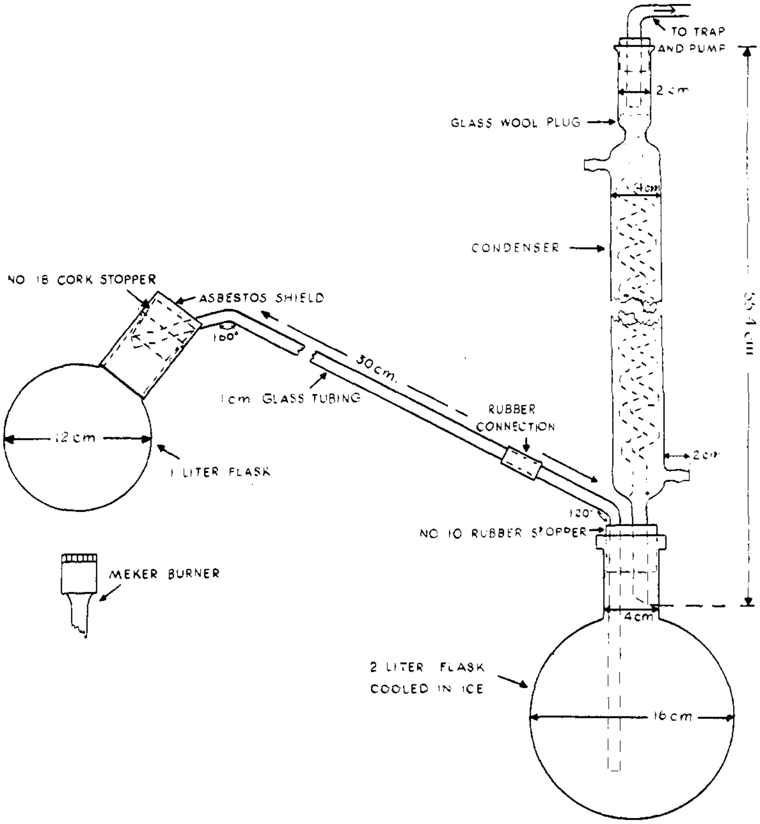

Fig. 1.

Anal. Calcd. for $C_6H_{10}O_5$: C, 44.44; H, 6.22. Found: C, 44.50; H, 6.28.

Hydrolysis of Acetone-D-mannosan and of D-Mannosan to D-Mannose.—(a) A solution of 0.5195 g. of acetone-D-mannosan in 50 cc. of 3% aqueous hydrochloric acid was heated for four hours on the steam-bath, at which time its rotation had become constant at +11.7° which corresponds to a rotation of +13.1° for a hexose, a value near that of D-mannose (+14.6°). From the hydrolyzed solution D-mannose phenylhydrazone was isolated and characterized by its melting point, mixed melting point with an

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(8) All rotations are specific rotations at 20° for the D-line of sodium, *c* is the concentration in grams in 100 cc. of solution, and the tube length was 4 dm. Each of the new substances was recrystallized to constant rotation.

(9) Elsner, *Ber.*, **61**, 2364 (1928).

authentic sample, and rotation in pyridine. (b) A solution of 0.6068 g. of D-mannosan in 50 cc. of *N* hydrochloric acid changed in rotation from −127.0° to a constant value of +12.8°, the latter calculated as D-mannose, upon heating for two hours on the steam-bath. From the strongly reducing hydrolyzate D-mannose phenylhydrazone was isolated in a yield of 0.8 g. (79%).

Conversion of Acetone-D-mannosan and of D-Mannosan to α-Methyl-D-mannopyranoside.—(a) A solution of 2.0 g. of acetone-D-mannosan in 35 cc. of 5% methyl alcoholic hydrochloric acid was refluxed for eight hours, the hydrochloric acid was removed with silver carbonate, and the residual solution was concentrated to crystallization. Upon recrystallization α-methyl-D-mannopyranoside melting at 193–194° (cor.) and rotating +79.1° (*c*, 1.04) in water was obtained in a yield of 1.5 g. (77%). (b) A similar experiment employing 1.62 g. of D-mannosan gave 1.6 g. of α-methyl-D-mannopyranoside (82%).

The Per-iodic Acid Oxidation of Acetone-D-mannosan.—To a solution of 1.3 g. of acetone-D-mannosan in 15 cc. of water, 30 cc. of 0.451 *M* aqueous per-iodic acid (2.10 molecular equivalents) was added and the solution adjusted to a volume of 50 cc. Over a period of twenty-two hours at 20° the rotation of the solution, calculated for acetone-D-mannosan, had changed from −55.6° to a constant value of −9.2°. A titration of an aliquot of the oxidized solution indicated that 2.02 moles of per-iodic acid had been consumed; evidently the ketal is hydrolyzed by the acidity of the solution, as would be expected, and the resulting D-mannosan is then oxidized normally. The latter rotation, assuming that the acetone-D-mannosan had been converted completely to L′-oxy-D-methylene-diglycolic aldehyde (III) would correspond to a rotation of −14.2° for the aldehyde, a value in good agreement with those obtained by Jackson and Hudson[5] from the per-iodic acid oxidation of levoglucosan (−15.0°) and Richtmyer and Hudson[6] from the similar oxidation of D-altrosan (−14.5°; −14.9°). A solution containing the aldehyde from 1.556 g. of acetone-D-mannosan was further oxidized by the methods employed by these workers and strontium L′-oxy-D-methylene-diglycolate trihydrate (IV)[10] was obtained in a yield of 1.1 g. (47%). When 0.5905 g. of the trihydrate was dissolved in 25 cc. of *N* hydrochloric acid the rotation of the resulting solution of free L′-oxy-D-methylene-diglycolic acid was +7.8°, in close agreement with the values of +8.0° and +7.9° that are known from the studies on levoglucosan and D-altrosan, respectively.

The Per-iodic Acid Oxidation of D-Mannosan.—To a solution of 0.5118 g. of D-mannosan in 12.5 cc. of water, 12.5 cc. of 0.5305 *M* per-iodic acid (2.10 molecular equivalents) was added. After twenty-four hours the rotation of the solution, calculated from the aldehyde content, was −13.2° and an analysis indicated that two moles of oxidant had been consumed.

The Sodium Metaperiodate Oxidation of D-Mannosan.—A sample of 0.5244 g. of D-mannosan was dissolved in 15 cc. of 0.453 *M* aqueous sodium metaperiodate (2.10 molecular equivalents) and the volume adjusted to 25 cc. After twenty-four hours the rotation of the solution, calculated for the aldehyde content, was −13.9° and titration of 5 cc. aliquots indicated that 1.98 moles of oxidizing agent had been consumed and 1.00 mole of formic acid had been produced.

Mono-acyl Derivatives of Acetone-D-mannosan.—(a) A solution of 4.04 g. of acetone-D-mannosan in a mixture of 12 cc. of pyridine and 12 cc. of acetic anhydride was allowed to stand overnight at room temperature and then poured into ice and water, when the **2,3-isopropylidene-4-acetyl-D-mannosan<1,5>β<1,6>** (**Va**) crystallized in a yield of 4.2 g. (86%). After recrystallization from three parts of methyl alcohol it was obtained in plates which melted at 101–102° (cor.) and rotated −72.2° (*c*, 1.6) in chloroform.

Anal. Calcd. for $C_{10}H_{16}O_6$: C, 54.09; H, 6.60; CH_3CO, 17.6. Found: C, 54.20; H, 6.77; CH_3CO, 17.9.

(b) **2,3-Isopropylidene-4-benzoyl-D-mannosan<1,5>β<1,6>** (**Vb**) was obtained in quantitative yield upon benzoylation of acetone-D-mannosan with pyridine and benzoyl chloride. It was recrystallized from ten parts of methyl alcohol as plates which melted at 134–135° (cor.) and rotated −103.5° (*c*, 1.4) in chloroform.

Anal. Calcd. for $C_{16}H_{18}O_6$: C, 62.73; H, 5.92; C_6H_5CO, 34.3. Found: C, 62.73; H, 5.94; C_6H_5CO, 34.8.

(c) **2,3-Isopropylidene-4-tosyl-D-mannosan<1,5>β<1,6>** (**Vc**) was obtained in quantitative yield by the action of tosyl chloride and pyridine on acetone-D-mannosan. It was crystallized from fifteen parts of methyl alcohol and separated in plates which melted at 144–145° (cor.) and rotated −39.8° (*c*, 1.17) in chloroform.

Anal. Calcd. for $C_{16}H_{20}O_7S$: C, 53.92; H, 5.66. Found: C, 53.94; H, 5.58.

2,3-Isopropylidene-4-methyl-D-mannosan<1,5>β<1,6> (**Vd**).—An acetone (25 cc.) solution of acetone-D-mannosan (25 g.) was refluxed with methyl iodide (25 cc.), drierite (25 g.) and silver oxide (45 g.) for twelve hours. The silver oxide was added in four equal portions at fifteen-minute intervals during the first hour. The solids were removed by filtration and the filtrate was concentrated to a sirup, which was dissolved in 20 cc. of ether and brought to crystallization by the addition of 60 cc. of iso-pentane, yield 17 g. (64%). Recrystallization from one part of ether by addition of three parts of isopentane gave pure 2,3-isopropylidene-4-methyl-D-mannosan<1,5>β<1,6> which melted at 53–54° and rotated −33.4° (*c*, 1.2) in chloroform.

Anal. Calcd. for $C_{10}H_{16}O_5$: C, 55.54; H, 7.46; OCH_3, 14.35. Found: C, 55.64; H, 7.54; OCH_3, 14.39.

4-Methyl-D-glucose Phenylosazone from 2,3-Isopropylidene-4-methyl-D-mannosan<1,5>β<1,6> (Vd).—A solution of 2 g. of the methyl-acetone-D-mannosan in 50 cc. of *N* hydrochloric acid, upon heating for four hours on the steam-bath, changed in rotation from −95.2° to a constant value of +16.9°, equivalent to a rotation of +18.8° for 4-methyl-D-mannose. Following removal of the hydrochloric acid as silver chloride, the solution was concentrated to a volume of 25 cc. and heated on a steam-bath for one hour with 3.5 cc. of phenylhydrazine and 3 cc. of glacial acetic acid. The 4-methyl-D-glucose phenylosazone (1.6 g., 47%) which

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[10] It has been observed that the water of hydration of strontium L′-oxy-D-methylene-diglycolate varies markedly depending upon atmospheric conditions. Stable mono-, tri-, tetra-, and pentahydrates analyzing correctly for strontium and water content and exhibiting correct rotations when calculated on the anhydrous basis, have been obtained.

separated on cooling was recrystallized from thirty parts of 50% acetone. It melted at 158–159° (cor.) and its alcoholic solution (*c*, 0.91) changed in rotation from −36.0° to −14.4° in twenty-one hours. Shinle[7] reports a melting point of 160° and a rotation change of −32.6° to −15.5° for the substance. The steps which are here described for preparing this useful reference osazone from the readily available acetone-D-mannosan involve much less labor than do those which have been necessary before in making it from glucose.

Anal. Calcd. for $C_{19}H_{24}O_4N_4$: C, 61.23; H, 6.49; OCH_3, 8.33. Found: C, 61.19; H, 6.63; OCH_3, 8.21.

Tri-acyl Derivatives of D-Mannosan.—(a) To an ice-cold solution of 5 g. of D-mannosan in 30 cc. of pyridine, 20 cc. of acetic anhydride was added and the solution allowed to stand overnight. The reaction mixture was poured into ice, extracted with chloroform and the extract concentrated to a sirup which was dissolved in 20 cc. of absolute alcohol. From the alcohol solution 6.8 g. (77%) of **2,3,4-tri-acetyl-D-mannosan<1,5>β<1,6>** (VIa) was obtained. Upon recrystallization from four parts of alcohol it separated in clusters of prismatic needles which melted at 90–91° (cor.) and rotated −123.6° (*c*, 1.79) in chloroform. Zemplén, Gerecs and Valatin[1] record a melting point of 86° and a rotation of −124.1° in chloroform.

Anal. Calcd. for $C_{12}H_{16}O_8$: C, 50.00; H, 5.60; CH_3CO, 44.8. Found: C, 50.04; H, 5.55; CH_3CO, 44.9.

(b) A solution of 5 g. of D-mannosan in a mixture of 40 cc. of pyridine and 14 cc. of benzoyl chloride (3.9 moles) was heated for one hour on the steam-bath. When the cooled solution was diluted with 100 cc. of water and 15 g. of sodium bicarbonate was added, crystallization of 14.5 g. (quantitative) of **2,3,4-tribenzoyl-D-mannosan<1,5>β<1,6>** (VIb) took place. It separated from its solution in eight parts of absolute alcohol in flat prisms which melted at 111–112° (cor.) and rotated −185.2° (*c*, 1.32) in chloroform.

Anal. Calcd. for $C_{27}H_{22}O_8$: C, 68.37; H, 4.67. Found: C, 68.30; H, 4.76.

(c) A solution of 1.62 g. of D-mannosan in 16 cc. of pyridine was cooled in ice and salt and 6.5 g. of *p*-toluene-sulfonyl chloride was added in portions. After reaching room temperature the reaction mixture was placed in an oven at 40° for forty-eight hours and then poured into 5% sodium bicarbonate solution, when **2,3,4-tritosyl-D-mannosan<1,5>β<1,6>** (VIc) separated in a yield of 6.2 g. (quantitative). The compound was recrystallized from 10 parts of 80% acetic acid in long needles which melted at 207–208° (cor.) and rotated +29.7° (*c*, 1.5) in chloroform.

Anal. Calcd. for $C_{27}H_{28}O_{11}S_3$: C, 51.91: H, 4.52. Found: C, 51.89; H, 4.72.

Thanks are expressed to Dr. Ernest L. Jackson for performing the per-iodic acid oxidations and to Dr. W. T. Haskins for making the microchemical analyses.

Summary

The pyrolysis of vegetable ivory under reduced pressure produces a water-soluble sirup from which, after its condensation with acetone, the new acetone-D-mannosan crystallizes in a yield of 8.3%. Mild treatment of this with aqueous acid removes the acetone and leads to crystalline D-mannosan<1,5>β<1,6>; the structure and configuration have been established by its conversion to D-mannose through full acid hydrolysis, and by its oxidation with per-iodic acid, which leads through customary reactions to the same strontium L′-oxy-D-methylene-diglycolate that has been obtained similarly from D-glucosan<1,5>β<1,6> (levoglucosan) and from D-altrosan<1,5>β<1,6>. The mannosan is thus the epimer of levoglucosan. Acetone-D-mannosan yields a crystalline mono-methyl ether, from which, after acid hydrolysis of the acetone group and the 1,6-ring, the known 4-methyl-D-glucose phenylosazone was prepared; the acetone is therefore attached to carbon atoms 2 and 3. Crystalline mono-acetyl, benzoyl and tosyl esters of acetone-D-mannosan and crystalline tri-acetyl, benzoyl and tosyl esters of D-mannosan are described. The relationship of our work to that which was published last year by Zemplén, Gerecs and Valatin[1] on the pyrolysis of vegetable ivory, is made clear. The new acetone-D-mannosan is a readily available substance which gives promise of extended usefulness in syntheses, particularly in those of disaccharides possessing the 4-linkage.

WASHINGTON, D. C. RECEIVED MARCH 25, 1941