and air-dried; yield 3.7 g. (55%). Recrystallization from methanol–chloroform–dioxane, or chloroform–petroleum ether (b.p. 30–60°) gave the analytically pure, orange-yellow nitrone, m.p. 192–194° (KHS).

Anal. Calcd. for $C_{15}H_{16}N_2O_4$: C, 62.50; H, 5.55; N, 9.73. Found: C, 62.18; H, 5.58; N, 9.98.

2 - (Hydroxymethyl) - 5 - methoxy - 4*H* - pyran-4-one (VII).—This substance was prepared by the method of Campbell and co-workers[6]; m.p. 159.5–161° (lit.,[6] m.p. 161°).

Comenaldehyde Methyl Ether (2-Formyl-5-methoxy-4*H*-pyran-4-one) (V). Method 1.—A 14-g. quantity of (5-methoxy-4*H*-pyran-4-on-2-yl)-*N*-(*p*-dimethylaminophenyl)-nitrone was suspended in 60 ml. of ice water mixture. To the well stirred mixture, cold cond. sulfuric acid was added dropwise until a color change from dark orange to light yellow occurred, and the aldehyde separated as a fine precipitate. Then an additional 20 ml. of sulfuric acid was added. The aldehyde was collected by filtration, and from chloroform extracts of the reaction mixture by solvent evaporation. Total yield of aldehyde ranged from 0.3 to 0.7 g., m.p. 202–203°. Analytically pure, colorless comenaldehyde methyl ether, m.p. 206–208°, was obtained by sublimation *in vacuo*.

Anal. Calcd. for $C_7H_6O_4$: C, 54.54; H, 3.90. Found: C, 54.53; H, 4.09.

Method 2.—A 4-g. quantity of freshly recrystallized 2-(hydroxymethyl)-5-methoxy-4*H*-pyran-4-one was dissolved in 300 ml. of *t*-butyl alcohol by gentle heating. To the cooled solution was added 16 g. of manganese dioxide catalyst, prepared from manganous carbonate by the method of Harfenist and co-workers.[7] The mixture was shaken on a platform shaker at room temperature for 8 days. Catalyst and inorganic by-products were removed by centrifugation in a high speed, automatic ultracentrifuge at 12,000 r.p.m. for 10 min. The combined decantates were distilled to near-dryness in a flash evaporator. Addition of 30 ml. of absolute ethanol, heating to boiling, cooling slightly, and addition of petroleum ether (b.p. 30–60°), gave a cloudy solution, which was permitted to stand in a refrigerator overnight. The white aldehyde was collected by filtration; yield, 2.5 g. (60%). The aldehyde was precipitated from chloroform–petroleum ether (b.p. 30–60°), or ethanol–petroleum ether (b.p. 30–60°) to give the substance, m.p. 196–199°. Vacuum sublimation gave the aldehyde, m.p. 205–206°, infrared spectrum identical with that of substance in method 1. The infrared spectrum (potassium bromide disk) contained absorption bands at 3100, 3050, 2950, 2900, 1705, 1655, 1620, 1594, 1495, 1435, 1408, 1295, 1235, 1190, 1165, 995, 935, 905, 870, and 810 cm.$^{-1}$.

Thiosemicarbazone of Comenaldehyde Methyl Ether.—Water was added to 1 g. of comenaldehyde methyl ether in absolute ethanol to faint turbidity, which was then removed with ethanol. To this solution, 1 g. of thiosemicarbazide and 1.5 g. of sodium acetate were added. The reaction mixture was shaken vigorously, placed in boiling water, and then allowed to cool. The thiosemicarbazone was collected by filtration; yield, 1.2 g. (60%). Recrystallization from ethanol–benzene gave analytically pure comenaldehyde methyl ether thiosemicarbazone, m.p. 244.5–246° (KHS).

Anal. Calcd. for $C_8H_9N_3O_3S$: C, 42.29; H, 4.00; N, 18.50. Found: C, 42.45; H, 4.22; N, 18.53.

Comenic Acid Methyl Ether.—A 1-g. quantity of comenaldehyde methyl ether was oxidized by the method of Campaigne and LeSuer[8] to give comenic acid methyl ether, m.p. 277–280° (lit.,[5] m.p. 280–282°); yield, 0.8 g. (75%). Mixture melting point with comenic acid methyl ether prepared by an independent synthesis showed no significant depression.

***p*-Dimethylaminoanil of Comenaldehyde Methyl Ether (IX).**—To 2 g. of comenaldehyde methyl ether in 25 ml. absolute ethanol was added 2.42 g. of *N*,*N*-dimethyl-*p*-phenylenediamine hydrochloride in 10 ml. of water. Additional ethanol was added to prevent the aldehyde from crystallizing. Then 20 ml. of 1 *N* sodium hydroxide were added dropwise to the cooled, stirred solution. A color change from grayish brown to red occurred, and the reddish orange anil precipitated after *ca.* 0.5 hr. The anil was collected and dried *in vacuo;* yield, 2 g. (45%). After recrystallization from absolute ethanol the m.p. was 177.0–177.5° (KHS).

Anal. Calcd. for $C_{15}H_{16}N_2O_3$: C, 66.44; H, 6.20; N, 10.47. Found: C, 66.18; H, 5.88; N, 10.30.

During heating of the sample on the hot stage, a crysta phase transition was noted at 165° (from wide large needles to short thin needles). Mixture melting point with (5-methoxy-4*H*-pyran-4-on-2-yl)-*N*-(*p*-dimethylaminophenyl)-nitrone was 164–167°.

Addition Polymerization of Anhydro Sugar Derivatives. V. Preparation and Attempted Polymerization of Various Levoglucosan Derivatives

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Received November 6, 1961

In a reinvestigation[1,2] of Pictet's[3] polymerization of levoglucosan it has been shown that highly branched glucans primarily linked to the number 6- and to a lesser degree to the 2,4- and probably 3-positions were formed. Both α- and β-anomeric forms have been shown to be present.[4,5]

The present investigation was undertaken to study the mechanism of polymerization of substituted levoglucosans and to ascertain the nature of any polymer formed. Three new derivatives of levoglucosan: 1,6-anhydro-β-D-glucopyranose 2,3,4-trinitrate; 1,6-anhydro-2,3,4-tri-*O*-mesyl-β-D-glucopyranose; and 1,6-anhydro-2,3,4-tri-*O*-tosyl-β-D-glucopyranose were prepared along with two known derivatives, *viz.*: 1,6-anhydro-2,3,4-tri-*O*-methyl-β-D-glucopyranose[6] and 1,6-anhydro-2,3,4-tri-*O*-acetyl-β-D-glucopyranose.[7]

The attempted polymerization of 1,6-anhydro-2,3,4-tri-*O*-methyl and 1,6-anhydro-2,3,4-tri-*O*-acetyl

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compounds was first carried out with a number of catalysts under different conditions (mentioned in the experimental part) and with several polyfunctional initiators including ethylene glycol, pentaerythritol, and glycerol. In general, either decomposition took place or unchanged monomer was recovered.

A number of explanations for this unreactivity can be given, the most obvious of which is steric hindrance. However, it seemed to us that reaction with a primary alcohol should be possible and we therefore considered another explanation: The attack of a hydroxyl on the C-1 carbon atom is probably ineffective unless the latter center is activated at the same time by the presence of a proton on the anhydro or pyranose ring oxygen. Since there are several other oxygen functions that have basic properties in both the triacetate and trimethyl ether of levoglucosan, the probability of finding a proton on the proper site when hydroxyl in another molecule attacks is not high. The basicity of nitrate and mesylate ester oxygens is substantially less than that of an acetal oxygen and the latter site should therefore compete effectively for a proton on those derivatives with the electronegative substituents. Thus, the probability of an effective collision between these protonated levoglucosan derivatives and an alcohol should be greater. Nevertheless, again only unchanged monomer or decomposition products were recovered. This result, therefore, extends the observation of Bhattacharya and Schuerch[8] that those 1,6-anhydro sugars that have been found to polymerize do so *via* a 1,2-anhydro intermediate.

The properties of the three new derivatives are given below.

This investigation has been supported by research grant RG-6168 from the Division of General Medical Sciences, National Institutes of Health.

Experimental

All specific rotations are equilibrium values and were determined at 20°. Melting points are corrected. Evaporations were carried out *in vacuo* at 40–45°.

Preparation of 1,6-Anhydro-2,3,4-trinitro-β-D-glucopyranose [cf. (9)].—Levoglucosan (10 g.) was suspended in acetic anhydride (25 ml.) and cooled to 0° in an ice bath. To this a nitrating mixture (50 ml. of acetic anhydride and 20 ml. of concentrated nitric acid cooled in ice bath) was added gradually at 0°. The reaction mixture was allowed to stand for an hour and then poured into a large volume of ice cold water and ethyl acetate mixture (1:1). The ethyl acetate layer was separated, treated with saturated sodium bicarbonate solution, washed with a large volume of cold water, dried over anhydrous sodium sulfate, and evaporated to a suitable volume. 2,3,4-Trinitrolevoglucosan was crystallized from ethyl acetate and after recrystallization had m.p. 94–95°, $[\alpha]^{20}D = -74°$ (*c* 2.7, chloroform).

Anal. Calcd. for $C_6H_7N_3O_{11}$: C, 24.3; H, 2.6; N, 14.1. Found: C, 24.3; H, 3.0; N, 13.2.

Preparation of 1,6-Anhydro-2,3,4-tri-*O*-mesyl-β-D-glucopyranose.[10]—Levoglucosan (10 g.) was dissolved in pyridine (25 ml.). To this an ice cold mixture of methanesulfonyl chloride (35 g.) in anhydrous chloroform (10 ml.) was added gradually with occasional shalking at 0°. The mixture was allowed to stand for an hour in an ice bath and for 24 hr. at room temperature. After this, water (5 ml.) was added and the solution was allowed to stand for 0.5 hr. More chloroform was added and then the chloroform layer was separated, washed with ice cold water, sulfuric acid (2%), bicarbonate, and water as needed, dried over anhydrous sodium sulfate, and evaporated to a suitable volume. The trimesyl derivative crystallized from chloroform and recrystallized from acetone had the m.p. 170–171°, $[\alpha]^{20}D = -3.2°$ (*c* 2.9, acetone).

Anal. Calcd. for $C_9H_{16}S_3O_{11}$: C, 27.7; H, 4.0; S, 24.2. Found: C, 27.7; H, 3.96; S, 23.6.

Preparation of 1,6-Anhydro-2,3,4-tri-*O*-tosyl-β-D-glucopyranose.[10]—This compound was prepared in the same way as the trimesyl derivative except for a longer period of cooking (72 hr.) with *p*-toluenesulfonyl chloride. When crystallized from acetone it had the m.p. 115–117°, $[\alpha]^{20}D = -15.3°$ (*c* 10, chloroform).

Anal. Calcd. S, 15.7. Found: S, 15.3.

Preparation of 1,6-Anhydro-2,3,4-tri-*O*-methyl- and 1,6-Anhydro-2,3,4-tri-*O*-acetyl-β-D-glucopyranose.—These compounds were prepared by published conventional methods. The methyl ether[6] had m.p. 63–64° and $[\alpha]^{20}D = -63.7°$ (*c* 2, water). The acetyl derivative[7] had a m.p. 109–110° and $[\alpha]^{20}D = -45.6°$ (*c* 2, alcohol).

Attempted Polymerizations of Substituted Levoglucosans.—Attempted polymerization was carried out as described by Carvalho, Prins, and Schuerch[2] but on a smaller scale. In the case of the nitro derivative, attempted polymerization was carried out in a tube with a narrow capillary opening instead of a sealed tube because of the danger of explosion from evolving gases. The catalysts used for the nitro and mesyl derivatives were trifluoroacetic acid, monochloroacetic acid, anhydrous zinc chloride, anhydrous aluminum chloride, sulfuric acid, antimony pentachloride, and phosphorus pentachloride and phosphorus pentafluoride. These were usually present to the extent of about 2–5% by weight and a number of alcohols including butanol-1, benzyl alcohol, ethylene glycol, and glycerol in about 2 mole % were present as initiators. The reaction was allowed to continue for 1–5 days over a temperature range of room temperature to 95°; and from 5 min. to 2 hr. at 168–170° in the case of nitro and mesyl derivatives, respectively. Attempted polymerization of the tri-*O*-methyl derivative was carried out with the following catalysts: platinum black, iodine crystals, aluminum chloride in nitrobenzene, boron trifluoride etherate in tetrahydrofuran, stannic iodide, zinc bromide, anhydrous zinc chloride, potassium hydroxide, sodium hydroxide, and sodium methylate. The polymerization temperature was varied from room temperature to 180° and the time from 1 hr. to 350 hr. For the tri-*O*-acetyl derivative the following catalysts were used: acid washed alumina, bentonite powder, iodine crystals, pumice powder, bismuth trichloride, calcium chloride, stannic iodide, zinc bromide, zinc chloride, trifluoroacetic acid, and phosphoric anhydride.

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