the Duolite A-4 column. Paper chromatographic examination of the sirup showed some D-*glycero*-D-*gulo*-octulose but no evidence of any unchanged octose.

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New Syntheses of Comenaldehyde Methyl Ether[1]

J. H. LOOKER and DUANE SHANEYFELT

Avery Laboratory, The University of Nebraska, Lincoln, Neb.

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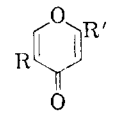
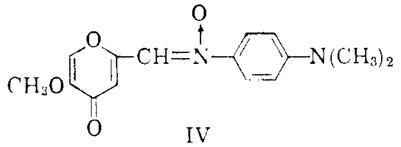
Recent interest has been shown in the synthesis of aldehydes containing the monocyclic γ-pyrone (4*H*-pyran-4-one) nucleus.[2,3] One report involves the preparation of the methyl ether of comenaldehyde (V) by oxidation of the carbinol VII.[3] We report the synthesis of V by two independent routes: from I *via* II, III, and IV in the Kröhnke aldehyde synthesis,[4] and from VII by manganese dioxide oxidation.

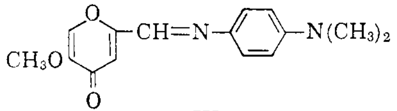
Methylation of chlorokojic acid (I) by the method of Yabuta[5] gave II. Interaction of II with pyridine at room temperature gave the very hygroscopic pyridinium salt III. Reaction of III and *p*-nitroso - *N*,*N* - dimethylaniline in cold aqueous ethanolic sodium hydroxide led to the orange-yellow nitrone IV. Hydrolysis of IV in cold sulfuric acid gave, in low yield, the colorless comenaldehyde methyl ether (V), m.p. 202–203°, raised after purification by sublimation *in vacuo* to 206–208°. The infrared spectrum of V contained the aldehyde carbonyl stretching band at 1705 (potassium bromide disk) and 1718 cm.$^{-1}$ (chloroform solution). In the potassium bromide disk spectrum, the pyrone carbonyl band was at 1655 cm.$^{-1}$.

Selective methylation of the enolic hydroxyl group of kojic acid (VI) by the method of Campbell[6] yielded the carbinol VII. Oxidation of VII to the aldehyde V was carried out in *t*-butyl alcohol solution by manganese dioxide, prepared from manganous carbonate by the method of Harfenist,[7] at room temperature for eight days. Yield of V, m.p. 205–206°, was 55–60%. This oxidation procedure differs from that of Becker[3] in method for preparation of manganese dioxide, temperature, solvent, and reaction period.





IV



IX

I. R = OH; R′ = CH_2Cl
II. R = OCH_3; R′ = CH_2Cl
III. R = OCH_3; R′ = $[(CH_2\overset{+}{N}C_5H_5)Cl^-]$
V. R = OCH_3; R′ = CHO
VI. R = OH; R′ = CH_2OH
VII. R = OCH_3; R′ = CH_2OH
VIII. R = OCH_3; R′ = COOH

The aldehyde V was characterized as a thiosemicarbazone, m.p. 244.5–246°, and as the anil IX, m.p. 177–177.5°. Silver oxide oxidation of V by the method of Campaigne and LeSuer[8] gave comenic acid methyl ether (VIII). Comparison of the properties of IV and IX shows that the nitrone, not the anil, is the intermediate in the preparation of V by the Kröhnke reaction.

Experimental

Melting points are uncorrected and were observed by the capillary tube method unless indicated by KHS, in which case Kofler hot stage was used. Analyses are by Micro-Tech Laboratories, Skokie, Ill., and Alfred Bernhardt, Mülheim, Germany.

Chlorokojic Acid Methyl Ether [2-(Chloromethyl)-5-methoxy-4*H*-pyran-4-one] (II).—This substance was prepared by the procedure of Yabuta[5]; m.p. 119-120° (lit.,[5] m.p. 119-121°).

(5-Methoxy-4*H*-pyran-4-on-2-yl)methyl Pyridinium Chloride (III).—A 9-g. quantity of very dry chlorokojic acid methyl ether in 150 ml. of pyridine (previously dried over potassium hydroxide) stood in a tightly stoppered flask for 24 hr. The pyridinium salt formed was collected by filtration, transferred immediately to a vacuum desiccator, and dried over concd. sulfuric acid; yield 12 g. (90%). Recrystallization from absolute ethanol–ether gave the analytically pure pyridinium salt (extremely hygroscopic), m.p. 200.5–201.5°.

Anal. Calcd. for $C_{12}H_{12}ClNO_3$: C, 56.70; H, 4.73; N, 5.51; Cl, 14.15. Found: C, 56.78; H, 4.95; N, 5.52; Cl, 13.79.

(5-Methoxy-4*H*-pyran-4-on-2-yl)-*N*-(*p*-dimethylaminophenyl)-nitrone (IV).—A solution of 6 g. of pyridinium salt III in 30 ml. of water was added to 3.6 g. of *p*-nitroso-*N*,*N*-dimethylaniline in 45 ml. of ethanol. To this mixture at 5° were added gradually with occasional shaking 25 ml. of 1 *N* sodium hydroxide. Then 200 ml. of ice water mixture were added to complete precipitation of the nitrone. After 1 hr., the crude nitrone was collected, washed with cold water,

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(1) This investigation was supported by a research grant (E-1703) from the National Institute of Allergic and Infectious Diseases, Public Health Service.

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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

A. JABBAR MIAN, EDWIN J. QUINN, AND CONRAD SCHUERCH

Department of Chemistry, State University College of Forestry at Syracuse University, Syracuse 10, N. Y.

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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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