with those used for the acetylation except that one equivalent of benzoyl chloride was used as the acylating agent. The product was crystallized in 15% yield as a brown solid, m.p. 95–102° from the ethanol–ethyl acetate solvent. On recrystallization from ethanol using decolorizing carbon, the pure product was obtained as rosettes of white needles, m.p. 110–111°, $[\alpha]^{25}D$ + 75° (*c* 2.54 in chloroform). Pedersen, *et al.*,[23] report m.p. 110–112°, $[\alpha]^{20}D$ +75.3 (chloroform); Zinner, *et al.*,[24] give 111–111.5°, $[\alpha]^{18}D$ +78° (chloroform).

From the original mother liquor, there was obtained a second crop (7%) of a lower-melting material, m.p. 78–82°. Further recrystallization from ethanol afforded white needles, m.p. 83–86°, $[\alpha]^{25}D$ − 20° (*c* 1.1 in chloroform). Pedersen, *et al.*,[23] found 84–87°, $[\alpha]^{20}D$ − 19.8° (chloroform). This isomer tended to be somewhat hygroscopic, especially in an impure state.

Anal. Calcd. for $C_{26}H_{22}O_7$: acyl. no., 3.0. Found: acyl. no., 3.05.

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF ARIZONA, TUCSON, ARIZ.]

Vinyl Ethers of Carbohydrates. I. Methyl 2-O-Vinyl-α-D-glucopyranoside[1]

BY ARCHIE J. DEUTSCHMAN, JR., AND HENRY W. KIRCHER

RECEIVED MAY 6, 1961

Crystalline methyl 2-*O*-vinyl-α-D-glucopyranoside was isolated as a product of the vinylation of methyl α-D-glucopyranoside with vinyl chloride or with acetylene. The structure of the compound was proved by methylation and hydrolysis to methyl 3,4,6-tri-*O*-methyl-α-D-glucoside and by hydrogenation and hydrolysis to 2-*O*-ethyl-D-glucose.

The preparation of vinyl ethers by the alkali-catalyzed addition of alcohols to acetylene has received considerable study and is the basis for a number of industrial processes. A review of the field[2] lists the preparation and properties of a large number of vinyl ethers derived from primary, secondary and tertiary alcohols.

The preparation of vinyl ethers from polyfunctional alcohols and carbohydrates also has been reported.[2–6] As a rule, the compounds were poorly characterized and, where partial substitution occurred, the positions of the vinyl groups were not established. 3-*O*-Vinyl-1,2;5,6-di-*O*-isopropylidene-D-glucose,[2] 3,5,6-tri-*O*-vinyl-1,2-*O*-isopropylidene-D-glucose[5] and methyl 2,3,4,6-tetra-*O*-vinyl-α-D-glucoside[6] are examples of the vinyl ethers of carbohydrates that have been prepared.

This paper deals with the preparation, isolation and proof of structure of methyl 2-*O*-vinyl-α-D-glucopyranoside (II). The initial vinylations of methyl α-D-glucopyranoside (I) were done with vinyl chloride[2] because facilities for handling acetylene under pressure were not available. Subsequent reactions with acetylene confirmed the results that were observed with vinyl chloride.

The reactions of I with vinyl chloride and sodium hydroxide or with acetylene and catalytic quantities of potassium hydroxide led to water-soluble reaction mixtures. These were mixed with Dry Ice to convert the hydroxides to the carbonates, evaporated to dryness, and extracted with acetone to yield a mixture of several vinylated products. Paper partition chromatography (*vide infra*) showed the presence of at least four vinylated compounds, two of low and two of high R_f. The pattern of spots observed from the acetylene reactions was the same as that observed from the vinyl chloride reactions.

The acetone-soluble portions of several reaction mixtures were redissolved in water and extracted continuously with benzene to yield a fraction that contained the substances of R_f 0.85 and 0.92. Subsequent continuous extraction of the aqueous solution with ether yielded a fraction that contained the components of R_f 0.68 and 0.72. The residual aqueous solution was evaporated to a sirup and extracted with chloroform. The chloroform extract evaporated to a sirup that crystallized upon standing a few days. Nucleation of the ether extract with these crystals caused a portion of it to crystallize. The material melted 122–126.5° after a single recrystallization from acetone, acetonitrile or ether. Recrystallization of this material from acetone gave large prisms, m.p. 126–127.5°, R_f 0.68, $[\alpha]^{25}D$ +136° (water).

The compound had all of the chemical characteristics that one would expect of a methyl mono-*O*-vinyl-α-D-glucopyranoside. It rapidly decolorized bromine and permanganate solutions, it yielded acetaldehyde and methyl α-D-glucopyranoside upon mild acid hydrolysis, and it was readily reduced with hydrogen. The vinyl derivative was methylated to a tri-*O*-methyl derivative (III) whose retention time on gas–liquid partition chromatography was very similar to that of methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucoside[7] (Fig. 1). The product of the methylation was hydrolyzed with dilute acetic acid at room temperature to a methyl tri-*O*-methyl-α-D-glucopyranoside (IV) (Fig. 1).

The four possible methyl tri-*O*-methyl-α,β-D-glucopyranosides were obtained from methylated starch (2,3,6),[7] methylated dextran (2,3,4),[7] 3-*O*-benzyl-D-glucose (2,4,6)[8] and from 3-*O*-methyl-D-glucose (3,4,6).[9] The separation diagrams of the four methyl tri-*O*-methyl-α,β-D-glucopyranosides are shown in Fig. 2.

(1) Presented at the 139th meeting of the A.C.S., St. Louis, Mo., March, 1961.

(2) W. Reppe, *et al.*, *Ann.*, **601**, 81 (1956).

(3) M. F. Shostakovskii, E. N. Prilezhaeva and L. V. Tsymbal, *Doklady Akad. Nauk S.S.S.R.*, **96**, 99 (1954); *C. A.*, **49**, 5312 (1955).

(4) M. F. Shostakovskii, E. N. Prliezhaeva and L. V. Tsymbal, *Zhur. Obshch. Khim.*, **26**, 739 (1956); *C. A.*, **50**, 14564 (1956).

(5) B. I. Mikhant'ev and V. L. Lapenko, *Zhur. Obshch. Khim.*, **27**, 2972, 2840 (1957); *C. A.*, **52**, 8054, 8055 (1958).

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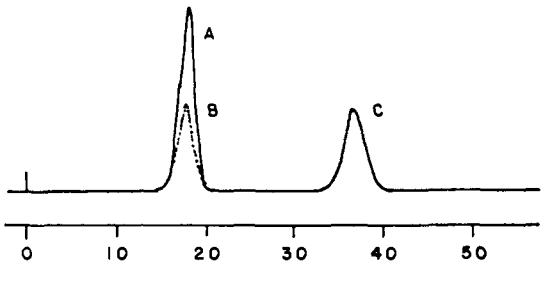
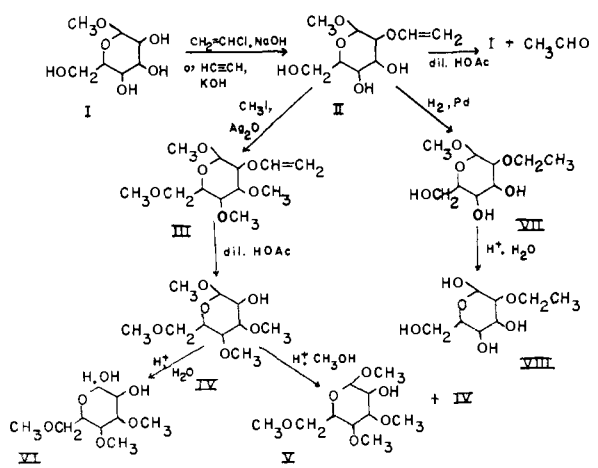


Fig. 1.—Separation diagram showing (200°, 2.04 atm. helium, 77 ml./min.): A, methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucoside; B, methyl *O*-vinyl-tri-*O*-methyl-α-D-glucoside; C, methyl tri-*O*-methyl-α-D-glucoside.

The methyl tri-*O*-methyl-α-D-glucopyranoside obtained from II corresponded in retention time with one of the peaks observed for methyl 3,4,6-tri-*O*-methyl-α,β-D-glucoside on a number of different gas chromatographic columns. Methanolysis of the unknown product to the α,β-mixture of glycosides (IV and V) followed by gas–liquid partition chromatography showed two peaks coincident in relative size and retention time with the two peaks shown by methyl 3,4,6-tri-*O*-methyl-α,β-D-glucoside. This indicated that the vinyl group had been in the two position.

2-*O*-Ethyl-D-glucose was prepared from methyl 3,5,6-tri-*O*-benzyl-α,β-D-glucofuranoside by the procedure outlined for 2-*O*-methyl-D-glucose.[10] It corresponded in both melting point and optical rotation with the *O*-ethyl-D-glucose (VIII) obtained by hydrogenation and hydrolysis of the crystalline methyl *O*-vinyl-α-D-glucoside. The crystalline material obtained from the reaction of methyl α-D-glucopyranoside with vinyl chloride or acetylene was therefore methyl 2-*O*-vinyl-α-D-glucopyranoside (II).



The presence of the three other possible mono-O-vinyl ethers of methyl α-D-glucopyranoside was shown by methylation of the ether extract that contained the components of R_f 0.68 and 0.72. After removal of the vinyl groups with dilute acetic acid, the resulting mixture of methyl tri-*O*-methyl-α-D-glucopyranosides was put through the gas chromatograph. The separation diagram (Fig. 3) showed peaks for methyl 3,4,6-, 2,3,4-, 2,3,6- and 2,4,6-tri-*O*-methyl-α-D-glucopyranoside. This indicated that the 2-, 6-, 4- and 3-O-vinyl ethers of methyl α-D-glucopyranoside were present in the ether extract. The sizes of the peaks in Fig. 3 are proportional to the amounts of each of these components in the mixture.

(10) F. Weygand and O. Trauth, *Chem. Ber.*, **88**, 57 (1952).

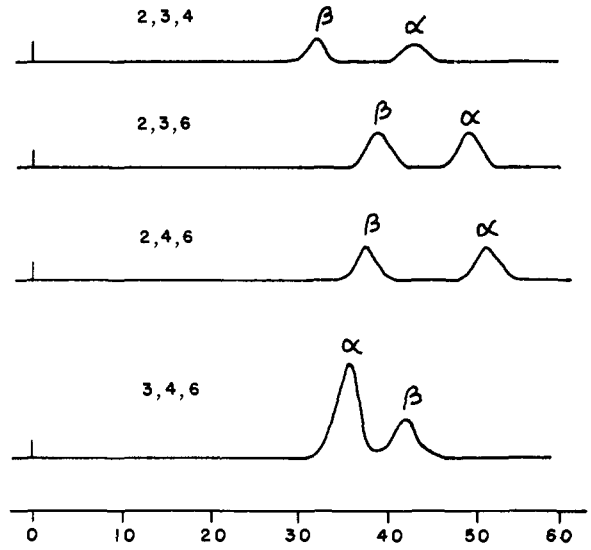


Fig. 2.—Separation diagrams showing the methyl tri-*O*-methyl-α,β-D-glucopyranosides; 200°, 2.04 atm. helium, 77 ml./min.

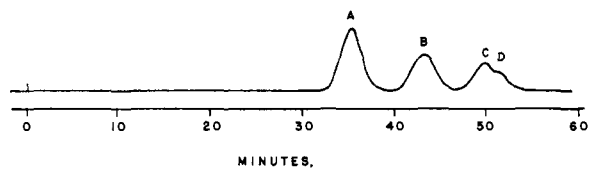


Fig. 3.—Separation diagram showing the products of methylation and dilute acid hydrolysis of the methyl mono-*O*-vinyl-α-D-glucopyranoside mixture (200°, 2.04 atm. helium, 77 ml./min.): A, methyl 3,4,6-tri-*O*-methyl-α-D-glucoside; B, methyl 2,3,4-tri-*O*-methyl-α-D-glucoside; C, methyl 2,3,6-tri-*O*-methyl-α-D-glucoside; D, methyl 2,4,6-tri-*O*-methyl-α-D-glucoside.

Two convenient techniques are therefore available for the determination of the position of the vinyl ether groups on carbohydrates. The compounds can be catalytically hydrogenated to the *O*-ethyl derivatives that can be prepared by classical techniques. The vinyl derivatives can also be fully methylated without disturbing the position of the vinyl groups. Dilute acid hydrolysis removes the latter; the resulting partially methylated carbohydrates then can be separated and identified by gas–liquid partition chromatography.

The vinyl ethers of methyl α-D-glucopyranoside were stable when stored in a desiccator over sodium hydroxide pellets. They were slowly hydrolyzed to acetaldehyde and methyl glucoside (over a period of months) when no precautions were taken to exclude atmospheric moisture and carbon dioxide.

Experimental

Chromatography.—Paper chromatography was performed in the descending manner with the upper phase of butanol–ethanol–water 4:1:5 (v./v.). The papers were dried in air and sprayed with 1% aqueous potassium permanganate. The vinylated products gave immediate yellow spots on a red background and methyl α-D-glucopyranoside gave a yellow spot after several minutes. The papers then were washed free of permanganate to prevent eventual yellowing of the background.

Gas–liquid partition chromatography of the methylated sugars was performed as recently described.[6,11] A 10-foot column, 20% butanediol succinate polyester on firebrick, was used in the Aerograph apparatus.

Vinylation of Methyl α-D-Glucopyranoside (I) with Vinyl Chloride.—The reactor[12] was charged with I (48 g., 0.25 mole), sodium hydroxide (50 g., 1.25 moles), tetrahydrofuran (60 ml.) and water (20 ml.). It was cooled in a Dry Ice-bath, evacuated, and liquified vinyl chloride (70 g., 1.1 moles) was admitted. The reaction mixture was heated to 130° and stirred for 10 hours. The pressure rose to and remained at 31.6 atm. After cooling, the reactor was vented; the odor of acetylene in the exhaust gases was confirmed by formation of cuprous acetylide.

The tacky orange residue in the reactor was dissolved in water (600 ml.) and treated with excess Dry Ice. The aqueous solution was evaporated to dryness and the residue extracted with methanol to yield a dark sirup (55 g.) that contained the products, unreacted methyl glucoside, and some salts. The products (35.6 g.) were extracted from the mixture with acetone. Paper chromatography of the acetone extract showed five spots, I (R_f 0.36) and spots of R_f 0.68, 0.72, 0.85 and 0.92. The products were distilled in a Hickman molecular still in vacuum, but no separation was obtained.

Vinylations with Acetylene.—Compound I (50 g.), powdered potassium hydroxide (2 or 4 g.), and solvent (100 ml. of water–tetrahydrofuran mixtures) were placed in the reactor. It was flushed with nitrogen and heated to 150°. The reactor was vented briefly and acetylene admitted at 25.5 atm. pressure. After 12 hours the reactor was cooled, vented, and the contents were dissolved in water. The solutions were carbonated with Dry Ice, adjusted to 500 ml., and aliquots (1–4 ml.) were removed for vinyl ether determinations with iodine.[13] The remaining solutions were worked up as described above. The results of the titrations are given in Table I; the figures represent the average number of vinyl ether groups per molecule of methyl α-D-glucopyranoside for the various runs. The occurrence of the highest substitution in 50:50 water–tetrahydrofuran illustrates the maximum effective solubility of the three components, sugar, alkali and acetylene, in this particular solvent.

TABLE I

AVERAGE DEGREE OF SUBSTITUTION

KOH, g.	Solvent composition (v./v., ml.) 100 H_2O	80 H_2O, 20 THF	50 H_2O, 50 THF	20 H_2O, 80 THF	100 THF
2	0.71	0.72	1.00	0.67	0.28
4	0.95	1.24	1.50	1.37	0.36

Isolation of Methyl 2-O-Vinyl-α-D-glucopyranoside (II).—The acetone-soluble portions of several reaction mixtures (80 g.) were dissolved in water (500 ml.) and extracted continuously for 3 days with benzene. Evaporation of solvent from the extract left a sirup (23 g.) that contained only the components of R_f 0.85 and 0.92. The aqueous solution was then extracted continuously for one day with ether. Evaporation of solvent from this extract left a sirup (7.5 g.) that contained vinylated components of R_f 0.92, 0.85, 0.72 and 0.68. The residual aqueous solution was then extracted continuously with ether for a week to yield a third sirup (24 g.) that contained only the components of R_f 0.68 and 0.72. Evaporation of the aqueous residue left a dark sirup (26 g.) composed mostly of methyl glucoside. This was extracted with chloroform to yield a colorless material that crystallized. When a portion (14 g.) of the second ether extract was seeded, more crystalline material formed. A total of 3.5 g. of methyl 2-O-vinyl-α-D-glucopyranoside was obtained, m.p. 126–127.5°, $[\alpha]^{25}D$ + 136° (*c* 2, H_2O), R_f 0.68.

Anal. Calcd. for $C_9H_{16}O_6$: C, 49.08; H, 7.34; mol. wt., 220. Found[14]: C, 48.83; H, 7.42; mol. wt. by iodine titration,[13] 231.

The compound (0.998 g.) was dissolved in 3% acetic acid (25 ml.) and allowed to stand at room temperature 24 hours. The acetaldehyde from the hydrolysis of the vinyl ether was transferred to a solution of 2,4-dinitrophenylhydrazine with a current of nitrogen and identified as acetaldehyde 2,4-dinitrophenylhydrazone, m.p. and mixed m.p. 159–161°. The dilute acetic acid solution was evaporated at reduced pressure in a tared flask to leave methyl α-D-glucopyranoside (0.853 g., calcd. 0.880 g.), m.p. and mixed m.p. 165°. The infrared spectrum of the compound in chloroform–ethanol showed a strong absorption at 1635 cm.$^{-1}$. *n*-Butyl vinyl ether showed a band at 1610 cm.$^{-1}$ and *sec*-butyl vinyl ether showed a band at 1625 cm.$^{-1}$.

Methyl 2-O-Vinyl-3,4,6-tri-O-methyl-α-D-glucoside (III).—The 2-*O*-vinyl derivative II (2 g.) in dimethylformamide (20 ml.) was methylated with methyl iodide (10 ml.) and silver oxide (10 g.). The reagents were added over a period of 2.5 hours in five equal aliquots. The mixture was stirred 24 hours, 100 ml. of ether was added and the solids filtered off and washed with ether. The ethereal solution was evaporated and the residue distilled in a vacuum. Gas-liquid partition chromatography showed a single peak for the derivative (Fig. 1) very close to methyl 2,3,4,6-tetra-*O*-methyl-α-D-glucoside in retention time.

Methyl 3,4,6-Tri-O-methyl-α-D-glucoside (IV).—The methylated derivative III (2 g.) was dissolved in aqueous acetone (100 ml.) and treated with glacial acetic acid (2 ml.) for 18 hours at room temperature. The solution was then evaporated at reduced pressure and the residual sirup distilled (b.p. 115° (0.01 mm.)) to yield a colorless product that crystallized in the receiver, m.p. 31–32°, $[\alpha]^{25}D$ + 173° (*c* 5, H_2O), $[\alpha]^{25}D$ + 177° (*c* 6, $CHCl_3$).

The 2-phenylazobenzoate of IV was prepared, m.p. 81.5–82.5° (lit.[15] m.p. 91°).

Gas–liquid partition chromatography of IV showed a single peak coincident in retention time with one of the peaks observed for methyl 3,4,6-tri-*O*-methyl-α,β-D-glucoside prepared by a standard synthesis[9] (Fig. 1). When IV was refluxed overnight with acidic methanol to form the α,β-mixture of glycosides (1V and V), the separation diagram obtained by gas chromatography was identical to that observed for the 3,4,6-tri-*O*-methyl derivative (Fig. 2).

3,4,6-Tri-O-methyl-D-glucose (VI).—The glucoside IV (0.7 g.) was hydrolyzed in 1 *N* sulfuric acid to yield a sirup that could not be crystallized. It yielded a polymorphic phenylosazone, m.p. 79–83°, 100–101°, 123–125°, depending upon crystallization medium and extent of handling (lit. m.p. 80°,[16] 80–82°,[17] 77–79° then 115–117°,[18] 130–132°[19]).

The optical rotation of VI, $[\alpha]^{25}D$ + 76.2° (*c* 2.6, H_2O) corresponded to the literature values, + 73.5°,[16] + 75°,[18] + 79°,[20] + 77.6°.[21]

2-O-Ethyl-D-glucose.—Methyl 3,5,6-tri-*O*-benzyl-α,β-D-glucofuranoside[10] (20 g.) in tetrahydrofuran (150 ml.) was stirred overnight with ethyl sulfate (20 ml.) and powdered potassium hydroxide (20 g.). The mixture was then refluxed, filtered and evaporated; the residual sirup was distilled at 235–239° (0.01 mm.) to yield methyl 2-*O*-ethyl-3,5,6-tri-*O*-benzyl-α,β-D-glucofuranoside (25.2 g.). This was dissolved in tetrahydrofuran (150 ml.), boiled with charcoal to remove a substance that inhibited hydrogenation, filtered, and evaporated to a sirup (21.5 g.).

(11) C. T. Bishop and F. P. Cooper, *Can. J. Chem.*, **38**, 388 (1960).

(12) Autoclave Engineers model ABE 300 bench scale autoclave.

(13) S. Siggia and R. L. Edsberg, *Anal. Chem.*, **20**, 762 (1948).

(14) Schwartzkopf Microanalytical Laboratory, Woodside 77, N. Y.

(15) G. H. Coleman, D. E. Rees, R. L. Sundberg and C. M. McCloskey, *J. Am. Chem. Soc.*, **67**, 381 (1945).

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(17) L. A. Boggs and F. Smith, *ibid.*, **78**, 1880 (1956).

(18) R. Kuhn, I. Low and H. Trishmann, *Chem. Ber.*, **90**, 203 (1957).

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(20) R. H. Farmer and R. A. Laidlaw, *ibid.*, 4201 (1955).

(21) H. B. Wood, Jr., R. Allerton, H. W. Diehl and H. G. Fletcher, *J. Org. Chem.*, **20**, 875 (1955).

The sirup in tetrahydrofuran (125 ml.) was hydrogenated over 10% palladium-on-charcoal (1 g.) at 90° and 8.2 atm. until a pressure drop corresponding to 31.3 atm. had been recorded (calcd. 26.4 atm.). The catalyst was removed and the solution evaporated to leave methyl 2-*O*-ethyl-α,β-D-glucofuranoside (10.8 g., calcd. 9.7 g.). The sirupy product was hydrolyzed with 1 *N* sulfuric acid and the 2-*O*-ethyl-D-glucose recrystallized from ethanol; m.p. 185–186°, $[\alpha]^{25}D$ + 95.4° → + 62.6°, equil. (*c* 2, H_2O) (lit.[22] m.p. 191–195°, $[\alpha]^{25}D$ + 65°).

Anal. Calcd. for $C_8H_{16}O_6$: C, 46.12; H, 7.75. Found[14]: C, 46.41; H, 7.85.

Methyl 2-O-Ethyl-α-D-glucopyranoside (VII).—Methyl 2-*O*-vinyl-α-D-glucopyranoside (II) (2 g.) in methanol (75 ml.) containing a little ammonia was hydrogenated over 5% palladium-on-charcoal (0.1 g.) at 5.4 atm. for 1.5 hours at room temperature. The product was recrystallized from acetone to yield VII (1.07 g.), m.p. 136°, $[\alpha]^{25}D$ + 144° (*c* 2, H_2O).

Anal. Calcd. for $C_9H_{18}O_6$: C, 48.65; H, 8.18. Found[14]: C, 48.79; H, 7.96.

A sample of the product was hydrolyzed to 2-*O*-ethyl-D-glucose (VIII), m.p. 184–185°, mixed m.p. 185–186°, $[\alpha]^{25}D$ + 87.3° → + 61.0°, equil., (*c* 4, H_2O).

Methylation of the Methyl Mono-O-vinyl-α-D-glucopyranosides.—A portion of the second ether extract (10 g.) that contained the components of R_f 0.68 and 0.72 was methylated in tetrahydrofuran (200 ml.) with powdered sodium hydroxide (24 g.) and methyl sulfate (24 ml.). The product obtained by filtration and evaporation of solvent was dissolved in water (110 ml.) and glacial acetic acid (1 ml.) was added. After 36 hours at room temperature, the solution was evaporated to a sirup. Gas–liquid partition chromatography showed the presence of four methyl tri-*O*-methyl-α-D-glucopyranosides (Fig. 3).

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH AND DEVELOPMENT DIVISION OF THE SCHERING CORP., BLOOMFIELD, N. J.]

Weak Acid-catalyzed Rearrangement of the Dihydroxyacetone Side Chain in Steroids

BY HERSHEL L. HERZOG, MARGARET JEVNIK GENTLES, HELEN MARSHALL AND E. B. HERSHBERG

RECEIVED MAY 4, 1961

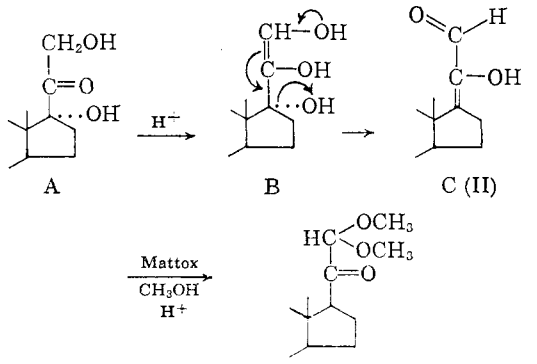
An enol aldehyde intermediate in the Mattox rearrangement of the steroidal dihydroxyacetone side-chain has been isolated and correlated with the proposed mechanism of Mattox. Proof is offered that the Norymberski reductive removal of the 17α-hydroxyl group in steroids bearing the dihydroxyacetone side-chain proceeds in its first stage *via* the Mattox rearrangement.

In the course of a study of microbiological 1-hydroxylation[1] of 4-pregnene-17α,21-diol-3,20-dione, evidence for the structure of the product was provided by the removal, by dehydration, of the 1-hydroxyl group in hot glacial acetic acid, which afforded 1,4-pregnadiene-17α,21-diol-3,20-dione (I). In this dehydration process, another, less polar product (II) was formed in minor amount. Compound II displayed an altered ultraviolet absorption spectrum in that, in addition to a peak at 246 mμ (ε 16,200) characteristic of the 1,4-diene-3-one, there was also a broad, flat peak between 260 and 280 mμ with an approximate maximum at 270 mμ (ε 14,000). The infrared spectrum of II showed bands at 2.94, 6.00, 6.16 and 6.23 μ from where the presence of 1,4-diene-3-one and hydroxyl was inferred. It was also noted that no evidence for a 20-carbonyl group remained since the customary band at about 5.85 μ was absent.

The same compound (II) was then prepared in about 40% yield by the action of refluxing glacial acetic acid on I for six hours, followed by chromatographic separation on Florisil. In addition to II, a smaller amount of the 21-acetate of I was formed. Compound II ($C_{21}H_{26}O_3$) contained one molecule of water less than I and gave a positive ferric chloride test. Acetylation with acetic anhydride in pyridine afforded a monoacetate (III) which, from its infrared spectrum, appeared free of hydroxyl groups and contained an enolic acetate (5.67 μ). The ultraviolet spectrum of III displayed no shoulder at 270 mμ, but the peak formerly at 245 mμ had shifted to 248 mμ, with a much enhanced intensity (ε 34,400). All these facts are consistent with the formulation of II as an enol aldehyde, as it is represented in the flow sheet.

The rearrangement product II was converted in poor yield to 1-dehydrodesoxycorticosterone by the action of lithium aluminum tri-*t*-butoxyhydride and by reduction with zinc and acetic acid, which confirmed the structure assigned to II.

A compound of structure similar to II has been described by Mattox[2] as part of a study of the action of methanolic hydrogen chloride on steroids containing the dihydroxyacetone side chain. In the Mattox reaction with pregnane-3α,17α,21-triol-11,20-dione 3,21-diacetate the rearrangement product was isolated as the dimethyl acetal (21,21-dimethoxypregnan-3α-ol-11,20-dione). Bromination (1 mole) of the latter in the presence of excess hydrogen bromide followed by treatment with sodium iodide in acetic acid afforded 17(20)-pregnen-3α,20-diol-11-one-21-al, $\lambda_{max}^{ethanol}$ 284 mμ (ε 14,200). The shift of this peak to 270 mμ in



(1) G. Greenspan, C. P. Schaffner, W. Charney, H. L. Herzog and E. B. Hershberg, *J. Am. Chem. Soc.*, **79**, 3922 (1957).

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