al.,[19] for the 21-benzylidene derivative of 3α,11α-dihydroxy-20-ketopregnane (ϵ_{2940} 24,000). 21-Benzal-3α-hydroxy-11,-20-diketopregnane[20] also exhibited a maximum at 295 mμ. Attempts to prepare the 2,4-dinitrophenylhydrazone were unsuccessful, due possibly to the instability of the reaction product which seemed to resinify and defied attempts at purification. Several attempts to prepare the oxime have been unsuccessful.

Ozonolysis of 16-Benzylidene-estrone-3-methyl Ether.—One millimole (366 mg.) of 16-benzylidene-estrone-3-methyl ether was dissolved in 25 ml. of glacial acetic acid, 2 ml. of water and 8 ml. of ethyl acetate. Ozone was bubbled through this solution for one hour. The yellow solution obtained was diluted with 30 ml. of water after 15 minutes at room temperature. The yellow color faded at once. The solution was allowed to stand at room temperature for 12 hours.

Most of the solvent was removed *in vacuo* with a minimum of heating. The concentrate was dissolved in ether which was then washed twice with water. The ether was extracted with 5% potassium carbonate solution and acidification of the carbonate extracts gave an oil which was dissolved in ether. After washing with water, the ether was evaporated to give 253 mg. (76%) of solid material. Several recrystallizations from aqueous acetone and aqueous ethanol gave glistening leaflets melting at 200–201°. A mixed melting point with an authentic sample of marrianolic acid-7-methyl ether (m.p. 200–201°) was not depressed.

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(19) W. P. Long, C. W. Marshall and T. F. Gallagher, *J. Biol. Chem.*, **165**, 197 (1946).

(20) Kindly supplied by Dr. S. L. Hsia of this department.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH AND DEVELOPMENT DIVISION OF SCHERING CORPORATION]

11-Oxygenated Steroids. XII. The Preparation of 17α-Hydroxycorticosterone 21-Acetate (Kendall's Compound F Acetate) via 11β-Formates[1]

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The synthesis of 17α-hydroxycorticosterone acetate from 3α,11β,17α-trihydroxypregnan-20-one *via* 11β-formates is described.

The 11β-hydroxyl group, long considered to be unreactive toward the usual esterifying agents,[2] was found by us to be acetylated in good yield under very mild conditions, using acetic anhydride and an acid catalyst.[3,4] This discovery led to the relatively simple synthesis of Compound F 11,21-diacetate and 11-acetate, but further hydrolysis to Compound F was not achieved. Attention was next turned to the corresponding 11β-formates, which were found to be not only hydrolysable to the parent 11β-hydroxy compound, but also to survive the reactions necessary to elaborate the dihydroxyacetone side-chain and the α,β-unsaturated ketone in the A-ring.[5]

Our preliminary studies were made on 11β,17α-dihydroxypregnane-3,20-dione (I). While formic acid alone produced no significant change, the addition of an acid catalyst (either *p*-toluenesulfonic acid or perchloric acid) gave a new compound, lacking in free hydroxyl groups, and therefore assumed to be 11β,17α-dihydroxypregnane-3,20-dione diformate (II). This compound was stable to attempted acid hydrolysis, but easily reverted to I in good yield on treatment with sodium hydroxide or potassium carbonate at room temperature overnight.

Treatment of 3α,11β,17α-trihydroxypregnan-20-one (III) with formic acid and an acid catalyst overnight gave the triformate IV in 43.5% yield. In the absence of the acid catalyst, the 3-monoformate V was obtained in 72% yield. Complete hydrolysis of IV to the starting triol III was accomplished with aqueous sodium hydroxide overnight at 30°. Reaction of IV with ethanol and *p*-toluenesulfonic acid gave the 11,17-diformate VI, which was oxidized easily with N-bromoacetamide in high yield to II. Partial hydrolysis of IV to 3α,11β,17α-trihydroxypregnan-20-one 11-formate (VII) was accomplished by either refluxing aqueous sodium bicarbonate, sodium methylate in tetrahydrofuran-methanol or Amberlite IRA-400 resin in methanol. The product VII, invariably a resin, was next brominated at C-21 with bromine in chloroform solution, and the bromine replaced by acetate by means of potassium acetate in refluxing acetone to give the 11-formate 21-acetate VIII in about 50% yield. Oxidation of VIII to 11β,17α,21-trihydroxypregnane-3,20-dione 11-formate 21-acetate (IX) was accomplished in good yield with N-bromoacetamide in *t*-butyl alcohol–methylene chloride.

The over-all yield of IX from IV was considerably improved if no purification of intermediates was attempted. Thus from 5 g. of IV there was obtained 3.37 g. of crude IX (*ca.* 67%) if no attempt was made to crystallize the intermediates V → VIII.

Hydrolysis of IX with sodium hydroxide in aqueous methanol at room temperature overnight, followed by acetylation with acetic anhydride and pyridine gave 11β,17α,21-trihydroxypregnane-3,-20-dione 21-acetate (X). This had been converted

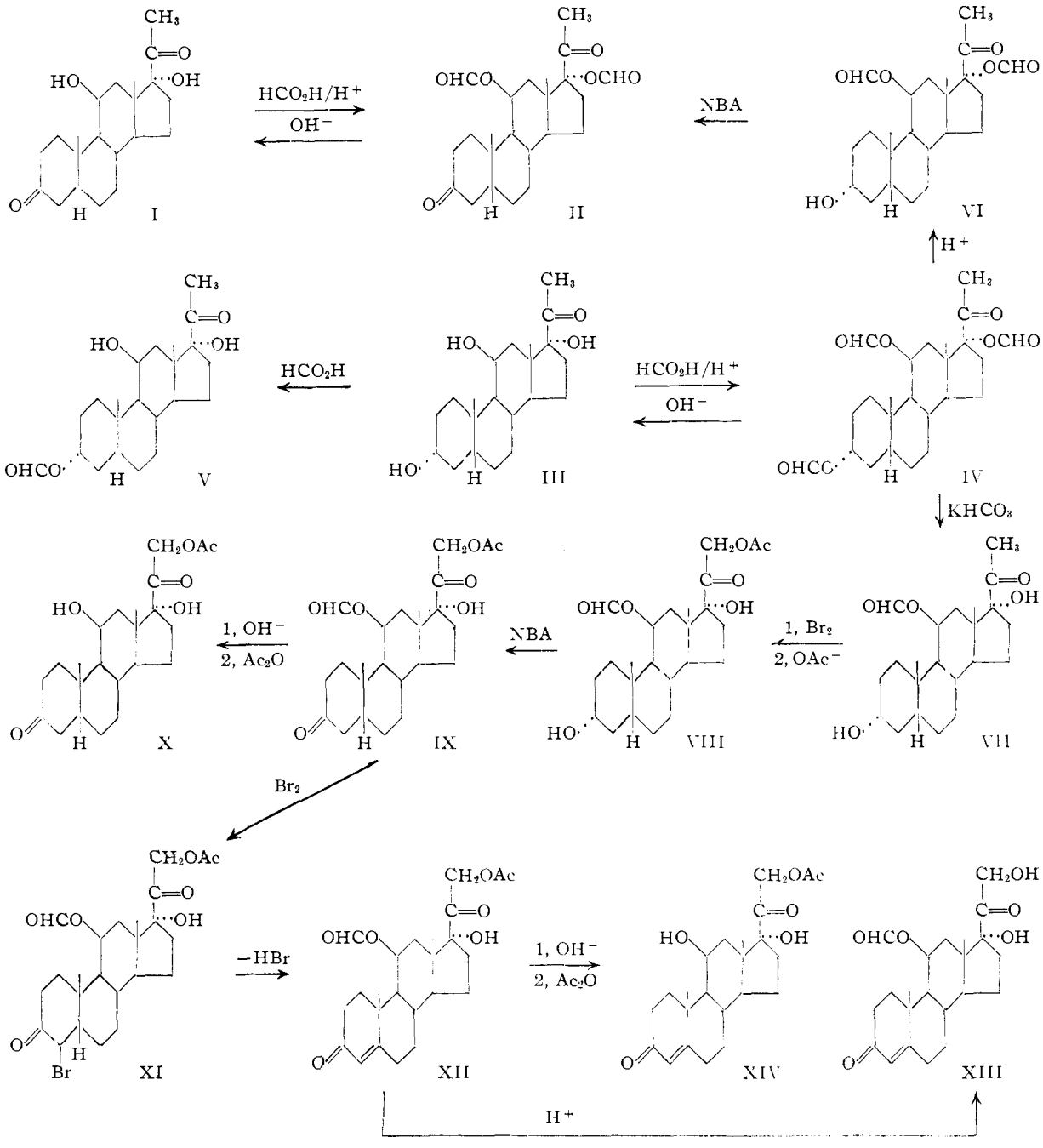
(1) A preliminary account of this work has appeared in *Arch. Biochem. Biophys.*, **49**, 244 (1954).

(2) T. F. Gallagher, *J. Biol. Chem.*, **162**, 539 (1946); L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, N. Y., 1949, pp. 408, 657. However, Dr. C. W. Shoppee has pointed out to us in a private communication that M. Steiger and T. Reichstein [*Helv. Chim. Acta*, **20**, 817 (1937)] converted 3β,11β-dihydroxyandrostan-17-one to its diacetate by warming with acetic anhydride and pyridine. See also A. Crawshaw, H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.*, 731 (1954), and A. Kemp, A. Kappas, I. Salamon, F. Herling and T. F. Gallagher, *J. Biol. Chem.*, **210**, 123 (1954).

(3) (a) E. P. Oliveto, C. Gerold and E. B. Hershberg, *Arch. Biochem. Biophys.*, **43**, 234 (1953); (b) E. P. Oliveto, C. Gerold, L. Weber, H. E. Jorgensen, R. Rausser and E. B. Hershberg, THIS JOURNAL, **75**, 5486 (1953).

(4) Soon after our original communication, A. Crawshaw, H. B. Henbest and E. R. H. Jones [ref. 2] described the acetylation of 11β-hydroxy steroids with acetyl chloride–dimethylaniline in chloroform.

(5) At about the same time, A. Lardon and T. Reichstein [*Helv. Chim. Acta*, **37**, 443 (1954)] prepared an 11β-formate with an acetic anhydride–formic acid mixture, and found that it could not only be saponified, but also was stable during the sequence of reactions elaborating the side-chain from an etio acid *via* the diazo ketone synthesis.



to 17α-hydroxycorticosterone 21-acetate previously.[6]

Bromination of IX at C-4, followed by dehydrobromination *via* the semicarbazone, proceeded in the normal fashion to give 11β,17α,21-trihydroxy-Δ^4-pregnene-3,20-dione 11-formate 21-acetate (XII, Compound F 11-formate 21-acetate). Acid hydrolysis gave Compound F 11-formate (XIII), while complete hydrolysis with sodium hydroxide, followed by acetylation gave Compound F 21-acetate (XIV).

The biological properties of XII and XIII will be reported elsewhere.

(6) N. L. Wendler, R. P. Graber, R. E. Jones and M. Tishler, THIS JOURNAL, **74**, 3630 (1952).

Experimental[7]

11β,17α-Dihydroxypregnane-3,20-dione 11,17-Diformate (II).—A solution of 1.00 g. of 11β,17α-dihydroxypregnane-3,20-dione (I) and 0.10 g. of *p*-toluenesulfonic acid monohydrate in 10 ml. of formic acid (98–100%) was allowed to stand overnight at 25°, then poured into water to precipitate 0.99 g. of crude II, m.p. 203–210°. One crystallization from acetone–hexane gave 0.80 g., m.p. 240–245°. The analytical sample, crystallized twice more, melted at 256–264°, $[\alpha]D$ +47.4° (dioxane). The infrared spectrum showed no hydroxyl or conjugated carbonyl bands.

Anal. Calcd. for $C_{23}H_{32}O_6$: C, 68.29; H, 7.97. Found: C, 68.47; H, 8.17.

(7) All m.p.'s are corrected. All rotations were taken in chloroform (except where noted) in a 1-dm. tube at 25° and at a concentration of about 1%. Analyses and optical data were obtained by the Microanalytical and Physical Chemistry Departments of these laboratories.

When the reaction was run in the absence of the *p*-toluenesulfonic acid, only the starting material I was obtained.

Hydrolysis Studies on II. (a).—A suspension of 1.00 g. of II in 80 ml. of C.P. methanol was treated with 10.0 ml. of 1 *N* aqueous sodium hydroxide and stirred for 19 hours at 25°. After neutralization with 1 ml. of acetic acid, the mixture was concentrated under reduced pressure until crystallization was substantially complete, then 200 ml. of water was added and the precipitate was collected by filtration to give 0.82 g., m.p. 200–210°. One crystallization from acetone–hexane gave 0.64 g., m.p. 214–222°. A mixture m.p. and the infrared spectrum indicated the product to be identical with I.

(b).—A mixture of 1.00 g. of II, 30 ml. of C.P. methanol, 1.00 g. of potassium carbonate and 6 ml. of water was stirred for 20 hours at 25°. After neutralization with 1.5 ml. of acetic acid, the solution was concentrated under reduced pressure. When crystallization began, the suspension was diluted with water and 0.82 g. of solid, m.p. 190–196°, was collected by filtration. Recrystallization from acetone–hexane yielded 0.55 g. of I, m.p. 211–214°, as shown by mixture m.p. and infrared spectrum.

3α,11β,17α-Trihydroxypregnan-20-one Triformate (IV).—A solution of 10.0 g. of 3α,11β,17α-trihydroxypregnan-20-one (III) in 100 ml. of 98–100% formic acid was treated with 4 ml. of 70–72% perchloric acid (or 1.0 g. of *p*-toluenesulfonic acid), then allowed to stand at 5° for 48 hours. The mixture was then poured into water and the precipitate collected by filtration: 11.26 g., m.p. 98–140°. One crystallization from methanol gave 5.38 g. of IV, m.p. 167–172°. The analytical sample, crystallized once more from methanol, melted at 174–177°, had $[\alpha]_D$ +57.0°, and showed no free hydroxyl band in its infrared spectrum.

Anal. Calcd. for $C_{24}H_{34}O_7$: C, 66.34; H, 7.89. Found: C, 66.50; H, 8.06.

3α,11β,17α-Trihydroxypregnan-20-one 3-Monoformate (V).—A solution of 1.0 g. of III in 10 ml. of 98–100% formic acid was allowed to stand overnight at 25°, then poured into water and the precipitate collected by filtration. One crystallization from acetone–hexane gave 0.80 g. of V, m.p. 184–188°. The analytical sample, crystallized twice more, melted at 187–190° and had $[\alpha]_D$ +43.9°.

Anal. Calcd. for $C_{22}H_{34}O_5$: C, 69.81; H, 9.05. Found: C, 69.91; H, 8.72.

The triformate IV could be obtained from V by treatment with formic acid and an acid catalyst.

Hydrolysis Studies on IV. Partial Hydrolysis. (a).—A mixture of 5.0 g. of IV and 0.5 g. of *p*-toluenesulfonic acid monohydrate in 100 ml. of absolute ethanol was stirred at 37–38° for 2 hours, then stored at 5° for 16 hours, water added and the clear solution extracted with methylene chloride. The organic extracts were washed with dil. sodium bicarbonate solution and water, dried over sodium sulfate and evaporated to dryness. The resinous residue, 4.6 g., crystallized easily upon trituration with ether; m.p. 168–182°. Recrystallization from acetone–hexane gave 2.31 g. of 3α,11β,17α-trihydroxypregnan-20-one 11,-17-diformate (VI), m.p. 187–190°, and a second crop of 0.74 g., m.p. 175–180°. Two additional crystallizations of the major portion raised the m.p. to 194–196°, $[\alpha]_D$ +47.5°.

Anal. Calcd. for $C_{25}H_{34}O_6$: C, 67.95; H, 8.43. Found: C, 67.78; H, 8.59.

This compound (VI) tended to solvate at times, but the solvate could be broken by heating at 90° under reduced pressure. The structure was established by oxidation with N-bromoacetamide to yield II. A solution of 0.5 g. of VI in 5 ml. of methylene chloride and 5 ml. of *t*-butyl alcohol was chilled in an ice-bath, treated with 0.5 g. of N-bromoacetamide and allowed to stand 5 hours in the dark at 5°. The solution then was washed with dilute sodium sulfite solution, the washes extracted twice with methylene chloride, the combined extracts washed twice with water, dried over sodium sulfate and evaporated to yield 0.5 g. of crystals, m.p. 260–265°. Recrystallization from acetone–hexane gave 0.42 g., m.p. 263–266°, which was shown to be identical with II by mixture m.p. and infrared spectrum.

(b).—A mixture of 5.0 g. of IV, 200 ml. of C.P. methanol, 2.90 g. of sodium bicarbonate and 40 ml. of water was refluxed for 2.5 hours. After neutralization with acetic acid, the solution was diluted with water and extracted several times with methylene chloride. The combined extracts were washed with water, dried over sodium sulfate and evaporated to dryness. The resin thus obtained was chromatographed on Florisil. The fraction eluted with methylene chloride was taken up in ether, treated with Darco, filtered, evaporated to dryness and thoroughly dried under vacuum. This material, still a resin, had $[\alpha]_D$ +38.0° and was presumed to be 3α,11β,17α-trihydroxypregnan-20-one 11-formate (VII).

Anal. Calcd. for $C_{22}H_{34}O_5$: C, 69.81; H, 9.05. Found: C, 69.69; H, 9.37.

This experiment was repeated several times and the final product was nearly always a resin which failed to crystallize on standing, on treatment with solvents or after chromatography. However, one run did yield some crystalline material on standing with ether: 0.25 g. with m.p. 160–166° was obtained from 1.0 g. of IV. The infrared spectrum of this material showed a stronger hydroxyl absorption and a weaker formate bond than that of VI; however, satisfactory carbon and hydrogen analyses could not be obtained. The infrared spectra of the resins obtained from this and the following hydrolyses matched each other exactly, and were very similar to that of the crystalline material; no important discrepancies existed.

(c).—A solution of 0.5 g. of IV in 25 ml. of tetrahydrofuran and 25 ml. of C.P. methanol was treated with a solution of 0.75 g. of sodium methylate in 10 ml. of C.P. methanol under an atmosphere of argon. After 5 minutes 0.72 ml. of water was added; 3 minutes later the excess alkali was neutralized by the addition of acetic acid. Concentration under reduced pressure and addition of water gave 0.37 g. of a gummy solid. Crystallization from ether–hexane gave 0.14 g., m.p. 158–162°. Its infrared spectrum matched exactly that of the crystals obtained in (b), but again no satisfactory analytical results could be obtained. Attempts to repeat the reaction invariably gave resins. Several variations were tried without success, among them the use of methanol alone as the solvent, allowing the reaction to take place at ice-bath temperature, and using only slightly more than the theoretical amount of sodium methylate.

(d).—A solution of 1.0 g. of IV in 50 ml. of C.P. methanol was stirred for 2 hours at 25° with 4.0 g. of Amberlite IRA-400 resin (basic form). The resin was removed by filtration and the filtrate evaporated to dryness, leaving 0.88 g. of a resin. Its infrared spectrum was identical with those of the resins obtained in (b) and (c).

Complete Hydrolysis. (a).—A mixture of 0.50 g. of IV, 40 ml. of C.P. methanol and 5 ml. of 1 *N* aqueous sodium hydroxide was stirred overnight at 30°. After neutralization with acetic acid, the solution was concentrated under reduced pressure, 200 ml. of water was added, and 0.21 g. of solid removed by filtration, m.p. 170–195°. Recrystallization from acetone–hexane yielded 0.11 g., m.p. 205–209°. Its infrared spectrum matched that of III.

3α,11β,17α,21-Tetrahydroxypregnan-20-one 11-Formate 21-Acetate (VIII).—The resinous product VII from the hydrolysis of 1.0 g. of IV as described in (a) was taken up in 20 ml. of C.P. chloroform and brominated by the dropwise addition of a solution of 0.41 g. of bromine in 10 ml. of C.P. chloroform. Two grams of potassium acetate was added, the solvent removed under reduced pressure, the residue treated with 50 ml. of acetone and 2 g. of potassium acetate, and the resulting suspension refluxed for 3 hours with stirring. The acetone was removed under reduced pressure, water added and the product collected by filtration: 1.14 g., m.p. 105–140° dec. An ether sludge gave 0.57 g., m.p. 125–160° dec. Recrystallization from aqueous methanol gave 0.40 g. of VIII, m.p. 160–165°. The analytical sample was crystallized twice more and had m.p. 185–190°, $[\alpha]_D$ +86.0°.

Anal. Calcd. for $C_{24}H_{36}O_7$: C, 66.03; H, 8.31. Found: C, 66.27; H, 8.35.

11β,17α,21-Trihydroxypregnane-3,20-dione 11-Formate 21-Acetate (IX).—A solution of 1.43 g. of VIII in 15 ml. of methylene chloride and 15 ml. of *t*-butyl alcohol was chilled in an ice-bath and 1.34 g. of N-bromoacetamide added. After 4 hours in the dark at 5°, the solution was worked up in the manner described above. The residue crystallized easily on treatment with ether: 1.43 g., m.p. 180–193°. Crystallization from acetone–hexane gave 0.80 g. of IX, m.p. 214–217°. The analytical sample, crystallized twice more, melted at 222–225°, $[\alpha]_D$ +90.0°.

Anal. Calcd. for $C_{24}H_{34}O_7$: C, 66.34; H, 7.89. Found: C, 66.00; H, 8.08.

It was found that purification of intermediates was not necessary in the preparation of IX from IV.

Thus starting with 5.0 g. of IV and carrying the material through the hydrolysis, bromination, acetoxylation and oxidation steps without isolation, there was obtained 3.37 g. of IX, m.p. 194–200°. One crystallization from acetone–hexane yielded 2.58 g., m.p. 209–212°.

11β,17α,21-Trihydroxypregnane-3,20-dione 21-Acetate (X).—A solution of 0.50 g. of IX in 20 ml. of C.P. methanol was combined with 6 ml. of water and 11.5 ml. of C.P. methanol containing 0.115 g. of sodium hydroxide, all under an argon atmosphere. The solution was allowed to stand for 18 hours at 27°, the excess alkali was neutralized with acetic acid, water added and the methanol removed under reduced pressure. Filtration yielded 0.21 g., m.p. 143–170°; this was acetylated with acetic anhydride and pyridine, and chromatographed on Florisil to give 30 mg. of X, m.p. 189–195°. Its infrared spectrum was identical with that of an authentic sample.[8]

4-Bromo-11β,17α,21-trihydroxypregnane-3,20-dione 11-Formate 21-Acetate (XI).—A solution of 3.0 g. of IX in 30 ml. of methylene chloride and 30 ml. of *t*-butyl alcohol at 25° was brominated by the dropwise addition of 1.14 g. of bromine in 25 ml. of methylene chloride. The bromine color discharged after standing 4 hours. The methylene chloride was removed under reduced pressure and the remaining solution poured into water. Filtration of the crystalline precipitate gave 3.76 g., m.p. 163–169° dec. Recrystallization from aqueous acetone gave 1.75 g. of XI, m.p. 185–187° dec., $[\alpha]_D$ +86.3° (acetone).

Anal. Calcd. for $C_{24}H_{33}O_7Br$: Br, 15.57. Found: Br, 15.37.

Debromination of the mother liquor gave 1.07 g. of X, m.p. 213–221°.

11β,17α,21-Trihydroxy-Δ⁴-pregnene-3,20-dione 11-Formate 21-Acetate (XII).—A suspension of 2.65 g. of XI in 53 ml. of *t*-butyl alcohol and 40 ml. of C.P. chloroform, stirred in an argon atmosphere, was treated with 0.81 g. of semicarbazide and stirring was continued for 2 hours. The reaction was concentrated under reduced pressure to *ca.* half-volume, water added and the distillation continued to the precipitation of solid. Filtration yielded 2.65 g., which was taken up in 25 ml. of acetic acid, combined with a solution of 1.22 g. of 94% pyruvic acid and 1.05 g. of sodium acetate in 7.5 ml. of water, and refluxed for 5 minutes. After the addition of 100 ml. of hot water, the mixture was chilled to precipitate 1.91 g. of XII, m.p. 190–200°. The analytical sample, crystallized several times from acetone–hexane, melted at 199–201°, $[\alpha]_D$ +176.1°, ϵ_{max} 15,100 at 239 mμ (95% EtOH).

Anal. Calcd. for $C_{24}H_{32}O_7$: C, 66.65; H, 7.46. Found: C, 66.46; H, 7.22.

11β,17α,21-Trihydroxy-Δ⁴-pregnene-3,20-dione 11-Formate (XIII).—A solution of 0.50 g. of XII in 5 ml. of C.P. chloroform and 17.5 ml. of C.P. methanol was chilled and combined with 1.0 ml. of concentrated hydrochloric acid in 1.8 ml. of water. The reaction was allowed to stand for 48 hours at 25°, diluted with water, and extracted with methylene chloride. The organic extracts were washed with dilute sodium bicarbonate solution and water, dried and evaporated. The resinous residue, 0.48 g., was taken up in benzene and chromatographed on Florisil. The fraction (0.17 g.) eluted with 1% methanol in methylene chloride crystallized on trituration with ether, m.p. 168–178°. Recrystallization from acetone–hexane yielded 0.08 g. of XIII, m.p. 184–187°, $[\alpha]_D$ +162.7°, ϵ_{max} 15,700 at 238 mμ (95% EtOH).

Anal. Calcd. for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.63; H, 7.92.

17α-Hydroxycorticosterone 21-Acetate (XIV).—Under an argon atmosphere, a mixture of 0.50 g. of XII in 30 ml. of C.P. methanol and 0.116 g. of sodium hydroxide in 6 ml. of water was allowed to react 20 hours at 25°. The excess alkali was neutralized with acetic acid, water was added and the methanol removed under reduced pressure. Only a small amount of solids separated, so the aqueous residue was extracted several times with methylene chloride, the extracts combined, dried and evaporated to give 0.37 g. This was acetylated with acetic anhydride and pyridine, then crystallized from acetone to give 0.11 g., m.p. 215–218°. Its infrared spectrum was identical with that of an authentic sample of XIV.

BLOOMFIELD, N. J.

(8) Kindly supplied by Merck and Co., Inc.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

6-O-β-Maltosyl-α-D-glucopyranose Hendecaacetate

BY A. THOMPSON[1] AND M. L. WOLFROM

RECEIVED JANUARY 13, 1955

The reaction mixture[2] obtained by treating 6-O-β-maltosyl-β-D-glucopyranose hendecaacetate successively with titanium tetrachloride, mercuric acetate and acetic anhydride–pyridine, has been investigated chromatographically and found to contain 6-O-β-maltosyl-α-D-glucopyranose hendecaacetate, β-maltose octaacetate and β-D-glucopyranose pentaacetate, in addition to the starting material. A proof of the identity of 6-O-β-maltosyl-α-D-glucopyranose hendecaacetate is presented.

The trisaccharides of D-glucose containing mixed (1 → 4)-α-D and (1 → 6)-α-D linkages are of interest in studies on the structure of amylopectin. Of the three possible trisaccharides, containing these linkages, that should be preformed in amylopectin, panose[3] (4-O-α-isomaltopyranosyl-D-glucose)[4] has been isolated from amylopectin.[5] An impure preparation of a second member of this group, 6-O-α-maltosyl-D-glucose hendecaacetate, has been reported by Asp and Lindberg[2] as resulting from the action of titanium tetrachloride on 6-O-β-maltosyl-β-D-glucopyranose hendecaacetate[6] with subsequent treatment with mercuric acetate and reacetylation with acetic anhydride and pyridine. Such a transformation of a (1 → 6)-β-D-glucosidic to the (1 → 6)-α-D form has been established by Lindberg[7] for the conversion of β-gentiobiose octaacetate to β-isomaltose octaacetate and has been verified in this Laboratory.

In the hope that we could obtain 6-O-α-maltosyl-β-D-glucopyranose hendecaacetate in a state of purity, we have made a chromatographic study of the reaction mixture obtained by Asp and Lindberg, at the stage in which all products appear as

(1) Corn Industries Research Foundation Associate.

(2) L. Asp and B. Lindberg, *Acta Chem. Scand.*, **5**, 665 (1951).

(3) S. C. Pan, A. A. Andreasen and P. Kolachov, *Science*, **112**, 115 (1950); S. C. Pan, L. W. Nicholson and P. Kolachov, THIS JOURNAL, **73**, 2547 (1951).

(4) M. L. Wolfrom, A. Thompson and T. T. Galkowski, *ibid.*, **73**, 4093 (1951).

(5) A. Thompson and M. L. Wolfrom, *ibid.*, **73**, 5849 (1951).

(6) S. H. Nichols, Jr., W. L. Evans and H. D. McDowell, *ibid.*, **62**, 1754 (1940).

(7) B. Lindberg, *Acta Chem. Scand.*, **3**, 1355 (1949).