was isolated from the hydrolysate by absorption from solution at pH 6–7 onto a column of Dowex 1-X8 (acetate form) and elution with *N* acetic acid. The fractions showing strong absorption at 260 mμ deposited crystals which were dissolved in water by bringing to pH 8 with sodium hydroxide and reprecipitated by adding hydrochloric acid to pH 3.7. The yield of colorless product was 26 mg., m.p. 241–242° dec.

Anal. Calcd. for $C_8H_{10}N_2O_3S$: C, 44.85; H, 4.70; N, 13.08. Found: C, 44.64; H, 4.94; N, 12.98.

B.—7-Aminocephalosporanic acid (6.81 g., 0.025 mole) dissolved in 100 ml. of water containing 4.20 g. (0.05 mole) of sodium bicarbonate was hydrogenated for 1.5 hr. at 4 kg./cm.^{2} over 27 g. of 5% palladium on barium sulfate.[14] The catalyst was removed and washed with dilute sodium bicarbonate. To the dark solution were added 60 ml. of 6 *N* hydrochloric acid and 9 g. of charcoal. Filtration gave a clear yellow solution which was cooled in ice and brought to pH 3.7 with 2 *N* sodium hydroxide to precipitate 3.32 g. (62%) of light tan crystals, sufficiently pure for the preparation of derivatives. A colorless product was obtained by dissolving in 0.5 *N* hydrochloric acid and reprecipitating by adding sodium hydroxide to pH 3.7. An analytical sample (reprecipitated as in method A) was indistinguishable by m.p., infrared spectrum and electrophoretic mobility from material prepared by method A.

Anal. Calcd. for $C_8H_{10}N_2O_3S$: C, 44.85; H, 4.70; N, 13.08. Found: C, 44.63; H, 4.75; N, 13.03.

7-Phenylacetamidodesacetoxycephalosporanic Acid (IId).—A solution of 4.29 g. (0.02 mole) of IIb in 200 ml. of water containing 5.04 g. (0.06 mole) of sodium bicarbonate was mixed with 300 ml. of acetone and stirred at −20° while 3.71 g. (0.024 mole) of phenylacetyl chloride was added. The reaction mixture was kept at −20° for 30 min. and then at 3° for 2 hr. Two washings with ether removed the acetone. The aqueous residue was acidified with 30 ml. of 6 *N* hydrochloric acid and extracted twice with ethyl acetate. The extracts were washed with a little 0.5 *N* hydrochloric acid and evaporated to dryness. The residual foam was triturated with ether to give 5.51 g. of white solid (IId as free acid). This was dissolved in 300 ml. of 1-propanol containing 5% of water and treated with 12 ml. of 1.65 *N* potassium 2-ethylhexanoate[15] in 2-propanol to precipitate 5.14 g. (65%) of the colorless **potassium salt** of the product. A sample recrystallized from water–1-propanol and air-equilibrated[16] had m.p. 212–213° dec.; lactam carbonyl stretching at 5.75 μ (Nujol).

Anal. Calcd. for $C_{16}H_{15}KN_2O_4S\cdot1.5H_2O$: C, 48.35; H, 4.56; N, 7.05. Found: C, 48.18; H, 4.43; N, 7.14.

7-(2-Thienylacetamido)desacetoxycephalosporanic Acid (IIe).—A procedure similar to that described in the foregoing experiment was used to acylate 1.07 g. (0.005 mole) of IIb with 2-thienylacetyl chloride[17] and to isolate the product as the free acid (1.25 g. of white solid). This was dissolved in 80 ml. of 2-propanol containing 5% of water and 2.7 ml. of 1.8 *M* sodium 2-ethylhexanoate[18] in 2-propanol was added to precipitate 1.17 g. (63%) of the colorless **sodium salt**. A sample recrystallized from water–2-propanol and air-equilibrated had m.p. 231–232° dec.; lactam carbonyl stretching at 5.75 μ (Nujol).

Anal. Calcd. for $C_{14}H_{13}N_2NaO_4S_2\cdot0.5H_2O$: C, 45.52; H, 3.82; N, 7.58. Found: C, 45.50; H, 3.66; N, 7.57.

7-Ureidodesacetoxycephalosporanic Acid (IIf).—A suspension of 2.14 g. (0.01 mole) of IIb in 20 ml. of water containing 0.811 g. (0.01 mole) of potassium cyanate was stirred for 7 hr. at room temperature. Acidification of the resulting clear solution to pH 0.5 with hydrochloric acid gave 1.95 g. of white solid (IIf as free acid). This was suspended in 70 ml. of methanol and stirred at 5° while cyclohexylamine was added to pH 7.3. The solid dissolved and the solution was evaporated to a foam which was crystallized from water–*tert*-butyl alcohol to give 1.74 g. (45%) of the colorless **cyclohexylammonium salt** of the product, m.p. 173–174° dec. after air-equilibration; lactam carbonyl stretching at 5.71 μ (Nujol).

Anal. Calcd. for $C_9H_{11}N_3O_4S\cdot C_6H_{13}N\cdot H_2O$: C, 48.11; H, 7.00; N, 14.96. Found: C, 48.17; H, 6.89; N, 14.68.

Acknowledgments.—The authors are indebted to Mrs. D. A. Rolston and her staff for the microanalyses reported herein, to Dr. W. E. Thompson for valuable discussions of the interpretation of n.m.r. spectra, and to Dr. C. A. Simpson for the determination of pK_a values. They also wish to thank Miss M. Dolan and her staff for carrying out the microbiological work.

(14) From Engelhard Industries, Inc., Newark, N. J. The catalyst was a brown powder. A gray-colored palladium on barium sulfate produced by the same company gave less satisfactory results, as did palladium on carbon.

(15) German Patent 965,703 (1957).

(16) Several weeks were required for equilibration. A shorter period gave material with propanol of crystallization.

(17) 2-Thienylacetic acid (J. H. Ford, G. C. Prescott, and D. R. Colingsworth, *J. Am. Chem. Soc.*, **72**, 2109 (1950)) was converted to the acid chloride (b.p. 52° at 0.2 mm.) by refluxing with thionyl chloride in benzene.

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Hypocholesterolemic Agents. IV.[1] 3α-Methoxy-5α-androstane Derivatives

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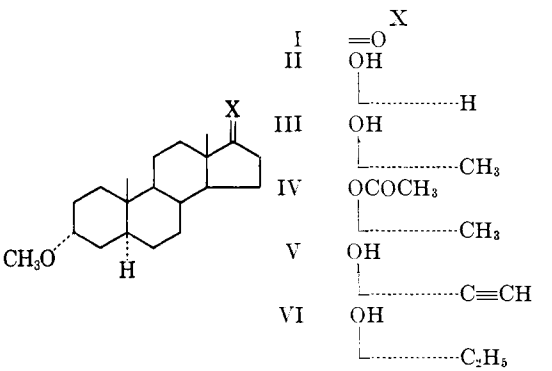
Received October 10, 1963

In 1959 Hellman and associates[2] demonstrated that the serum cholesterol levels of hypercholesterolemic patients could be reduced by the parenteral administration of androsterone (3α-hydroxy-5α-androstan-17-one). Later studies by Cohen, *et al.*,[3,4] however, showed that this hypocholesterolemic effect was not achieved when the steroid was given orally. As a consequence of these findings, a program was initiated in our Laboratories aimed at preparing an orally active androsterone analog having a good separation of hypocholesterolemic and androgenic properties. Since it had been previously shown[4,5] that orally administered androsterone is rapidly conjugated in the liver and excreted predominantly as the 3-glucuronide, it was felt that etherification of the 3α-hydroxyl group would inhibit this conjugation and lead to orally effective compounds. As a result, a series of 3α-methoxy-5α-androstane derivatives was synthesized and biologically evaluated.



The methyl ether of androsterone (I)[6] was readily prepared (74% yield) from epiandrosterone (3β-hy-

(1) Paper III: R. E. Counsell, P. D. Klimstra, and R. E. Ranney, *J. Med. Pharm. Chem.*, **5**, 1224 (1962).

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(5) O. Crépy, M. F. Jayle, and F. Meslin, *Compt. rend. soc. biol.*, **151**, 234 (1957).

(6) Since completion of this work, this compound has been prepared in essentially the same manner by R. Gardi, R. Vitalli, and A. Ercoli, *Gazz. Chim. Ital.*, **92**, 632 (1962).

droxy-5α-androstan-17-one) by methanolysis of the 3β-tosylate. Column chromatography revealed that 5α-androst-2-en-17-one (21% yield) and androsterone (0.9% yield) were also formed as by-products. Reduction of I with sodium borohydride in isopropyl alcohol furnished 3α-methoxy-5α-androstan-17β-ol (II). Similarly, methylation and ethynylation of I by conventional methods gave the 17α-methyl (III) and 17α-ethynyl (V) homologs, respectively. Catalytic hydrogenation of V afforded the 17α-ethyl derivative VI. In view of the potent oral hypocholesterolemic activity displayed by III (see below), the corresponding 3β-epimer (VII) was synthesized for biological comparison. This compound was prepared conveniently by catalytic hydrogenation of known 3β-methoxy-17α-methylandrost-5-en-17β-ol.

Preliminary Biological Results.[7]—The noted inability of androsterone to produce a hypocholesterolemic effect in various laboratory animals[8,9] has contributed to the difficulty in evaluating compounds for androsterone-like activity. Recently, however, Ranney and Saunders[10] observed a decrease in serum cholesterol levels when androsterone was administered subcutaneously to rats made hypercholesterolemic with 6-propylthiouracil. As was the case with humans, no effect was noticed when the compound was given orally. Similarly, in contrast with our initial hopes, I also showed a low order of cholesterol-lowering activity when given orally. In fact, of all the products described, only III[11] was found to have appreciable oral hypocholesterolemic activity. This substance caused a reduction in serum cholesterol of about 10% at a dose of 1 mg./kg. This oral potency was slightly greater than the parenteral potency of androsterone. Moreover, intramuscular administration of III to castrated male rats indicated it to have only $^1/_{20}$ the androgenicity of testosterone propionate. Interestingly, 17α-methyl-5α-androstane-3α,17β-diol, the corresponding free alcohol, was not only essentially devoid of hypocholesterolemic activity but possessed also approximately 10 times the androgenicity of III. The 3β-epimer (VII) of III also was found to lack significant hypocholesterolemic activity even at doses as high as 10 mg./kg. Clinical evaluation of III as a hypocholesterolemic agent is currently in progress and these results will be reported elsewhere.

Experimental[12]

3α-Methoxy-5α-androstan-17-one (I).—3β-Hydroxy-5α-androstan-17-one tosylate[13] (50 g.) was added to methanol (600 ml.) and the mixture heated on a steam bath. The tosylate gradually dissolved and the solution was refluxed for 72 hr. The solvent was removed by distillation under reduced pressure and the residue taken up in ether. The ether solution was washed successively with water, 5% sodium carbonate solution, and water. After drying the organic phase over a mixture of anhydrous potassium carbonate and Darco, the solvent was removed by distillation. Crystallization of the residue from hexane gave I (17.5 g.), m.p. 121–124°. Recrystallization from heptane gave an analytical sample, m.p. 124.5–126.5°, $[\alpha]^{28}D$ +82° (reported[8] m.p. 124–126°, $[\alpha]^{23}D$ + 81° [dioxane]).

Anal. Calcd. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.60. Found: C, 79.05; H, 10.42.

The mother liquor was concentrated to dryness, the residue dissolved in hexane, and the solution adsorbed onto silica gel (1300 g.). Elution with hexane–benzene (1:1) gave 5α-androst-2-en-17-one (6.3 g.), m.p. 104–106° (reported[13] m.p. 105–106°). Further elution with benzene–ethyl acetate (19:1) gave I (7.8 g.) identical with that described above. In addition to these products a small amount of androsterone (0.3 g.), m.p. 185–188° was eluted with benzene–ethyl acetate (4:1).

3α-Methoxy-5α-androstan-17β-ol (II).—To a solution of I (1.0 g.) in isopropyl alcohol (25 ml.) was added a solution of sodium borohydride (0.8 g.) in water (1.5 ml.) and isopropyl alcohol (10 ml.). The mixture was stirred at room temperature for 2.5 hr. and then poured into ice–water. The resulting precipitate was collected by filtration, washed with water, and air-dried. Recrystallization from methanol–water gave pure II (0.9 g.), m.p. 147–149°, $[\alpha]^{26}D$ +7°.

Anal. Calcd. for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.66; H, 11.25.

3α-Methoxy-17α-methyl-5α-androstan-17β-ol (III).—To a solution of 3 *M* methylmagnesium bromide in ether (40 ml.) was added dropwise with stirring a solution of I (2.0 g.) in ether (60 ml.). The mixture was refluxed with stirring for 6 hr. and allowed to stand overnight at room temperature. A solution of ammonium chloride (4 g.) in water (30 ml.) was added dropwise with stirring to the cooled reaction mixture. The ether phase was separated, washed with water, and dried over a mixture of anhydrous potassium carbonate and Darco. Removal of the solvent *in vacuo* and crystallization of the residue from methanol–water gave pure III (1.2 g.), m.p. 141.5–143°, $[\alpha]_D^{26}$ −14°.

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32. Found: C, 78.42; H, 11.17.

The 17-acetate (IV) was prepared by refluxing a solution of III (1 g.) in pyridine (14 ml.) and acetic anhydride (7 ml.) for 7 hr. The solution was allowed to stand overnight at room temperature and poured into ice–water. The precipitate was collected, washed with water, and air-dried. Recrystallization from methanol–water gave pure IV (0.9 g.), m.p. 131–133°, $[\alpha]^{28}D$ −3.5°.

Anal. Calcd. for $C_{23}H_{38}O_3$: C, 76.19; H, 10.57. Found: C, 76.46; H, 10.30.

17α-Ethynyl-3α-methoxy-5α-androstan-17β-ol (V).—Potassium hydroxide flakes (36 g.) was added with stirring to a solution of diethyleneglycol dimethyl ether (180 ml.) and diethylene glycol monoethyl ether (10 ml.) previously heated to 130°. The stirred reaction mixture was allowed to cool slowly in order to provide a fine dispersion of the potassium hydroxide. The reaction vessel was surrounded by an ice–alcohol bath and acetylene gas passed into the rapidly stirred mixture for 3 hr. A solution of I (6.5 g.) in diethylene glycol dimethyl ether (50 ml.) was then added slowly with stirring. The addition of acetylene gas and stirring were continued for another hour. Water (100 ml.) was added slowly with stirring and the contents were poured slowly into ice–water (1200 ml.) containing concentrated hydrochloric acid (55 ml.). The crude products was dissolved in acetone–ether (1:3, 200 ml.) and the solution decolorized with Darco. The solvent was evaporated under a stream of nitrogen and the residue crystallized from methanol–water. This afforded pure V (5.9 g.) as the methanol solvate, m.p. 62–65°, $[\alpha]^{28}D$ −38.5°.

Anal. Calcd. for $C_{22}H_{34}O_2 \cdot CH_3OH$: C, 76.19; H, 10.57. Found: C, 76.52; H, 10.16.

17α-Ethyl-3α-methoxy-5α-androstan-17β-ol (VI).—A solution of V (1.5 g.) in 95% ethanol (20 ml.) was hydrogenated at atmospheric pressure and 25° over 5% palladium-on-carbon (0.15 g.).[14] When hydrogen uptake was complete (0.5 hr.), the catalyst was removed by filtration and washed well with 95% ethanol. The filtrate was concentrated to dryness *in vacuo* and the resulting residue crystallized from ethanol–water. This afforded pure VI (1.4 g.), m.p. 107–108°, $[\alpha]^{25}D$ −11.5°.

(7) We are grateful to Drs. R. E. Ranney, F. J. Saunders, and E. F. Nutting of our Biological Research Division for furnishing us with this information.

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(9) L. Hellman, H. L. Bradlow, B. Zumoff, D. K. Fukushima, and T. F. Gallagher, *Acta Endocrinol., Suppl.*, **51**, 873 (1960).

(10) R. E. Ranney and F. J. Saunders, *Endocrinology*, in press.

(11) For a more complete description of the biological properties of this compound see ref. 10.

(12) The elemental analyses and optical rotations (in chloroform) were furnished by our Analytical Department under the supervision of Dr. R. T. Dillon. The melting points were obtained on a Fisher-Johns apparatus and are corrected.

(13) J. Iriarte, G. Rosenkranz, and F. Sondheimer, *J. Org. Chem.*, **20**, 542 (1955).

(14) We are indebted to Mr. J. D. Clark for performing this catalytic hydrogenation.

Anal. Calcd. for $C_{22}H_{38}O_2$: C, 78.98; H, 11.45. Found: C, 78.85; H, 11.25.

3β-Methoxy-17α-methyl-5α-androstan-17β-ol (VII).—To a solution of 3β-methoxy-17α-methylandrost-5-en-17β-ol[15] (1.0 g.) in 95% ethanol (35 ml.) was added 5% palladium-on-carbon (0.1 g.). The mixture was hydrogenated at atmospheric pressure and room temperature.[14] Hydrogen uptake was complete after 3 hr. and the catalyst was removed by filtration and washed with ethanol. The solvent was removed from the filtrate and the residue crystallized from 95% ethanol. This gave VII (0.8 g.), m.p. 178–179°, and a second crop (0.15 g.), m.p. 176–178°. Recrystallization from methanol–water afforded an analytical sample, m.p. 180–181°, $[\alpha]^{26}D$ −16.5°.

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32. Found: C, 78.71; H, 11.35.

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Acknowledgment.—We wish to thank Dr. F. B. Colton for his interest and comments during the course of this work.

New Compounds

Synthesis of the Three Isomeric 7-Pyridylbenz(a)anthracenes

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Received September 30, 1963

In view of the suspected causal relationship between certain polynuclear compounds related to benz(a)anthracene found in some polluted air and lung cancer,[2] we decided to prepare the three isomeric 7-pyridylbenz(a)anthracenes and have them screened for possible carcinogenic activity. The synthetic route to these compounds involves extensions to useful cyclodehydration reactions previously recorded.[3,4]

Experimental[5]

2-(1-Naphthylmethyl)phenyl 4-Pyridyl Ketone.—A Grignard reagent was prepared in dry ether from 1.6 g. (0.068 mole) of magnesium and 20 g. (0.068 mole) of 2-(1-naphthylmethyl)-bromobenzene.[6] When the reaction was complete, a solution of 7.0 g. (0.068 mole) of 4-cyanopyridine[7] in dry ether was added dropwise and the mixture was then heated under reflux overnight. It was then cooled, decomposed with dilute hydrochloric acid, stirred, and heated under reflux for 4 hr. The aqueous layer was separated, made basic with sodium hydroxide, and extracted with an acetone–ether mixture. The organic portions were combined, dried over anhydrous magnesium sulfate, and concentrated. The residue was distilled; yield, 13.5 g. (62%), b.p. 246–254° (3 mm.). The viscous oil crystallized on standing and was recrystallized twice from ethanol, m.p. 107–108°.

Anal. Calcd. for $C_{23}H_{17}NO$: C, 85.45; H, 5.30; N, 4.33. Found: C, 85.12; H, 5.28; N, 4.29.

The 3- and 2-pyridyl isomers were prepared in a similar manner. The 3-isomer, b.p. 248–255° (3 mm.) was obtained in 48% yield as a viscous red oil. The analytical sample was taken from a redistilled portion, b.p. 237–239° (0.5 mm.).

Anal. Calcd. for $C_{23}H_{17}NO$: C, 85.45; H, 5.30; N, 4.33. Found: C, 85.82; H, 5.28; N, 3.90.

The 2-isomer, b.p. 250–253° (2 mm.) was obtained in 40% yield as a viscous red oil. The analytical sample was taken from a redistilled portion, b.p. 225–226° (0.5 mm.).

Anal. Calcd. for $C_{23}H_{17}NO$: C, 85.45; H, 5.30; N, 4.33. Found: C, 85.59; H, 5.38; N, 4.37.

7-(4-Pyridyl)benz(a)anthracene.—A mixture of 1 g. (0.0031 mole) of 2-(1-naphthylmethyl)phenyl 4-pyridyl ketone and 7 g. of dihydrogen phenyl phosphate was heated at 190° for 5 hr. The mixture was cooled and made alkaline with sodium hydroxide solution. The precipitate which resulted was collected and dried; 0.9 g. (96%), m.p. 243–244°. The material was recrystallized from ethanol giving light tan plates; m.p. 245–246°.

Anal. Calcd. for $C_{23}H_{15}N$: C, 90.46; H, 4.95; N, 4.59. Found*: C, 90.29; H, 4.92; N, 4.47.

The same product was obtained in 87% yield using a previously described standard acid mixture.[8]

The 3-pyridyl isomer, m.p. 221–222°, was obtained in 69% yield (45%, by standard acid mixtures[8]). It was recrystallized from ethanol and formed white plates, m.p. 222–223°.

Anal. Calcd. for $C_{23}H_{15}N$: C, 90.46; H, 4.95; N, 4.59. Found*: C, 90.24; H, 4.86; N, 4.57.

Anal. Calcd. for $C_{23}H_{15}N$: C, 90.46; H, 4.95; N, 4.59.

The 2-isomer, m.p. 151–152°, was obtained in 45% (80%[8]) yield. It was recrystallized from ethanol as white plates, m.p. 152.5–153.5°.

Anal. Calcd. for $C_{23}H_{15}N$: C, 90.46; H, 4.95; N, 4.59. Found*: C, 90.18; H, 4.99; N, 5.64.

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α-Alkyloximinocarboxamides for Biological Testing

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Received October 2, 1963

The title compounds, not previously reported, were prepared according to the procedure outlined by Woolley and co-workers.[1] At present the compounds are being screened for biological activity.

Amide	% Amide based on acid	M.p., °C.	% Nitrogen[a] Calcd.	% Nitrogen[a] Found
α-Benzyloximino-butyramide	70.4	59–61	13.59	13.80
α-Benzyloximino-β-phenylpropionamide	37[b]	86–88	10.44	10.47
α-Benzyloximino-propionamide	86.7	91–94	14.58	14.72
α-Methyloximino-propionamide	35.1	68–71	24.13	23.82
α-Benzyloximino-phenylacetamide	80.4	100–102	11.02	11.00

[a] Nitrogen analyses were obtained from the Coleman Nitrogen Analyzer. [b] Prepared from α-benzyloximino-β-phenylpropionyl chloride and aqueous ammonia. Acids were prepared from substituted malonic esters by established procedures.[2,3]

Acknowledgment.—The author wishes to thank the University of Illinois Research Board for financial assistance and G. W. Adelstein, P. V. Halushka, and S. R. Janik for technical assistance.

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(3) C. K. Bradsher, *J. Am. Chem. Soc.*, **62**, 486 (1940).

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(5) All melting points were taken on a Fisher-Johns melting point block and are corrected; all the analyses were carried out by Geller Laboratories Bardonia, New York, except those marked with an asterisk which were carried out by Galbraith Laboratories, Knoxville, Tennessee.

(6) A Grignard reaction between 2-bromobenzaldehyde and 1-naphthylmagnesium bromide gave a mixture which was reduced to 2-(1-naphthylmethyl)bromobenzene. For details see P. Polss, Ph.D. dissertation, Virginia Polytechnic Institute, Blacksburg, Va., 1962.

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