Anal. Calcd. for $C_{14}H_{18}N_6O_4$ (334): C, 50.3; H, 5.4; N, 25.1. Found: C, 50.5; H, 5.7; N, 25.1.

2-Methylthio-3-(2-carbethoxyethyl)-6,7-dimethyl-4(3H)-pteridinone (XV). A solution of 1 g. (4.5 mmoles) of 2-methylthio-4-hydroxy-6,7-dimethylpteridine[1] (XIV) in 60 ml. of 50% aqueous pyridine containing 2 ml. of ethyl acrylate was heated to reflux for 33 hr. Two-milliliter portions of ethyl acrylate were added at 6-hr. intervals until a total of 10 ml. had been added. The solvents were removed *in vacuo* and the resulting oil taken up in absolute alcohol, treated with Norit, and filtered. An oil came out of the dark solution which crystallized on standing; yield 0.55 g. (38%). After two recrystallizations from isopropyl alcohol the yield was 0.30 g. (20.6%), m.p. 156–159°. R_f 0.87 (dark purple absorption) in butanol–5 *N* acetic acid (7–3). Ultraviolet absorption spectra in 0.1 *N* NaOH, λ_{max} 249 mμ (ε 13,100), 288 mμ (ε 12,300), 335 mμ (ε 7720); 0.1 *N* HCl, λ_{max} 246 mμ (ε 13,200), 287 mμ (ε 14,630), 335 mμ (ε 7900).

Anal. Calcd. for $C_{14}H_{18}N_4O_3S$ (322.3): C, 52.2; H, 5.6; N, 17.4; S, 10.0. Found: C, 52.2; H, 6.1; N, 17.0; S, 9.9.

2-Methylthio-3-(2-carboxamidoethyl)-6,7-dimethyl-4(3H)-pteridinone (XVI). Seven hundred and fifty milligrams (2.3 mmoles) of compound XV was dissolved in 75 ml. of methanol, cooled to −3°, and anhydrous ammonia passed in for 20 min. (final temperature 14°). The solution was chilled overnight (protected with Drierite) then allowed to stand at room temperature for several hours during which time some crystals appeared. In order to ensure complete reaction the mixture was heated to reflux for 1 hr. and then evaporated to about 20 ml. and cooled; yield 0.35 g. (52%), m.p. 261–264°. Recrystallization of the product from 20 ml. of water containing 4 ml. of ethanol gave 0.26 g. (39%), m.p. 265–267°. R_f 0.61 (absorption) in 3% NH_4Cl; 0.57 (dark purple fluorescence) in butanol–5 *N* acetic acid (7:3). Ultraviolet absorption spectra in 0.1 *N* NaOH, λ_{max} 245 mμ (ε 10,900), 288 mμ (ε 11,200), 333 mμ (ε 6950); 0.1 *N* HCl, λ_{max} 247 mμ (ε 13,800), 287 mμ (ε 14,900), 335 mμ (ε 8210).

Anal. Calcd. for $C_{12}H_{15}O_2N_5S$ (293.3): C, 49.1; H, 5.2 N, 23.9; S, 10.9. Found: C, 49.0; H, 5.2; N, 23.8; S, 10.8.

3-(2-Carboxyethyl)6,7-dimethyl-2,4-(1H,3H)-pteridinedione (XVII). 2-Methylthio-3-(2-carbethoxyethyl)-6,7-dimethyl-4(3*H*)-pteridinone (XV) (100 mg., 0.31 mmole) was heated on a steam bath for 2.5 hr. in 5 ml. of 1.0 *N* hydrochloric acid. The hot solution was treated with Norit, filtered, and chilled, yield 50 mg. (60%); m.p. 287–293° dec. R_f 0.88 (blue fluorescence) in 0.5% Na_2CO_3. Ultraviolet absorption spectra in 0.1 *N* NaOH, λ_{max} 247 mμ (ε 17,500), 271 mμ (ε 11,350), 361 mμ (ε 7540); 0.1 *N* HCl, λ_{max} 232 mμ (ε 12,500), 330 mμ (ε 10,300).

Anal. Calcd. for $C_{11}H_{12}N_4O_4$ (264.2): C, 50.0; H, 4.6; N, 21.1. Found: C, 50.3; H, 4.8; N, 21.3.

Acknowledgment. We wish to thank Mr. Louis Brancone and staff for the microanalyses reported and also Mr. William Fulmor and Mr. George Morton for the ultraviolet and infrared absorption spectra.

PEARL RIVER, N. Y.

[CONTRIBUTION FROM THE RESEARCH INSTITUTE FOR TROPICAL MEDICINE, CAIRO]

Some Pyrido[1,2-*a*]pyrimidones

H. ANTAKI

Received September 20, 1961

The facile reaction of ethyl α-ethoxyethylidenecyanoacetate with 2-aminopyridine and its 3- and 4-methyl derivatives to yield the corresponding 4*H*-pyrido[1,2-*a*]pyrimidones is ascribed to hyperconjugation. The ultraviolet spectra of several 4*H*-pyrido[1,2-*a*]pyrimidones are reported and display a band with λ_{max} at *ca.* 245 mμ ascribed to the —C=C—C=O chromophore of the pyrimidine moiety. This observation is extended to the spectra of 5*H*-thiazolo[3,2-*a*]pyrimidine-5-one and *s*-triazolo[2,3-*a*]pyrimidine-7-one. The condensation of ethyl acetaminomalonate with 2-aminopyridine and its 4-methyl derivative is reported.

The thermal facile cyclization of ethyl 2-pyridylaminocrotonate[1] as compared with the α-substituted β-2-pyridylaminoacrylate,[2] which could only be cyclized by distillation under reduced pressure, prompted the synthesis of similarly substituted crotonic esters to determine whether this effect may be attributed to the unsaturated α-substituent or to hyperconjugation.[3]

Refluxing ethyl orthoacetate with ethyl cyanoacetate in acetic anhydride solution gave ethyl α-ethoxyethylidenecyanoacetate in moderate yield. Reaction of the latter ester with 2-aminopyridine and its 3- and 4-methyl derivatives at 150° gave by condensation followed by smooth cyclization 2-methyl, 2,9-, and 2,8-dimethyl-3-cyano-4*H*-pyrido[1,2-*a*]pyrimidine-4-one in excellent yield. The effect of hyperconjugation on ease of cyclization is thus clearly evidenced.

The ultraviolet spectra in absolute ethanol are reported in Figure 1. It is to be remarked that the absorption spectrum of 3-cyano-2,8-dimethyl-4*H*-pyrido[1,2-*a*]pyrimidine-4-one exhibits the normal three bands characteristic of 4*H*-pyrido[1,2-*a*]pyrimidine-4-one bearing an unsaturated 3-substituent (Fig. 1).

The previously observed rearrangement[2] of ethyl 4-methyl-2-pyridylaminomethylenecyanoacetate to ethyl *N*-(4-methyl-2-imino-1,2-dihydropyridyl)methylenecyanoacetate led by cyclization to the isomeric 3-cyano-8-methyl-2*H*-pyrido[1,2-*a*]pyrimidine-2-one, which displayed an anomalous ultraviolet spectrum. Such a rearrangement is partly dependent on the thermal lability of the —C—N= bond. The effect of electron release due

(1) H. Antaki and V. Petrow, *J. Chem. Soc.*, 551 (1951).
(2) H. Antaki, *J. Am. Chem. Soc.*, **80**, 3066 (1958).
(3) R. S. Mulliken, *J. Am. Chem. Soc.*, **63**, 41–56 (1941); *J. Chem. Phys.*, **7**, 339 (1939).

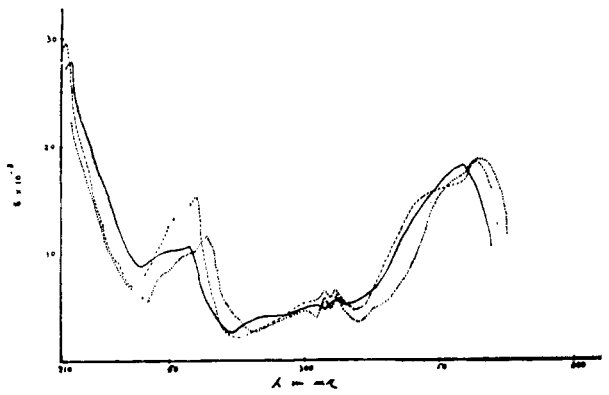


Fig. 1. Ultraviolet spectra of 3-cyano-2-methyl (---), 3-cyano-2,8-dimethyl (—), and 3-cyano-2,9-dimethyl-4*H*-pyrido[1,2-*a*]pyrimidine-4-one (. . . . . .)

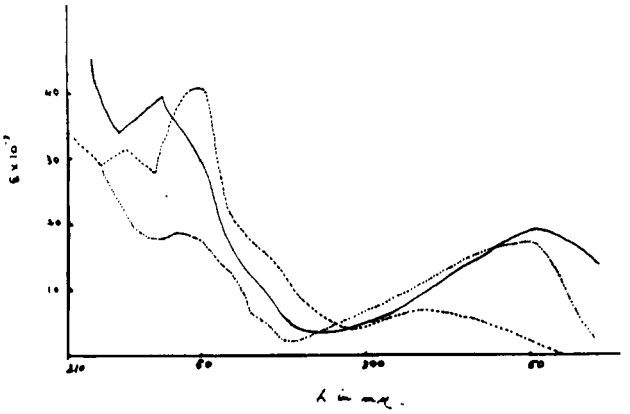


Fig. 2. Ultraviolet spectra of 2,8-dimethyl (. . . .), 8-carboxamido-2-methyl (—), and 8-methyl-2,3-dihydro-2-oxo-4*H*-pyrido[1,2-*a*]pyrimidine-4-one (---)

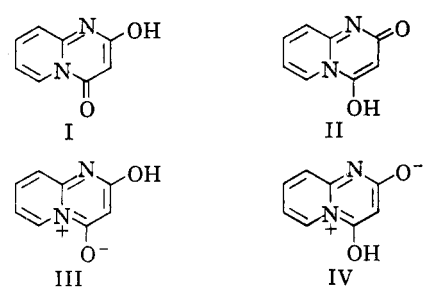
to hyperconjugation will result in additional strength of this bond while facilitating cyclization.

As illustrated by the absorption curve of the 2,8-dimethyl derivative (Fig. 2) the spectrum of 4*H*-pyrido[1,2-*a*]pyrimidine-4-one[4,5] displays two bands one with λ_{max} at *ca.* 350 mμ previously ascribed to the *N*-substituted pyridone-2-imine chromophore.[2] The second band with λ_{max} at *ca.* 245 mμ is now attributed to the $-\overset{|}{C}=\overset{|}{C}-C=O$ chromophore of the pyrimidine moiety. The introduction of an unsaturated substituent in the 3- position results in a bathochromic shift of this band λ_{max} occurring at 258–264 mμ due to extended conjugation (Fig. 1). A new region of absorption with λ_{max} at *ca.* 308 mμ pertaining to the β-amino-α,β-unsaturated carbonyl or cyano chromophore also appears.[2]

Pyrimidines with carboxamide groups lacking unsaturated linkages in the ring such as alloxan or dialuric acid exhibit only end absorption at *ca.* 230 mμ characteristic of the carboxamide group.[6,7] Uracil with a $-\overset{|}{C}=\overset{|}{C}-C=O$ chromophore has a characteristic band with λ_{max} at 260 mμ (ϵ 9000). Barbituric acid where such a chromophore can be established by enolization of either of the two carboxamide groups displays a band with an intense hyperchromic effect (ϵ 24,000) indicative of such tautomerism.[6]

In order to determine the role played by the $-\overset{|}{C}=\overset{|}{C}-C=O$ chromophore in the absorption spectrum of 4*H*-pyrido[1,2-*a*]pyrimidine-4-one, the introduction of a second group was considered. This was achieved by the condensation of 6-aminonicotinamide with ethyl β-aminocrotonate to give 8-carboxamido-2-methyl-4*H*-pyrido[1,2-*a*]pyrimidine-4-one in good yield. As shown in Figure 2, whereas the *N*-substituted pyridone-2-imine band is chiefly unaffected the $-\overset{|}{C}=\overset{|}{C}-C=O$ band has doubled in intensity. The low intensity of absorption of the carboxamide chromophore, as displayed in the pyrimidines referred to above, is clear evidence that the observed hyperchromic effect in 8-carboxamido-2-methyl-4*H*-pyrido[1,2-*a*]pyrimidine-4-one is to be attributed essentially to the $-\overset{|}{C}=\overset{|}{C}-C=O$ chromophore.

Further corroborative evidence was obtained from the study of the ultraviolet spectra of 2,3-dihydro - 2 - oxo - 4*H* - pyrido[1,2-*a*]pyrimidine-4-one and its 8-methyl derivative. The absorption curve of the latter is shown in Figure 2 and exhibits an intense hyperchromic effect of the $-\overset{|}{C}=\overset{|}{C}-C=O$ band, previously observed as cited above in barbituric acid, and ascribed to tautomeric enolization. Considerable lowering of the intensity of the pyridone-2-imine band is indicative of the contribution of fully aromatic zwitterionic structures (III, IV) to the resonance state of the molecule which is best represented by structures I to IV. Such a view has previously been advanced solely on



(4) H. Antaki, "Contribution to the Chemistry of Heterocyclic Compounds," Ph.D. thesis, London (1950).

(5) R. Adams and I. Pachter, *J. Am. Chem. Soc.*, **74**, 5491 (1952).

(6) F. Heyroth and J. R. Loofbourow, *J. Am. Chem. Soc.*, **56**, 1728 (1934).

(7) L. F. Cavalier and A. Bendich, *J. Am. Chem. Soc.*, **72**, 2587 (1950).

(8) A. E. Tschtschibabin, *Ber.*, **57**, 1168 (1924); *J. Russ. Phys. Chem. Soc.*, **57**, 399 (1926).

(9) H. R. Snyder and M. M. Robison, *J. Am. Chem. Soc.*, **74**, 4910 (1952).

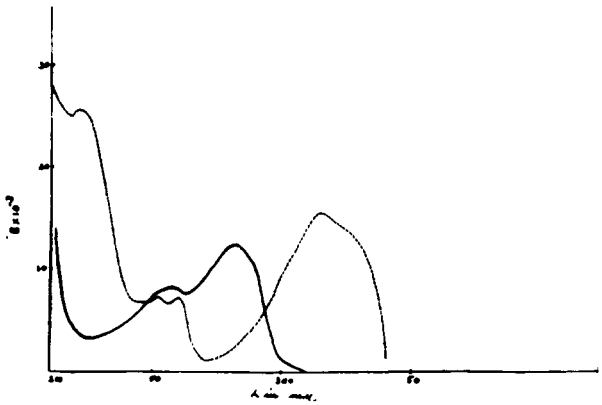
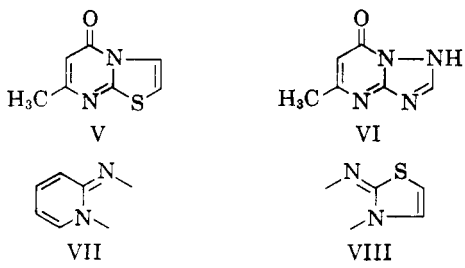


Fig. 3. Ultraviolet spectra of 7-methyl-5-thiazolo[3,2-*a*]pyrimidine-5-one (---), and 5-methyl-*s*-triazolo[2,3-*a*]-pyrimidine-7-one (—)

the basis of chemical and infrared spectral evidence.[9]

In support of the above interpretation of the two band spectrum of 4*H*-pyrido[1,2-*a*]pyrimidine-4-one, the absorption spectra of 7-methyl-5*H*-thiazolo[3,2-*a*]pyrimidine-5-one (V) and 5-methyl-*s*-triazolo[2,3-*a*]pyrimidine-7-one were investigated[10] (VI). As indicated in Figure 3 the $-\overset{|}{C}=\overset{|}{C}-C=O$ band of the pyrimidine moiety is the common feature in the spectra of this class of compounds derived by condensation of cyclic amidines with either β-keto esters or one of their derivatives or α-ethoxymethylene carboxylic esters. The second band is dependent on the cyclic amidine chromophore, in the former, case 2-imino-2,3-dihydrothiazole and in the latter 3-imino-2,3-dihydro-1,2,4-triazole with λ_{max} 315 mμ (ε 15,300) and λ_{max} 285 mμ (ε 12,000), respectively.



V VI

VII VIII

Replacement of a $-\overset{|}{C}=\overset{|}{C}-$ group in (VII) (λ_{max} 340, ε 17,000) by —S— in (VIII) (λ_{max} 315, ε 15,300) results in a hypsochromic shift with a slight hypochromic effect in the absorption characteristics of the chromophore.

In continuation of previous work on the schistosomicidal activity in the pyrido[1,2-*a*]pyrimidine series, the synthesis of some basic derivatives was considered. Ethyl acetaminomalonate reacted with 2-aminopyridine and its 4-methyl derivative to give 3-acetamido-2,3-dihydro-4*H*-pyrido[1,2-*a*]pyrimidine-2,4-dione and its 8-methyl derivative, respectively. The former substance crystallized from 90% ethanol with one molecule of water of crystallization. However, the poor yields obtained precluded further synthetic work along these lines. Other approaches to this problem will be reported in a separate publication.

EXPERIMENTAL

Ethyl α-ethoxyethylidenecyanoacetate. Ethyl cyanoacetate (11.3 g., 0.1 mole), ethyl orthoacetate (16.2 g., 0.1 mole), and acetic anhydride (150 cc.) were refluxed for 7 hr. After removal of the anhydride by distillation, the residue was distilled under reduced pressure to give a colorless oil, b.p. 200° (16 mm.), which solidified on cooling. Crystallization from benzene–petroleum ether (b.p. 60–80°) gave colorless needles, m.p. 48°; yield 27%.

Anal. Calcd. for $C_9H_{13}O_3N$: C, 59.0; H, 7.1; N, 7.6. Found: C, 58.8; H, 7.0; N, 7.5.

3-Cyano-2-methyl-4H-pyrido[1,2-a]pyrimidine-4-one. 2-Aminopyridine (0.9 g., 0.01 mmole) and ethyl α-ethoxyethylidenecyanoacetate (1.8 g.) were heated in an oil bath at 150° until the reaction mass solidified. Crystallization of the product from alcohol gave yellow needles, m.p. 243°; yield 74%.

Anal. Calcd. for $C_{10}H_7ON_3$: C, 64.9; H, 3.8; N, 22.7. Found: C, 65.1; H, 4.1; N, 22.8.

The 2,8-dimethyl derivative similarly prepared separated from alcohol in yellow plates, m.p. 222°; yield, 72%.

Anal. Calcd. for $C_{11}H_9ON_3$: C, 66.3; H, 4.6; N, 21.1. Found: C, 66.4; H, 4.7; N, 21.4.

The 2,9-dimethyl derivative crystallized in yellow needles from alcohol, m.p. 183°; yield 84%.

Anal. Calcd. for $C_{11}H_9ON_3$: C, 66.3; H, 4.6; N, 21.1. Found: C, 66.2; H, 4.6; N, 21.1.

8-Carboxamido-2-methyl-4H-pyrido[1,2-a]pyrimidine-4-one. 6-Aminonicotinamide (1.4 g., 0.01 mole) and ethyl β-aminocrotonate (1.3 g., 0.01 mole) were heated in an oil bath until the temperature rose to 260–270°. The temperature was maintained until the reaction mass solidified. After cooling it was crystallized from alcohol–acetic acid to give yellow platelets, m.p. above 300°; yield 87%.

Anal. Calcd. for $C_{10}H_9O_2N_3$: C, 59.1; H, 4.5; N, 20.7. Found: C, 59.1; H, 4.6; N, 20.3.

8-Methyl-2,3-dihydro-4H-pyrido[1,2-a]pyrimidine-2,4-dione. 4-Methyl-2-aminopyridine (5.4 g., 0.05 mole) and ethyl malonate (8 g., 0.05 mole) were heated in an oil bath at 70° for several hours. After cooling the reaction mass was crystallized from alcohol to give yellow needles, m.p. 256° dec.; yield 72%.

Anal. Calcd. for $C_9H_8O_2N_2$: C, 61.3; H, 4.5; N, 15.9. Found: C, 61.1; H, 4.4; N, 15.8.

2,3-Dihydro-4H-pyrido[1,2-a]pyrimidine-2,4-dione similarly prepared crystallized from alcohol in buff yellow platelets, m.p. 305° dec. The substance is reported to melt at 295–298° dec.[8,9] on rapid heating.

5-Methyl-s-triazolo[2,3-a]pyrimidine-7-one. 3-Amino-1,2,4-triazole (0.8 g., 0.01 mole) and ethyl β-aminocrotonate (1.3 g., 0.01 mole) were heated in an oil bath at 150°; the reaction mass rapidly solidified. The white crystalline mass crystallized from alcohol in white needles, m.p. 271°; the yield was nearly theoretical. The substance is identical with that prepared from 3-amino-1,2-4-triazole and ethyl acetoacetate by refluxing in ethanol in presence of piperidine as catalyst.[11]

(10) H. Allen *et. al., J. Org. Chem.*, **24**, 779 (1959).

(11) C. Bulow and K. Haas, *Ber.*, **42**, 4638 (1907). The spectra reported in Figure 3 were determined in this laboratory in 1958 in conjunction with work carried out on the ultraviolet spectra of pyrido[1,2-*a*]pyrimidones. Delay in publication awaited completion of this and other works.

3-Acetamido-2,3-dihydro-4H-pyrido[1,2-a]pyrimidine-2,4-dione. 2-Aminopyridine (1 g., 0.01 mole) and ethyl acetaminomalonate (2.2 g., 0.01 mole) were heated in an oil bath at 70° for 3 hr. The temperature was then raised to 200° and maintained for 2 hr. Purification of the reaction product from alcohol benzene–petroleum ether followed by crystallization from 90% ethanol gave bright yellow platelets, m.p. 270° dec.; yield 14%.

Anal. Calcd. for $C_{10}H_9O_3N_3 \cdot H_2O$: C, 50.6; H, 4.6; N, 17.7. Found: C, 50.3; H, 4.8; N, 17.6.

The 8-methyl derivative similarly prepared separated from benzene–petroleum ether in pale yellow prisms, m.p. 274° dec.; yield 10%.

Anal. Calcd. for $C_{11}H_{11}O_3N_3$: C, 56.6; H, 4.7; N, 18.0. Found: C, 56.5; H, 4.6; N, 17.9.

AGOUZA, CAIRO, EGYPT

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH, PUBLIC HEALTH SERVICE, U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE]

Steroids with Functional Sulfur Groups. I. 9α-Thiocyanocortisone and -cortisol[1]

TOSHIO KAWASAKI[2] AND ERICH MOSETTIG

Received October 16, 1961

The synthesis 9α-thiocyanocortisone and -cortisol and their acetates from the appropriate 9β,11β-epoxides is described. By an analogous route 9α,11α-epoxy-5β-pregnane-17α,21-diol-3,20-dione acetate was converted to the expected 3α,9α-epoxy-11β-thiocyano derivatives.

This paper and following ones of this series describe our efforts toward the partial synthesis of various steroid hormone analogs in which the oxygen of functional groups is replaced by sulfur.

A considerable number of sulfur analogs of steroids have been described in the recent literature. The majority of them are steroids with the sulfur-containing group in the 3-position,[3] and specifically corticoids and androgens with sulfur functions attached to C-21[4] or to C-17.[5] A few other types worthy of mentioning are the pregnane-20-thiones,[6] 6β-isothiocyano-3α,5-cyclo-5α-cholestane,[7] and the 1α- and 7α-acylthio(or thiol)- and the 1α,7α-diacylthio(or thiol)-Δ⁴-3-keto steroids.[8,9]

The present study was undertaken primarily with the aim of synthesizing corticoids or androgens with a sulfur-containing substituent at C-11. A few of the negative attempts toward this end may be mentioned cursorily. The direct conversion of an epoxide to an episulfide with potassium thiocyanate[10] could not be realized when attempted with 11β,12β-epoxy-23a-bromotigogenin acetate and 9β,11β-epoxy-Δ⁴-pregnene-17α,21-diol-3,20-dione acetate.[11] Attempts at adding thiolacetic acid or trichlorothiolacetic acid to the 9,11-double bond (of Δ⁹⁽¹¹⁾-tigogenin acetate or of Δ⁴,⁹⁽¹¹⁾-pregnadiene-17α,21-diol-3,20-dione acetate) were unsuccessful in spite of a wide variation of experimental conditions including irradiation with incandescent light (G.E. Photospot lamp). Only starting material was recovered. Equally unsuccessful were the attempts of replacing the 11α-bromine (in 11α,23a-dibromo-12-ketotigogenin acetate and 11α,23a-dibromo-12β-

(1) A preliminary account of this paper was published by T. Kawasaki and E. Mosettig, *J. Org. Chem.*, 24, 2071 (1959).

(2) Visiting Scientist (1957–1959), National Institutes of Health, under the sponsorship of the Cancer Chemotherapy National Service Center, National Cancer Institute.

(3) (a) T. Wagner-Jauregg and T. Lennartz, *Ber.*, 74, 27 (1941); L. C. King, R. M. Dodson and L. A. Subluskey, *J. Am. Chem. Soc.*, 70, 1176 (1948); J. Strating and H. J. Backer, *Rec. trav. chim.*, 69, 638 (1950). (b) S. Bernstein and K. Sax, *J. Org. Chem.*, 16, 679 (1951); J. A. K. Butsman and P. Westerhof, *Rec. trav. chim.*, 71, 925 (1952). (c) R. Bourdon, *Bull. soc. chim. France*, 722 (1958). (d) R. Bourdon, *Bull. soc. chim. France*, 1117 (1958).

(4)(a) L. H. Sarett, *J. Am. Chem. Soc.*, 71, 1175 (1949). (b) C. Djerassi and A. L. Nussbaum, *J. Am. Chem. Soc.*, 75, 3700 (1953).

(5)(a) R. M. Dodson and P. B. Sollman (to G. D. Searle & Co.) U. S. Patent 2,763,669 (1956); *Chem. Abstr.*, 51, 5134a (1957). (b) R. M. Dodson and P. B. Sollman (to G. D. Searle & Co.) U. S. Patent 2,837,538 (1958); *Chem. Abstr.*, 53, 4357c (1959).

(6) R. M. Dodson and P. B. Sollman (to G. D. Searle & Co.) U. S. Patent 2,837,539 (1958); *Chem. Abstr.*, 53, 3282 (1959).

(7) R. Charonnat and R. Bourdon, *Bull. soc. chim. France*, 719 (1958).

(8)(a) R. C. Tweit and R. M. Dodson, *J. Org. Chem.*, 24, 277 (1959). (b) R. M. Dodson and R. C. Tweit, *J. Am. Chem. Soc.*, 81, 1224 (1959).

(9) While this part of our work has been prepared for the regular full-length publication there appeared a series of papers dealing with thio analogs of a variety of steroids by members of the Research Laboratory, Shionogi & Co., Ltd., Imafuku, Amagasaki, Hyogo-ken: (a) K. Takeda and T. Komeno, *Chem. Pharm. Bull.* (Japan), 8, 468 (1960); (b) K. Takeda, T. Kubota, and J. Kawanami, *ibid.* p. 615; (c) K. Takeda, T. Komeno, and J. Kawanami, *ibid.* p. 621; (d) T. Komeno, *ibid.* p. 668; (e) T. Komeno, *ibid.* p. 672; (f) T. Komeno, *ibid.* p. 680. The compounds described therein are 19-C, 21-C, 24-C, and 27-C steroids substituted in positions 5, 6, 11, 12, and 16, with thiocyano and thiol groups.

(10) (a) E. E. van Tamelen, *J. Am. Chem. Soc.*, 73, 3444 (1951). (b) E. E. van Tamelen, *Org. Syntheses*, 32, 39 (1952).

(11) A successful preparation of an 11,12β-episulfide from methyl 3α-acetoxy-11β-thiocyano-12α-chlorocholanate has been reported by Takeda *et al.*, see ref. 9c.