(*Anal.* Calcd. for $C_{11}H_{10}O_3N_4S$: C, 47.50; H, 3.59; N, 20.12; S, 11.52. Found : C, 47.54; H, 3.68; N, 19.98; S, 11.10), respectively.

These results suggest the possibility of the use of 5-bromopyrimidines for the syntheses of new derivatives of amino- or hydroxy-pyrimidines. The details of these reactions and further examples in other pyrimidines will be published later.

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Synthesis of the Ethynylated Steroids
(Studies on Acetylenic Compounds)

Recently, several works on the alkylated steroids bearing methyl group at the 1-,[1] 2-,[2] 4-,[3] 6-,[4] 7-,[5] 11-,[6] 14-,[7] or 16-[8] position have been reported. Some of these alkylated steroids, especially, 6- and 16-methyl compounds are significant in enhancing hormonal activity as compared with the mother steroids.

Considering that 17-ethynylated steroid is more important in variety of its actions, the following steroids ethynylated at 6-, 7-, or 16-position have been prepared from the corresponding oxosteroids.

Addition of 16-oxo-5-androstene-3β,17α-diol 3-methyl ether[9] to lithium acetylide (LiC≡CH) in liquid ammonia and subsequent stirring at -40° for 5 hr. yielded 16α-ethynyl-5-androstene-3β,16β,17α-triol 3-methyl ether (I) of m.p. 191~194°, $[\alpha]_D^{22}$ −66°(in $CHCl_3$), which was converted into 16,17-acetonide by the action of acetone and hydrochloric acid at room temperature.

Analogously 7ξ-ethynyl-5-cholestene-3β,7ξ-diol 3-acetate (III) of m.p. 152.5~154°, $[\alpha]_D^{25}$ −104.3°(in $CHCl_3$), was prepared from 7-oxocholesterol[10] by the action of lithium acetylide and subsequent acetylation.

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7) W. Vosea, *et al.* : Helv. Chim. Acta, **36**, 299(1953).
8) A. Wettstein : *Ibid.*, **27**, 1803(1944); H. Mori, *et al.* : Yakugaku Zasshi, **78**, 813(1958); G. E. Arth, *et al.* : J. Am. Chem. Soc., **80**, 3160, 3161(1958); E. P. Oliveto, *et al.*: *Ibid.*, **80**, 4428, 4431(1958); D. Taub, *et al.* : *Ibid.*, **80**, 4435(1959).
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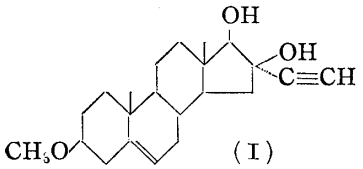
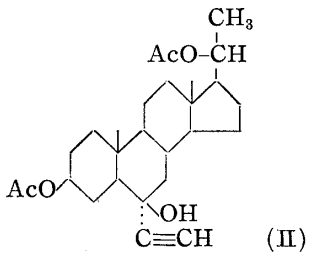
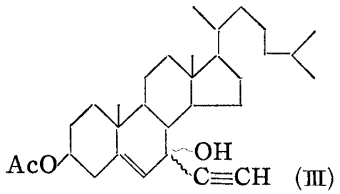
10) A. Windaus : Ann., **520**, 98(1935); K. Heusler, A. Wettstein : Helv. Chim. Acta, **35**, 284(1952).

Nitration of 5-pregnene-3β,20β-diol 3,20-diacetate by the usual method[11] gave 6-nitro-5-pregnene-3β,20β-diol 3,20-diacetate of m.p. 152~155°, $[\alpha]_D^{22.5}$ −98° (in $CHCl_3$), which on reduction by zinc in acetic acid gave 6-oxoallopregnane-3β,20β-diol 3,20-diacetate of m.p. 175~176°. Analogous ethynylation of this compound and successive acetylation afforded 6α-ethynylallopregnane-3β,6β,20β-triol 3,20-diacetate (II) of m.p. 199~200°, $[\alpha]_D^{22}$ +2.7° (in $CHCl_3$).

The resulting compounds of these reactions are summarized below.

	m.p. (uncorr.) (°C)	$[\alpha]_D$	Analysis (%)
 (I)	191~194	$[\alpha]_D^{22}$ −66° (in $CHCl_3$)	Calcd. for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36; O, 13.93. Found : C, 76.95; H, 9.08; O, 19.83.
 (II)	199~200	$[\alpha]_D^{22}$ +2.7° (in $CHCl_3$)	Calcd. for $C_{27}H_{40}O_5$: C, 72.94; H, 9.07. Found : C, 73.35; H, 8.91.
 (III)	152.5~154	$[\alpha]_D^{25}$ −104.3°(in $CHCl_3$)	Calcd. for $C_{31}H_{48}O_3$: C, 79.44; H, 10.32; O, 10.42. Found : C, 79.58; H, 10.09; O, 10.81.

Conversion of these compounds to the hormonally active 3-oxo-Δ^4-steroids and further synthesis of the steroids ethynylated at 6-, 7-, and 16-positions in the other physiologically active steroidal series are being carried out in this laboratory. Details will be published elsewhere.

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