(*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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Research Laboratory,
Shionogi & Co., Ltd.,
Imafuku, Amagasaki,
Hyogo-ken.

Mahiko Horiuchi (堀内真彦)

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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-3 β ,17 α -diol 3-methyl ether⁹⁾ to lithium acetylide ($LiC\equiv CH$) in liquid ammonia and subsequent stirring at -40° for 5 hr. yielded 16 α -ethynyl-5-androstene-3 β ,16 β ,17 α -triol 3-methyl ether (I) of m.p. $191\sim 194^\circ$, $[\alpha]_D^{25} -66^\circ$ (in $CHCl_3$), which was converted into 16,17-acetonide by the action of acetone and hydrochloric acid at room temperature.

Analogously 7 ξ -ethynyl-5-cholestene-3 β ,7 ξ -diol 3-acetate (III) of m.p. $152.5\sim 154^\circ$, $[\alpha]_D^{25} -104.3^\circ$ (in $CHCl_3$), was prepared from 7-oxocholesterol¹⁰⁾ by the action of lithium acetylide and subsequent acetylation.

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Nitration of 5-pregnene-3 β ,20 β -diol 3,20-diacetate by the usual method¹¹⁾ gave 6-nitro-5-pregnene-3 β ,20 β -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-3 β ,20 β -diol 3,20-diacetate of m.p. 175~176°. Analogous ethynylation of this compound and successive acetylation afforded 6 α -ethynylallopregnane-3 β ,6 β ,20 β -triol 3,20-diacetate (II) of m.p. 199~200°, $[\alpha]_D^{22}$ $+2.7^\circ$ (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 $\text{C}_{22}\text{H}_{32}\text{O}_3$: C, 76.70; H, 9.36; O, 13.93. { Found: C, 76.95; H, 9.08; O, 19.83.
(II)	199~200	$[\alpha]_D^{22}$ $+2.7^\circ$ (in CHCl_3)	{ Calcd. for $\text{C}_{27}\text{H}_{40}\text{O}_5$: 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 $\text{C}_{31}\text{H}_{48}\text{O}_3$: 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.

Takamine Research Laboratory,
Sankyo Co., Ltd.,
Nishi-Shinagawa,
Shinagawa-ku, Tokyo.

Issei Iwai (岩井一成)
Tetsuo Hiraoka (平岡哲夫)

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