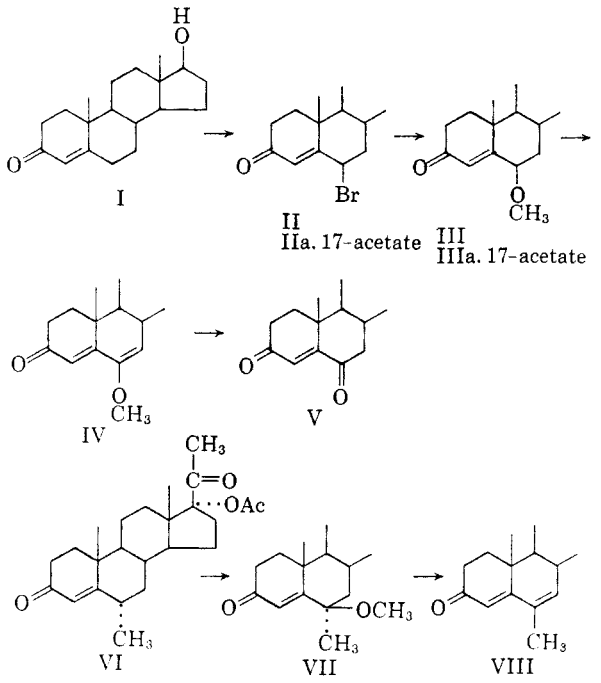

6-dehydro-6-methyl-17α-acetoxyprogesterone.[8] In the Clauberg assay, when given orally, VII was approximately as active as Norlutin (17α-ethynyl-19-nortestosterone) as a progestational agent.[9]

In view of the above reactions, it seems probable that cupric bromide supplies bromine at low concentration[10] for the selective ionic bromination of the steroid at C-6, and that this bromide, in the presence of cupric bromide, is solvolyzed to the 6β-alkoxy compound.

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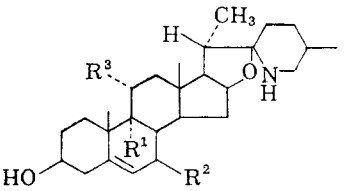
Microbiological Hydroxylation of Steroidal Alkaloids

Sir:

The hydroxylation of steroids by microorganisms has been extensively applied to the C_{19} and C_{21} steroids of adrenal and sex hormonal origin.[1,2] More recently this technique has been extended to the cardiac lactones.[3,4] The steroidal sapogenins,[5] on the other hand, do not appear to hydroxylate readily.

The hydroxylation of the amino analogs of these sapogenins, the steroidal alkaloids solasodine and tomatidine, has not been reported so far. We wish now to report the microbiological hydroxylation of these alkaloids. The incubation of solasodine (I) (R^1, R^2, R^3 = H) with *Helicostylum piriforme* (A.T.C.C. 8992) resulted in the formation of 9α-hydroxysolasodine (II) (R^1 = OH; R^2, R^3 = H), m.p. 213–215°, $[\alpha]_D^{20}$ −138° (chloroform) (found: C, 75.38; H, 9.99) (yield *ca.* 27%); 11α-hydroxysolasodine (III) (R^3 = OH; R^1, R^2 = H) m.p. 200–203°, $[\alpha]_D^{20}$ −110° (chloroform) (found: C, 75.41; H, 10.41) (yield *ca.* 1%); 7ξ-hydroxysolasodine (IV) (R^2— = ~~OH; R^1, R^3 = H) m.p. 234–238° dec., $[\alpha]_D^{20}$ −82.4° (chloroform)



I. (R^1, R^2, R^3 = H)
II. (R^1 = OH; R^2, R^3 = H)
III. (R^3 = OH; R^1, R^2 = H)
IV. (R^2— = ~~OH; R^1, R^3 = H)
VI. (R^1, R^3 = H; R^2— = O=)

(found: C, 76.73; H, 10.58) (yield *ca.* 1%) and an unidentified dihydroxysolasodine (V), m.p. 256–259° dec., $[\alpha]_D^{20}$ −43.1° (ethanol) (found: C, 72.56; H, 10.02) (yield *ca.* 0.5%). The identity of II was established by its conversion to 9α-hydroxyprogesterone[6] by the degradative procedure previously reported from our laboratory.[7] Substance III was likewise identified as 11α-hydroxysolasodine by conversion into 11-oxo-16-dehydroprogesterone[8] and into 11α-hydroxyprogesterone[9] in an analogous manner. The structure of IV was deduced from the fact that it was very readily converted into the α,β-unsaturated carbonyl derivative, 7-oxosolasodine (VI) (R^1, R^3 = H; R^2— = O=) m.p. 188–191°, 238 mμ (log ϵ 3.95) by allylic oxidation with

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(4) Ch. Tamm and A. Gubler, *Helv. Chim. Acta*, **41**, 1762 (1958); **42**, 239, 473 (1959).

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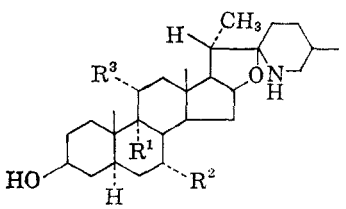
manganese dioxide in chloroform at room temperature. Although the molecular rotation data is suggestive of a 7β configuration (ΔM_D, +114°),[10] a definite assignment awaits further study.

In contrast to solasodine, the incubation of tomatidine (VII) (R^1, R^2, R^3 = H) with *Helicostylum piriforme* affords a preponderant amount of the diol, 7α,11α-dihydroxytomatidine (VIII) (R^1 = H; R^2, R^3 = OH) m.p. 266–270° dec., $[\alpha]_D^{20}$ +23° (ethanol) (found: C, 72.42; H, 10.43) (yield *ca.* 20%); a lesser amount of the monohydroxy compound, 7α-hydroxytomatidine (IX) (R^1, R^3 = H; R^2 = OH) m.p. 238–242° dec., $[\alpha]_D^{20}$ −3.5° (chloroform) (found: C, 75.22; H, 10.68) (yield *ca.* 5%), and a third component (X) (R^2, R^3 = H; R^1 = OH) m.p. 188–191° (found: C, 74.50; H, 11.02) (yield *ca.* 0.5%) to which we tentatively ascribe a 9α-hydroxytomatidine structure. The assignment of a 7α,11α-diol formulation to VIII was based on the degradation of VIII into the known allopregnane-3,11,20-trione[11] and allopregnane-3,7,11,20-tetrone.[12] The 7-hydroxylic function is apparently easily removed during the degradation. The assignment of α-configurations to both the 7- and 11-hydroxyl moieties was based on the conversion of the intermediate 3,7,11-trihydroxy-20-one derivative into 7α,11α-dihydroxyallopregnane-3,20-dione, whose structure has been fully elucidated.[13] The structure of IX was determined by its degradative conversion into the known 3β-acetoxyallopregnane-7,20-dione.[14] Molecular rotation data (ΔM_D, −39°) and the fact that IX only partially acetylates under normal acetylating conditions support the assignment of the 7α-configuration. Compound X acetylates to yield only the 3β-*O*,*N*-diacetyl derivative. In view of the tertiary nature of the second hydroxyl moiety, reminiscent of its solasodine counterpart, II, the 9α position is tentatively assigned to substance X. The homogeneity of all of the hydroxylated compounds was tested by paper and gas chromatography.[15]



VII. (R^1, R^2, R^3 = H)
VIII. (R^1 = H; R^2, R^3 = OH)
IX. (R^1, R^3 = H; R^2 = OH)
X. (R^2, R^3 = H; R^1 = OH)

It is of some interest to note that 7α-hydroxylation in the steroids of the C-5 allo series is an unique occurrence. The hydroxylation of these steroidal alkaloids enhances their usefulness as starting material for the preparation of biologically active hormones. The fungus, *Helicostylum piriforme*, is capable of transforming other steroidal alkaloids (*e.g.*, solanidine). Further work along these lines is being pursued.

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(13) Forthcoming publication of one of the authors (Hayakawa).

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(15) We are greatly indebted to Dr. W. J. A. VandenHeuvel of the National Heart Institute, National Institutes of Health, for running the gas chromatograms of these substances.

(16) Visiting Scientist, National Institutes of Health.

A New Reaction for Forming Carbon-Phosphorus Bonds

Sir:

We wish to report a new general method for forming carbon-phosphorus bonds by adding phosphorus trichloride to an olefin in the presence of aluminum chloride. The reaction is quite general and has been applied to various types of olefins, including highly branched structures such as trimethylpentene, propylene trimers, tetramers, and hexamers, α-olefins and olefins with centrally located double bonds such as methyl oleate and tricosene.

Previous reports on the formation of carbon-phosphorus bonded compounds from aliphatic olefins are limited to such examples as Kharasch's free radical-catalyzed addition of phosphorus trichloride,[1] the addition of phosphorus pentachloride to primary olefins to yield unsaturated phosphonic acids,[2] the free radical-catalyzed addition of dialkyl phosphites,[3,4] or Willstaetter's oxidative phosphonation.[5,6]

The reaction is carried out at ordinary temperatures in a solvent such as methylene chloride, using one mole of phosphorus trichloride and one mole of

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