by the catalytic desulfurization, and a catalytic reduction of carbon–carbon unsaturated compounds, carbonyl and nitro compounds derivatives etc., in addition to biotin and its related compounds. Moreover, it will be very interesting to investigate the mechanisms of these reductive tritiation whether the tritium atoms introduced into *d*–dethiobiotin are derived from the solvent (water) or the catalyst (Raney nickel).

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The Structure of Tomentogenin

Previously, Mitsuhashi, *et al.*,[1] proposed the structure 3*β*,12*β*,14*β*,17*β*,20*ξ*–pentahydroxypregnane (I) for tomentogenin isolated from *Marsdenia tomentosa* DENCE (Asclepiadaceae, Japanese name: Kijoran), but there remains some ambiguity for the configuration of C–17 hydroxyl group.

We now wish to describe the establishment of the configuration of the C–17 hydroxyl group by partial synthesis of tomentogenin (I) from hecogenin acetate. Hecogenin acetate was converted to 3*β*,12*β*,20*ξ*–trihydroxy–5*α*–pregn–16–ene (II)[2] according to the procedures by Cameron, *et al.*[3] and by Adams, *et al.*,[4] and the product, after acetylation with acetic anhydride–pyridine, was treated with dibromodimethylhydantoin[5] to give 3*β*,12*β*,20*ξ*–trihydroxy–5*α*–pregna–14,16–diene 3,12–diacetate (IV), mp 176–178°, $[\alpha]_D^{22}$ +111.3° (c=0.88, $CHCl_3$), UV λ_{max}^{EtOH} mμ (log ε): 262 (3.98), IR ν_{max}^{Nujol} cm^{-1}: 3580 (OH), 1740, 1710, 1265, 1240 (OAc). Oxidation of IV with MnO_2 gave the dienone[6] (V), mp 155—157°, UV λ_{max}^{EtOH} mμ (log ε): 305 (4.30). Epoxidation of V with monoperphthalic acid gave the 14*β*,15*β*–epoxide (VI),[6] mp 150—153°, UV λ_{max}^{EtOH} mμ (log ε): 243 (3.65), and further epoxidation of VI with alkaline–H_2O_2 gave the bisepoxide (VII), mp 146.5—147.5°, ORD (c=0.17, MeOH) $[\alpha]$(mμ): positive Cotton effect, +173.1° (285) (trough) +358.4° (314) (peak), +45.8° (589), IR ν_{max}^{Nujol} cm^{-1}: 1745, 1730, 1240 (OAc), 1710 (methylketone), NMR ($CDCl_3$) τ: 9.18 (19–CH_3), 8.57 (18–CH_3), 8.05, 8.02 (OAc), 8.00 (21–CH_3), 6.30 (1H, broad singlet, C–15–proton), 6.05 (1H, broad singlet, C–16–proton).

Djerassi, *et al.*,[7] reported that the Cotten effect of 16,17–epoxy–20–oxopregnane showed the opposite sign to the Cotton effect observed on the corresponding 20–ketopregnane. Since the compound (VII) showed the positive Cotton effect, while 3*β*,12*β*–diacetoxy–14*β*,15*β*–epoxy–5*α*,17*α*–pregnan–20–one[8] showed the negative Cotton effect, and since the compound

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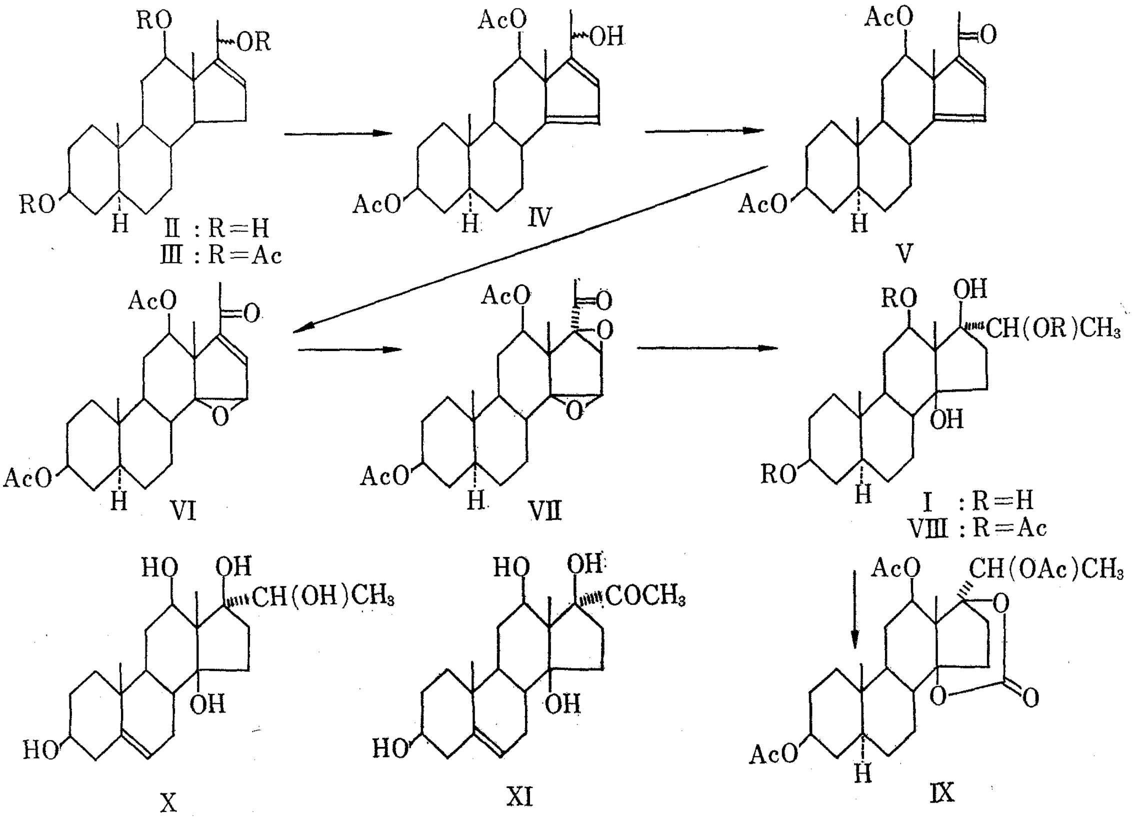
1) H. Mitsuhashi, I. Takemori, Y. Shimizu, T. Nomura, and E. Yamada, *Chem. Pharm. Bull.* (Tokyo), **10**, 804 (1962); H. Mitsuhashi, T. Sato, T. Nomura, and I. Takemori, *ibid.*, 13, 267 (1965).
2) Satisfactory analytical results were obtained for all compounds described in this communication. All melting points were measured with a Kofler hot stage microscope and are uncorrected.
3) A.E.B. Cameron, R.M. Evans, J.C. Hamlet, J.S. Hunt, and P.G. Jones, *J. Chem. Soc.*, **1955**, 2807.
4) W.J. Adams, D.N. Kirk, D.K. Patel, V. Petrow, and I.A. Stuart-Webb, *J. Chem. Soc.*, **1955**, 870.
5) M. Fukuoka and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **15**, 2007 (1967).
6) H. Mitsuhashi and T. Nomura, *Chem. Pharm. Bull* (Tokyo), **13**, 1332 (1965).
7) C. Djerassi, W. Klyne, T. Norin, G. Oholoff, and E. Klein, *Tetrahedron*, **21**, 163 (1965).
8) H. Mitsuhashi, T. Nomura, and M. Fukuoka, *Steroids*, **4**, 483 (1964).



(VII) could be converted to the cyclic carbonate (IX), the configuration of the epoxide at the position C-16 and 17 was considered to be 16β,17β-type.

Successive reduction of VII with $NaBH_4$ and $LiAlH_4$, gave tomentogenin (I), mp 256.5—259.5°, $[\alpha]_D^{19}$ +40.0° (c=1.0, MeOH), which was identical with an authentic sample[1] by a mixed melting point, comparisons of thin-layer and paper chromatography, and IR spectra.

Acetylation of I with Ac_2O-pyridine gave the corresponding triacetate (VIII), mp 290—293°, ORD (c=0.11, MeOH) [α] (mμ): a positive plane curve, +354.7° (210), +87.3° (230), 0° (300). Treatment of VIII with 30% phosgene-chloroform gave quantitatively a cyclo carbonate (IX), mp 261—263°, ORD (c=0.11, MeOH) [α] (mμ): a negative Cotton effect,[9] 0° (210), −353.9° (228) (though), −88.4° (300), IR ν_{max}^{Nujol} cm^{-1}: 1755, 1750, 1735, 1725, 1245, NMR ($CDCl_3$) τ: 9.18 (19-CH_3), 8.68 (18-CH_3), 8.64 (21-CH_3, d, J=6 cps), 7.97, 7.89 (OAc). These characteristics correspond to the formula IX.

These results established the structure of tomentogenin to be 3β,12β,14β,17β,20 ξ-pentahydroxy-5α-pregnane (I).

Since the correlation of tomentogenin and utendin (X) and pergularin (XI) was report by Abisch, *et al.*,[10] and by Mistuhashi, *et al.*,[11] the structures of utendin and pergularin were established to be the formula X and XI, respectively.

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9) This Cotton effect was agreeable with the lactone sectars rule (J.P. Jennings, W. Klyne, and P.M. Scopes, *J. Chem. Soc.*, **1965**, 7211, 7230).

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Isolation of Insect Moulting Substances from *Osmunda japonica* and *Osmunda asiatica*

During our screening tests on vegitable materials by means of bioassay, it has been noticed that the crude extracts of ferns especially show insect-moulting hormone activity in high frequency. Therefore, we have investigated the constituents of varieties of ferns whose extracts exhibit the biological activity, and isolated a number of active steroids.[1] We have further observed that the methanol extracts of *Osmunda japonica* Thunberg and *O. asiatica* Ohwi[2] (Osmundaceae) grown in Japan are positive in the *Sarcophaga* assay. The polar fraction of each extract was submitted to column chromatography resulted in the isolation of the following substances: ponasterone A, mp 266—268°, ecdysone, mp 241.5—242°, and ecdysterone, mp 239—240°, from *O. japonica,* and ponasterone A, mp 260—261°, ecdysone, mp 243—244°, and ecdysterone, mp 242—243°, from *O. asiatica.*

It is of interest to note that the known plant sources of ecdysone, the first insect-moulting hormone, are all ferns, *Pteridium aquilinum* Kuhn,[3] *Polypodium vulgare* Linné,[4] and *Lemmaphyllum microphyllum* Presl.[1d]

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