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-thiobiotin 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 3β,12β,14β,17β,20α–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 3β,12β,20α–trihydroxy–5α–pregn–16–ene (II)9 according to the procedures by Cameron, et al.9) and by Adams, et al.,4) and the product, after acetylation with acetic anhydride–pyridine, was treated with dibromomethylhydantoin9 to give 3β,12β,20α–trihydroxy–5α–pregna–14,16–dien–3,12–diacetate (IV), mp 176–178°, [α]D +111.3° (c = 0.88, CHCl3), UV λmax (log e): 262 (3.98), IR νmax cm⁻¹: 3580 (OH), 1740, 1710, 1265, 1240 (OAc). Oxidation of IV with MnO₂ gave the dienone9) (V), mp 155–157°, UV λmax (log e): 305 (4.30). Epoxidation of V with monoperoxphosphatic acid gave the 14β,15β–epoxide (VI),9) mp 150–153°, UV λmax (log e): 243 (3.65), and further epoxidation of VI with alkali–H₂O₂ gave the bisepoxide (VII), mp 146.5–147.5°, ORD (c = 0.17, MeOH)[a]D (methyl): positive Cotton effect, +173.1° (285) (tough) +358.4° (314) (peak), +45.8° (588), IR νmax cm⁻¹: 1745, 1730, 1240 (OAc), 1710 (methylketone), NMR (CDCl₃) τ: 9.18 (19–CH₃), 8.57 (18–CH₃), 8.05, 8.02 (OAc), 8.00 (21–CH₃), 6.30 (1H, broad singlet, C-15–proton), 6.05 (1H, broad singlet, C-16–proton).

Djerassi, et al.,7) reported that the Cotton effect of 16,17–epoxy–20–oxopregna showed the opposite sign to the Cotton effect observed on the corresponding 20–ketopregnan. Since the compound (VII) showed the positive Cotton effect, while 3β,12β–diacetoxy–14β,15β–epoxy–5α,17α–pregnan–20–one9) showed the negative Cotton effect, and since the compound

2) Satisfactory analytical results were obtained for all compounds described in this communication. All melting points were measured with a Kofer hot stage microscope and are uncorrected.
(VII) could be converted to the cyclic carbonate (IX), the configuration of the epoxide at the position C–18 and 17 was considered to be 1β,17β-type.

Successive reduction of VII with NaBH₄ and LiAlH₄ gave tomentogenin (I), mp 256.5—259.5°C, [α]D² +40.0° (c=1.0, MeOH), which was identical with an authentic sample³ by a mixed melting point, comparisons of thin-layer and paper chromatography, and IR spectra.

Acetylation of I with Ac₂O-pyridine gave the corresponding triacetate (VIII), mp 290—293°C, ORD (c=0.11, MeOH) [α] (μ): a positive plane curve, +354.7° (210), +87.3° (230), 0° (300). Treatment of VIII with 30% phosphene–chloroform gave quantitatively a cyclo carbonate (IX), mp 261—263°C, ORD (c=0.11, MeOH) [α] (μ): a negative Cotton effect,⁹ 0° (210), −353.9° (288) (though), −88.4° (300), IR νmax cm⁻¹: 1755, 1750, 1735, 1725, 1245, NMR (CDCl₃) τ: 9.18 (19-CH₃), 8.68 (18-CH₃), 8.64 (21-CH₃), 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,20β-penta-hydroxy-5α-pregnane (I).

Since the correlation of tomentogenin and utendin (X) and pergularin (XI) was report by Abisch, et al.,¹⁰ and by Misutahashi, 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).
Isolation of Insect Moulting Substances from Osmunda japonica and Osmunda asiatica

During our screening tests on vegetal 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. We have further observed that the methanol extracts of Osmunda japonica Thunberg and O. asiatica Onw (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 260–268°, 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, Polypodium vulgare Linné, and Lemmaphyllum microphyllum Presl.

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2) Japanese names: zemmai and yamadori-zemmai, respectively.