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Studies on the Constituents of Asclepiadaceae Plants. XXXVI.[1] Component of *Marsdenia tomentosa* Decne: Structure of Tomentonin, Tomentodin, and Dehydrotomentosin and Difference in the Reactivity between Utendin and Tomentogenin Diesters on Mild Alkaline Hydrolysis

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Three new polyoxypregnane derivatives, tomentonin (12β-*O*-dihydrotigloyl-20-*O*-acetyltomentogenin), tomentodin (12β-*O*-cinnamoyl-20-*O*-acetyltomentogenin), and dehydrotomentosin (12β-*O*-tigloyl-20-*O*-acetylutendin), were isolated from the stem of *Marsdenia tomentosa* Decne. Dehydrotomentosin underwent an internal acyl migration from C-12β-OH to C-20-OH on mild alkaline hydrolysis to afford a monoester, but tomentonin and tomentodin did not. The remarkable difference in the reactivity between toementogenin and utendin diesters on this condition was discussed. Tomentonin is the first example of a tomentogenin derivative with an ester linking of dihydrotiglic acid or 2-methylbutyric acid isolated from Asclepiadaceae plants.

Our previous papers reported the isolation and characterization of tomentosin[3] (I), tomentin, and dehydrotomentin,[1] new polyoxypregnane derivatives possessing a tomentogenin or an utendin skeleton, from the stem of *Marsdenia tomentosa* Decne, and the presence of several unidentified ester type compounds. We now report the isolation and structural elucidation of three new polyoxypregnane derivatives, tentatively named compounds A, B, and F, and the marked difference in the reactivity between tomentogenin and utendin diesters on mild alkaline hydrolysis to afford a monoester.

The aglycone mixture, obtained by a mild acid hydrolysis of the crude glycoside,[4] was separated and purified by silica gel column chromatography and preparative thin-layer chromatography (TLC). These procedures yielded three fine crystalline substances, compounds A, B, and F. Compound A (II) showed mp 158—161°, $[\alpha]_D^{18}$ +38° (c=0.3, $CHCl_3$). The molecular formula $C_{28}H_{46}O_7$ was given for II from its elemental analysis and mass spectrum (M^+-H_2O at m/e 476). Infrared (IR) spectrum of II showed absorptions for hydroxyl groups at 3400 and 1040 cm^{-1}, and saturated esters at 1735, 1720, 1260, and 1240 cm^{-1}. The nuclear magnetic resonance (NMR) spectrum of II showed signals for two tertiary methyl groups at δ 0.78 (s) and 1.20 (s), two secondary methyl groups at 0.96 (d, J=6 Hz) and 1.16 (d, J=7 Hz), one primary methyl group at 1.22 (t, J=6 Hz), one acetyl group at 1.94 (s), three hydroxymethines at 3.60 (br. m), 4.52 (q, J=6 Hz), and 4.68 (d,d. J=6, 11 Hz), and no olefinic proton. The mass spectral peaks of II at m/e 392 ($M^+-C_5H_{10}O_2$), 85 (C_5H_9O), and 57 (C_4H_9) as well as m/e 434 (M^+-CH_3COOH) and 43 ($COCH_3$) showed the presence of a dihydrotigloyl group and an acetyl group, respectively.

1) Part XXXV: H. Seto, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **23**, 2397 (1975).
2) Location: *Kita-12-jo, Nishi-6-chome, Kita-ku, Sapporo, 060, Japan.*
3) H. Seto, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **23**, 1552 (1975).
4) *a*) H. Mitsuhashi, I. Takemori, Y. Shimizu, T. Nomura, and E. Yamada, *Chem. Pharm. Bull.* (Tokyo), **10**, 804 (1962); *b*) H. Mitsuhashi, T. Sato, T. Nomura, and I. Takemori, *ibid.*, **13**, 267 (1965); *c*) M. Fukuoka, and H. Mitsuhashi, *ibid.*, **16**, 1634 (1968); *d*) T. Sasaki, K. Hayashi, and H. Mitsuhashi, *ibid.*, **20**, 628 (1972).

Hydrolysis of II with 5% methanolic potassium hydroxide afforded tomentogenin[4c,5] (III) as a neutral product. Acetylation of II with acetic anhydride-pyridine afforded an acetate (IV), mp 223—225°. Mild alkaline hydrolysis of II with saturated methanolic potassium carbonate gave a monoester (V), mp 210—214°. The NMR spectrum of V showed a shift of the siganl for the hydroxy-methine at δ 4.52 to 4.40 and a disappearance of that for an acetyl group at 1.94. These results suggested that an acetate moiety was at C-20 of tomentogenin, which was supported by the mass spectrum of V at *m/e* 407 (M^+-45).[6]

Acetylation of the monoester (V) with acetic anhydride-pyridine afforded a diacetate, which was identical with compound A acetate (IV) from mixed mp and spectral data. Hydrogenation of tomentosin (I) with 10% palladium-carbon afforded a dihydro derivative, which was identical with II from mixed mp and spectral data. From these evidences, compound A (II) was determined as 12β-*O*-dihydrotigloyl-20-*O*-acetyltomentogenin and was named tomentonin. This is the first example of a tomentogenin derivative with a dihydrotiglic acid, 2-methylbutyric acid, ester linking to be isolated from a plant of the family Asclepiadaceae. (Fig. 1).

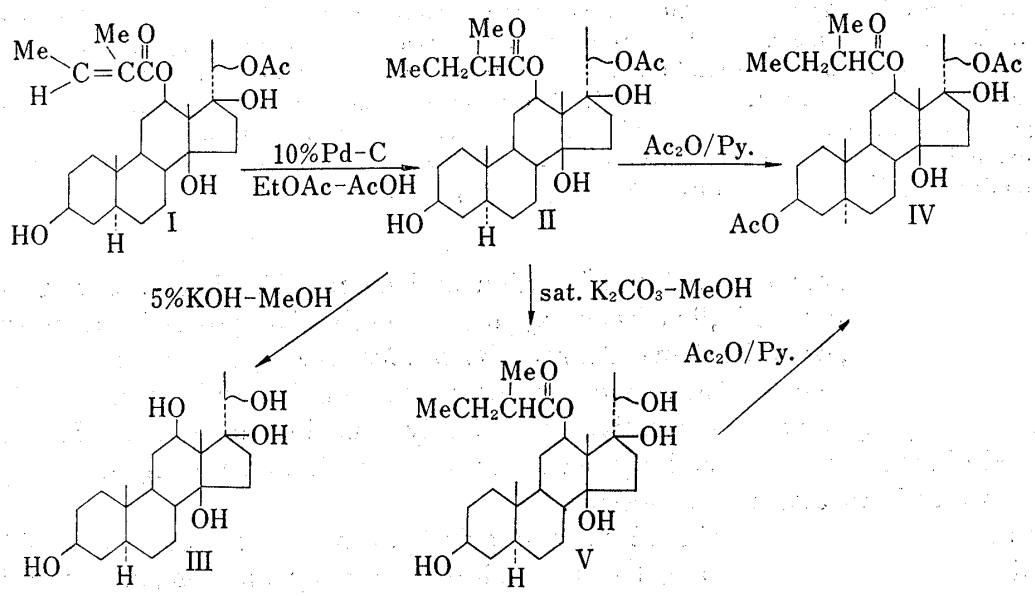

Fig. 1

Compound B (VI) showed mp 140—144°, $[\alpha]_D^{20}$ +45° (c=0.35, $CHCl_3$). The molecular formula $C_{32}H_{44}O_7$ was given for VI from elemental analysis and mass spectrum (M^+ at *m/e* 540). IR spectrum of VI showed absorptions for hydroxyl groups at 3400 and 1040 cm^{-1}, a saturated ester at 1730 and 1255 cm^{-1}, and an α,β-unsaturated ester at 1710, 1680, 1635, and 1165 cm^{-1}.

The NMR spectrum of VI showed signals for two tertiary methyl groups at δ 0.80 (s) and 1.29 (s), one secondary methyl group at 1.23 (d, J=6 Hz), one acetyl group at 2.02 (s), three hydroxy-methines at 3.60 (br. m), 4.52 (q, J=6 Hz), and 4.68 (d.d, J=6, 11 Hz), and seven olefinic protons at 6.24 (1H, d, J=16 Hz), 7.40 (5H, m), and 7.56 (1H, d, J=16 Hz). Hydrolysis of VI with 5% methanolic potassium hydroxide afforded tomentogenin (III) as a neutral product. Prominent mass spectral peaks indicative of acetate and cinnamate functional groups were observed at *m/e* 43 (acetyl cation) and 131 (cinnamoyl cation). Further substantiation was obtained from mass spectral peaks of VI at 522 (M^+-H_2O), 480 (M^+–AcOH), 462 (M^+-H_2O–AcOH), 453 (M^+–CHOAc·Me),[6] 392 (M^+—cinnamic acid), 332 (M^+—AcOH

5) H. Mitsuhashi, T. Sato, T. Nomura, and I. Takemori, *Chem. Pharm. Bull.* (Tokyo), **12**, 981 (1964).
6) M. Fukuoka, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **19**, 1469, (1971).

cinnamic acid), and 305 (M^+–CHOAc·Me–cinnamic acid), which was supported by ultraviolet (UV) absorptions at 217 (log ε 4.27), 223 (4.22), and 278 (4.38) nm. The peak at *m/e* 453 definitely suggested that the acetate moiety was at C-20 of tomentogenin (III), thus placing the cinnamate group at C-12.

Acetylation of VI with acetic anhydride-pyridine afforded an acetate (VII), mp 165—169°. Mild alkaline hydrolysis of VI with saturated methanolic potassium carbonate gave a monoester (VIII), mp 208—210°, whose IR spectrum showed absorptions for an α,β-unsaturated ester at 1710, 1690, 1630, and 1160 cm^{-1}, which was supported by UV absorptions at 215 (log ε 4.35) and 275 nm (4.30). In order to confirm the position of ester linkages of VI, the monoester (VIII) was acetylated with acetic anhydride-pyridine and afforded a diacetate, which was identical with compound B acetate (VII) from mixed mp and comparison of spectral data. On the basis of these results, it is determined that the structure of compound B (VI) is 12β-*O*-cinnamoyl-20-*O*-acetyltomentogenin and was named tomentodin. The internal acyl migration between C-12 and C-20-OH[7] on mild alkaline hydrolysis did not occur in tomentonin (II) and tomentodin (VI) as in the case of tomentosin (I) (Fig. 2).

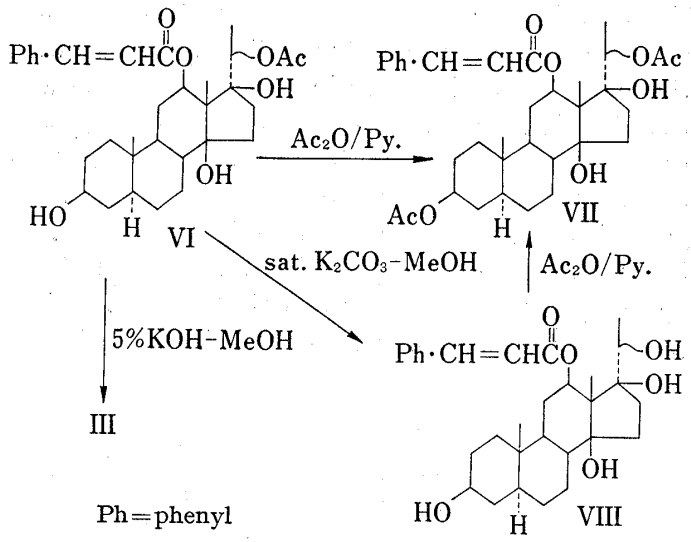

Fig. 2

Compound F (IX) showed mp 180—183°, $[\alpha]_D^{19}$ +42° (c=0.6, $CHCl_3$). The molecular formula $C_{28}H_{42}O_7$ was given for IX from elemental analysis and mass spectrum (M^+ at *m/e* 490). The IR spectrum of IX showed absorptions for hydroxyl groups at 3350 and 1070 cm^{-1}, a saturated ester at 1730 and 1260 cm^{-1}, and an α,β-unsaturated ester at 1700, 1680, 1640, and 1150 cm^{-1}, and the latter was supported by ultraviolet (UV) absorption at 214 nm (log ε 4.08). The NMR spectrum of IX showed signals for two tertiary methyl groups at δ 0.93 (s) and 1.21 (s), one secondary methyl group at 1.22 (d, J=6 Hz), two vinyl-methyl groups at 1.82 (d, J=6 Hz) and 1.83 (s), one acetyl group at 1.91 (s), three hydroxy-methines at 3.54 (br. m), 4.56 (q, J=6 Hz), and 4.62 (d.d, J=6, 11 Hz), and two olefinic protons at 5.34 (d, J=3.5 Hz) and 6.82 (d, J=6 Hz).

Hydrolysis of IX with 5% methanolic potassium hydroxide afforded utendin[8] (XIII). Prominent mass spectral peaks indicative of acetate and tiglate groups were observed at *m/e* 83 (tigloyl cation) and 43 (acetyl cation), which suggested that compound-F (IX) is a diester of utendin with acetic acid and tiglic acid. Acetylation of IX with acetic anhydride-pyridine afforded an acetate (X), mp 220—223°.

Mild alkaline hydrolysis of IX with saturated methanolic potassium carbonate gave a monoester (XI), mp 251—254°, whose IR spectrum showed absorptions for an α,β-unsaturated ester at 1720, 1690, 1650, and 1150 cm^{-1}, which was supported by UV absorption at 217 nm (log ε 4.10). The mass spectral peaks of XI at *m/e* 321 (M^+–127)[7] definitely suggested that tigloyl moiety was located at C-20 on the monoester (XI), which was supported by the NMR spectrum showing disappearance of a signal for the acetyl group at δ 1.91 and upfield shift of the hydroxy-methine of IX at 4.62 to 3.75. Acetylation of XI with acetic anhydride-

7) T. Yamagishi, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **20**, 2289 (1972).
8) E. Abisch, Ch. Tamm, and T. Reichstein, *Helv. Chim. Acta*, **42**, 1014 (1959).

pyridine afforded a diacetate (XII), mp 233—235°, which was evidently different from compound-F acetate (X) in mp and spectral data.

These evidences indicate that the tigloyl moiety at C-20 in the monoester (XI) was originally located at C-12β in IX it migrated to C-20 during the mild alkaline hydrolysis. From these results, it was concluded that compound-F (IX) is 12β-*O*-tigloyl-20-*O*-acetylutendin and was named dehydrotomentosin. This is the first example of polyoxypregnane derivatives which affords only 20-*O*-monoester through the internal acyl migration[7] on mild alkaline hydrolysis. Tomentosin (I) and dehydrotomentosin (IX) afforded 12β-*O*-tigloyl- and 20-*O*-tigloyl monoesters, respectively, on mild alkaline hydrolysis with potassium carbonate. This fact indicates the remarkable difference in the reactivity between utendin and tomentogenin diesters and that the tiglate group at C-12β in IX is hydrolysed partially on this condition, but it migrates to C-20 immediately and irreversibly when C-20 hydroxyl group becomes free. In contrast, the tiglate and other acyl groups at C-12β in I are hardly hydrolysed and even if C-20 hydroxyl group becomes free, they do not migrate to C-20. These facts were supported by the evidence that the mild alkaline hydrolysis of tomentosin (I) afforded 12β-*O*-tigloyl monoester exclusively and only a trace of tomentogenin[4c,5] (III), while dehydrotomentosin (IX) afforded utendin (XIII) and its 20-*O*-monoester (XI) in the ratio of 2: 5 (Fig. 3).

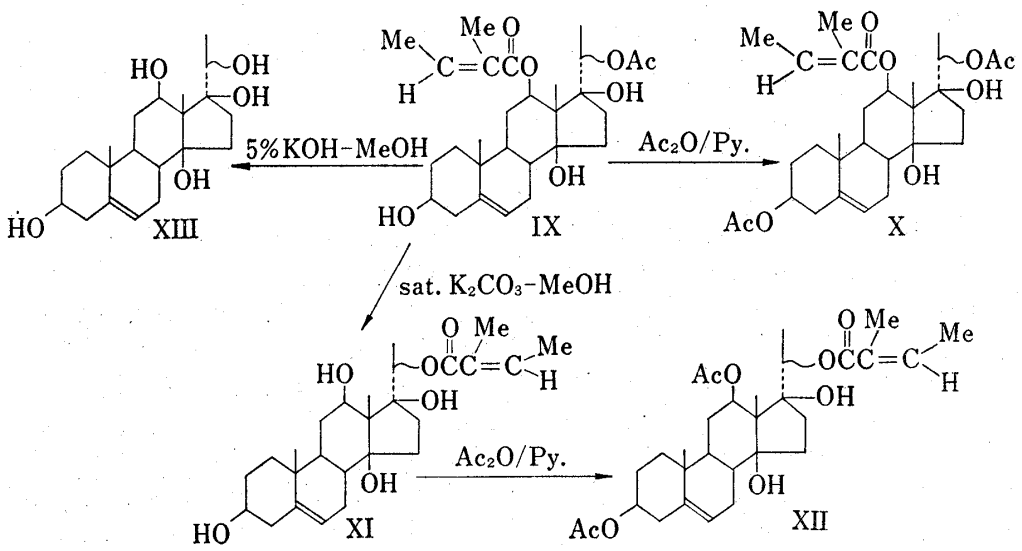

Fig. 3

Experimental

Melting points were determined on a Kofler hot stage and are uncorrected. Optical rotations were measured in $CHCl_3$ solution with a Hitachi S 115—4 polarimeter. NMR spectra were determined on a JEOL PS-100 spectrometer operating at 100 MHz with tetramethylsilane (TMS) as an internal standard, mass spectra with a Hitachi RMU-7 mass spectrometer, IR spectra were taken in Nujol mull on a Hitachi 215 spectrometer, and UV spectra were determined in EtOH solution on a Hitachi EPS-3T spectrometer. TLC was performed on Silica gel HF_{254} (Merck, Type 60), and silica gel 0.05—0.2 mm (Merck, 70—325 mesh ASTM) was used for column chromatography.

Tomentonin (II)——From 15 g of the ester-type aglycone mixture that obtained in the same procedure as reported previously,[3] 85 mg of tomentonin (II) was obtained by column chromatography and preparative TLC. II was recrystallized from hexane–$(CH_3)_2CO$ to plates, mp 158—161°, $[\alpha]_D^{18}$ +38° (c=0.3, $CHCl_3$). Mass Spectrum *m/e*: 476 (M^+–H_2O), 458 (M^+–$2H_2O$), 440 (M^+–$3H_2O$), 434 (M^+—acetic acid), 416 (M^+–H_2O–acetic acid), 407 (M^+–CHOAc·Me), 398 (M^+–$2H_2O$–acetic acid), 392 (M^+—2-methylbutyric acid), 374 (M^+—H_2O—2-methylbutyric acid), 332 (M^+—acetic acid—2-methylbutyric acid), 262,[1] 249, 244, 220, 95, 57 (base peak), 43. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1735, 1720, 1260, 1240, 1080, 1040. NMR (δ) $CDCl_3$: 0.78 (3H, s, 18-Me), 0.96 (3H, d, J=6 Hz, 21-Me), 1.16 (3H, d, J=7 Hz, sec-Me), 1.20 (3H, s, 19-Me), 1.22 (3H, t, J=6 Hz, prim-Me), 1.94 (3H, s, OAc), 3.60 (1H, m, 3α-H), 4.52 (1H, q, J=6 Hz, 20-H), 4.68 (1H, d.d, J=6,11 Hz, 12α-H). *Anal.* Calcd for $C_{28}H_{46}O_7$: C, 67.98; H, 9.37. Found: C, 67.71; H, 9.20.

Alkaline Hydrolysis of Tomentonin (II)——A solution of 8 mg of tomentonin (II) in 2 ml of 5% MeOH–KOH was allowed to stand for 24 hr at room temperature and the reaction mixture was purified directly by preparative TLC (MeOH: $CHCl_3$, 1: 19). The product was recrystallized from $(CH_3)_2CO$–MeOH to 5 mg of tomentogenin (III) as prisms, mp 263—267°. Mass Spectrum *m/e*: 368 (M^+), 350 (M^+-H_2O), 332 (M^+-2H_2O) 323 (M^+–CHOH·Me), 305 (M^+-H_2O–CHOH·Me, base peak), 262, 249, 244, 242, 226. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1040. NMR (δ) pyridine-d_5: 0.76 (3H, s, 18-Me), 1.54 (3H, d, J=6 Hz, 21-Me), 1.64 (3H, s, 19-Me), 3.74 (1H, d.d., J=6, 11 Hz, 12α-H), 3.80 (1H, m, 3α-H), 4.38 (1H, q, J=6 Hz, 20-H).

Acetylation of Tomentonin (II)——A solution of 20 mg of tomentonin (II), 1 ml of Ac_2O, and 1 ml of pyridine was allowed to stand for 18 hr at room temperature, and poured into ice water. A white powder that appeared was collected and recrystallized from $(CH_3)_2CO$–MeOH to afford 20 mg of tomentonin acetate (IV), mp 223—225° Mass Spectrum *m/e* 518 (M^+-H_2O), 500 (M^+-2H_2O), 476 (M^+—acetic acid), 458 (M^+-H_2O-acetic acid), 440 (M^+-2H_2O—acetic acid), 434 (M^+—2-methylbutyric acid), 416 ($M^+-2\times$acetic acid), 374 (M^+—acetic acid—2-methylbutyric acid), 314 ($M^+-2\times$acetic acid—2-methylbutyric acid), 304, 291, 286, 226, 85 (base peak), 57, 43. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1730, 1710, 1240, 1080, 1025. NMR (δ) $CDCl_3$: 0.80 (3H, s, 18-Me), 0.98 (3H, d, J=6 Hz, 21-Me), 1.20 (3H,s, 19-Me), 1.22 (3H, d, J=7 Hz, sec-*Me*), 1.24 (3H, t, J=6 Hz, prim-Me), 1.98 (3H, s, OAc), 2.02 (3H, s, OAc), 4.52 (1H, q, J=6 Hz, 20-H), 4.56 (1H, d.d, J=6, 11 Hz, 12α-H), 4.60 (1H, m, 3α-H).

Partial Hydrolysis of Tomentonin (II)——A solution of 50 mg of tomentonin (II) in 2 ml of saturated MeOH–K_2CO_3 was allowed to stand for 12 hr at room temperature. The reaction mixture was purified directly by preparative TLC (MeOH: $CHCl_3$, 1: 19) to afford 5 mg of monoester (V) and 40 mg of II. V was recrystallized from $(CH_3)_2CO$–hexane to needles, mp 210—214°. Mass Spectrum *m/e*: 452 (M^+), 434 (M^+-H_2O), 416 (M^+-2H_2O), 407 (M^+-45), 398 (M^+-3H_2O), 389 (M^+-45-H_2O), 350 (M^+—-2-methylbutyric acid,) 332 (M^+-H_2O—2- methylbutyric acid), 305 (M^+—45-—2-methylbutyric acid), 262, 249, 244, 226, 141 (base peak), 85, 57. IR ν_{max}^{Nujol} cm^{-1}: 3400, 3175, 1730, 1270, 1080. NMR (δ) pyridine-d_5: 0.63 (3H, s, 18-Me), 1.12 (3H, d, J=6 Hz, 21-Me), 1.54 (3H, t, J=6 Hz, prim-Me), 1.55 (3H, d, J=7 Hz, *sec*-Me), 1.57 (3H, s, 19-Me), 3.60 (1H, m, 3α-H), 4.40 (1H, m, 20-H), 4.70 (1H, m,12α-H).

Acetylation of Monoester (V)——A solution of 10 mg of V in 1 ml of Ac_2O and 1 ml of pyridine was allowed to stand for 18 hr at room temperature and worked up in the same way as in the acetylation of II to yield 8 mg of diacetate. Recrystallization of the diacetate from $(CH_3)_2CO$–MəOH gave needles, mp 225—228°. Mass Spectrum *m/e*: 518 (M^+-H_2O), 500 (M^+-2H_2O), 476 (M^+—acetic acid), 458 (M^+-H_2O—acetic acid), 440 (M^+-2H_2O—-acetic acid), 434 (M^+—2-methylbutyric acid), 416 ($M^+-2\times$acetic acid), 374 (M^+—acetic acid-2- methylbutyric acid), 314 ($M^+-2\times$acetic acid-2—methylbutyric acid), 304, 291, 286, 226, 85 (base peak), 57, 43. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1730, 1710, 1240, 1080, 1025. NMR (δ) $CDCl_3$: 0.78 (3H, s, 18-Me), 0.98 (3H, d, J=6 Hz 21-Me), 1.18 (3H, s, 19-Me), 1.20 (3H, d, J=7 Hz, *sec*-Me), 1.22 (3H, t, J=6 Hz, prim-Me), 1.96 (3H, s, OAc), 2.00 (3H, s, OAc). 4.60 (3H, m,3 α-H+12α-H+20-H).

Hydrogenation of Tomentosin (I)——A solution of 80 mg of tomentosin (I) in 10 ml of EtOAc–AcOH (3: 1) was hydrogenated over 150 mg of 10% Pd-C at atmospheric pressure at 20°. It consumed 1 molar equiv. of H_2 (10 ml) during 3 hr. After the catalyst was removed, the reaction mixture was purified by preparative TLC ($(C_2H_5)_2O$) to yield 58 mg of a dihydro derivative, which was recrystallized from $(CH_3)_2CO$–hexane to needles, mp 184—186°, $[\alpha]_D^{19}$ +40° (c=0.5, $CHCl_3$). Mass Spectrum *m/e*:476 (M^+-H_2O), 458 (M^+-2H_2O), 440 (M^+-3H_2O), 434 (M^+—acetic acid), 416 (M^+-H_2O—acetic acid), 407 (M^+—CHOAc·Me), 398 (M^+-2H_2O- acetic acid), 392 (M^+—2-methylbutyric acid), 374 (M^+—-H_2O—2-methylbutyric acid), 332 (M^+—-acetic acid-2—methylbutyric acid), 262, 249, 244, 226, 85, 57 (base peak) 43. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1735, 1710, 1685, 1650, 1260, 1240, 1080, 1040. NMR (δ) $CDCl_3$ 0.79 (3H, s, 18-Me), 0.99 (3H, d, J=6 Hz, 21-Me), 1.16 (3H, d, J=7 Hz, *sec*-Me), 1.20 (3H, s, 19-Me), 1.22 (3H, t, J=6 Hz, prim-Me), 1.98 (3H, s, OAc), 3.60 (1H, m, 3α-H), 4.58 (1H, q, J=6 Hz, 20-H), 4.74 (1H, d.d, J=6, 11 Hz, 12α-H). *Anal.* Calcd. for $C_{28}H_{46}O_7$: C, 67.98; H, 9.37. Found: C, 67.81; H, 9.19.

Tomentodin (VI)——From the more polar fraction than that of tomentonin (II), 38 mg of tomentodin (VI) was obtained by repeated preparative TLC ($(C_2H_5)_2O$, MeOH: $CHCl_3$=1: 99). VI was recrystallized from $(CH_3)_2CO$–hexane to needles, mp 140—144°, $[\alpha]_D^{20}$ +45 (c=0.3, $CHCl_3$). Mass Spectrum *m/e*: 540 (M^+), 522 (M^+-H_2O), 480 (M^+—-acetic acid), 462 (M^+-H_2O—acetic acid), 453 (M^+—CHOAc·Me), 444 (M^+-2H_2O—acetic acid), 435 (M^+—-H_2O—CHOAc·Me), 417 (M^+-2H_2O—CHOAc·Me), 392 (M^+—cinnamic acid), 374 (M^+-H_2O—cinnamic acid), 356(M^+-2H_2O—cinnamic acid), 332(M^+—-acetic acid-cinnamic acid), 305(M^+—CHOAc·Me—cinnamic acid), 262, 249, 244, 226, 148, 147, 131 (base peak), 103, 43. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1730, 1710, 1680, 1635, 1255, 1165, 1040, 1020. UV λ_{max}^{EtOH} nm (log ε): 217 (4.29), 223 (4.22), 278 (4.38). NMR (δ) $CDCl_3$: 0.80 (3H, s, 18- Me), 1.23 (3H, d, J=6 Hz, 21-Me), 1.29 (3H, s, 19-Me), 2.02 (3H, s, OAc), 3.60 (1H, m, 3α-H), 4.54 (1H, q, J=6 Hz, 20-H), 4.68 (1H, d.d, J=6, 11 Hz, 12α-H), 6.24 (1H, d, J=16 Hz), 7.40 (5H, m, aromatic protons), 7.56 (1H, d, J=16 Hz). *Anal.* Cacld for $C_{32}H_{44}O_7$: C, 71.08; H, 8.20. Found; C, 71.21; H, 8.26.

Alkaline Hydrolysis of Tomentodin (VI)——A solution of 5 mg of tomentodin (VI) in 1 ml of 5% MeOH–KOH was allowed to stand for 24 hr at room temperature and worked up in the same way as in the hydrolysis of II to yield 3 mg of tomentogenin (III), mp 262—265°. Mass Spectrum *m/e*: 368 (M^+), 350 (M^+-H_2O), 332 (M^+-($2H_2O$), 323 (M^+—CHOH·Me), 305 (M^+-H_2O—CHOH·Me, base peak) 262, 249, 244, 242, 226. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1040.

Partial Hydrolysis of Tomentodin (VI)——A solution of 30 mg of tomentodin (VI) in 2 ml of saturated MeOH-K_2CO_3 was allowed to stand for 16 hr at room temperature and worked up in the same manner as in the partial hydrolysis of II to afford 3 mg of monoester (VIII) and 25 mg of VI. VIII was recrystallized from $(CH_3)_2CO$–hexane to needles, mp 208—210°. Mass Spectrum *m/e*: 480 (M^+-H_2O), 462 (M^+-2H_2O), 453 (M^+—CHOH·Me), 444 (M^+-3H_2O), 435 (M^+-H_2O—CHOH·Me), 426 (M^+—$-4H_2O$), 417 (M^+-2H_2O—CHOH·Me), 350 (M^+—cinnamic acid), 332 (M^+-H_2O—cinnamic acid), 305 (M^+—CHOH·Me—cinnamic acid), 262, 249, 244, 226, 148, 147, 131 (base peak), 103. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1710, 1690, 1630, 1160, 1080, 1030. UV λ_{max}^{EtOH} nm (log ε): 215 (4.35), 275 (4.30).

Acetylation of Monoester (VIII)——A solution of 5 mg of VIII in 0.5 ml of pyridine and 0.5 ml of Ac_2O was allowed to stand for 24 hr at room temperature and worked up in the usual manner to afford 3 mg of diacetate (VII) as needles, from $(CH_3)_2CO$–MeOH, mp 163—167°. Mass Spectrum *m/e*: 564 (M^+-H_2O), 522 (M^+—acetic acid), 504 (M^+-H_2O—acetic acid), 495(M^+—CHOAc·Me), 486(M^+—$-2H_2O$—acetic acid), 434(M^+—cinnamic acid), 416 (M^+-H_2O—cinnamic acid), 374 (M^+—-acetic acid—cinnamic acid), 314 ($M^+-2\times$acetic acid—cinnamic acid), 304, 291, 286, 226, 148, 147, 131, 103, 43 (base peak). IR ν_{max}^{Nujol} cm^{-1}: 3400, 1730, 1710 1690, 1640, 1250, 1170, 1080, 1070, 1030.

Acetylation of Tomentodin (VI)——A solution of 10 mg of VI in 1 ml of pyridine and 1 ml of Ac_2O was allowed to stand for 18 hr at room temperature and worked up in the usual manner to afford 8 mg of tomentodin acetate (VII) as needles from $(CH_3)_2CO$–MeOH, mp 165—169°. Mass Spectrum *m/e*: 582 (M^+), 564 (M^+-H_2O), 522 (M^+—acetic acid), 504 (M^+-H_2O—acetic acid), 495 (M^+—CHOAc·Me), 486(M^+-2H_2O—acetic acid), 434(M^+—cinnamic acid), 416(M^+-H_2O—cinnamic acid), 374(M^+—acetic acid—cinnamic acid), 314(M^+—$2\times$acetic acid—cinnamic acid), 304, 291, 286, 226, 148, 147, 131, 103, 43 (base peak). IR ν_{max}^{Nujol} cm^{-1}: 3400, 1730, 1710, 1690, 1640, 1250, 1170, 1080, 1070, 1030. NMR (δ) $CDCl_3$: 0.80 (3H, s, 18-Me), 1.23 (3H, d, J=6 Hz, 21-Me), 1.25 (3H, s, 19-Me), 2.02 (3H, s, OAc), 2.16 (3H, s, OAc), 4.54 (1H, q, J=6 Hz, 20-H), 4.60 (1H, m, 3α-H), 4.68 (1H, d.d, J=6, 11 Hz, 12α-H), 6.24 (1H, d, J=16 Hz), 7.40 (5H, m, aromatic protons), 7.56 (1H, d, J= 16 Hz).

Dehydrotomentosin (IX)——From the less polar fraction than that of II, 105 mg of dehydrotomentosin (IX) was obtained by column chromatography and repeated preparative TLC ($(C_2H_5)_2O$, $CHCl_3$: MeOH=99: 1). IX was recrystallized from hexane–$(CH_3)_2CO$ to afford needles, mp 180—183°, $[\alpha]_D^{19}$ +42 (c=0.6, $CHCl_3$). Mass Spectrum *m/e*: 490 (M^+), 472 (M^+-H_2O), 454 (M^+-2H_2O), 436 (M^+—$-3H_2O$), 436 (M^+—acetic acid), 412 (H^+-H_2O—acetic acid), 390 (M^+—tiglic acid), 372 (M^+—-H_2O—tiglic acid), 330(M^+—acetic acid—tiglic acid), 312 (M^+-H_2O—acetic acid—tiglic acid), 294 ($M^+-2\times H_2O$—-acetic acid—tiglic acid), 242, 209, 145, 105, 83 (base peak), 55, 43. IR ν_{max}^{Nujol} cm^{-1}: 3350, 1730, 1700, 1680,1640, 1260, 1150, 1070, 1040. UV λ_{max}^{EtOH} 214 nm (log ε 4.08). NMR (δ) $CDCl_3$: 0.93 (3H, s, 18-Me), 1.21 (3H, s, 19-Me), 1.22 (3H, d, J=6 Hz, 21-Me), 1.82 (3H, d, J=6 Hz, vinyl- Me), 1.83 (3H, s, vinyl-Me), 1.91 (3H, s, OAc), 3.54 (1H, m, 3α-H), 4.56 (1H, q, J=6 Hz, 20-H), 4.62 (1H, d.d, J=6, 11 Hz, 12α-H), 5.34 (1H, d, J=3.5 Hz, Δ^5-olefinic-H), 6.82 (1H, d, J=6 Hz). *Anal.* Calcd. for $C_{28}H_{42}$- O_7: C, 68.54; H, 8.63. Found: C, 68.32; H, 8.88.

Alkaline Hydrolysis of Dehydrotomenttosin (IX)——A solution of 10 mg of dehydrotomentosin (IX) in 1 ml of 5% MeOH–KOH was allowed to stand for 24 hr at room temperature and the reaction mixture was purified directly by preparative TLC (MeOH: $CHCl_3$, 1: 19) to afford 6 mg of utendin (XIII). XIII was recrystallized from MeOH–$(CH_3)_2CO$ to prisms, mp 240—243° (reported mp 247—251°).[8] Mass Spectrum *m/e*: 366 (M^+), 348 (M^+-H_2O), 330 (M^+—$-2H_2O$), 321 (M^+—CHOH·Me).[6] 312 (M^+-3H_2O), 303 (M^+—CHOH·Me—H_2O), 285 (M^+ CHOH—Me—$2H_2O$), 267 (M^+—CHOH·Me—$3H_2O$), 260, 234, 159, 145. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1070, 1050, 1035. NMR (δ) d_5-pyridine: 0.96 (3H, s, 18-Me), 1.32 (3H, d, J=6 Hz, 21-Me), 1.36 (3H, s, 19-Me), 3.60 (1H, m, 3α-H), 3.64 (1H, d.d, J=6, 11 Hz, 12α-H), 4.16 (1H, q, J=6 Hz, 20-H), 5.36 (1H, Δ^5-olefinic-H).

Acetylation of Dehydrotomentosin (IX)——A solution of 20 mg of dehydrotomentosin (IX), 1 ml of Ac_2O, and 1 ml of pyridine was allowed to stand for 24 hr at room temperature, and poured into ice-water. A white powder that appeared was collected and was recrystallized from hexane–$(CH_3)_2CO$ to afford 17 mg of dehydrotomentosin acetate (X) as needles, mp 220—223°. Mass Spectrum *m/e*: 532 (M^+), 514 (M^+-H_2O), 496 (M^+-2H_2O), 472 (M^+—acetic acid), 454 (M^+-H_2O—acetic acid), 412 (M^+—$-2\times$acetic acid), 394 ($M^+-H_2O-2\times$acetic acid), 372 (M^+—acetic acid—tiglic acid), 354 (M^+-H_2O—-acetic acid—tiglic acid), 336 (M^+-2H_2O—acetic acid—tiglic acid), 312 ($M^+-2\times$acetic acid-tiglic acid), 294 ($M^+-H_2O-2\times$acetic acid—-tiglic acid), 276 (M^+— $2H_2O-2\times$acetic acid—tiglic acid), 224, 209, 145, 105, 83 (base peak), 55, 43. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1740, 1725, 1700, 1650, 1270, 1235, 1150, 1075, 1045, 1030. NMR (δ) $CDCl_3$: 0.95 (3H, s, 18-Me), 1.21 (3H, s, 19-Me), 1.22 (3H, d, J=6 Hz, 21-Me), 1.80 (3H, d, J=6 Hz, vinyl-Me), 1.83 (3H, s, vinyl-Me), 1.90 (3H, s, OAc), 2.00 (3H, s, OAc), 4.58 (1H, q, J=6 Hz, 20-H), 4.60 (1H, m, 3α-H), 4.62 (1H, d.d, J=6, 11 Hz, 12α-H), 5.40 (1H, Δ^5-olefinic-H) 6.83 (1H, d, J=6 Hz).

Partial Hydrolysis of Dehydrotomentosin (IX)——A solution of 70 mg of dehydrotomentosin (IX), in 2 ml of saturated MeOH-K_2CO_3 was allowed to stand for 15 hr at room temperature and the reaction mixture was separated and was purified by preparative TLC (MeOH: $CHCl_3$, 1: 19) to afford 55 mg of IX, 7 mg of a monoester (XI), and 3 mg of utendin (XIII). XI was recrystallized from MeOH to needles, mp 251—254°. Mass Spectrum *m/e*: 448 (M^+), 430 (M^+—$-H_2O$), 412 (M^+-2H_2O), 395 (M^+-3H_2O), 348 (M^+—tiglic acid), 330 (M^+-H_2O—tiglic acid), 321($M^+-CHOC_5H_7O$·Me), 312 (M^+—$-2H_2O$—tiglic acid), 303($M^+-H_2O-CHOC_5H_7O$·

Me), 294 (M^+-3H_2O-tiglic acid), 267($M^+-3H_2O-CHOC_5H_7O\cdot Me$), 242, 209, 141, 83(base peak), 55. IR ν_{max}^{Nujol} cm^{-1}: 3350, 1720, 1690, 1650, 1150, 1080, 1060, 1030. NMR (δ) d_5-pyridine: 1.07 (3H, s, 18-Me), 1.52 (3H, d, $J=6$ Hz, 21-Me), 1.62 (3H, d, $J=6$ Hz, vinyl-Me), 1.73 (3H, s, 19-Me), 1.89 (3H, s, vinyl-Me), 3.72 (1H, m, 3α-H), 3.75 (1H, d.d, $J=6$, 11 Hz, 12α-H), 5.42 (1H, Δ^5-olefinic-H), 5.86 (1H, q, $J=6$ Hz, 20-H), 7.08 (1H, d, $J=6$ Hz).

Acetylation of Monoester (XI)——A solution of 15 mg of monoester (XI) in 0.5 ml of Ac_2O and 0.5 ml of pyridine was allowed to stand for 24 hr at room temperature and worked up in the same way as for the acetylation of II to yield 12 mg of an amorphous diacetate (XII). XII was recrystallized from MeOH–$(CH_3)_2CO$ to needles, mp 233—235°. Mass Spectrum *m/e*: 432 (M^+-tinglic acid), 414 (M^+-H_2O-tinglic acid), 412 ($M^+-2\times$ acetic acid), 405 ($M^+-CHOC_5H_7O\cdot Me$), 396 (M^+-2H_2O-tinglic acid), 387($M^+-H_2O-CHOC_5H_7O\cdot Me$), 376 ($M^+-2H_2O-2\times$acetic acid), 372 ($M^+-$acetic acid-tiglic acid), 369 (M^+-2H_2O--$CHOC_5H_7O\cdot Me$), 354 (M^+-H_2O-acetic acid$-$tiglic acid), 345 (M^+-acetic acid$-CHOC_5H_7\cdot Me$), 312 ($M^+-2\times$acetic acid$-$-tiglic acid), 294 ($M^+-H_2O-2\times$acetic acid$-$tiglic acid), 242, 224, 211, 209, 145, 141, 105, 83 (base peak), 55, 43. IR ν_{max}^{Nujol} cm^{-1}: 3450, 3350, 1735, 1690, 1650, 1260, 1250, 1150, 1080, 1035. NMR (δ) $CDCl_3$: 1.00 (3H, s, 18-Me), 1.15 (3H, s, 19-Me), 1.31 (3H, d, $J=6$ Hz, 21-Me), 1.80 (3H, d, $J=6$ Hz, vinyl-Me), 1.85 (3H, s, vinyl-Me), 1.90 (3H, s, OAc), 2.05 (3H, s, OAc), 4.60 (1H, m, 3α-H), 4.62 (1H, d.d, $J=6$, 11 Hz, 12α-H), 5.30 (1H, q, $J=6$ Hz, 20-H), 5.42 (1H, d, $J=3.5$ Hz, Δ^5-olefinic-H), 6.88 (1H, d, $J=6$ Hz).

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