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Studies on the Constituents of Asclepiadaceae Plants. XXXIX.[1] Component of *Marsdenia tomentosa* Decne: Structure of Deacetyldehydrotomentodin, 20-*O*-Acetylpenupogenin, Deacetylkidjoladinin, and Kidjoladinin

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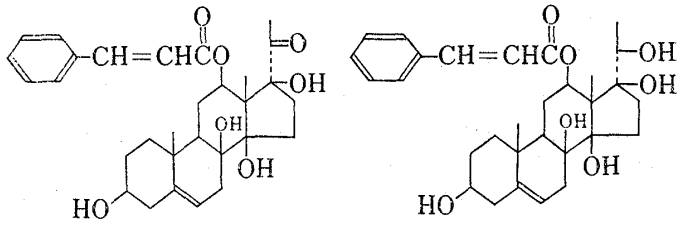
Four new polyoxypregnane derivatives, deacetyldehydrotomentodin (12β-*O*-cinnamoylutendin) (III), 20-*O*-acetylpenupogenin (12β-*O*-cinnamoyl-20-*O*-acetylsarcostin) (V), deacetylkidjoladinin (12β-*O*-tigloylsarcostin) (VIII), and kidjoladinin (12β-*O*-tigloyl-20-*O*-acetylsarcostin) (IX), were isolated from the stem of *Marsdenia tomentosa* Decne. Deacetyldehydrotomentodin is the first example of a monoester possessing the utendin skeleton to be isolated from the Asclepiadaceae plants.

Our previous papers reported the isolation and characterization of tomentosin,[3] tomentin,[4] dehydrotomentin,[4] tomentonin,[5] tomentodin,[5] dehydrotomentosin,[5] deacetyltomentosin,[6] and tomentidin,[6] the new polyoxypregnane derivatives possessing tomentogenin or utendin skeleton from the stem of *Marsdenia tomentosa* Decne. In this paper, we report some later findings on the components of this plant.

The aglycone mixture, obtained by a mild acid hydrolysis of the crude glycoside,[7] was chromatographed over silica gel and separated into several main fractions. Preparative thin-layer chromatography (TLC) of the most polar fraction yielded six crystalline substances, tentatively named compounds I, J, K, L, M, and N.

Among these, compounds I (I) and J (II) were identical with kidjolanin[7a] and penupogenin,[7a,8] respectively, from the comparison of spectral data and mixed mp with authentic samples. Compound K (III) mp 210—215°, $[\alpha]_D^{20}$ +7° (c=0.8, $CHCl_3$), with a molecular formula of $C_{30}H_{40}O_6$ from its elemental analysis and mass spectrum of m/e 496 (M^+) ,whose infrared (IR) spectrum showed absorptions for hydroxyl groups at 3450 and 1070 cm ^{1}, and an α,β-unsaturated ester at 1710, 1690, 1635, and 1150 cm^{-1}. The nuclear magnetic resonance (NMR) spectrum of III showed signals for two tertiary methyl groups at δ 1.00 (s) and 1.32 (s), one secondary methyl group at 1.12 (d, J=6 Hz), three hydroxy-methines at 3.50 (m),



kidjolanin (I) penupogenin (II)

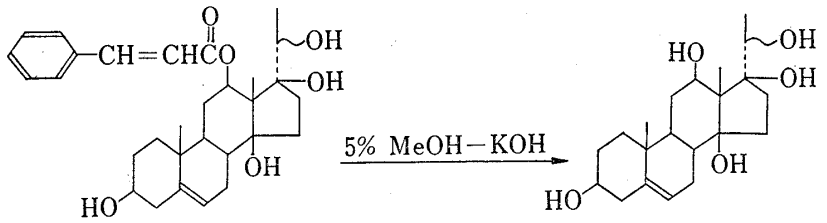
Fig. 1

1) Part XXXVIII: H. Bando, T. Yamagishi, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **24**, 1842 (1976).
2) Location: *Kita-12-jo, Nishi-5-chome, Kita-ku, Sapporo, 060, Japan.*
3) H. Seto, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **23**, 1552 (1975).
4) H. Seto, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **23**, 2397 (1975).
5) H. Seto, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **24**, 443 (1976)
6) H. Seto, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **24**, 1552 (1976).
7) *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).
8) H. Mitsuhashi and Y. Shimizu, *Chem. Pharm. Bull.* (Tokyo), **8**, 565 (1960).

3.62 (q, J=6 Hz), and 4.70 (d.d, J=6, 11 Hz), and eight olefinic protons at 5.36 (1H, t, J=3.5 Hz), 6.40 (1H, d, J=16 Hz), 7.40 (5H, m), and 7.70 (1H, d, J=16 Hz). The mass spectrum of III showed the presence of a cinnamoyl group at m/e 348 ($M^+-C_9H_8O_2$), 148, 131, and 103 which was supported by ultraviolet (UV) absorptions at 217 (log ε 4.30), 223 (4.28) and 279 nm (4.15).

Hydrolysis of III with 5% methanolic potassium hydroxide afforded utendin[9] (IV) as a neutral product. These facts suggest that III is a monoester of utendin with cinnamic acid, and mass spectral peak of III at m/e 451 (M^+-45)[10] definitely indicated that cinnamate moiety was not at C-20 of utendin.

The NMR spin decoupling experiments were carried out to confirm the position of the ester linkage of III. Irradiation of 21-Me group protons at δ 1.12 collapsed the quartet at δ 3.62 to a singlet but the double-doublet at δ 4.70, while that of the hydroxy-methine at δ 3.62 collapsed 21-Me group protons to a singlet, so that the hydroxy-methines at 3.62 and 4.70 (d.d, J=6, 11 Hz) correspond to 20- and 12α-H,[11] respectively. From these evidences, the structure of compound K (III) was determined as 12β-*O*-cinnamoylutendin and was named deacetyldehydrotomentodin, which is the first example of a monoester possessing an utendin skeleton to be isolated from a plant of the Asclepiadaceae family. Compound L (V), mp



deacetyldehydrotomentodin (III) utendin (IV)

Fig. 2

142—145°, $[\alpha]_D^{18}$ +52° (c=0.4,$CHCl_3$), with a molecular fornula of $C_{32}H_{42}O_8$ from its elemental analysis, and mass spectrum of m/e 494 (M^+—AcOH), whose IR spectrum showed absorptions for hydroxyl groups at 3400 and 1050 cm^{-1}, a saturated ester at 1730 and 1260 cm^{-1}, and an α,β-unsaturated ester at 1710, 1680, 1635, and 1170 cm^{-1}. The NMR spectrum of V showed signals for two tertiary methyl groups at δ 1.14 (s) and 1.46 (s), one secondary methyl group at 1.20 (d, J=6 Hz), one acetyl group at 1.95 (s), three hydroxy-methines at 3.60 (m), 4.62 (q, J=6 Hz), and 4.68 (d.d, J=6, 11 Hz), and eight olefinic protons at 5.40 (1H, t, J=3.5), 6.34 (1H, d, J=16 Hz), 7.50 (5H, m), and 7.66 (1H, d, J=16 Hz). The mass spectral peaks of V at m/e ($M^+-C_9H_8O_2$), 131 (C_9H_7O), and 103 (C_8H_6), as well as m/e 494 (M^+—AcOH) and 43 ($COCH_3$), showed the presence of a cinnamoyl group and an acetyl group, respectively. The presence of cinnamoyl group was supported by UV absorptions at 217 (log ε 4.29), 223 (4.22), and 278 nm (4.38).

Hydrolysis of V with 5% methanolic potassium hydroxide afforded sarcostin[12] (VI) as a neutral product. These facts suggest that V is a diester of sarcostin (VI) with acetic acid and cinnamic acid. Acetylation of V with acetic anhydride–pyridine afforded a monoacetate (VII), which was identical with 3β,20-*O*,*O*-diacetylpenupogenin (3β,20-*O*,*O*-diacetyl-12β-*O*-cinnamoylsarcostin). From these evidences, the structure of compound L (V) was determined as 12β-*O*-cinnamoyl-20-*O*-acetylsarcostin and was named 20-*O*-acetylpenupogenin, which

9) E. Abisch, Ch. Tamm, and T. Reichstein, *Helv. Chim. Acta*, **42**, 1014, (1959).
10) M. Fukuoka, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **19**, 1469 (1971).
11) N.S. Bhacca and D.H. Williams, "Application of NMR Spectroscopy in Organic Chemistry—Illustrations from Steroid Field," Holden-Day, Inc., San Francisco, 1964.
12) J.W. Cornforth and J.C. Earl, *J. Chem. Soc.*, **1939**, 737.

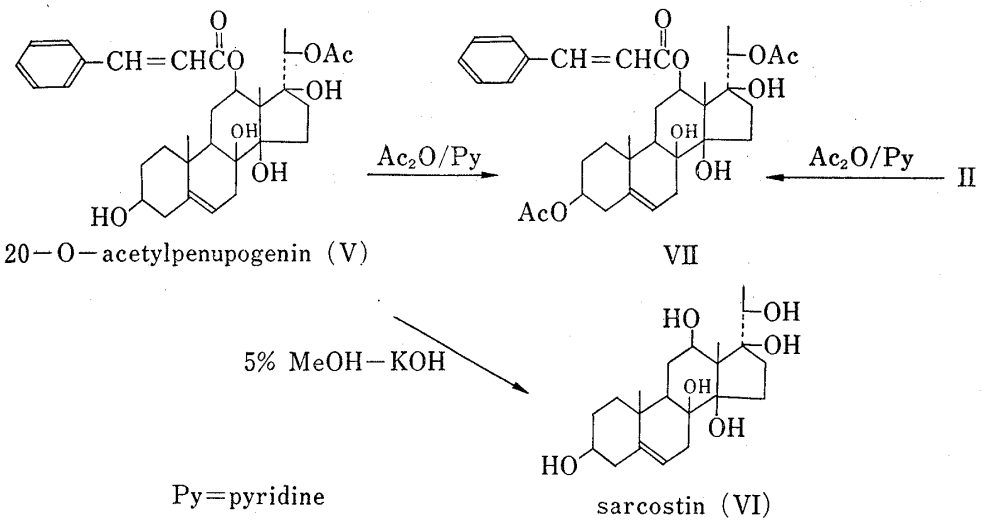


Fig. 3

corresponds to the acylgenin of amplexoside A isolated from *Asclepias amplexicaulis* by Piatak.[13] Compound M (VIII), mp 205—209°, $[\alpha]_D^{19}$ +9.5° (c=0.85, $CHCl_3$), with molecular formula of $C_{26}H_{40}O_7$ from its elemental analysis and mass spectrum of m/e 464 (M^+), whose IR spectrum of VIII showed absorptions for hydroxyl groups at 3400 and 1035 cm^{-1}, and an α,β-unsaturated ester at 1710, 1690, 1640, and 1140 cm^{-1}, which was supported by UV absorption at 215 nm (log ε 3.9). The NMR spectrum of VIII showed signals for two tertiary methyl groups at δ 1.12 (s) and 1.46 (s), one secondary methyl group at 1.20 (d, J=6 Hz), two vinyl methyl groups at 1.82 (d, J=6 Hz), and 1.83 (s), three hydroxy methines at 3.58 (q, J=6 Hz), 3.60 (m), 4.64 (d.d, J=6, 11 Hz), and two olefinic protons at 5.40 (t, J=3.5 Hz), and 6.86 (d, J=6 Hz).

Hydrolysis of VIII with methanolic potassium hydroxide afforded sarcostin (VI) as a neutral product. Prominent mass spectral peaks of VIII indicative of tiglate functional group were observed at m/e 83 (C_5H_7O) and 55 (C_4H_7). Further evidences were secured from the mass spectral peaks of VIII, since there were a faint parent ion at m/e 464 and other fragments at 446 (M^+-H_2O), 419 (M^+—CHOH·Me),[10] 374 (M^+-5H_2O), 364 (M^+—tiglic acid), 346 (M^+—tiglic acid−H_2O), and 83 (tigloyl cation). These evidences indicated that VIII is a monoester of sarcostin (VI) with tiglic acid. The mass spectral peak at m/e 419, and the chemical shift and coupling constant[11] of the NMR spectrum at δ 4.64 (d.d, J=6, 11 Hz) definitely indicated that tiglate moiety was not at C-20 but at C-12β of sarcostin.

In order to confirm the position of ester linkage of VIII, the NMR spin decoupling experiments were carried out. Irradiation of 21-Me group protons (δ 1.20, 3H, d, J=6 Hz) collapsed the quartet at δ 3.58 to a singlet but not the double-doublet at 4.64 and that of the hydroxy-methine at δ 3.58 collapsed 21-Me to a singlet, so that the hydroxy-methines at 3.58 and 4.64 correspond to 20- and 12α-H,[11] respectively. From these results, the structure of compound M (VIII) was determined as 12β-*O*-tigloyl sarcostin and was named deacetylkidjoladinin.

Compound N (IX), mp 250—255°, $[\alpha]_D^{15}$ +43.4° (c=1.0, $CHCl_3$), with a molecular formula of $C_{28}H_{42}O_8$ from its elemental analysis and mass spectrum of m/e 506 (M^+), whose IR spectrum showed absorptions for hydroxyl groups at 3500, 3430, and 1070 cm^{-1}, a saturated ester at 1710 and 1280 cm^{-1}, and an α,β-unsaturated ester at 1700, 1645 and 1145 cm^{-1}. The NMR spectrum of IX showed signals for two tertiary methyl groups at δ 1.15 (s) and 1.44 (s), one secondary methyl group at 1.23 (d, J=6 Hz), two vinyl-methyl groups at 1.85 (s) and 1.86 (d, J=6 Hz), one acetyl group at 1.95 (s), three hydroxy-methines at 3.52 (m), 4.63 (d.d, J=

13) A.M. Ahsan, D.M. Piatak, and P.D. Sorensen, *Experientia*, **29**, 788 (1973).

6, 11 Hz), 4.65 (q, J=6 Hz), and two olefinic protons at 5.35 (t, J=3.5 Hz) and 6.85 (q, J=6 Hz).

Hydrolysis of IX with methanolic potassium hydroxide afforded sarcostin (VI) as a neutral product. The mass spectrum of IX showed the presence of a tigloyl group at *m/e* 406 ($M^+-C_5H_8O_2$), 83 (C_5H_7O), and 55 (C_4H_7), and an acetyl group at *m/e* 446 (M^+—AcOH) and 43 ($COCH_3$). The presence of tigloyl group was supported by UV absorption at 214 nm (log ε 4.14). These facts indicate that IX is a diester of sarcostin (VI) with acetic acid and tiglic acid. Acetylation of IX with acetic anhydride–pyridine afforded a monoacetate (X), which was identical with deacetylkidjolanin diacetate. From these results, the structure of compound N (IX) was determined as 12β-*O*-tigloyl-20-*O*-acetylsarcostin and was named kidjoladinin.

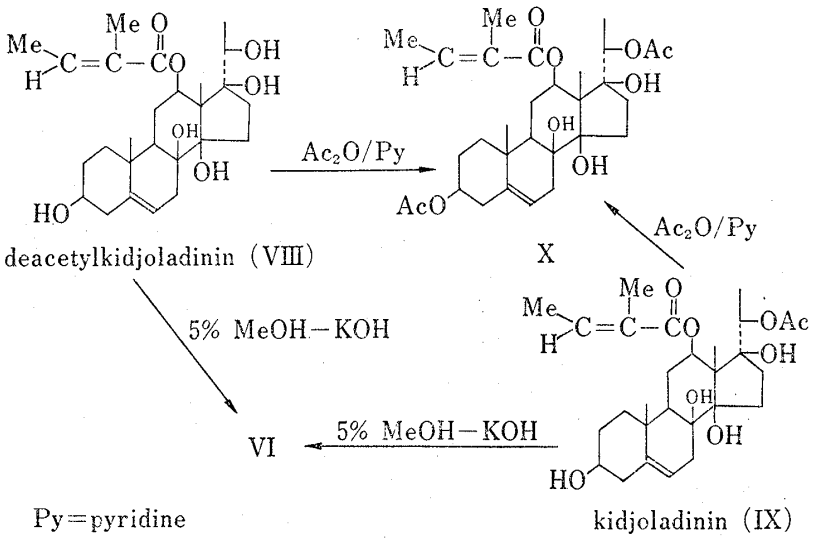


Fig. 4

Experimental

Melting points were determined on a Kofler hot stage and are uncorrected. Optical rotations were measured in $CHCl_3$ solution on a Hitachi S115-4 polarimeter. NMR spectra were determined on a JEOL PS-100 spectrometer operating at 100 MHz with tetramethylsilane (TMS) as an internal standard. Mass spectra were determined on a Hitachi RMU-7 mass spectrometer, IR spectra in Nujol mull on a Hitachi 215 spectrometer, and UV spectra 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.

Deacetyldehydrotomentodin (III)——From 15 g of the ester-type aglycone mixture obtained by the same procedure as reported previously,[3] 74 mg of deacetyldehydrotomentodin (III) was obtained by silica gel column chromatography and preparative TLC ($CHCl_3$: MeOH=19: 1, cyclohexane: EtOAc=1: 1). III was recrystallized from acetone–hexane to prisms, mp 210—215°, $[\alpha]_D^{20}$ +7° (c=0.8, $CHCl_3$). Mass Spectrum *m/e*: 496 (M^+), 478 (M^+-H_2O), 460 (M^+-2H_2O), 451 (M^+—CHOH·Me), 442 (M^+-3H_2O), 433 (M^+—CHOH·Me—H_2O), 415 (M^+—CHOH·Me—$2H_2O$), 397 (M^+—CHOH·Me—$3H_2O$), 348 (M^+—cinnamic acid), 330 (M^+—cinnamic acid—H_2O), 312 (M^+—cinnamic acid—$2H_2O$), 303 (M^+—cinnamic acid—CHOH·Me), 294 (M^+—cinnamic acid—$3H_2O$), 285 (M^+—cinnamic acid—CHOH·Me—H_2O), 267 (M^+—cinnamic acid—CHOH·Me—$2H_2O$), 249 (M^+—cinnamic acid—CHOH·Me—$3H_2O$), 148, 147, 131 (base peak), 105, 103. IR ν_{max}^{Nujol} cm^{-1}: 3450, 1710, 1690, 1635, 1575, 1280, 1150, 1070, 1050. UV λ_{max}^{EtOH} nm (log ε): 217 (4.30), 223 (4.28), 279 (4.15). NMR $\delta_{ppm}^{CDCl_3}$: 1.00 (3H, s, 19-Me), 1.12 (3H, d, J=6 Hz, 21-Me), 1.32 (3H, s, 18-Me), 3.50 (1H, m, 3α-H), 3.62 (1H, q, J=6 Hz, 20-H), 4.70 (1H, d.d, J=6, 11 Hz, 12α-H), 5.36 (1H, t, J=3.5 Hz, Δ^5-olefinic proton), 6.40 (1H, d, J=16 Hz), 7.40 (5H, m, aromatic protons), 7.70 (1H, d, J=16 Hz). *Anal.* Calcd. for $C_{30}H_{40}O_6$: C, 72.55; H, 8.12. Found: C, 72.63; H, 7.95.

Alkaline Hydrolysis of Deacetyldehydrotomentodin (III)——A solution of 20 mg of deacetyldehydrotomentodin (III) in 1 ml of 5% MeOH–KOH was refluxed for 30 min and the reaction mixture was purified directly by preparative TLC (MeOH: $CHCl_3$=9: 1). Recrystallization from acetone gave 10 mg of utendin

(IV) as prisms, mp 240—243°. Mass Spectrum *m/e*: 366 (M^+), 348 (M^+-H_2O), 330 (M^+-2H_2O), 321 (M^+—CHOH·Me), 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.

20-*O*-Acetylpenupogenin (V)——From the same column chromatographic fraction which contained III, 55 mg of 20-*O*-acetylpenupogenin (V) was obtained by preparative TLC (ether, $CHCl_3$: MeOH=99: 1). V was recrystallized from acetone–hexane to fine needles, mp 142—145°, $[\alpha]_D^{18}$ +52° (c=0.4, $CHCl_3$). Mass Spectrum *m/e*: 494 (M^+—AcOH), 476 (M^+—AcOH—H_2O), 467 (M^+—CHOAc·Me), 458 (M^+—AcOH—$2H_2O$), 449 (M^+—CHOAc·Me—H_2O), 440 (M^+—AcOH—$3H_2O$), 431 (M^+—CHOAc·Me—$2H_2O$), 406 (M^+—cinnamic acid), 346 (M^+—cinnamic acid—AcOH), 328 (M^+—cinnamic acid—AcOH—H_2O), 319 (M^+—cinnamic acid—CHOAc·Me), 301 (M^+—cinnamic acid—CHOAc·Me—H_2O), 283 (M^+—cinnamic acid—CHOAc·Me—$2H_2O$), 265 (M^+—cinnamic acid—CHOAc·Me—$3H_2O$), 148, 147, 131 (base peak), 103, 43. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1730, 1710, 1680, 1635, 1260, 1170, 1050. UV λ_{max}^{EtOH} nm (log ε): 217 (4.29), 223 (4.22), 278 (4.38). NMR $\delta_{ppm}^{CDCl_3}$: 1.14 (3H, s, 19-Me), 1.20 (3H, d, J=6 Hz, 21-Me), 1.46 (3H, s, 18-Me), 1.95 (3H, s, OAc), 3.60 (1H, m, 3α-H), 4.62 (1H, q, J=6 Hz, 20-H), 4.68 (1H, d.d, J=6, 11 Hz, 12α-H), 5.40 (1H, t, J=3.5 Hz, Δ^5-olefinic proton), 6.34 (1H, d, J=16 Hz), 7.50 (5H, m, aromatic protons), 7.66 (1H, d, J=16 Hz), *Anal.* Calcd. for $C_{32}H_{42}O_8$: C, 69.29; H, 7.63. Found: C, 69.07; H, 7.85.

Alkaline Hydrolysis of 20-*O*-Acetylpenupogenin (V)——A solution of 15 mg of 20-*O*-acetylpenupogenin (V) 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: 9). Recrystallization from MeOH–acetone gave 6 mg of sarcostin (VI) as prisms, mp 245—250°. Mass Spectrum *m/e*: 382 (M^+), 364 (M^+-H_2O), 346 (M^+-2H_2O), 337 (M^+—CHOH·Me), 328 (M^+-3H_2O), 319 (M^+—CHOH·Me—H_2O), 310 (M^+-4H_2O), 301 (M^+—CHOH·Me—$2H_2O$), 283 (M^+—CHOH·Me—$3H_2O$), 265 (M^+—CHOH·Me—$4H_2O$), 244 (M^+-138),[10,14] 226 ($M^+-138-H_2O$), 161, 138, 114, 105, 43. IR ν_{max}^{Nujol} cm^{-1}: 3470, 3380, 3250, 175, 1045, 1040.

Acetylation of 20-*O*-Acetylpenupogenin (V)——A solution of 20 mg of 20-*O*-acetylpenupogenin (V) in 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 recrystallized from acetone–hexane to afford 18 mg of an acetate (VII) as needles, mp 137—139°. Mass Spectrum *m/e*: 536 (M^+—AcOH), 518 (M^+—AcOH—H_2O), 500 (M^+—AcOH—$2H_2O$), 476 ($M^+-2\times$AcOH), 448 (M^+—cinnamic acid), 388 (M^+—cinnamic acid—AcOH), 370 (M^+—cinnamic acid—AcOH—H_2O), 352 (M^+—cinnamic acid—AcOH—$2H_2O$), 328 (M^+—cinnamic acid—2×AcOH), 310 (M^+—cinnamic acid—2×AcOH—H_2O), 292 (M^+—cinnamic acid—2×AcOH—$2H_2O$), 148, 147, 131 (base peak), 120, 103, 43. IR ν_{max}^{Nujol} cm^{-1}: 3450, 1725, 1705, 1690, 1635, 1245, 1160, 1070, 1030. NMR $\delta_{ppm}^{CDCl_3}$: 1.16 (3H, s, 19-Me), 1.20 (3H, d, J=6 Hz, 21-Me), 1.46 (3H, s, 18-Me), 2.02 (3H, s, OAc), 2.18 (3H, s, OAc), 4.60 (3H, m, 3α-H+12α-H+20-H), 5.36 (1H, t, J=3.5 Hz, Δ^5-olefinic proton), 6.24 (1H, d, J=16 Hz), 7.40 (5H, m, aromatic protons), 7.56 (1H, d, J=16 Hz). *Anal.* Calcd. for $C_{34}H_{44}O_9$: C, 68.43; H, 7.43. Found: C, 68.28; H, 7.34.

Acetylation of Penupogenin (II)——A solution of 55 mg of penupogenin (II) in 1 ml of Ac_2O and 1 ml of pyridine was allowed to stand for 19 hr at room temperature and worked up in the same manner as in the acetylation of V to produce 50 mg of an amorphous product, which was recrystallized from acetone–hexane to needles, mp 136—138.5°, and miexd mp with VII 135—139°. All spectral data were identical with those of VII.

Deacetylkidjoladinin (VIII)——From the same column chromatographic and thin-layer chromatographic fraction which contained V, 37 mg of deacetylkidjoladinin (VIII) was obtained by preparative TLC (ether, $CHCl_3$: MeOH=99: 1). VIII was recrystallized from acetone–hexane to prisms, mp 205—209°, $[\alpha]_D^{19}$ +9.5° (c=0.85, $CHCl_3$). Mass Spectrum *m/e*: 464 (M^+), 446 (M^+-H_2O), 428 (M^+-2H_2O), 419 (M^+—CHOH·Me), 413 (M^+-2H_2O—Me), 410 (M^+-3H_2O), 401 (M^+—CHOH·Me—H_2O), 392 (M^+-4H_2O), 383 (M^+—CHOH·Me—$2H_2O$), 374 (M^+-5H_2O), 365 (M^+—CHOH·Me—$3H_2O$), 364 (M^+—tiglic acid), 346 (M^+—tiglic acid—H_2O), 328 (M^+—tiglic acid—$2H_2O$), 310 (M^+—tiglic acid—$3H_2O$), 301 (M^+—tiglic acid—CHOH·Me—H_2O), 277, 240, 208, 83 (base peak), 55. IR ν_{max}^{Nujol} cm^{-1}: 3400, 1710, 1690, 1640, 1280, 1140, 1070, 1035. UV λ_{max}^{EtOH} 215 nm (log ε 3.93). NMR $\delta_{ppm}^{CDCl_3}$: 1.12 (3H, s, 19-Me), 1.20 (3H, d, J=6 Hz, 21-Me), 1.46 (3H, s, 18-Me), 1.82 (3H, d, J=6 Hz, vinyl-Me), 1.83 (3H, s, vinyl-Me), 3.58 (1H, q, J=6 Hz, 20-H), 3.60 (1H, m, 3α-H), 4.64 (1H, d.d, J=6, 11 Hz, 12α-H), 5.40 (1H, d, J=3.5 Hz, Δ^5-olefinic proton), 6.86 (1H, d, J=6 Hz). *Anal.* Calcd. for $C_{26}H_{40}O_7$: C, 67.21; H, 8.68. Found: C, 67.09; H, 8.75.

Alkaline Hydrolysis of Deacetylkidjoladinin (VIII)——A solution of 7 mg of deacetylkidjoladinin (VIII) in 0.5 ml of 5% MeOH–KOH was allowed to stand for 18 hr at room temperature and worked up in the same manner as in the hydrolysis of V to afford 3 mg of sarcostin (VI) as prisms.

Acetylation of Deacetylkidjoladinin (VIII)——A solution of 20 mg of deacetylkidjoladinin (VIII) in 1 ml of Ac_2O and 1 ml of pyridine was allowed to stand for 23 hr at room temperature and worked up in the same manner as in the acetylation of V to afford 20 mg of a diacetate (X), which was recrystallized from acetone–hexane to plates, mp 231—236°. Mass Spectrum *m/e*; 488 (M^+—AcOH), 470 (M^+—AcOH—H_2O), 452 (M^+—AcOH—$2H_2O$), 448 (M^+—tiglic acid), 434 (M^+—AcOH–$3H_2O$), 430 (M^+—tiglic acid—H_2O), 428 ($M^+-2\times$

14) M. Fukuoka and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **17**, 2448 (1969).

AcOH), 410 ($M^+-2\times AcOH-H_2O$), 392 ($M^+-2\times AcOH-2H_2O$), 388 (M^+-tiglic acid$-$AcOH), 370(M^+-tiglic acid$-$AcOH$-H_2O$), 352 (M^+-tiglic acid$-$AcOH$-2H_2O$), 328 (M^+-tiglic acid$-2\times$AcOH), 310 (M^+-tiglic acid$-2\times$AcOH$-H_2O$), 292 (M^+-tiglic acid$-2\times$AcOH$-2H_2O$), 274 (M^+-tiglic acid$-2\times$AcOH$-3H_2O$), 120, 105, 83 (base peak), 55, 43. IR ν_{max}^{Nujol} cm^{-1}: 3450, 1730, 1705, 1690, 1640, 1260, 1240, 1150, 1070, 1030. NMR $\delta_{ppm}^{CDCl_3}$: 1.14 (3H, s, 19-Me), 1.20 (3H, d, $J=6$ Hz, 21-Me), 1.42 (3H, s, 18-Me), 1.82 (3H, d, $J=6$ Hz, vinyl-Me), 1.83 (3H, s, vinyl-Me), 1.94 (3H, s, OAc), 2.01 (3H, s, OAc), 4.60 (1H, m, 3α-H), 4.64 (1H, d.d, $J=6$, 11 Hz, 12α-H), 4.66 (1H, q, $J=6$ Hz, 20-H), 5.38 (1H, t, $J=3.5$ Hz, Δ^5-olefinic proton), 6.82 (1H, d, $J=6$ Hz).

Kidjoladinin (IX)——From the same column chromatographic and thin-layer chromatographic fractions which contained V, 52 mg of kidjoladinin (IX) was obtained by preparative TLC (ether, $CHCl_3$: MeOH=99:1). Recrystallization of IX from acetone-hexane gave needles, mp 250—252°, $[\alpha]_D^{15}$ +43.4° ($c=1.0$, $CHCl_3$). Mass Spectrum *m/e*: 506 (M^+), 488 (M^+-H_2O). 470 (M^+-2H_2O), 452 (M^+-3H_2O), 446 (M^+-AcOH), 428 (M^+-AcOH$-H_2O$), 413 (M^+-AcOH$-H_2O-$Me), 410 (M^+-AcOH$-2H_2O$), 406 (M^+-tiglic acid), 395 (M^+-AcOH$-2H_2O-$Me), 388 (M^+-tiglic acid$-H_2O$), 370 (M^+-tiglic acid$-2H_2O$), 368 (M^+-138), 352 (M^+-tiglic acid$-3H_2O$), 350 ($M^+-138-H_2O$), 346 (M^+-tiglic acid$-$AcOH), 332 ($M^+-138-2H_2O$), 328 (M^+-tiglic acid$-$AcOH$-H_2O$), 314 ($M^+-138-3H_2O$), 310 (M^+-tiglic acid$-$AcOH$-2H_2O$), 190 (M^+-tiglic acid$-138-2H_2O$), 120, 105, 83 (base peak), 55, 43. IR ν_{max}^{Nujol} cm^{-1}: 3500, 3430, 1710, 1700, 1650, 1645, 1280, 1145, 1070, 1050. UV λ_{max}^{EtOH}: 214 nm (log ε 4.14). NMR $\delta_{ppm}^{CDCl_3}$: 1.15 (3H, s, 19-Me), 1.23 (3H, d, $J=6$ Hz, 21-Me), 1.44 (3H, s, 18-Me), 1.85 (3H, s, vinyl-Me), 1.86 (3H, d, $J=6$ Hz, vinyl-Me), 1.95 (3H, s, OAc), 3.52 (1H, m, 3α-H), 4.63 (1H, d.d, $J=6$, 11 Hz, 12α-H), 4.65 (1H, q, $J=6$ Hz, 20-H), 5.35 (1H, t, $J=3.5$ Hz, Δ^5-olefinic proton), 6.85 (1H, d, $J=6$ Hz). *Anal.* Calcd. for $C_{28}H_{42}O_8$: C, 66.38; H, 8.36. Found: C, 66.64; H, 8.44.

Alkaline Hydrolysis of Kidjoladinin (IX)——A solution of 10 mg of kidjoladinin (IX) in 0.5 ml of 5% MeOH–KOH was allowed to stand for 24 hr at room temperature and worked up in the same manner as in the hydrolysis of V to afford 4 mg of sarcostin (VI) as prisms.

Acetylation of Kidjoladinin (IX)——A solution of 25 mg of kidjoladinin (IX) in 1 ml of Ac_2O and 1 ml of pyridine was allowed to stand for 24 hr at room temperature and worked up in the same manner as in the acetylation of V to afford 23 mg of an amorphous product, which was recrystallized from acetone-hexane to plates, mp 230—233° and mixed mp with X, 230—235°. All spectral data were identical with those of X.

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