Studies on the Constituents of Asclepiadaceae Plants. XXXIX.\(^1\) Component of *Marsdenia tomentosa* Decne: Structure of Deacetyldehydrotomentodin, 20-O-Acetylpenupogenin, Deacetylkidjolanin, and Kidjolanin

HIDEO SETO, TAMIKO SASAKI, KOJI HAYASHI, and HIROSHI MITSUHASHI

Faculty of Pharmaceutical Sciences, Hokkaido University\(^2\)

(Received January 5, 1976)

Four new polyoxy pregnane derivatives, deacetyldehydrotomentodin (12β-O-cinnamoylutentudin) (III), 20-O-acetylpenupogenin (12β-O-cinnamoyl-20-O-acetylsarcostin) (V), deacetylkidjolanin (12β-O-tigloylsarcostin) (VIII), and kidjolanin (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,\(^4\) tomentoin,\(^5\) tomentodin,\(^5\) dehydrotomentosin,\(^6\) and tomentidin,\(^6\) the new polyoxy preg nan 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\(^8\) and penupogenin,\(^8\) respectively, from the comparison of spectral data and mixed mp with authentic samples. Compound K (III) mp 210–215°, \([α]_D^20 +7^\circ (c=0.8, \text{CHCl}_3)\), with a molecular formula of C\(_{36}\)H\(_{50}\)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),

![Fig. 1](image)

\(^2\) Location: Kita-12-jo, Nishi-5-chome, Kita-ku, Sapporo, 060, Japan.
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+C₆H₅O₂), 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 utendin⁹ (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)⁹⁰ 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-methylene 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-cinnamylutendin and was named deacetyldehydrotomendotin, 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

![Diagram](image)

Fig. 2

142—145°, [α]D₂⁰ +52° (c=0.4, CHCl₃), with a molecular formula of C₃₂H₄₅O₈ 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⁺-C₆H₅O₂), 131 (C₆H₄O), and 103 (C₅H₃), as well as m/e 494 (M⁺-AcOH) and 43 (CO₂H), 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 sarcostin¹² (VI) as a neutral product. These facts suggest that V is a diester of sarcostine (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,0-diacytylenupogenin (3β,20-O,0-diacytyl-12β-O-cinnamoylsarcosin). From these evidences, the structure of compound L (V) was determined as 12β-O-cinnamyl-20-O-acetylsarcostin and was named 20-O-acetylpenogenin, which

---

corresponds to the acylgenin of amplexoside A isolated from Asclepias amplexicaulis by Piatak.\textsuperscript{13} Compound M (VIII), mp 205–209°, $[x]_D^{25} +9.5^\circ$ ($c=0.85$, CHCl$_3$), with molecular formula of C$_{28}$H$_{46}$O$_4$, 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 $\alpha,\beta$-unsaturated ester at 1710, 1690, 1640, and 1140 cm$^{-1}$, which was supported by UV absorption at 215 nm (log $\varepsilon$ 3.9 ). The NMR spectrum of VIII showed signals for two tertiary methyl groups at $\delta$ 1.12 (s) and 1.46 (s), one secondary methyl group at 1.20 (d, $J=6$ Hz), two vinyl methyl groups at 1.89 (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$_6$H$_7$O) and 55 (C$_4$H$_7$). 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 ($M^+-\text{H}_2$O), 419 ($M^+-\text{CHOH-Me}$),\textsuperscript{10} 374 ($M^+-5\text{H}_2$O), 364 ($M^+-\text{tiglic acid}$), 346 ($M^+-\text{tiglic acid-}$H$_2$O), 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\textsuperscript{11} of the NMR spectrum at $\delta$ 4.64 (d,d, $J=6, 11$ Hz) definitely indicated that tiglate moiety was not at C-20 but at C-12$\beta$ 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 ($\delta$ 1.20, 3H, d, $J=6$ Hz) collapsed the quartet at $\delta$ 3.58 to a singlet but not the double-doublet at 4.64 and that of the hydroxy-methine at $\delta$ 3.58 collapsed 21-Me to a singlet, so that the hydroxy-methines at 3.58 and 4.64 correspond to 20- and 12$\alpha$-H,\textsuperscript{11} respectively. From these results, the structure of compound M (VIII) was determined as 12$\beta$-O-tigloyl sarcostin and was named deacetylkidjoladinin.

Compound N (IX), mp 250–255°, $[x]_D^{25} +43.4^\circ$ ($c=1.0$, CHCl$_3$), with a molecular formula of C$_{28}$H$_{45}$O$_5$, 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 $\alpha,\beta$-unsaturated ester at 1700, 1645 and 1145 cm$^{-1}$. The NMR spectrum of IX showed signals for two tertiary methyl groups at $\delta$ 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, $J=$

\textsuperscript{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_3H_2O_2), 83 (C_6H_5O), and 55 (C_4H_7), and an acetyl group at m/e 446 (M^+ - AcOH) and 48 (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 deacetylkindjoladin diacetate. From these results, the structure of compound N (IX) was determined as 12α-O-tigloyl-20-O-acetylsarcostin and was named kindjoladinin.

![Fig. 4](image)

**Experimental**

Melting points were determined on a Kofer 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 FS-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 H_{60} (Merck, Type 60), and silica gel 0.05—0.2 mm (Merck, 70—235 mesh ASTM) was used for column chromatography.

**Deacetyldehydrometotin (III)**—From 15 g of the ester-type aglycone mixture obtained by the same procedure as reported previously,^a^ 74 mg of deacetyldehydrometotin (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°, [α]_D^20 +7° (c=0.8, CHCl_3). Mass Spectrum m/e: 496 (M^+), 478 (M^+ - H_2O), 460 (M^+ - 2H_2O), 451 (M^+ - CHO-Me), 442 (M^+ - 3H_2O), 433 (M^+ - CHO-Me - H_2O), 415 (M^+ - CHO-Me - 2H_2O), 397 (M^+ - CHO-Me - 3H_2O), 348 (M^+ - cinnamic acid), 330 (M^+ - cinnamic acid - H_2O), 312 (M^+ - cinnamic acid - 2H_2O), 303 (M^+ - cinnamic acid - CH-OH-Me), 294 (M^+ - cinnamic acid - 3H_2O), 285 (M^+ - cinnamic acid - CH-OH-Me - H_2O), 267 (M^+ - cinnamic acid - CH-OH-Me - 2H_2O), 249 (M^+ - cinnamic acid - CH-OH-Me - 3H_2O), 148, 147, 131 (base peak), 105, 103. IR ν_{max} cm⁻¹: 3450, 1710, 1690, 1635, 1575, 1280, 1150, 1070, 1050. UV λ_{max} nm (log ε): 217 (4.30), 223 (4.28), 279 (4.19). NMR δ ppm: 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, J=6 Hz, 11 Hz, 12α-H), 5.36 (1H, t, J=3.5 Hz, δ-olefinic proton), 6.46 (1H, d, J=16 Hz), 7.40 (5H, m, aromatic protons), 7.70 (1H, d, J=16 Hz). Anal. Calcd. for C_{29}H_{34}O_7: C, 72.55; H, 8.12. Found: C, 72.63; H, 7.85.

**Alkaline Hydrolysis of Deacetyldehydrometotin (III)**—A solution of 20 mg of deacetyldehydrometotin (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.
Alkaline Hydrolysis of 20-O-Acetylpenuogenin (V)—A solution of 15 mg of 20-O-acetylpenuogenin (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: CHCl₃=1:9). Recrystallization from MeOH−acetone gave 6 mg of sarcotin (VI) as prisms, mp 245−250°. Mass Spectrum m/e: 382 (M⁺), 364 (M⁺−H₂O), 346 (M⁺−2H₂O), 337 (M⁺−CHOH−Me), 328 (M⁺−3H₂O), 319 (M⁺−4H₂O), 310 (M⁺−CH(OH)−Me−2H₂O), 283 (M⁺−CHOH−Me−3H₂O), 265 (M⁺−CHOH−Me−4H₂O), 244 (M⁺−138), 226 (M⁺−138−H₂O), 161, 138, 114, 105, 43.

Acetylation of 20-O-Acetylpenuogenin (V)—A solution of 20 mg of 20-O-acetylpenuogenin (V) in 1 ml of Ac₂O 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−H₂O), 500 (M⁺−AcOH−2H₂O), 476 (M⁺−2×AcOH), 448 (M⁺−cinnamic acid), 388 (M⁺−cinnamic acid−AcOH), 370 (M⁺−AcO−AcOH−H₂O), 352 (M⁺−AcO−AcOH−2H₂O), 328 (M⁺−cinnamic acid−2×AcOH), 310 (M⁺−cinnamic acid−2×AcOH−H₂O), 292 (M⁺−cinnamic acid−2×AcOH−2H₂O), 248, 143, 105, 43.

Acetylation of Penuogenin (II)—A solution of 55 mg of penuogenin (II) in 1 ml of Ac₂O 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 136−135.5°, and mixed mp with VII 135−139°. All spectral data were identical with those of VII.

Deacetylkjoladin (VIII)—From the same column chromatographic and thin−layer chromatographic fraction which contained V, 37 mg of deacetylkjoladin (VIII) was obtained by preparative TLC (ether: CHCl₃: MeOH=99:1). VIII was recrystallized from acetone−hexane to prisms, mp 205−209° (c=0.85, CHCl₃). Mass Spectrum m/e: 464 (M⁺), 446 (M⁺−H₂O), 428 (M⁺−2H₂O), 419 (M⁺−CHOH−Me), 413 (M⁺−2H₂O−Me), 410 (M⁺−3H₂O), 401 (M⁺−CHOH−Me−H₂O), 392 (M⁺−4H₂O), 383 (M⁺−CHOH−Me−2H₂O), 374 (M⁺−5H₂O), 365 (M⁺−CHOH−Me−3H₂O), 364 (M⁺−tiglic acid), 346 (M⁺−tiglic acid−H₂O), 328 (M⁺−tiglic acid−2H₂O), 310 (M⁺−tiglic acid−3H₂O), 301 (M⁺−tiglic acid−CHOH−Me−H₂O), 277, 249, 208, 83 (base peak), 55. IR νmax cm⁻¹: 3400, 1710, 1600, 1640, 1280, 1140, 1070, 1035. UV λmax nm (log e): 319 (1.14), 282 (1.20), 257 (1.30), 218 (1.46), 190 (1.52). NMR δCH₃ cm⁻¹: 8.73. Found: C, 68.28; H, 7.34.

Acetylation of Penuogenin (II)—A solution of 55 mg of penuogenin (II) in 1 ml of Ac₂O 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 136−135.5°, and mixed mp with VII 135−139°. All spectral data were identical with those of VII.

Deacetylkjoladin (VIII)—From the same column chromatographic and thin−layer chromatographic fraction which contained V, 37 mg of deacetylkjoladin (VIII) was obtained by preparative TLC (ether: CHCl₃: MeOH=99:1). VIII was recrystallized from acetone−hexane to prisms, mp 205−209° (c=0.85, CHCl₃). Mass Spectrum m/e: 464 (M⁺), 446 (M⁺−H₂O), 428 (M⁺−2H₂O), 419 (M⁺−CHOH−Me), 413 (M⁺−2H₂O−Me), 410 (M⁺−3H₂O), 401 (M⁺−CHOH−Me−H₂O), 392 (M⁺−4H₂O), 383 (M⁺−CHOH−Me−2H₂O), 374 (M⁺−5H₂O), 365 (M⁺−CHOH−Me−3H₂O), 364 (M⁺−tiglic acid), 346 (M⁺−tiglic acid−H₂O), 328 (M⁺−tiglic acid−2H₂O), 310 (M⁺−tiglic acid−3H₂O), 301 (M⁺−tiglic acid−CHOH−Me−H₂O), 277, 249, 208, 83 (base peak), 55. IR νmax cm⁻¹: 3400, 1710, 1600, 1640, 1280, 1140, 1070, 1035. UV λmax nm (log e): 319 (1.14), 282 (1.20), 257 (1.30), 218 (1.46), 190 (1.52). NMR δCH₃ cm⁻¹: 8.73. Found: C, 68.28; H, 7.34.

Alkaline Hydrolysis of Deacetylkjoladin (VIII)—A solution of 7 mg of deacetylkjoladin (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 sarcotin (VI) as prisms.

Acetylation of Deacetylkjoladin (VIII)—A solution of 20 mg of deacetylkjoladin (VIII) in 1 ml of Ac₂O 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−H₂O), 452 (M⁺−AcOH−2H₂O), 448 (M⁺−tiglic acid), 434 (M⁺−AcOH−3H₂O), 430 (M⁺−tiglic acid−H₂O), 428 (M⁺−2×

AcOH), 410 (M+\(\text{–}2\times\text{AcOH}–\text{H}_2\text{O}\)), 392 (M+\(\text{–}2\times\text{AcOH}–2\text{H}_2\text{O}\)), 388 (M+\text{–}tiglic acid–\text{AcOH}), 370 (M+\text{–}tiglic acid–\text{AcOH}–\text{H}_2\text{O}), 352 (M+\text{–}tiglic acid–\text{AcOH}–2\text{H}_2\text{O}), 328 (M+\text{–}tiglic acid–2\times\text{AcOH}), 310 (M+\text{–}tiglic acid–2\times\text{AcOH}–\text{H}_2\text{O}), 292 (M+\text{–}tiglic acid–2\times\text{AcOH}–2\text{H}_2\text{O}), 274 (M+\text{–}tiglic acid–2\times\text{AcOH}–3\text{H}_2\text{O}), 120, 105, 83 (base peak), 55, 43. IR \(\nu_{\text{max}}^\text{cm}^{-1}\): 3450, 1730, 1690, 1640, 1260, 1240, 1150, 1070, 1030. NMR \(\delta_{\text{H}}\): 1.14 (3H, s, 19-Me), 1.20 (3H, d, \(J=6\text{ Hz}\), 21-Me), 1.42 (3H, s, 18-Me), 1.82 (3H, d, \(J=6\text{ Hz}\), vinyl-Me), 1.83 (3H, s, vinyl-Me), 1.94 (3H, s, OAc), 2.01 (3H, s, OAc), 4.60 (1H, m, 3z-H), 4.64 (1H, d.d, \(J=6, 11\text{ Hz}\), 12z-H), 4.66 (1H, q, \(J=6\text{ Hz}\), 20-H), 5.38 (1H, t, \(J=3.5\text{ Hz}\), d\text{–}olefinic proton), 6.82 (1H, d, \(J=6\text{ Hz}\)).

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\(^\circ\), \(\nu_{\text{max}}^\text{cm}^{-1}\) 4344 (\(\omega\), 1390, 1230, 1150, 1040, 810. NMR \(\delta_{\text{H}}\): 1.18 (3H, s, 19-Me), 1.20 (3H, d, \(J=6\text{ Hz}\), 21-Me), 1.42 (3H, s, 18-Me), 1.82 (3H, d, \(J=6\text{ Hz}\), vinylMe), 1.83 (3H, s, vinyl-Me), 1.94 (3H, s, OAc), 2.01 (3H, s, OAc), 4.60 (1H, m, 3z-H), 4.64 (1H, d.d, \(J=6, 11\text{ Hz}\), 12z-H), 4.66 (1H, q, \(J=6\text{ Hz}\), 20-H), 5.38 (1H, t, \(J=3.5\text{ Hz}\), d\text{–}olefinic proton), 6.82 (1H, d, \(J=6\text{ Hz}\)).

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 sarcoxin (VI) as prisms.

Acetylation of Kidjoladinin (IX)—A solution of 25 mg of kidjoladinin (IX) in 1 ml of Ac\(_2\text{O}\) 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\(^\circ\) and mixed mp with X, 230–235\(^\circ\). All spectral data were identical with those of X.

Acknowledgement The plant material was kindly collected by Mr. M. Kawaguchi and we express our sincere gratitude. We also thank Miss M. Takahashi for mass spectral measurements Miss T. Obara, Miss A. Maeda, and Mrs. H. Matsumoto for elemental analyses and Miss T. Okayama for NMR spectral measurements.