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Studies on the Constituents of Asclepiadaceae Plants. XXXII.[1] Aglycones from *Cynanchum wilfordi* Hemsley

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Structures of two new polyoxypregnane ester-type aglycones; 12-O-cinnamoyl-20-O-ikemaoylsarcostin (VII) and 12-O-cinnamoyl-20-O-tigloylsarcostin (VIII), from the glycoside of *C. wilfordi* Hemsley, were elucidated by chemical and physicochemical analyses. Kidjoranin (IV), caudatin (V) and penupogenin (VI) were also obtained.

In 1966, our laboratory members reported the presence of polyoxypregnane ester glycoside mixture in *Cynanchum wilfordi* Hemsley (Asclepiadaceae). They isolated three polyoxypregnane derivatives; sarcostin (I), deacylmetaplexigenin (II), and lineolon (III), from the deacylated aglycone fraction.[3] In this paper, we describe the separation and the structure elucidation of five polyoxypregnane esters derived from the aglycone mixture of the glycoside of this plant. Two of them are new esters and others are known esters.

The aglycone mixture, obtained from the glycoside after a mild acid hydrolysis, was submitted to silica gel column and preparative thin-layer chromatography (TLC). These procedures yielded five polyoxypregnane ester derivatives, named aglycone-A, -B, -C, -D, and -E.

Aglycone-A, -B, and -C were obtained from the same column chromatographic fractions followed by preparative TLC with several solvent systems, and identified respectively with kidjoranin[4] (IV), mp 148—149°, $[\alpha]_D$+63.2°, caudatin[5] (V), mp 158—160/190—195°, $[\alpha]_D$ +19.5°, and penupogenin[6] (VI), mp 147—149°.

Aglycone-D (VII) and aglycone-E (VIII) were obtained from the less polar fractions than the fractions containing IV, V, and VI. Aglycone-D[7] (VII) shows the following properties: mp 158—163°, $[\alpha]_D$+107° (c=1.05, chloroform), bluish violet coloration with antimony trichloride. The elemental analysis of VII indicate the composition of $C_{37}H_{50}O_8$. Ultraviolet (UV) maxima at 217 nm (log ε, 4.43), 223 (4.39), and 280 (4.33), and infrared (IR) absorption bands at 3550, 3380, 1708, 1643, 1580, 1500, and 1180 cm^{-1} indicate the presence of α,β-unsaturated ester, aromatic and hydroxyl groups. Nuclear magnetic resonance (NMR) spectrum of VII shows the signals at δ 6.24 and 7.60 ppm as AB-type quartet (J=16 Hz) and δ 7.36 ppm corresponding to five aromatic protons as a multiplet, so that the cinnamic acid ester linkage was recognized. Hydrolysis of VII with 5% methanolic potassium hydroxide gave sarcostin (I) and cinnamic acid, whose mother liquor fraction showed the presence of ikemaic acid (3,4-dimethyl-2-pentenoic acid) by gas chromatographic examination. The NMR spectrum

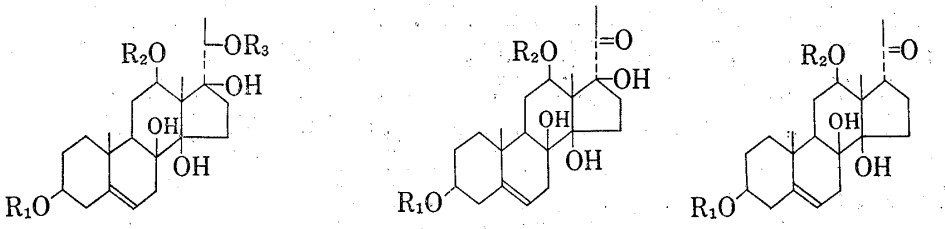
1) Part XXXI: H. Bando, K. Hayashi, Y. Kitaichi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **22**, 1209 (1974).
2) Location: *Kita-12-jo, Nishi-6-chome, Kita-ku, Sapporo, 060, Japan.*
3) H. Mitsuhashi, K. Sakurai, T. Nomura, and N. Kawahara, *Chem. Pharm. Bull.* (Tokyo), **14**, 712 (1966).
4) T. Sasaki, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **20**, 628 (1972).
5) T. Yamagishi and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **20**, 625 (1972).
6) H. Mitsuhashi and Y. Shimizu, *Chem. Pharm. Bull.* (Tokyo), **10**, 725 (1962).
7) In the previous communication, we reported this compound as wilforine [*Chem. Pharm. Bull.* (Tokyo), **20**, 2065 (1972)]. However, this name had been used for an alkaloid from *Tripterygium wilfordii* by M. Beroza [*J. Am. Chem. Soc.*, **74**, 3636 (1952)] and from *Maytenus senegalensis* by M. Tin-wa, *et al.* [*Lloydia*, **34**, 79 (1971)] as pointed out by Dr. N.R. Farnsworth [*J. Pharm. Sci.*, 1028 (1973)]. We apologize for this inattention and the name will no longer be used for VII.

of VII also supported this fact on the basis of the signals at δ 0.99 and 1.03 ppm for geminal dimethyl doublets, at 1.81 ppm for vinylic methyl singlet, and 5.69 ppm for vinylic proton singlet. The signals originating from the steroid ring appear at δ 1.15 ppm (C-19 Me), 1.23 (C-21 Me, doublet, J=6 Hz), 1.53 (C-18 Me), 3.50 (C-3α proton), 4.76 (C-12α proton, double doublet, J=12 and 4 Hz), 4.63 (C-20 proton, quartet, J=6 Hz), and 5.35 (C-6 vinylic proton).

These facts suggest that aglycone-D (VII) is a diester of I with cinnamic and ikemaic acids linked at C-12 and/or C-20 hydroxyl groups of I on the basis of the chemical shift. The mass spectrum of VII showed no parent peak at *m/e* 622, but, other peaks agreed with the above suggestion; *m/e* 604 (M^+-H_2O), 586 (M^+-2H_2O), 474 (M^+—cinnamic acid), 456 (474—H_2O), 438 (474—$2H_2O$), 346 (474—ikemaic acid), 328 (346—H_2O), 310 (346—$2H_2O$), 208 (346—138),[8] 190 (208—H_2O), 131 (cinnamoyl cation), and 111 (ikemaoyl cation).

Acetylation of VII with acetic anhydride in pyridine afforded a monoacetate (IX), mp 126—132°, showing δ 2.03 ppm (–OAc singlet) and the signal of C-3α proton of VII at δ 3.50 ppm (multiplet) shifted to δ 4.7 ppm.

Reduction of VII with equimolar amount of lithium aluminium hydride in dioxane only gave I and recovered VII. When the hydrolysis of VII under the above described conditions was stopped before the complete disappearance of VII, two kinds of partially hydrolyzed compounds were obtained in a very low yield. These two compounds lacked cinnamoyl but had ikemaoyl chromophore on the basis of the absorption maximum at 217 nm. One of them (X) (12-O-ikemaoylsarcostin), mp 160—170°, showed the peaks at *m/e* 492 (M^+), 474 (M^+-H_2O), 456 (M^+-2H_2O), 447 (M^+-45), *etc.*, on the mass spectrum. It is well known that the ion M^+-45 originates from the cleavage of the glycol between C-17 and C-20 of pregnane derivatives indicating the presence of free hydroxyl group at C-20.[9] We found that the acyl migration occurred reversively between the C-12β hydroxyl and the C-20 hydroxyl groups on 17-β-H C/D-*cis*-pregnane derivatives under alkaline or acidic condition.[10] Therefore, the other partially hydrolyzed product seems to be 20-O-ikemaoylsarcostin (XI). From these results, it is deduced that descinnamoyl aglycone-D (X or XI) is formed first from VII and the subsequent migration of the ikemaoyl group causes the formation of another ikemaoylsarcostin (XI or X) under an alkaline condition.



I: R_1=R_2=R_3=H
VI: R_1=R_3=H, R_2=Cin.
VII: R_1=H, R_2=Cin., R_3=Ikem.
VIII: R_1=H, R_2=Cin., R_3=Tig.
IX: R_1=Ac, R_2=Cin., R_3=Ikem.
X: R_1=R_3=H, R_2=Ikem.
XI: R_1=R_2=H, R_3=Ikem.
XIII: R_1=Ac, R_2=Ikem., R_3=H
XIV: R_1=Ac, R_2=Ikem., R_3=Cin.
XV: R_1=Ac, R_2=Cin., R_3=Tig.

II: R_1=R_2=H
IV: R_1=H, R_2=Cin.
V: R_1=H, R_2=Ikem.
XII: R_1=Ac, R_2=Ikem.

III: R_1=R_2=H

Cin.: cinnamoyl
Ikem.: ikemaoyl
Tig.: tigloyl

Chart 1

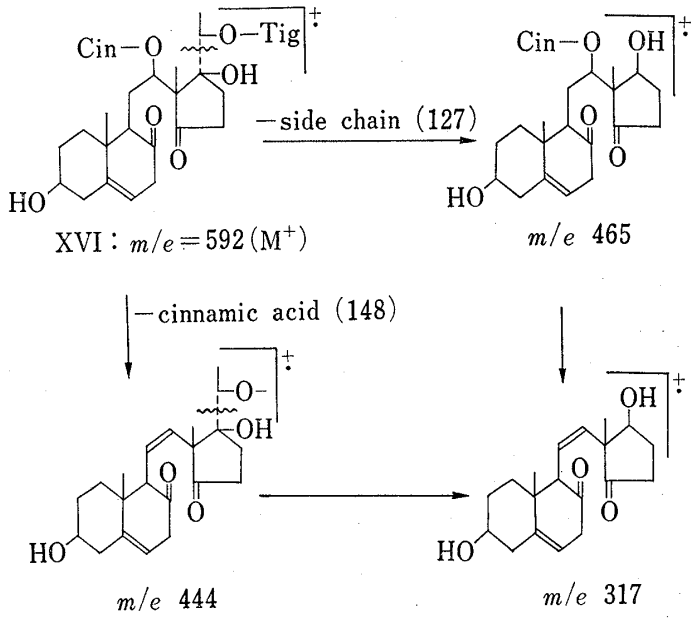
In order to confirm the position of the ester linkages in VII, the following experiments were carried out. Caudatin acetate (XII) was reduced with sodium borohydride, and the

8) Retro-Diels-Alder cleavaged fragment at Δ^5 double bond.
9) M. Fukuoka, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **19**, 1469 (1971).
10) T. Yamagishi, K. Hayashi, and H. Mitsuhashi, *Chem. Pharm. Bull.* (Tokyo), **20**, 2289 (1972).

product (XIII), mp 193—199°, exhibiting the signals of doublet methyl at δ 1.16 ppm and a quartet methine at δ 3.62 ppm, was treated with cinnamoyl chloride in pyridine to give 3-O-acetyl-12-O-ikemaoyl-20-O-cinnamoylsarcostin (XIV), which was not identified with aglycone-D acetate (IX) by TLC and other spectral data. This finding suggests that the structure of aglycone-D can be expressed by the formula VII.

Aglycone-E (VIII), $[\alpha]_D$+136.6°, a vitreous substance, possesses a cinnamoyl ester linkage on the basis of IR bands at 1710 and 1645 cm^{-1} for α,β-unsaturated ester and aromatic group at 1580 and 1500 cm^{-1}, the absorption maxima at 217 nm (log ε, 4.26), 223 (4.14), and 280 (4.20), and the NMR signals at δ 6.22 and 7.55 ppm (AB-quartet, J=16 Hz) and five aromatic protons as a multiplet at 7.4 ppm. Hydrolysis of XV with 5% methanolic potassium hydroxide gave I and cinnamic acid, and tiglic acid was also detected by GLC from the mother liquor of the cinnamic acid fraction. The proton signals originating from tigloyl moiety appeared at 1.68 ppm (doublet methyl), 1.72 (singlet methyl), and 6.76 (collapsed quartet vinylic proton).

Acetylation of VIII with acetic anhydride in pyridine gave a monoacetate (XV) (δ 2.02 ppm, -OAc methyl). The signal corresponding to C-3α proton (δ 3.50 ppm, broad multiplet in the spectrum of VIII) had shifted down field (δ 4.7 ppm) in XV. The mass spectrum of VIII showed no parent peak m/e 594 ($C_{35}H_{46}O_8$), but the following peaks were observed: m/e 558 (M^+-3H_2O), 446 (M^+-cinnamic acid), 428 (446–H_2O), 410 (446–$2H_2O$), 346 (446–tiglic acid), 328 (346–H_2O), 310 (346–$2H_2O$), 208,[8] 190, 131, 83 (tigloyl cation), *etc.*



XVI: m/e=592 (M^+) m/e 465

m/e 444 m/e 317

Chart 2

These results indicate that aglycone-E (VIII) is a diester of I with cinnamic and tiglic acids. The ester linkages exist at C-12β and C-20 hydroxyl groups of I on the basis of the chemical shifts and the patterns of both protons at δ 4.80 ppm (double doublet, J=12 and 4 Hz) and δ 4.70 (quartet, J=6 Hz).

Oxidative cleavage of 8β—14β glycol of VIII with lead tetra-acetate afforded a diketone (XVI), which showed IR bands at 1735, 1700, and 1662 cm^{-1}. The mass spectrum of XVI shows the parent peak at m/e 592, and considerable peaks at m/e 465 (M^+—127) and 317 (465—cinnamic acid). The latter peaks were derived from the cleavage between C-17 and C-20 with C-20 tigloyl moiety shown as Chart 2. Therefore, aglycone-E is 12-O-cinnamoyl-20-O-tigloyl-sarcostin formulated as VIII.

Experimental

All melting points were taken on a Kofler hot stage apparatus and are uncorrected. IR absorption spectra were obtained with a Hitachi Model 215. UV spectra were determined with a Hitachi EPS-3T spectrometer. NMR spectra were taken on a JOEL PS-100 in $CDCl_3$ solution with tetramethylsilane as internal standard. Chemical shifts are given in δ values and signal multiplicities were abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Mass spectra were recorded on a Hitachi RMU-6 mass spectrometer. Gas chromatograph apparatus used was a Shimadzu Model GC-4BPF, a 25% diethylene glycol succinate on Chromosorb W column (glass, 2.1 m), N_2 as a carrier gas at 60 ml/min. Thin-layer chromatography was performed on Merck Kieselgel HF_{254}. Column chromatography was performed with Merck Kieselgel-60. Material: The aglycone mixture was obtained by the procedure reported previously from the radix of *C. wilfordi*.[3]

Acid Hydrolysis of Crude Glycoside——To a solution of 50 g of the glycoside mixture in 450 ml of methanol, 150 ml of 0.2 N sulfuric acid was added and heated under reflux for 45 min. After addition of 450 ml of water, methanol was evaporated *in vacuo*, and the aqueous layer was extracted with ether. The solution was washed successively with water, 5% sodium bicarbonate solution, and water, and dried over anhydrous sodium sulfate. Evaporation of ether gave 22 g of foamy aglycone mixture. These procedures were repeated three times, and 72 g of the aglycone mixture was obtained from 150 g of the glycoside. The aglycone was submitted to silica gel column chromatography as shown in Table I.

Table I. Column Chromatography of the Koikema-Aglycone

Fr. No.	Solvent	Volum (liter)	Weight (g)
I	Chf.	2	3.48
II	Chf.	1	2.53
III	Chf.	2	5.89
IV	1% MeOH/Chr.	1.5	2.28
V	1% MeOH/Chr.	1	3.75
VI	1% MeOH/Chr.	1.5	4.21
VII	2% MeOH/Chf.	2	3.37
VIII	2% MeOH/Chr.	2	2.59
IX	5% MeOH/Chf.	3	7.14

Separation of Aglycone-A (IV), -B (V), and -C (VI)——The fractions VI—VIII in the Table I gave similar chromatograms on TLC. Therefore, they were combined and submitted to preparative TLC by monitoring with UV absorption. When the development was carried out with ether, the mixture was separated into aglycone-A fraction and the mixed fraction of aglycone-B and -C. The latter fraction was separated into each compound by development with hexane–acetone (6: 4) solution three times. Aglycone A, mp 148—149° (from ether), $[\alpha]_D$ +63.2° (c=0.244, methanol), was identified with kidjoranin by mixed fusion with an authentic sample. Aglycone-B, mp 158—160°/190—195°, $[\alpha]_D$ +19.4° (c=0.325, methanol), was identified with caudatin by mixed fusion with an authentic sample. Aglycone-C, mp 147—149°, was identified with penupogenin by mixed fusion with an authentic sample.

Separation of Aglycone-D (VII) and -E (VIII)——Preparative TLC of fr. III by developing with 5% methanol in chloroform gave a fraction containing two components absorbing UV-rays. However, this fraction was contaminated by an impurity with no UV absorption, which was removed by developing with ethyl acetate. Further preparative TLC with ether afforded two components, aglycone-D (VII), more mobile on TLC, and aglycone-E (VIII).

Aglycone-D (VII)——mp 158—163° (from acetone/hexane), $[\alpha]_D$ +107° (c=1.05, chloroform). *Anal.* Calcd. for $C_{37}H_{50}O_8$: C, 71.35; H, 8.09. Found: C, 71.25; H, 8.08. IR ν_{max}^{Nujol} cm^{-1}: 3550, 3380, 1708, 1643, 1580, 1500, 1180. UV λ_{max}^{EtOH} nm (log ε): 217 (4.43), 223 (4.39), 280 (4.33). NMR: δ ($CDCl_3$): 0.99 (3H, d., J=6 Hz), 1.03 (3H, d., J=6 Hz), 1.15 (3H, s), 1.23 (3H, d., J=6 Hz), 1.53 (3H, s), 1.81 (3H, s), 3.50 (1H, m), 4.63 (1H, q, J=6 Hz), 4.76 (1H, d.d., J=12 and 4 Hz), 5.35 (1H, broad s), 5.69 (1H, s), 6.24 and 7.60 (2H, AB q, J=16 Hz), 7.38 (5H, m). Mass Spectrum m/e: 604, 586, 474, 456, 438, 346, 328, 310, 292, 208, 190, 131, 111.

Alkali Hydrolysis of VII——Aglycone-D (VII) (120 mg) was dissolved in 5 ml of 5% potassium hydroxide in methanol solution and refluxed for 12 hr on a water bath. Excess water was added to the mixture and methanol was evaporated under a reduced pressure. The residual solution was extracted by a continuous liquid–liquid extractor to give needles (42 mg), mp 150—155°/255°, from acetone/methanol, identified with sarcostin (I). The water layer was then acidified with 40% phosphoric acid and extracted with ether. After removal of the solvent, recrystallization of the residue from diluted ethanol gave plates, mp 131—133°, identified with cinnamic acid. The mother liquor fraction of the acid was submitted to GLC (column: 25% diethylene glycol succinate on Chromosorb W, 2.1 m glass, temp. 180°, N_2 as carrier, 60 ml/min): t_R 8.4 min and 7.2 min (minor peak) identified with ikemaic acid. The authentic sample also showed two peaks.

Acetylation of VII——Aglycone-D (VII) (56.7 mg) was dissolved in 1.2 ml of pyridine, 0.6 ml of acetic anhydride was added, and the mixture was kept for 6 hr at room temp. The mixture was poured into ice-water and extracted with ether. The organic layer was washed successively with 2 N hydrochloric acid, 5% sodium bicarbonate, and sodium chloride–saturated water solution and dried over sodium sulfate. Removal of the solvent and recrystallization of the residue from acetone–hexane gave 37.3 mg of colorless prisms (IX), mp 126—132°, NMR δ ($CDCl_3$): 1.03 (6H, d, J=7 Hz), 1.18 (3H, s), 1.23 (3H, d., J=7 Hz), 1.55 (3H, s), 1.84 (3H, s), 2.02 (3H, s), 4.7 (3H, m), 5.40 (1H, broad s), 5.68 (1H, s), 6.24 and 7.58 (2H, AB q, J=16 Hz), 7.4 (5H, m). *Anal.* Calcd. for $C_{39}H_{52}O_9$: C, 70.45; H, 7.88. Found: C, 70.27; H, 7.84.

Short-time Hydrolysis of VII——Aglycone-D (VII) (119 mg) was dissolved in 6 ml of 5% potassium in methanol and the mixture was kept for 6 hr at room temp. After addition of excess water, methanol was

evaporated *in vacuo*, and residual aqueous solution was extracted with ether. The organic solution was worked up as usual and the residual material was submitted to preparative TLC to recovered the starting VII (97.9 mg). The less mobile fraction than VII gave 1.8 mg of a powder consisting of two components detected by TLC. Each spot on TLC absorbed UV-rays (254 nm) and the mixture showed absorption maximum at 217 nm. The less polar material between them was obtained by further preparative TLC as colorless prisms (X), mp 160—170°. Mass Spectrum *m/e*: 492 (M^+), 474 (M^+-H_2O), 456 (M^+-2H_2O), 447 (M^+–45), 441 (M^+-2H_2O–Me), 111 (ikemaoyl cation).

Conversion of Caudatin Acetate (XII) into 3-O-Acetyl-12-O-ikemaoyl-20-O-cinnamoylsarcostin (XIV)——To a solution of 360 mg of caudatin acetate (XII) in 3.5 ml of dimethylformamide, 57 mg of sodium borohydride was added with stirring during 3 hr. After decomposition of the excess reagent with acetic acid, the mixture was poured into water and extracted with ether, followed by usual working up of the ether solution to give 366 mg of a white foamy substance, which was submitted to preparative TLC. The reduced product (XIII) was obtained as rods, mp 193—199°, and the starting material was recovered (132 mg) which was reduced again under the same conditions to give 64.3 mg of XIII. *Anal.* Calcd. for $C_{30}O_{46}O_8$: C, 67.39; H, 8.67. Found: C, 67.15; H, 8.76.

Alkaline hydrolysis of a small amount of XIII gave sarcostin (I) identified by coloration with antimony trichloride and *Rf* value on TLC. To a solution of 62 mg of XIII in 4 ml of pyridine, cinnamoyl chloride (150 mg) was added and the mixture was stirred for 18 hr at room temp. The reaction mixture was poured into water and extracted with ether. The organic layer was washed successively with 2 N hydrochloric acid, 5% sodium bicarbonate solution, and water saturated with sodium chloride and dried over magnesium sulfate. Evaporation of the solvent and purification of the residue by preparative TLC gave 34.2 mg of vitreous mass (XIV). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550, 3400, 1710, 1640, 1580, 1500, 1180. NMR δ ($CDCl_3$): 1.04 (3H, d, J=6 Hz), 1.06 (3H, d, J=6 Hz), 1.14 (3H, s), 1.28 (3H, d, J=6 Hz), 1.53 (3H, s), 2.02 (3H, s), 2.13 (3H, s), 4.6 (3H, broad, m), 5.39 (1H, broad, m), 5.44 (1H, broad, s), 6.46 and 7.65 (2H, AB q, J=16 Hz), 7.4 (5H, m). This compound (XIV) did not correspond to (IX) on TLC with several solvent systems.

Aglycone-E (VIII)——$[\alpha]_D$ +136.6° (c=0.467, methanol). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1710, 1645, 1580, 1500. UV λ_{max}^{MeOH} nm (log ε): 217 (4.26), 223 (4.14), 280 (4.20). NMR δ ($CDCl_3$): 1.13 (3H, s), 1.22 (3H, d, J=6 Hz), 1.55 (3H, s), 1.68 (3H, d, J=6 Hz), 1.72 (3H, s), 3.50 (1H, broad, m), 4.70 (1H, q, J=6 Hz), 4.80 (1H, d.d, J=12 and 4 Hz), 5.33 (1H, broad, s), 6.22 (1H, d, J=16 Hz), 6.76 (1H, broad q, J=6 Hz), 7.4 (5H, m), 7.55 (1H, d, J=16 Hz). Mass Spectrum *m/e*: 558 (M^+-3H_2O), 446 (M^+–cinnamic acid), 428 ($446-H_2O$), 410 ($446-2H_2O$), 346 (446–tiglic acid), 328 ($346-H_2O$), 310 ($346-2H_2O$), 292 ($346-3H_2O$), 208 (346–138), 190 ($208-H_2O$), 131, 83 (tigloyl cation). *Anal.* Calcd. for $C_{35}H_{46}O_8$: C, 70.68; H, 7.80. Found: C, 69.86; H, 7.73.

Alkali Hydrolysis of VIII——A solution of 120 mg of aglycone-E (VIII) in 6 ml of 5% potassium hydroxide in methanol was refluxed for 18 hr on a water bath. After addition of excess water and evaporation of methanol *in vacuo*, the mixture was extracted with ether by a continuous liquid–liquid extractor to give 39 mg of needles, mp 150—154°/250—255° (from acetone/methanol) identified with sarcostin (I). The aqueous layer was acidified with 40% phosphoric acid and extracted with ether. After removal of the solvent, recrystallization of the residue gave plates (from dil ethanol), mp 132—134°, identified with cinnamic acid. The mother liquor fraction was submitted to GLC examination (column: 25% diethylene glycol succinate on Chromosorb W, 2.1 m glass column, 180°): t_R 6.0 min identified with tiglic acid.

Acetylation of VIII——A solution of ester-E (VIII) (102.9 mg) dissolved in a mixture of 1 ml of pyridine and 0.8 ml of acetic anhydride was kept for 5 hr at room temp. The solution was poured into ice-water and extracted with ether. After usual working-up, the ether layer was dried over magnesium sulfate. Evaporation of the solvent and purification of the residue by preparative TLC gave 58.9 mg of monoacetate (XV). NMR δ ($CDCl_3$): 1.18 (3H, s), 1.23 (3H, d, J=7 Hz), 1.56 (3H, s), 1.71 (3H, d, J=6 Hz), 1.73 (3H, s), 2.02 (3H, s), 4.7 (3H, m), 5.42 (1H, m), 6.24 (1H, d, J=16 Hz), 6.80 (1H, broad, q, J=6 Hz), 7.4 (5H, m), 7.56 (1H, m).

Lead Tetraacetate Oxidation of VIII——To a solution of aglycone-E (VIII) (87 mg) in 4 ml of benzene, 203 mg of lead tetraacetate was added and the mixture was stirred for 30 min at room temp. To the mixture, water was added and extracted with ether. The ether solution was washed successively with 5% sodium bicarbonate solution and water, and dried over magnesium sulfate. After removal of the solvent and purification of the residue by preparative TLC, 62.6 mg of diketone (XVI) was obtained. $[\alpha]_D$ +68.8° (c=0.782, methanol), IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 1735, 1700, 1628, 1570. NMR δ ($CDCl_3$): 0.83 (3H, s), 1.36 (3H, d, J=7 Hz), 1.40 (3H, s), 1.72 (3H, d, J=6 Hz), 1.76 (3H, s), 3.56 (1H, m), 4.97 (1H, q, J=7 Hz), 5.3 (1H, m), 5.39 (1H, broad, t), 6.32 (1H, d, J=16 Hz), 6.75 (1H, m), 7.4 (5H, m), 7.58 (1H, d, J=16 Hz). Mass Spectrum *m/e*: 592 (M^+), 465 (M^+–127), 444 (M^+–cinnamic acid), 344 (444–tiglic acid), 317 (444–127), 131, 83.

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