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Studies on the Constituents of Zizyphi Fructus. II. Structure of New *p*-Coumaroylates of Maslinic Acid

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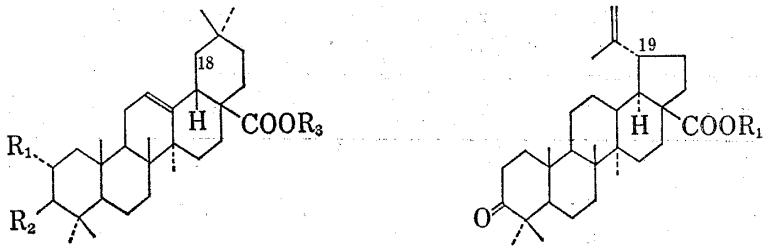
A new *p*-coumaroylate of maslinic acid was isolated from the fruits of *Zizyphus jujuba* (Rhamnaceae) together with known triterpenoid acids: betulonic, oleanonic, maslinic and 3-O-*trans*-*p*-coumaroyl maslinic acid. The structure of V was characterized to be 3-O-*cis*-*p*-coumaroyl maslinic acid on the basis of chemical and spectral evidence.

Keywords——*Zizyphus jujuba*; Rhamnaceae; new *p*-coumaroylates of maslinic acid; 3-O-*trans*-*p*-coumaroyl maslinic acid; 3-O-*cis*-*p*-coumaroyl maslinic acid

On the study of pharmacological active principles in the fruits of *Zizyphus jujuba* (Rhamnaceae) 2-O-*trans*-, 3-O-*trans*- and 3-O-*cis*-*p*-coumaroylalphitolic acids were identified.[2] Further examination on triterpenoid acids provided new *p*-coumaroylates of maslinic acid together with known triterpenoid acids. This paper deals with the structure elucidation on these esters.

The dried fruits were treated as described in the experimental section to yield compounds A to E. Attempt to isolate compound A (I) and B (II) by means of repeated chromatographies was in failure, but after methylating the mixture with diazomethane, the mixture of



II: R_1=H, R_2=O, R_3=H
IIa: R_1=H, R_2=O, R_3=Me
III: R_1=OH, R_2=OH, R_3=H
IIIa: R_1=OH, R_2=OH, R_3=Me
IIIb: R_1=OAc, R_2=OAc, R_3=H
IIIc: R_1=OAc, R_2=OAc, R_3=Me

I: R_1=H
Ia: R_1=Me

IV: R_1=OH, R_2=O-CO-CH=CH-(C$_6$H$_4$)-OH, R_3=H
IVa: R_1=OH, R_2=O-CO-CH=CH-(C$_6$H$_4$)-OMe, R_3=Me
V: R_1=OH, R_2=O-CO-CH=CH-(C$_6$H$_4$)-OH, R_2=H

Fig. 1

1) Location: *a*) *Maidashi, Higashi-ku, Fukuoka*; *b*) *Tashiro, Tosu, Saga.*
2) A. Yagi, N. Okamura, Y. Haraguchi, K. Noda, and I. Nishioka, *Chem. Pharm. Bull.* (Tokyo), 26, 1798 (1978).

the corresponding esters was successfully separated over repeated chromatographies to afford two monomethyl esters of I and II (Ia and IIa).

Ia, mp 168—169°, $[\alpha]_D^{23}$ +10.5° ($CHCl_3$), $C_{31}H_{48}O_3$, *m/e* 468 (M^+), gave positive Liebermann-Burchard and Legal tests and showed ester carbonyl (1730 cm^{-1}), carbonyl (1705 cm^{-1}) and isopropenyl (880 cm^{-1}) absorption bands on the infrared (IR) spectrum. On the nuclear magnetic resonance (NMR) spectrum Ia exhibited the signals due to tertiary methyl and isopropenyl protons. Two olefinic proton signals (J=2 Hz), two multiplet methylene proton signals of α-position to carbonyl group and a methine proton signal due to C_{19}–H (J=10; 10; 4 Hz) appeared at δ 4.62, 4.75, 2.24, 2.42 and 3.00, respectively. The assignment of the signal (δ 3.00) to C_{19}–H is based on the NMR spectral analysis that the proton at C_{19} position indicating the coupling constant (J=10; 10; 4 Hz) is found down-field because of the effect by isopropenyl and carboxyl groups.[3] The above spectral data indicated Ia to be methly betulonate[4] and the examination of mass spectral fragment ion peaks (*m/e* 262 and 205)[5] supported above conclusion. By direct comparison with an authentic sample which was synthesized from betulinic acid by Jones oxidation followed by methylation Ia was identified to be methyl betulonate.

IIa, mp 182—184°, $[\alpha]_D^{23}$ +30° ($CHCl_3$), $C_{31}H_{48}O_3$, *m/e* 468 (M^+), gave positive Liebermann-Burchard and Legal tests and showed ester carbonyl (1720 cm^{-1}) and carbonyl (1700 cm^{-1}) absorption bands on the IR spectrum. On the NMR spectrum IIa indicated the signals due to methylene protons adjacent to carbonyl group and a triplet olefinic proton (J=4 Hz) at δ 2.38, 2.52 and 5.30, respectively besides tertiary methyl proton signals. The appearance of a methine proton signal at C_{18} position (J=14; 4 Hz) which discriminates oleanane type from ursane type triperpenoid acid at δ 2.87 on the NMR spectrum[6] disclosed that IIa is methyl oleanonate. The examination of mass spectral fragment ion peaks (*m/e* 262 and 205) supported IIa to be methyl oleanonate or ursonate.[5] By direct comparison with an authentic sample which was synthesized from oleanolic acid by Jones oxidation followed by methylation IIa was identified to be methyl oleanonate.

Table I. Nuclear Magnetic Resonance Spectral Data of C_2 and C_3 Methine Protons

Compounds	III	IIIa	IIIb	IIIc	IV	IVa	V
Solvent	A	B	B	B	A	B	A
C_2	3.74 a	3.66 c	5.10 a	5.11 a	3.98 a	3.90 c	3.84 a
C_3	3.08 b	2.97 b	4.72 b	4.73 b	4.70 b	4.63 b	4.61 b

a, sextet, J=10; 10; 4 Hz b, doublet, J=10 Hz c, multiplet.
Solvent A: $CDCl_3$–pyridine-d_5 (10: 1).
Solvent B: $CDCl_3$.
The spectra were determined in solvent A or B with Me_4Si as an internal standard at 100 MHz.

Compound C (III), mp 258—260°, $[\alpha]_D^{18}$ +30.8° (pyridine), $C_{30}H_{48}O_4$, *m/e* 472 (M^+) gave a positive Liebermann–Burchard test and showed carboxylic acid absorption (1690 cm^{-1}) band

3) Comparison of NMR spectral data. Chemical shift (δ) and coupling constant (Hz) of C_{19}–H are shown in parentheses. lupeol (2.38, J=10; 10; 4), betuline (2.36, J=10; 10; 4), diacetyl betulin (2.40, m), acetyldihydrobetulinic acid (2.35, m), methyl betulinate (2.98, J=10; 10; 4), acetylbetulinic acid (3.02, J=10; 10; 4), methyl betulinate acetate (2.98, J=10; 10; 4), diacetylalphitolic acid (2.98, J=10; 10; 4), methyl alphitolate (2.97, m), methyl alphitolate diacetate (2.99, J=10; 10; 4).
4) H.T. Cheung and D.G. Williamson, *Tetrahedron*, **25**, 119 (1969).
5) H. Budzikiewicz, J.M. Wilson, and C. Djerassi, *J. Am. Chem. Soc.*, **85**, 3688 (1963).
6) H.T. Cheung and T.C. Yan, *Aust. J. Chem.*, **25**, 2003 (1972).

on the IR spectrum. On the NMR spectrum an olefinic proton signal (J=4 Hz) and two methine proton signals which are assigned to the protons at C_3 (J=10 Hz) and C_2 (J=10; 10; 4 Hz) appeared at δ 5.38, 3.08 and 3.74, respectively. On methylation with diazomethane III afforded methyl ester of III, IIIa, mp 232—233°, $C_{31}H_{50}O_4$, *m/e* 486 (M^+) which indicated ester absorption (1730 cm^{-1}) band on the IR spectrum and a methyl proton signal (δ 3.59) of methoxycarbonyl on the NMR spectrum.

On acetylation Ac_2O and pyridine III gave IIIb, mp 236—238°, $C_{34}H_{52}O_6$, *m/e* 556 (M^+). On the NMR spectrum two proton signals due to the methine attached to each acetoxyl group appeared at δ 4.72 ($J_{3a,2a}$=10 Hz) and 5.10 ($J_{2a,1a}=J_{2a,3a}$=10 Hz; $J_{2a,1e}$=4 Hz), and a proton signal assigned to the methine at C_{18} position which discriminates oleanane type from ursane type triterpenoid acids appeared at δ 2.83 (J=14; 4 Hz). The methyl ester diacetate, IIIc mp 165—168°, $C_{35}H_{54}O_6$, *m/e* 570 (M^+) showed the proton signals due to a methoxycarbonyl (δ 3.61) and two acetoxy methyl (δ 1.99 and 2.06) proton signals on the NMR spectrum. Based on the above physical and spectral data it is concluded that III is maslinic acid.[7] The examination of mass spectral fragment ion peaks of III and its derivatives supported above conclusion. By direct comparison with an authentic sample (NMR and mixed melting point) the structure of III was identified to be maslinic acid.

Compound D (IV), mp 278—282°, $[\alpha]_D^{20}$ +0.95° (pyridine), $C_{39}H_{54}O_6$, *m/e* 618 (M^+), gave positive Liebermann–Burchard and benzidine tests. IV showed ester carbonyl (1695 cm^{-1}) and carboxylic acid (1730 cm^{-1}) absorption bands on the IR spectrum. On the NMR spectrum IV exhibited the signals due to the AB type signal of aromatic protons at δ 6.88 (J=8 Hz) and 7.38 (J=8 Hz) and *trans* olefinic protons conjugated with aromatic ring (δ 6.29 and 7.63; J=16 Hz) in which a proton at β-position to carbonyl group appeared in the lower-field, and two methine proton signals of C_2 and C_3–H appeared at δ 3.98 and 4.70. On alkaline hydrolysis IV afforded III and *p*-coumaric acid which were identified with authentic samples. On the basis of these findings IV is assumed to be 3-O-*p*-coumaroyl ester of III. On treatment with diazomethane IV gave methyl ester of IV, IVa, mp 205—206.° On the NMR spectrum a methoxycarbonyl and a methoxyl proton signals appeared at δ 3.62 and 3.84. By direct comparison with an authentic sample (mixed melting point and TLC) the structure of IVa was identified to be methyl 3-O-*trans*-4′-methoxycinnamoyl maslinate.[8] Thus, the structure of IV was established to be 3-O-*trans*-*p*-coumaroyl maslinic acid.

Compound E (V), mp 190—195° $[\alpha]_D^{20}$ +9.1° (pyridine), $C_{39}H_{54}O_6$, *m/e* 618 (M^+) gave same positive Liebermann–Burchard and benzidine tests to those of IV. V showed ester carbonyl (1690 cm^{-1}) and carboxylic acid (1715 cm^{-1}) absorption bands on the IR spectrum. On the NMR spectrum V exhibited *cis* conjugated olefinic proton signals (δ 5.82 and 6.82, J=12 Hz) instead of those of *trans* in IV and two pair of proton at C_2, and C_6,, and C_3, and C_5, in aromatic ring appeared at δ 7.66 and 6.83, respectively. On alkaline hydrolysis V afforded *p*-coumaric acid and III which were identified by direct comparison. On the basis of the NMR spectral analysis the position of *p*-coumaroyl moiety in V was determined at C_3. On heating at 100° for 24 hr, V was converted to IV which was identified by direct comparison (NMR). Above results led to the conclusion that *cis* *p*-coumaroyl moiety is located at C_3 position in III. Thus, the structure of V was established to be 3-O-*cis*-*p*-coumaroylmaslinic acid. The isolation of 2α-hydroxy-3β-O-*trans*-*p*-coumaroyl urs-12-en-28-oic acid (*Jacaranda caucan*),[9] 3β-O-*trans*-*p*-coumaroyl maslinic acid (*Lyonia ovalifolia* var. *elliptica*),[8] and 3β-O-*trans*-*p*-coumaroyl ursolic acid (*Tripetaleia paniculata*)[10] had been reported. The occurrence of 3β-O-*cis*-*p*-coumaroyl maslinic and alphitolic acids together with those of *trans* isomers presents biological interests.

7) H.T. Cheung and M.C. Feng, *J. Chem. Soc.* (*C*), **1968**, 1047.
8) M. Yasue, J. Sakakibara, and T. Kaiya, *Yakugaku Zasshi*, **91**, 1200 (1971).
9) M. Ogura, G.H. Cardell, and N.R. Farnsworth, *Phytochemistry*, **16**, 286 (1977).
10) M. Yasue, J. Sakakibara, and H. Ina, *Yakugaku Zasshi*, **93**, 687 (1973).

Experimental

Melting points were determined on a Yanagimoto melting point apparatus and uncorrected. IR spectra were obtained with a KOKEN DS-301 and NMR spectra were taken with a JEOL C-100H spectrometer and chemical shifts are given in δ scale with Me_4Si as an internal standard and coupling constants (J) in Hz. Abbreviation used, s, singlet; d, doublet; t, triplet; q, quartet; sex, sextet, m, multiplet; br, broad. Unless otherwise indicated solvent used was $CDCl_3$. Optical rotation was measured on JASCO DIP-SL automatic polarimeter. Mass spectra were recorded on a JMS-01SG mass spectrometer with an accelerating potential of 6.3 kV, an ionizing potential of 75 eV and a source temperature of 190°. Thin-layer chromatography (TLC) was performed on Kieselgel G (Merck) using solvent systems, $CHCl_3$–EtOAc (8: 1) (TLC 1), C_6H_6–acetone (10: 1) (TLC 2), C_6H_6–acetone (3: 1) (TLC 3), C_6H_6–acetone (5: 1) (TLC 4) and the spot was monitored with UV lamp (Toshiba PAN UV Lamp PUV-B). As coloring reagents 10% H_2SO_4 and benzidine solutions were used. Column chromatography was performed with Kieselgel 60 (75—230 mesh, Mearck). The following gas chromatographic analysis employing Shimadzu GC-4BM was carried out. Column, 1.5% SE 52 on chromosorb W (60—80 mesh) 2 m×3 mm ϕ, glass column; Column temperature, 255—275° (programmed temperature 1°/min); Detector temperature, 280°, N_2 gas (1.9 kg/cm²), H_2 gas 0.6 kg/cm², Air 1.0 kg/cm².

Isolation of Triterpenoid Acids——The dried fruits (20 kg) of this plant were extracted with boiling EtOH for 1 hr, four times. The EtOH extract (11.2 kg) suspended in H_2O was extracted with BuOH. The BuOH extract (240 g) was chromatographed over silica gel using C_6H_6 and C_6H_6–acetone (7: 3) as solvent to give resinous substance (112 g). The resinous substance was partitioned between 2% Na_2CO_3 and EtOAc and the EtOAc layer was evaporated to dryness. The residue (64 g) was chromatographed over silica gel using $CHCl_3$–EtOAc as solvent to give fraction A (25.8 g) [eluation with $CHCl_3$–EtOAc (95: 5)], fraction B (9.6 g) [eluation with $CHCl_3$–EtOAc (85: 5)] and fraction C (19.2 g) [eluation with $CHCl_3$–EtOAc (1: 1)]. Fraction A (25.8 g) was subjected to the repeated chromatographies using $CHCl_3$–EtOAc as solvent to yield fraction A-1 (4.2 g) [eluation with $CHCl_3$–EtOAc (15: 1)] and fraction A-2 (8.9 g) [eluation with $CHCl_3$–EtOAc (10: 1)]. From fraction A-2 betulinic acid and a mixture of oleanolic and ursolic acids were obtained. Fraction B (9.6 g) was fractionated to fraction B-1 (2.2 g) [eluation with $CHCl_3$–EtOAc (10: 1)] and fraction B-2 (3.1 g) [eluation with $CHCl_3$–EtOAc (5: 1)]. Fraction C (19.2 g) was chromatographed over silica gel using C_6H_6–acetone (3: 1) as solvent to afford III (1.22 g) and alphitolic acid (1.15 g).

Isolation of Betulonic Acid (I) and Oleanonic Acid (II)——Fraction A-1 was chromatographed over silica gel using hexane–acetone (8: 1) to give a mixture of I and II. The mixture dissolved in MeOH was methylated with CH_2N_2 at room temperature for 30 min and the product was chromatographed over silica gel using hexane–C_6H_6–acetone (20: 5: 1) as solvent to give Ia (270 mg) and IIa (340 mg).

Methyl Betulonate (Ia)——mp 168—169° (recrystallized from MeOH), colorless needles, $[\alpha]_D^{23}$ +10.5° ($CHCl_3$, c=1.0), MS m/e: 468.358 (M^+, Calcd. for $C_{31}H_{48}O_3$ 468.360), 453, 409, 262, 249, 218, 205, 203, 189, 133. IR ν_{max}^{KBr} cm^{-1}: 1730, 1705, 1640, 880. NMR δ: 0.92, 0.96, 0.98, 1.02, 1.07, 1.70 (each s, CH_3), 2.24, 2.42, (each 1H, m, C_2–H), 3.00 (1H, sex, J=10; 10; 4, C_{19}–H), 3.67 (3H, s, $COOCH_3$), 4.62, 4.75 (each 1H, d, J=2, C_{29}–H).

Synthesis of Methyl Betulonate——To a solution of betulinic acid (50 mg) dissolved in acetone (20 ml) Jones reagent (1 ml) was added and the reaction mixture was stirred for 20 min at room temperature. The product extracted with EtOAc was washed with H_2O and evaporated to dryness. The residue dissolved in $CHCl_3$ was methylated with CH_2N_2 at room temperature for 30 min. The methylate was recrystallized from MeOH to give colorless needles Ia (25 mg).

Methyl Oleanonate (IIa)——mp 182—184° (recrystallized from MeOH), colorless needles, $[\alpha]_D^{23}$ +30.0° ($CHCl_3$, c=1.05), MS m/e: 468.362 (Calcd. for $C_{31}H_{48}O_3$ 468.360), 453, 409, 408, 262, 249, 205, 203, 189, 133. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1700. NMR δ: 0.77, 0.89, 0.92 (each 3H, s, CH_3), 1.04 (6H, s, CH_3×2), 1.08, 1.13 (each 3H, s, CH_3), 2.38, 2.52 (each 1H, m, C_2–H), 2.87 (1H, dd, J=14: 4, C_{18}–H), 3.61 (3H, s, $COOCH_3$), 5.30 (1H, t, J=4, C_{12}–H).

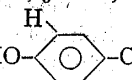
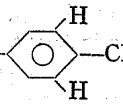
Synthesis of Methyl Oleanonate——To a solution of oleanolic acid (50 mg) dissolved in acetone (20 ml) Jones reagent (1 ml) was added and the same procedure as that for Ia was carried out to give colorless needles IIa (30 mg) (recrystallized from MeOH).

Maslinic Acid (III)——mp 258—260° (recrystallized from EtOH), colorless amorphous powders, $[\alpha]_D^{18}$ +30.8° (pyridine, c=0.65), MS m/e: 472.351 (Calcd. for $C_{30}H_{48}O_4$ 472.355), 454, 426, 408, 248, 235, 233, 223, 219, 203, 189, 133. IR ν_{max}^{KBr} cm^{-1}: 3440, 1690. NMR [$CDCl_3$–pyridine-d_5 (10: 1)] δ: 0.85, 0.89, 0.93, 1.10, 1.19 (each 3H, s, CH_3), 0.98 (6H, s, CH_3×2), 3.00 (1H, dd, J=14; 4, C_{18}–H), 3.08 (1H, d, J=10, C_3–H), 3.74 (1H, sex, J=10; 10; 4, C_2–H), 5.38 (1H, t, J=4, C_{12}–H).

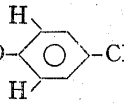
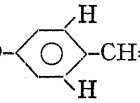
Methyl Maslinate (IIIa)——III (30 mg) dissolved in $CHCl_3$–MeOH (1: 1, 1 ml) was methylated with CH_2N_2 at room temperature for 30 min. The product was recrystallized from C_6H_6 to give colorless needles IIIa (27 mg). mp 232—233°, MS m/e: 486.367 (Calcd. for $C_{31}H_{50}O_4$ 486.370), 468, 426, 409, 262, 249, 233, 223, 203, 189, 133. IR ν_{max}^{KBr} cm^{-1}: 3360, 1730. NMR δ: 0.71, 0.81, 0.89, 0.92, 0.97, 1.02, 1.12 (each 3H, s, CH_3), 2.85 (1H, dd, J=14; 4, C_{18}–H), 2.97 (1H, d, J=10, C_3–H), 3.59 (3H, s, $COOCH_3$), 3.66 (1H, m, C_2–H), 5.28 (1H, t, J=4, C_{12}–H).

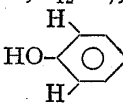
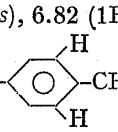
Diacetylmaslinic Acid (IIIb)——III (60 mg) was acetylated with Ac_2O (10 ml) and pyridine (10 ml) at room temperature for 24 hr. The product was recrystallized from hexane to give colorless needles IIIb (50 mg). mp 236—238°, MS *m/e*: 556.380 (Calcd. for $C_{34}H_{52}O_6$ 556.376), 541, 510, 307, 248, 235, 233, 219, 203, 189, 173, 133. NMR δ: 0.75, 0.92, 1.07, 1.13 (each 3H, s, CH_3), 0.91 (9H, s, $CH_3\times3$), 2.00, 2.07 (each 3H, s, CH_3COO), 2.83 (1H, dd, J=14; 4, C_{18}–H), 4.72 (1H, d, J=10, C_3–H), 5.10 (1H, sex, J=10; 10; 4, C_2–H), 5.26 (1H, t, J=4, C_{12}–H).

Methyl Maslinate Diacetate (IIIc)——IIIb (25 mg) dissolved in $CHCl_3$ (1 ml) was methylated with CH_2N_2 at room temperature for 30 min. The product was recrystallized from hexane to give colorless amorphous powders IIIc (18 mg). mp 165—168°. MS *m/e*: 570.390 (Calcd. for $C_{35}H_{54}O_6$ 570.392), 555, 510, 450, 435, 262, 249, 233, 215, 203, 189, 173, 133. IR ν_{max}^{KBr} cm^{-1}: 1745, 1725. NMR δ: 0.72, 1.05, 1.13 (each 3H, s, CH_3), 0.91 (12H, s, $CH_3\times4$), 1.99, 2.06 (each 3H, s, $CH_3COO\times2$), 2.87 (1H, dd, J=14; 4, C_{18}–H), 3.61 (3H, s, $COOCH_3$), 4.73 (1H, d, J=10, C_3–H), 5.11 (1H, sex, J=10; 10; 4, C_2–H), 5.28 (1H, t, J=4, C_{12}–H).

3-O-*trans*-*p*-Coumaroylmaslinic Acid (IV)——Fraction B-2 was chromatographed over silicagel using C_6H_6–acetone (5: 1) to afford IV (37 mg) and V (63 mg). mp 278—282° (recrystallized from C_6H_6–acetone), colorless needles $[\alpha]_D^{20}$ +0.95° (pyridine, c=1.05), MS *m/e*: 618.394 (Calcd. for $C_{39}H_{54}O_6$ 618.392), 454, 436, 408, 371, 248, 235, 233, 223, 219, 203, 189, 165, 163, 147, 133. IR ν_{max}^{KBr} cm^{-1}: 3400, 1730, 1695, 1630, 1605, 1590. NMR [$CDCl_3$–pyridine-d_5 (10: 1)] δ: 0.84, 1.03, 1.20 (each 3H, s, CH_3), 0.96 (12H, s, $CH_3\times4$), 2.97 (1H, dd, J=14; 4, C_{18}–H), 3.98 (1H, sex, J=10; 10; 4, C_2–H), 4.70 (1H, d, J=10, C_3–H), 5.36 (1H, t, J=4, C_{12}–H), 6.29 (1H, d, J=16, Ar–CH=CH– *trans*), 6.88 (2H, d, J=8, HO-  -CH=CH–), 7.38 (2H, d, J=8, HO-  —CH=CH), 7.63 (1H, d, J=16, Ar–CH=CH– *trans*).

Hydrolysis of IV——IV (50 mg) was saponified with 2% KOH–EtOH (10 ml) for 1 hr. The reaction mixture was partitioned between EtOAc and H_2O. The EtOAc layer was evaporated to dryness and the residue was recrystallized from $CHCl_3$–MeOH to give III which was identified by direct comparison (mixed melting point and TLC). The H_2O layer was neutralized with dil. HCl and extracted with EtOAc. After the evaporation of solvent the residue was recrystallized from H_2O to give colorless needles of *p*-coumaric acid which was identified by direct comparison (mixed melting point and TLC).

Methyl 3-O-*trans*-4′-methoxycinnamoylmaslinic Acid (IVa)——IV (20 mg) dissolved in $CHCl_3$–MeOH (1: 1, 1 ml) was methylated with CH_2N_2 at room temperature for 30 min. The product was recrystallized from EtOH to give colorless needles IVa (11 mg). mp 205—206°, IR ν_{max}^{KBr} cm^{-1}: 3400, 1730, 1690, 1635, 1605, 1575. NMR δ: 0.75, 0.92, 1.03, 1.16 (each 3H, s, CH_3), 0.95 (9H, s, $CH_3\times3$), 2.89 (1H, dd, J=14; 4, C_{18}–H), 3.62, 3.84 (each 3H, s, $COOCH_3$ and CH_3O), 3.90 (1H, m, C_2–H), 4.63 (1H, d, J=10, C_3–H), 5.30 (1H, t, J=4, C_{12}–H), 6.37 (1H, d, J=16, Ar–CH=C<u>H</u>–, *trans*), 6.89 (2H, d, J=8, HO-  -CH=CH), 7.48 (2H, d, J=8, HO-  -CH=CH), 7.68 (1H, d, J=16, Ar–CH=CH–, *trans*).

3-O-*cis*-*p*-Coumaroylmaslinic Acid (V)——mp 190—195° (recrystallized from hexane–acetone), colorless amorphous powders, $[\alpha]_D^{20}$ +9.1° (pyridine, c=1.1), MS *m/e*: 618.392 (Calcd. for $C_{39}H_{54}O_6$ 618.392), 454, 436, 408, 371, 248, 235, 233, 219, 205, 203, 189, 165, 163, 147, 133. IR ν_{max}^{KBr} cm^{-1}: 3400, 1715, 1690, 1625, 1600, 1585. NMR [$CDCl_3$–pyridin-d_5 (10: 1)] δ: 0.84, 1.17 (each 3H, s, CH_3), 0.93 (6H, s, $CH_3\times2$), 0.98 (9H, s, $CH_3\times3$), 2.95 (1H, dd, J=14; 4, C_{18}–H), 3.84 (1H, sex, J=10; 10; 4, C_2–H), 4.61 (1H, d, J=10, C_3–H), 5.32 (1H, t, J=4, C_{12}–H), 5.82 (1H, d, J=12, Ar–CH=C<u>H</u>–, *cis*), 6.82 (1H, d, J=12, Ar–C<u>H</u>=CH–, *cis*), 6.83 (2H, d, J=8, HO-  -CH=CH–), 7.66 (2H, d, J=8, HO-  -CH=CH–).

Hydrolysis of V——V (50 mg) was saponified as same procedure as that of IV to give III and *p*-coumaric acid which were identified by direct comparison (mixed melting point and TLC).

Conversion of V to IV——V (20 mg) dissolved in dioxane (10 ml) was refluxed for 24 hr and the product was identified to be IV by direct comparison (NMR and TLC).

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