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Studies on Constituents of Medicinal Plants. XIV.[1] Constituents of *Schizandra nigra* Max. (1)

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A new triterpene acid, schizandronic acid was isolated from the wooden part of *Schizandra nigra* Max. and the structure of the acid was elucidated to be *cis*-3-oxo-cycloart-24-ene-26-oic acid (I) by chemical and spectral evidences.

There have been a few reports regarding the constituents of *Schizandra nigra*. From the wooden part, methyl-*n*-undecylketone, bornyl acetate, methyl-nonylketone, β-pinene, and palmitic acid have been isolated.[3] This paper deals with the structural elucidation of a new triterpene acid of the cycloartene type. The methanolic extract of the wooden part of *Schizandra nigra* (Matsubusa in Japanese) afforded colorless triangular crystals $C_{30}H_{46}O_3$ (I) of mp 167—168.5°, $[\alpha]_D^{27}=+15°$ (c=2.00, $CHCl_3$), to be named schizandronic acid hereafter. Substance I gave methyl ester $C_{31}H_{48}O_3$ (II) of mp 105° on treatment with diazomethane and dihydroschizandronic acid $C_{30}H_{48}O_3$ (III) of mp 148—149° on hydrogenation over Pd-C catalyst. Treatment of III with diazomethane gave methyl ester $C_{31}H_{50}O_3$ (IV) of mp 90—91°. Acid I shows the ultraviolet (UV) maximum at 222.5 nm (log ε 3.86), assignable to an α,β-unsaturated C=O group. The infrared (IR) spectra of these compounds indicate that I has a six-membered ring C=O, and α,β-unsaturated COOH, and a conjugated double bond. Ester II shows the nuclear magnetic resonance (NMR) signals (δ-value) at 0.58 (d, 1H, J=4 Hz) and at 0.80 (d, 1H, J=4 Hz) and the IR band at 3050 cm^{-1}, suggesting the presence of a cyclopropane ring[4] in the molecule of II (Table I). The mass (MS) spectrum of II (Chart 1 and Table II) shows peaks at m/e 313.248 (D, $C_{22}H_{33}O$) and m/e 155.109 ($C_9H_{15}O_2$), suggesting that these fragment-ions were produced by the fission of a side chain and also II has a six-membered ring C=O, and an α,β-unsaturated $COOCH_3$ on the side chain. Especially, a peak at m/e 330.257 (A, $C_{22}H_{34}O_2$), characteristic of the cycloartenol-type triterpenoids containing a 9,19-cyclopropane ring,[5] and that at m/e 175.149 (E, A—$C_9H_{15}O_2$) indicate that II has a C=O group on the ring A, and an α,β-unsaturated $COOCH_3$ group on the side chain (Chart 2).

The optical rotatory dispersion curve (ORD) of I shows the negative Cotton effect and is nearly similar to that of cycloartenone,[6] suggesting that I is related to a 3-oxocycloartene-type triterpenoid. The $NaBH_4$ reduction of I gave schizandrolic acid $C_{30}H_{48}O_3$ (V) of mp 164—165° and isoschizandrolic acid $C_{30}H_{48}O_3$ (V′) of mp 162—163°. The reaction of V with diazomethane produced methyl ester $C_{31}H_{50}O_3$ (VI) of mp 130°, which yielded an acetylated methyl ester $C_{33}H_{52}O_4$ (VII) of mp 141° on treatment with acetic anhydride. The fact that VI exhibits the IR band of OH group and the NMR signal at 3.28 (q, 1H, $W_{h/2}$=16.5 Hz) and that VII reveals the NMR signal at 4.58 (q, 1H, $W_{h/2}$=17 Hz) indicates that the newly formed OH group is in β-configuration. The isomeric acid (V′) shows the NMR signal at

1) Part XIII: K. Takahashi, S. Kawaguchi, K. Nishimura, K. Kubota, Y. Tanabe, and M. Takani, *Chem. Pharm. Bull.* (Tokyo), **22**, 650 (1974).
2) Location: *Takaramachi, Kanazawa, 920, Japan.*
3) T. Sengoku, *Yakugaku Zasshi*, **53**, 947 (1933); *idem, ibid.*, **57**, 920 (1937).
4) A.P.H. Cole, *J. Chem. Soc.*, **1954**, 3810.
5) R.T. Alpin and G.M. Hornby, *J. Chem. Soc.*, (*B*), **1966**, 1078.
6) C. Djerassi, O. Halpern, V. Halpern, and B. Riniker, *J. Am. Chem. Soc.*, **80**, 4001 (1958).

TABLE I. The NMR Data (δ-Value, J in Hz, 100 Mc)

	H H	C–CH_3						–CHOH or –CHOAc	$COOCH_3$	CH_2OH	=CH–	OH
		C_{30}	C_{31}	C_{18}	C_{32}	C_{21}	C_{27}					
II	0.58, d, 1H, J=4 0.80, d, 1H, J=4	1.05 s 3H	1.10 s 3H	0.91 s 3H	1.00 s 3H	0.91 d 3H J=5	1.89 d 3H J=1.5		3.74 s 3H		5.91 t 1H	
IV	0.59, d, 1H, J=5 0.81, d, 1H, J=5	1.07 s 3H	1.12 s 3H	0.93 s 3H	1.03 s 3H	0.87 d 3H J=6	1.16 d 3H J=6		3.68 s 3H			
VI	0.33, d, 1H, J=4 0.56, d, 1H, J=4	0.96 s 3H	0.89 s 3H	0.81 s 3H	0.96 s 3H	0.89 d 3H J=5	1.88 d 3H J=1.5	3.28 q 1H J=11;5.5 $W_{h/2}$=16.5	3.74 s 3H		5.92 t 1H J=8	1.50 s
VII	0.34, d, 1H, J=4 0.58, d, 1H, J=4	0.90 s 3H	0.90 s 3H	0.85 s 3H	0.96 s 3H	0.90 d 3H J=7	1.89 d 3H J=1.5	4.58 q 1H J=11;5.5 $W_{h/2}$=17	3.75 s 3H		5.91 t 1H J=7	2.06 s 3H OAc
VIII	0.32, d, 1H, J=4 0.56, d, 1H, J=4	0.96 s	0.89 s	0.80 s	0.96 s	*a*) 0.83	*a*)	3.28 q 1H J=10;5 $W_{h/2}$=16		3.46 m 2H		1.59 s
X	0.33, d, 1H, J=5 0.55, d, 1H, J=5	0.96 s 3H	0.88 s 3H	0.80 s 3H	0.96 s 3H	0.88 d 3H J=6	1.79 d 3H J=1.5	3.30 q 1H J=10;5 $W_{h/2}$=17		4.14 s 2H	5.30 t 1H J=7	1.35 s
V′	0.34, d, 1H, J=4 0.52, d, 1H, J=4	0.91 s	0.96 s	0.89 s	0.94 s	*a*) 0.86	1.92 s-like 3H	3.48 m 1H $W_{h/2}$=6			6.08 t 1H J=7	
VIII′	0.35, d, 1H, J=5 0.53, d, 1H, J=5	0.92 s	0.96 s	0.89 s	0.96 s	0.90 d J=7	*a*)	3.47 m*b*) $W_{h/2}$=9.5		3.47 m*b*)		1.48 s
X′	0.35, d, 1H, J=4 0.53, d, 1H, J=4	0.91 s 3H	0.96 s 3H	0.89 s 3H	0.96 s 3H	0.90 d 3H J=5	1.80 d 3H J=1	3.47 m 1H $W_{h/2}$=6.5		4.13 s 2H	5.29 t 1H J=7	1.44 s

a) The signals are overlapped with other methyl signals.
b) These two signals are overlapped with each other and equivalent to three protons in total.
Abbreviation: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

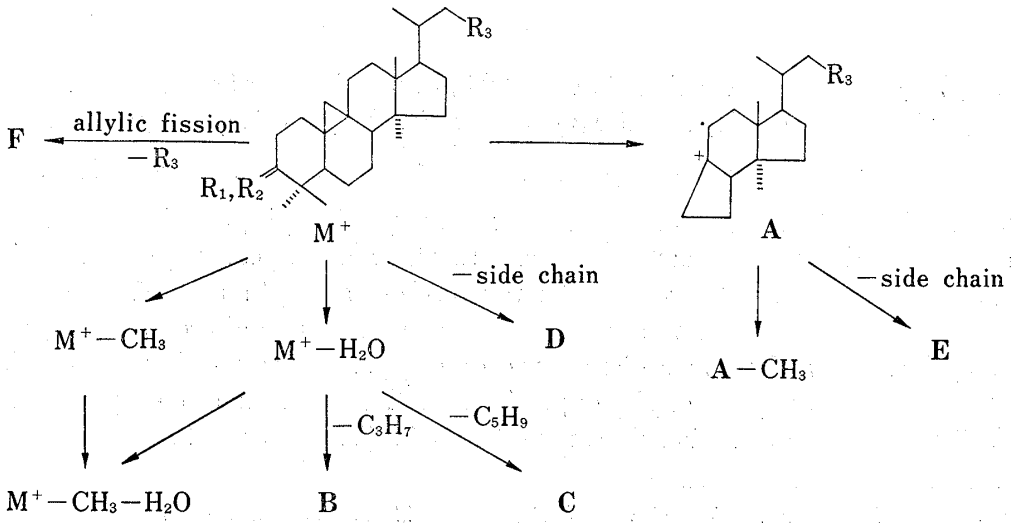
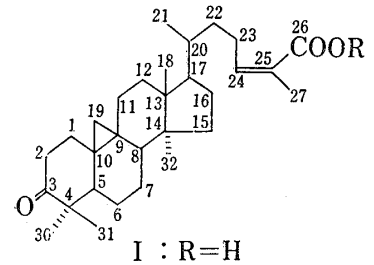


Chart 1

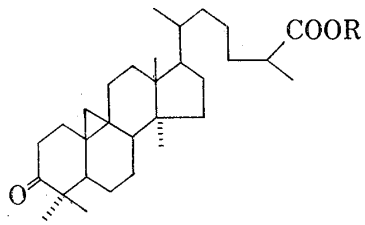
Table II. The MS Data

	M^+	M^+-15	M^+-18	$M^+-15-18$	A	A−15	E	B	C	D	D−18	F	Side-chain
II	468.350 (100)	453.337 (13)	—	—	330.257 (20)	315.233 (5)	175.149 (10)	—	—	313.248 (33)	—	355.289 (22)	155.109 (3)
IV	470 (100)	455 (21)	—	—	332 (32)	317 (5)	175 (41)	—	—	313 (42)	—	—	157 (2)
VI[a]	470 (75)	455 (40)	452 (97)	437 (89)	330 (97)	315 (35)	175 (31)	409 (26)	383 (36)	315 (35)	297 (17)	357 (13)	155 (10)
VIII	444 (60)	429 (43)	426 (95)	411 (73)	304 (100)	289 (22)	175 (39)	383 (30)	357 (37)	315 (37)	297 (28)	—	129 (5)
[VIII']	[100]	[81]	[59]	[38]	[63]	[14]	[56]	[9]	[8]	[52]	[38]		[7]
X	442 (90)	427 (28)	424 (100)	409 (61)	302 (56)	287 (13)	175 (31)	381 (24)	355 (19)	315 (15)	297 (15)	357 (5)	127 (4)
[X']	[64]	[40]	[100]	[80]	[40]	[12]	[60]	[61]	[24]	[20]	[22]	[12]	[6]

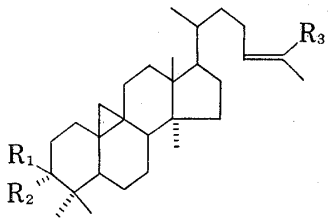
The figures in square brackets are relative intensities of fragment-ions of VIII' and X', respectively.
a) base peak: *m/e* 95



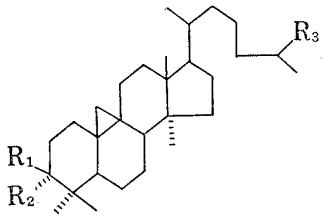
I : R=H
II : R=CH_3



III : R=H
IV : R=CH_3



V : R_1=OH, R_2=H, R_3=COOH
V' : R_1=H, R_2=OH, R_3=COOH
VI : R_1=OH, R_2=H, R_3=$COOCH_3$
VII : R_1=OAc, R_2=H, R_3=$COOCH_3$
X : R_1=OH, R_2=H, R_3=CH_2OH
X' : R_1=H, R_2=OH, R_3=CH_2OH



VIII : R_1=OH, R_2=H, R_3=CH_2OH
VIII' : R_1=H, R_2=OH, R_3=CH_2OH
IX : R_1=OH, R_2=H, R_3=COOH
XI : R_1=OH, R_2=H, R_3=CH_3
XII : R_1=OAc, R_2=H, R_3=CH_3

Chart 2

3.48 (m, 1H, $W_{h/2}$=6 Hz), indicating that the OH group is in α-configuration. Ester II shows the NMR signals at 1.89 (d, 3H, J=1.5 Hz) and 5.91 (t, 1H, J=8 Hz), assignable to the methyl and the β-olefinic protons of a $-CH_2-HC=C\langle^{COOCH_3}_{CH_3}$ system. It is well known[7] that in such a system the β-olefinic proton *cis* to the methoxycarbonyl group is, without exception, significantly more deshielded than that *trans* to the methoxycarbonyl group. The NMR signals of II (5.91) and VI (5.92) are similar to those[7] of methyl masticadienonate (5.91) and methyl angelate (5.98), but do not resemble those of methyl mangiferolate (6.63) and methyl tiglate (6.73), indicating that the β-olefinic proton of the side chain of both II and VI is *trans* with respect to the methoxycarbonyl group. The $LiAlH_4$ reduction of methyl dihydroschizandronate (IV) produced dihydrodiol derivative $C_{30}H_{52}O_2$ (VIII) of mp 152—154° and $C_{30}H_{52}O_2$

7) S. Corsano and E. Mincione, *Tetrahedron Letters*, **1965**, 2377. The sample of the diol derivative was furnished through the courtesy of Prof. E. Mincione.

(VIII') of mp 149°. The former (VIII) was proved by the NMR spectra to have a β-OH group and the latter (VIII'), an α-OH group. The physical properties of VIII closely resemble those of dihydrodiol derivative of mangiferonic acid.[7] The *Rf* value of VIII was identical with that of one of the catalytic hydrogenation products of the diol derivative[7] of mangiferonic acid. Catalytic reduction of schizandrolic acid (V) gave dihydroschizandrolic acid $C_{30}H_{50}O_3$ (IX) of mp 171—173°. On the other hand, I was reduced with $LiAlH_4$ to give diol derivative $C_{30}H_{50}O_2$ (X) of mp 173—174° and its isomer $C_{30}H_{50}O_2$ (X') of mp 147°. The NMR spectra (Table I) of these diols reveal that X has a β-OH group and X', an α-OH group. Compound X was hydrogenated over Pd-C to give $C_{30}H_{52}O$ (XI) of mp 100° and dihydrodiol (VIII). Treatment of XI with acetic anhydride gave acetate $C_{32}H_{54}O_2$ (XII) of mp 133—135°, $[\alpha]_D^{17}=+52°$ ($c=0.97$, $CHCl_3$), which was proved to be identical with cycloartanol acetate[8] by the mixed fusion and comparison of the IR spectrum. The NMR signals of II and VI closely resemble those[9] of methyl mangiferonate and methyl mangiferolate, respectively, except for signals of the β-olefinic protons (Table I). The chemical and spectral evidence indicates that shizandronic acid (I) is *cis*-3-oxo-cycloart-24-ene-26-oic acid, which has the β-olefinic proton *trans* to the carboxy group on the side chain. Consequently, compounds I—XII could be formulated as shown in Chart 2. Their NMR spectra could be interpreted as shown in Table I, taking the NMR of 25-hydroxy-cycloartanol[10] into consideration, and their MS as shown in Chart 1 and Table II.

Experimental

The following instruments were used for the physical data. Melting point: Yanagimoto Micro-Melting apparatus (a hot-stage type); UV spectra: Hitachi EPS-2U recording spectrometer in *n*-hexane; IR spectra: Nippon Bunko IR-G spectrometer in KBr; NMR spectra: JNM-PS-100 high resolution instrument at 100 MHz in $CDCl_3$ with $(CH_3)_4Si$ as an internal reference; Mass spectra: JMS-0ISG mass spectrometer; ORD: Nippon Bunko Optical Rotatory Dispersion Curve Recorder ORD/UV-5; Optical rotation: Nippon Bunko automatic polarimeter DIP-SL.

Schizandronic Acid (I)——Dried, cut wooden part (5 kg) of *Schizandra nigra* was extracted with methanol four times and the extract (60 liters) was concentrated to 500 ml *in vacuo* and filtered. The filtrate was chromatographed on a column of silica gel (750 g), and the column was eluted with *n*-hexane (10 liters), benzene (10 liters), $CHCl_3$ (10 liters), AcOEt (8 liters), acetone (4 liters) and methanol (2 liters), successively. The fraction eluted with *n*-hexane and benzene were chromatographed over silica gel with $CHCl_3$–MeOH (100: 1) and the fraction of *Rf* 0.38 gave triangular crystals (I) of mp 167—168.5° on recrystallization from methanol. Yield: 5.8 g. IR ν_{max} cm^{-1}: 3050 (cyclopropane), 1710 (six-membered ring C=O), 1675 (α,β-unsatd. C=O), 1630 (conjugated double bond). ORD[6]: ($c=0.205$, MeOH, 21°) $[\phi]_{350}=-66°$, $[\phi]_{330}=-664°$, $[\phi]_{314}=-1262°$ (trough), $[\phi]_{272}=+1993°$ (peak), $[A]=-32.55$. *Anal.* Calcd. for $C_{30}H_{46}O_3$: C, 79.24; H, 10.20. Found: C, 79.51; H, 10.15.

Methyl Schizandronate (II)——Acid I (100 mg) in ether was methylated with diazomethane to give colorless triangular crystals (II) of mp 105° (from MeOH). $[\alpha]_D^{32}=+15.5°$ ($c=1.01$, $CHCl_3$). IR ν_{max} cm^{-1}: 3050 (cyclopropane), 1715 (ester), 1710 (ring C–O), 1640 (conjugated double bond). *Anal.* Calcd. for $C_{31}H_{48}O_3$: C, 79.43; H, 10.32. Found: C, 79.09; H, 10.19.

Catalytic Hydrogenation of I——Acid I (0.5 g) in ethyl acetate (120 ml) was hydrogenated over Pd-C (0.5 g) for 1 hr and then the mixture was filtered and evaporated to give colorless triangular crystals (III) of mp 148—149° (from MeOH). IR ν_{max} cm^{-1}: 3050 (cyclopropane), 1710 (ring C=O and COOH). *Anal.* Calcd. for $C_{30}H_{48}O_3$: C, 78.89; H, 10.59. Found: C, 78.52; H, 10.53.

Methylation of III——Compound III (200 mg) in ether was methylated with diazomethane to give colorless triangular crystals (IV) of mp 90—91° (from MeOH). $[\alpha]_D^{32}=+21.4°$ ($c=1.01$, $CHCl_3$). IR ν_{max} cm^{-1}: 3040 (cyclopropane), 1735 (ester), 1710 (ring C=O). *Anal.* Calcd. for $C_{31}H_{50}O_3$: C, 79.10; H, 10.71. Found: C, 78.87; H, 10.53.

$NaBH_4$ Reduction of I——A solution of I (200 mg) in methanol (40 ml) was poured into a suspension of $NaBH_4$ (100 mg) in six drops of water and the mixture was allowed to stand overnight. After evaporating of the methanol, the residue was mixed with water, and the mixture was acidified with dil. HCl and

8) M. Shimizu and G. Ohta, *Chem. Pharm. Bull.* (Tokyo), **8**, 108 (1960). The sample was furnished through the courtesy of Dr. Ohta.
9) S. Corsano and E. Mincione, *Ann. Chim.* (Roma), **57**, 508 (1967).
10) T. Endo, S. Naito, and Y. Inaba, *Yukagaku*, **19**, 298, 302 (1970).

extracted with AcOEt. The AcOEt-soluble fraction was chromatographed over silicic acid with benzene–AcOEt (8: 1). The fraction of *Rf* 0.38 (silica gel impregnated with 0.1 N $(COOH)_2$, benzene–AcOEt=8: 1) gave colorless needles (V′) of mp 162—163° (from MeOH). Yield: 27 mg. $[\alpha]_D^{16}=+28.5°$ ($c=0.58$, $CHCl_3$). IR ν_{max} cm^{-1}: 3500 (OH), 3050 (cyclopropane), 1670 (α,β-unsatd. COOH), 1630 (conjugated double bond), 1055 (secondary OH). *Anal.* Calcd. for $C_{30}H_{48}O_3$: C, 78.89; H, 10.59; Found. C, 78.46; H, 10.50.

The fraction of *Rf* 0.32 gave colorless needles (V) of mp 164—165° (from MeOH). Yield: 120 mg. $[\alpha]_D^{15}=+35°$ ($c=1.00$, $CHCl_3$). IR ν_{max} cm^{-1}: 3400 (OH), 3050 (cyclopropane), 1690 (α,β-unsatd. COOH), 1640 (conjugated double bond), 1020 (secondary OH). *Anal.* Calcd. for $C_{30}H_{48}O_3$: C, 78.89; H, 10.59. Found: C, 78.65; H, 10.31.

Methylation of V——Schizandrolic acid (V) (250 mg) in methanol was methylated with diazomethane to give colorless needles (VI) of mp 130° (from MeOH). IR ν_{max} cm^{-1}: 3550 (OH), 3050 (cyclopropane), 1695 (α,β-unsatd. $COOCH_3$), 1645 (conjugated double bond), 1020 (secondary OH). *Anal.* Calcd. for $C_{31}H_{50}O_3$: C, 79.10; H, 10.71. Found: C, 79.32; H, 10.69.

Acetylation of VI——A mixture of VI (125 mg), pyridine (1 ml), and acetic anhydride (1.3 ml) was allowed to stand overnight and the mixture was poured into ice water to give colorless needles (VII) of mp 141° (from MeOH). IR ν_{max} cm^{-1}: 3050 (cyclopropane), 1725, 1250 (OAc), 1715 (α,β-unsatd. $COOCH_3$), 1635 (conjugated double bond). *Anal.* Calcd. for $C_{33}H_{52}O_4$: C, 77.29; H, 10.22. Found: C, 77.04; H, 10.13.

$LiAlH_4$ Reduction of IV——To a solution of IV (1 g) in dry ether (200 ml), 2 g of $LiAlH_4$ was added portionwise and the resulting mixture was refluxed for 3 hr. Under ice cooling, water and dil. H_2SO_4 were added dropwise and the mixture was extracted with ether. The ether-soluble fraction was chromatographed over silica gel with benzene–AcOEt (10: 1). The fraction of *Rf* 0.33 gave colorless needles (VIII′) of mp 149° (from MeOH). $[\alpha]_D^{16}=+20.5°$ ($c=1.05$, $CHCl_3$). Yield: 15 mg. IR ν_{max} cm^{-1}: 3400 (OH), 3050 (cyclopropane), 1065 (secondary OH), 1030 (primary OH). *Anal.* Calcd. for $C_{30}H_{52}O_2$: C, 81.02; H, 11.79. Found: C, 80.77; H, 11.67.

The fraction of *Rf* 0.25 gave colorless needles (VIII) of mp 152—154° (from MeOH). $[\alpha]_D^{15}=+45°$ ($c=1.01$, $CHCl_3$). IR ν_{max} cm^{-1}: 3400 (OH), 3050 (cyclopropane), 1040 (secondary OH), 1025 (primary OH). *Anal.* Calcd. for $C_{30}H_{52}O_2$: C, 81.02; H, 11.79. Found: C, 81.14; H, 11.52.

Catalytic Hydrogenation of V——Compound V (135 mg) in AcOEt (30 ml) was hydrogenated over 15% Pd-C (135 mg) to give colorless triangular crystals (IX) of mp 171—173° (from MeOH). $[\alpha]_D^{19}=+39.5°$ ($c=1.00$, $CHCl_3$). IR ν_{max} cm^{-1}: 3400 (OH), 3050 (cyclopropane), 1705 (COOH), 1040 (secondary OH). *Anal.* Calcd. for $C_{30}H_{50}O_3$: C, 78.55; H, 10.99. Found: C, 78.47; H, 10.83.

$LiAlH_4$ Reduction of I——Compound I (0.4 g) in dry ether (150 ml) was reduced with $LiAlH_4$ (1 g) and the mixture was treated as mentioned in the case of $LiAlH_4$ reduction of IV. The ether-soluble fraction was chromatographed over silica gel with benzene–AcOEt (5: 1). The fraction of *Rf* 0.37 gave colorless needles (X′) of mp 147° (from MeOH). Yield: 16 mg. $[\alpha]_D^{19}=+29.3°$ ($c=0.70$, $CHCl_3$). IR ν_{max} cm^{-1}: 3300 (OH), 3050 (cyclopropane), 1065 (secondary OH), 1010 (primary OH), 1630 (conjugated double bond). *Anal.* Calcd. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 81.06; H, 11.08. The fraction of *Rf* 0.30 gave colorless needles (X) of mp 173—174° (from MeOH). Yield: 235 mg. $[\alpha]_D^{19}=+43.8°$ ($c=0.96$, $CHCl_3$). IR ν_{max} cm^{-1}: 3300 (OH), 3050 (cyclopropane), 1030 (secondary OH), 1000 (primary OH), 1630 (conjugated double bond). *Anal.* Calcd. for $C_{30}H_{50}O_2$: C, 81.39; H, 11.38. Found: C, 81.42; H, 11.26.

Catalytic Hydrogenation of X——Compound X (150 mg) in AcOEt (40 ml) was hydrogenated over 15% Pd-C and the crude product was chromatographed over silica gel with benzene–AcOEt (20: 1). The fraction of *Rf* 0.30 gave colorless triangular crystals (XI) of mp 100° (from MeOH). $[\alpha]_D^{19°}=+48.5°$ ($c=1.01$, $CHCl_3$). IR ν_{max} cm^{-1}: 3400 (OH), 3050 (cyclopropane), 1380, 1370 (isopropyl), 1040 (secondary OH). *Anal.* Calcd. for $C_{30}H_{52}O$: C, 84.04; H, 12.23. Found: C, 83.55; H, 11.95. The fraction of *Rf* 0.06 gave dihydrodiol (VIII) of mp 150°. (IR, TLC, and mixed fusion).

Acetylation of XI——A mixture of XI (70 mg), pyridine (0.5 ml), and acetic anhydride (1 ml) was allowed to stand overnight. The reaction product was chromatographed over silica gel with benzene–AcOEt (40: 1). The fraction of *Rf* 0.69 gave colorless needles (XII) of mp 133—135° (from MeOH). It was proved to be identical with an authentic sample of cycloartanol acetate[8] by IR, TLC, and the mixed fusion. IR ν_{max} cm^{-1}: 3050 (cyclopropane), 1735, 1250 (acetate), 1380, 1370 (isopropyl). *Anal.* Calcd. for $C_{32}H_{54}O_2$: C, 81.64; H, 11.56. Found: C, 81.33; H, 11.23.

Catalytic Hydrogenation of the Diol Derivative of Mangiferonic Acid——Diol derivative[7] (7 mg) in AcOEt (7 ml) was hydrogenated over 15% Pd-C (7 mg). The filtered and concentrated solution showed two spots of *Rf* 0.44 and 0.33 on thin-layer chromatogram (silica gel impregnated with 5% $AgNO_3$, benzene–AcOEt=20: 1). Under the same conditions, cycloartanol, VIII, and the diol derivative showed spots of *Rf* 0.44, 0.33, and 0.31, respectively.

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