Triterpenoid Constituents of *Huperzia miyoshiana*

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Thirteen triterpenoids, including three new ones, miyoshianols A (1), B (2) and C (3), were isolated from *Huperzia miyoshiana*. The structures of these new compounds were established as 3-*O*-dihydroferuloyltohogenol (1), 16-oxo-3β,21β-dihydroxy-serrat-14-en-24-ferulate (2) and 16-oxo-3α, 21β-dihydroxy-serrat-14-en-24-ferulate (3), respectively, on the basis of their spectroscopic analysis.

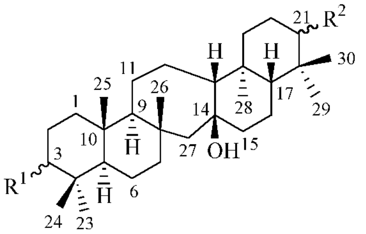
Keywords *Huperzia miyoshiana*, triterpenoids, miyoshianols A, B and C

Introduction

Serratenediol (**5**), a representative serratene-type triterpenoid with 7-membered ring-C and 7 tertiary methyls, was firstly isolated from the Japanese club moss *Lycopodium serratum* (= *Huperzia serrata*) in 1964.[1,2] Subsequently intense activities in this field have led to the discovery of a series of this type triterpenoids from diverse plants, such as conifers (especially *Pinus* and *Picea* species),[3,4] club moss (*Lycopodium* and *Huperzia* species),[3,4] ferns[5] and the liverwort (*Nardia scalaris*).[6] Recently, we reported three new triterpenoids with serratane-type from *Huperzia serrata*.[7] As a continuous interest in this species, we investigated the non-alkaloid constituents of *Huperzia miyoshiana* (Makino) Ching (Huperziaceae), a club moss gsows merely in the middle part of Asia, obtaining three new triterpenoids, miyoshianols A (**1**), B (**2**) and C (**3**), together with 10 known compounds, 3-*O*-acetyltohogenol (**4**),[8] 3β-hydroxy-serrat-14-en-21α-ol (**5**),[9] serrat-14-en-3β,21α-diyl-acetate (**6**),[10] 21α-hydroxy-serrat-14-en-3β-yl-acetate (**7**),[8] 21β-hydroxy-serrat-14-en-3β-yl-acetate (**8**),[8] 3β-hydroxy-serrat-14-en-21β-ol (**9**),[9] 16-oxo-3α-hydroxy -serrat-14-en-21β-ol (**10**),[11] 3β, 21β-dihydroxy-serrat-14-en-29-ol (**11**),[12] 3α,21β-dihydroxy-serrat-14-en-24-ol (**12**) and 3β,21α-dihydroxy-serrat-14-en-24-ol (**13**).[13] The chemical components of this plant was reported for the first time. In this paper, we describe the isolation and structure elucidation of above-mentioned new compounds.

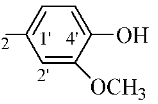
Results and discussion

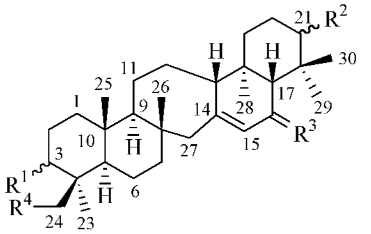
The planar structure of compound **4** was deduced to



	R1	R2
1	β-dihydroferuloxyl	α-OH
4	β-OAc	α-OH
14	β-OAc	α-OAc

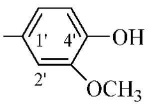
dihydroferuloxyl = $OCO(CH_2)_2$—





	R1	R2	R3	R4
2	β-OH	β-OH	O	feruloxyl
3	α-OH	β-OH	O	feruloxyl
5	β-OH	α-OH	H_2	H
6	β-OAc	α-OAc	H_2	H

feruloxyl = OCOCH=CH—



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be the same with 3-*O*-acetyltohogenol[8] by means of IR, EIMS and NMR (^{1}H, ^{13}C NMR, HMQC and HMBC) analyses. The configuration of **4** was elucidated through chemical conversions. Acetylation of **4** with Ac_2O afforded **14**, dehydration of **14** with $SOCl_2$-pyridine gave the sole product **6**. These results confirmed compound **4** to be 3-*O*-acetyltohogenol with 14β-OH.[14] The ^{1}H and ^{13}C NMR signals (Tables 1 and 2) were assigned completely for the first time.

The molecular formula $C_{40}H_{62}O_6$ of miyoshianol A (**1**) is deduced from the HREIMS. The IR spectrum of **1** resembles that of **4** with the exception of the extra signals for an aromatic ring (1518, 1463 and 1369 cm^{-1}). The ^{1}H and ^{13}C NMR (Tables 1 and 2) spectra show signals for seven tertiary methyl groups, a methine (δ_H 4.65, dd, J = 11.4, 4.7 Hz; δ_C 80.8) geminal to an ester group with equatorial orientation, a methine (δ_H 3.55, dd, J = 11.3, 4.3 Hz; δ_C 78.4) connected with an equatorial hydroxyl, and an oxygenated quaternary carbon (δ_C 74.9). Comparison of the ^{1}H and ^{13}C NMR spectra of **1**

Table 1 ^{1}H NMR spectral data of compounds **1—4** in C_5D_5N^{a}

Site	**1**	**2**	**3**	**4**
H-1	1.70^b, 1.00^b	1.80^b, 1.03^b	1.80^b, 1.56^b	1.68^b, 0.99^b
H-2	1.70^b, 1.70^b	1.95^b, 1.95^b	2.17^b, 1.95^b	1.64^b, 1.71^b
H-3	4.65 (dd, J = 11.4, 4.7 Hz)	3.62 (dd, J = 11.4, 4.6 Hz)	4.19 (br.s)	4.58 (dd, J = 11.1, 4.7 Hz)
H-5	0.92^b	1.00^b	1.90^b	0.90^b
H-6	1.41^b, 1.36^b	1.84^b, 1.84^b	1.41^b, 1.26^b	1.42^b, 1.42^b
H-7	1.73^b, 1.42^b	1.40^b, 1.20^b	1.38^b, 1.21^b	1.73^b, 1.41^b
H-9	1.65^b	0.85^b	1.00^b	1.65^b
H-11	2.05^b, 1.60^b	1.90^b, 1.21^b	1.84^b, 1.15^b	2.01^b, 1.60^b
H-12	1.88^b, 1.67^b	1.97^b, 1.15^b	1.90^b, 1.12^b	1.85^b, 1.65^b
H-13	1.09^b	2.50 (d, J = 8.6 Hz)	2.48 (br.d, J = 8.6 Hz)	1.10^b
H-15	1.93^b, 1.65^b	5.95 (s)	5.94 (s)	1.92^b, 1.62^b
H-16	1.72^b, 1.20^b	—	—	1.74^b, 1.17^b
H-17	0.98^b	3.03 (s)	3.04 (s)	0.98^b
H-19	1.90^b, 1.12^b	2.29 (br.t, J = 11.3 Hz) 1.59 (dd, J = 11.4, 4.8 Hz)	2.26 (td, J = 13.1, 3.0 Hz) 1.55 (m)	1.88^b, 1.12^b
H-20	1.93^b, 2.02^b	2.03^b, 1.88^b	2.03^b, 1.82^b	1.95^b, 1.95^b
H-21	3.55 (dd, J = 11.3, 4.3 Hz)	3.60 (br.s)	3.59 (br.s)	3.54 (dd, J = 11.1, 4.8 Hz)
H-23	0.83 (s, 3H)	1.51 (s, 3H)	1.48 (s, 3H)	0.81 (s, 3H)
H-24	0.91 (s, 3H)	5.02 (d, J = 11.7 Hz) 4.78 (d, J = 11.7 Hz)	4.69 (d, J = 11.2 Hz) 4.40 (d, J = 11.2 Hz)	0.88 (s, 3H)
H-25	0.84 (s, 3H)	0.96 (s, 3H)	0.89 (s, 3H)	0.82 (s, 3H)
H-26	1.02 (s, 3H)	0.77 (s, 3H)	0.73 (s, 3H)	1.00 (s, 3H)
H-27	1.74 (d, J = 14.8 Hz) 1.58 (d, J = 14.8 Hz)	2.40 (d, J = 14.7 Hz) 1.95 (d, J = 14.7 Hz)	2.34 (d, J = 14.7 Hz) 1.87 (d, J = 14.7 Hz)	1.72 (d, J = 14.9 Hz) 1.55 (d, J = 14.9 Hz)
H-28	1.35 (s, 3H)	0.91 (s, 3H)	0.89 (s, 3H)	1.34 (s, 3H)
H-29	1.14 (s, 3H)	1.38 (s, 3H)	1.38 (s, 3H)	1.13 (s, 3H)
H-30	1.30 (s, 3H)	1.85 (s, 3H)	1.71 (s, 3H)	1.28 (s, 3H)
H-2′	7.00 (br.s)	7.33 (br.s)	7.38 (d, J = 1.7 Hz)	2.04 (s, 3H, OAc)
H-5′	7.21 (d, J = 7.6 Hz)	7.19 (d, J = 8.7 Hz)	7.23 (d, J = 8.2 Hz)	—
H-6′	6.92 (br.d, J = 7.6 Hz)	7.23 (d, J = 8.7 Hz)	7.27 (dd, J = 8.2, 1.7 Hz)	—
H-7′	3.07 (br.t, J = 7.6 Hz)	8.06 (d, J = 15.8 Hz)	8.05 (d, J = 15.8 Hz)	—
H-8′	2.80 (t, J = 7.6 Hz)	6.82 (d, J = 15.8 Hz)	6.78 (d, J = 15.8 Hz)	—
OCH_3	3.80 (s, 3H)	3.72 (s, 3H)	3.78 (s, 3H)	—

^{a} Values were recorded at 400 MHz, J in Hz. ^{b} The signals were either multiplets or overlapping with other peaks, and assignments were performed by measuring the center of cross peaks in the 2D NMR spectra.

with those of **4** indicates that both have the same serratane-type triterpenoid moiety. The remained signals in the ^{1}H and ^{13}C NMR spectra of **1** disclose a dihydroferulic acid ester group[12] by exhibiting signals for three ABX pattern aromatic protons (δ_H 7.00, br.s; 7.21, d, $J = 7.6$ Hz; 6.92, br. d, $J = 7.6$ Hz), two methylene groups with A_2B_2 system (each 2H, t, $J = 7.6$ Hz, δ_H 3.07 and 2.80) and a phenolic methoxy group (δ_H 3.80, s, 3H; δ_C 56.0). Therefore, miyoshianol A is the dihydroferulate of tohogenol. The HMBC spectrum displays the correlations of C-27/H_3-26, C-9/H_3-25, H_3-26, C-5/H_3-23, H_3-24, H_3-25, C-3/H_3-23, H_3-24 and C-9′/H-3, affirming **1** to be 3-*O*-dihydroferuloyltohogenol.

Table 2 ^{13}C NMR spectral data of compounds **1—4** in C_5D_5N[a]

Site	δ_C				HMBC (C to H)	
	1	**2**	**3**	**4**	**1**	**2**
C-1	38.2 t	39.2 t	33.8 t	38.0 t	Me-25, H-2	Me-25, H-2
C-2	24.3 t	28.4 t	26.7 t	24.1 t	—	—
C-3	80.8 d	78.1 d	69.9 d	80.7 d	Me-23, 24	Me-23, H-2, 24
C-4	38.1 s	43.1 s	42.7 s	38.0 s	Me-23, 24, H-3, 6	Me-23, H-5, 24
C-5	55.6 d	56.4 d	50.0 d	55.4 d	Me-23, 24, 25, H-6	Me-23, 25, H-24
C-6	19.3 t	20.8 t	19.4 t	19.2 t	H-7	Me-25
C-7	44.6 t	45.9 t	45.6 t	44.5 t	Me-26, H-6, 27	Me-26, H-6
C-8	38.3 s	38.1 s	38.3 s	38.1 s	Me-28, H-9, 27	Me-26, H-6, 27
C-9	59.5 d	62.9 d	62.6 d	59.3 d	Me-25, 26, H-27	Me-25, 26, H-27
C-10	38.5 s	38.5 s	38.5 s	38.4 s	Me-25, H-1	Me-25, H-1, 5, 9
C-11	19.4 t	25.3 t	25.3 t	19.3 t	H-9, 12	—
C-12	26.3 t	26.9 t	27.0 t	26.2 t	—	—
C-13	60.5 d	59.0 d	59.1 d	60.4 d	Me-28, H-27	Me-28, H-27, 28
C-14	74.9 s	163.5 s	163.6 s	74.8 s	H-15, 27	H-27
C-15	46.0 t	129.1 d	129.1 d	45.9 t	H-27	H-27
C-16	25.7 t	201.4 s	201.4 s	25.6 t	—	H-17
C-17	56.1 d	59.6 d	59.6 d	56.0 d	Me-28, 29, 30	Me-28, 29, 30
C-18	39.0 s	44.8 s	44.8 s	38.8 s	Me-28, H-17, 19	Me-28, H-17
C-19	39.0 t	32.1 t	32.0 t	39.0 t	Me-28, H-20	Me-28, H-21
C-20	28.5 t	26.0 t	26.0 t	28.4 t	—	H-21
C-21	78.4 d	76.0 d	76.0 d	78.3 d	Me-29, 30	Me-29, 30
C-22	39.8 s	37.7 s	37.7 s	39.7 s	Me-29, 30	Me-29, 30, H-17
C-23	28.1 q	23.4 q	23.6 q	28.0 q	Me-24, H-3	H-24
C-24	16.7 q	66.5 t	68.1 t	16.6 q	Me-23, H-3	Me-23, 25
C-25	16.7 q	16.0 q	16.4 q	16.6 q	H-9	—
C-26	23.4 q	19.9 q	20.0 q	23.3 q	H-9, 27	H-27
C-27	62.2 t	55.9 t	56.0 t	62.0 t	Me-26	Me-26, H-15
C-28	16.5 q	15.3 q	15.3 q	16.4 q	—	H-17, 19
C-29	16.8 q	22.3 q	22.2 q	16.7 q	Me-30, H-21	Me-30, H-17
C-30	29.2 q	29.1 q	29.1 q	29.1 q	Me-29, H-21	Me-29, H-17
C-1′	132.3 s	126.7 s	126.7 s	170.6 s (C=O)	H-2′, 6′, 7′, 8′	H-6′, 7′, 8′
C-2′	113.1 d	111.6 d	111.7 d	21.2 q (OAc)	H-6′, 7′	H-6′, 7′
C-3′	148.8 s	149.0 s	149.6 s	—	H-2′, 5′, OCH_3	H-2′, 5′, OCH_3
C-4′	146.8 s	151.2 s	151.2 s	—	H-2′, 5′, 6′	H-2′, 5′, 6′
C-5′	116.7 d	117.0 d	117.0 d	—	H-6′	H-6′
C-6′	121.6 d	123.0 d	123.1 d	—	H-2′, 7′	H-2′, 5′, 7′
C-7′	31.3 t	145.6 d	145.7 d	—	H-2′, 6′, 8′	H-2′, 6′
C-8′	37.1 t	116.0 d	115.6 d	—	H-7′	H-7′
C-9′	172.8 s	168.1 s	168.0 s	—	H-7′, 8′, 3	H-7′, 8′, 24
OCH_3	56.0 q	56.0 q	56.0 q	—	—	—

[a] Values were recorded at 100 MHz, and assignments were from DEPT and 2D NMR spectra.

The molecular ion at m/z 648.4009 in the HREIMS discloses the molecular formula $C_{40}H_{56}O_7$ for miyoshianol B (**2**) ($C_{40}H_{56}O_7$ requires 648.4026). The IR spectrum of **2** suggests the presence of hydroxyl group (3417 cm^{-1}) and α,β-unsaturated carbonyl group (1702 and 1666 cm^{-1}). The ^1H NMR spectrum (Table 1) of **2** reveals signals for six tertiary methyl groups, a proton (δ_H 3.03, s, H-17) of a methine neighbored to a ketone, a vinylic proton (δ_H 5.95, s, H-15), an axial proton (δ_H 3.62, dd, J = 11.4, 4.6 Hz, H-3) geminal to a hydroxyl group, an equatorial proton (δ_H 3.60, br.s, H-21) geminal to a hydroxyl group, and a pair of AB model protons (δ_H 4.78 and 5.02, each 1H, d, J = 11.7 Hz, H_2-24), indicating a 16-oxoserratriol-type triterpenoid.[11] Furthermore, the ^1H NMR spectrum exhibits signals due to a 1,3,4-trisubstituted benzene ring (δ_H 7.33, br.s; 7.23, d, J = 8.7 Hz; and 7.19, d, J = 8.7 Hz), two *trans*-conjugated olefinic protons at δ_H 8.06 and 6.82 (each 1H, d, J = 15.8 Hz) and a phenolic methoxyl group at δ_H 3.72 (s, 3H), indicating the existence of a ferulic acid ester group.[12] The 40 carbons signals observed in the ^{13}C NMR spectrum (Table 2) are characterized by the DEPT experiment, suggesting that **2** has an ester carbonyl, a ketone, four sp^2 quaternary carbons, six sp^2 methines, two oxymethines, an oxymethylene, five sp^3 quaternary carbons, four sp^3 methines, nine methylenes, six tertiary methyls and a phenolic methoxy group.

The above evidences demonstrate **2** to be a 16-oxoserratene triol ferulate. Further structural information is discovered from extensive 2D NMR (HMQC, HMBC and NOESY) analyses. The HMBC (Table 2) spectrum shows the correlations from the methylene protons (δ_H 5.02 and 4.78) to the carbonyl carbon of ferulic acid (δ_C 168.1), from H-17 (δ_H 3.03) to C-16 (δ_C 201.4), C-28 (δ_C 15.3), C-29 (δ_C 22.3) and C-30 (δ_C 29.1), from H_3-26 (δ_H 0.77) to C-27 (δ_C 55.9), and from H_3-25, H_3-26 (δ_H 0.96, 0.77) to C-9 (δ_C 62.9), suggesting that the ferulic acid ester group is located at C-23 or C-24. The feruloxyl group attached to C-24 is constructed on the basis of NOE (Fig. 1) correlations between H_a-24 (δ_H 4.78) and H_3-25, and between H_b-24 (δ_H 5.02) and H-6. Therefore, **2** is formulated as 16-oxo-3β,21β-dihydroxy-serrat-14-en-24-ferulate.

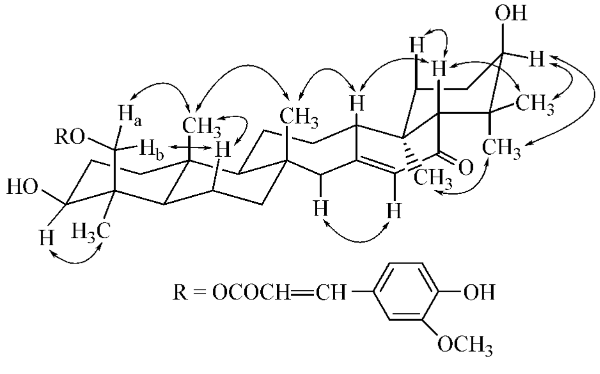

Fig. 1 Key NOE correlations of **2**.

Miyoshianol C (**3**) is assigned the molecular formula $C_{40}H_{56}O_7$ by the HREIMS (calcd for 648.4026, found 648.4044). Its IR spectrum is similar to that of **2**. The ^1H NMR (Table 1) spectrum is nearly superposed with that of **2**, excluding a proton signal at δ_H 4.19 (br.s) instead of the H-3 signal (δ_H 3.62, dd, J = 11.4, 4.6 Hz) of **2**, indicating the proton attached to C-3 to be equatorial (β-configuration) rather than axial. Moreover, in contrast with the ^{13}C NMR data of **2**, those differences ($\Delta\delta_{2-3}$: C-1, −5.4 and C-5, −6.4) are attributed to the γ-gauche effect from the axial-hydroxyl attached to C-3 of **3**, validating **3** to be 16-oxo-3α,21β-dihydroxy-serrat-14-en-24-ferulate.

Experimental

General

All melting points were determined on a Fisher-Johns melting point apparatus and were uncorrected. The optical rotations were measured using a Perkin-Elmer 241 MC polarimeter in $CHCl_3$ or C_5H_5N. The IR spectra were taken on a Nicolet Magna 750 FTIR (KBr) spectrophotometer. The NMR spectra were recorded on a Bruker AM-400 instrument. The chemical shift values were reported in units (δ) with TMS as internal standard, and coupling constants (J) are given in Hz. EIMS and HREIMS data were obtained with an MAT-95 mass spectrometer. Silica gel (200—300, 400 mesh) and precoated plates of silica gel ($HSGF_{254}$) (Qingdao Haiyang Chemical Group Co. Ltd, Qingdao, China) were used for column chromatography (CC) and TLC, respectively.

Plant material

Fresh whole plants of *Huperzia miyoshiana* (Makino) Ching (Huperziaceae) were collected at Changbai Mountain, Jilin Province, China in August 2000 and identified by Dr. Xiao-Qiang Ma of this institute. A voucher specimen has been deposited at the herbarium of this institute (No. 2000-79).

Extraction and isolation

Air-dried and powdered whole plants (4.3 kg) of *H. miyoshiana* were extracted with 95% EtOH (3 × 10 L) at room temperature. The EtOH extraction was concentrated under reduced pressure, then extracted with aqueous 1% HOAc (3 × 1.5 L). After filtration, the filter residue was successively partitioned with petroleum ether, $CHCl_3$, Me_2CO and EtOH (each 3 × 1 L). Then the $CHCl_3$ extract (70 g) was subjected to CC over silica gel (100—200 mesh, 1500 g) with gradient eluent of petroleum ether-$CHCl_3$ (50:1 to 0:1) and $CHCl_3$-Me_2CO (25:1 to 0:1) to give frs. 1—8. Fr. 1 (300 mg) yielded needles, were recrystallized with CH_2Cl_2-Me_2CO （5∶1），affording **6** （15 mg）. Fr. 2 （5 g） was chromatographed with petroleum ether-ether （4∶1，1∶1，each 1500 mL） as eluent，affording **7** （500 mg） and **8** （20 mg）. Fr. 3 （1.5 g） furnished solid crystals，were recrystallized with CH_2Cl_2-Me_2CO （5∶1） to yield **9** （50 mg）. The concentrated mother liquor （800 mg） was purified with $CHCl_3$ （500 mL） to give **4** （130 mg） and **5** （30 mg）. Repeated chromatography on fr. 4 （4.0 g） with increasing polarity eluent of CH_2Cl_2-Me_2CO （15∶1，10∶1，5∶1，each 500 mL） afforded **1** （50 mg）. Fr. 5 （5.2 g） was followed by silica gel CC with CH_2Cl_2-Me_2CO （2∶1 to acetone） as eluate to give 3 subfractions：frs. 5.1—5.3，frs. 5.4—5.7 and frs. 5.8—5.12. Further purification on frs. 5.1—5.3，frs. 5.4—5.7 and frs. 5.8—5.12 resulted in **2** （17 mg），**3** （6 mg），**10** （8 mg） and **11** （50 mg），respectively. Fr. 6 （2.2 g） was purified on silica gel （CH_2Cl_2-Me_2CO，3∶1，1500 mL） to afford **12** （40 mg） and **13** （75 mg）.

Acetylation of 3-*O-acetyltohogenol* （**4**） *to tohogenol diacetate* （**14**） 3-*O*-acetyltohogenol （30 mg） in pyridine （2 mL） was acetylated with Ac_2O （1 mL） for 1 h at room temperature. Then the solution was poured into ice water，and extracted with CH_2Cl_2. The organic extract was washed with 5% HCl and water，dried over Na_2SO_4，and concentrated to give a residue，which was crystallized from CH_2Cl_2 to afford tohogenol diacetate （27 mg） as prisms，m.p. 306—308 ℃；^1H NMR （C_5D_5N，400 MHz） δ：4.76 （dd，J = 10.5，5.2 Hz，1H，H-3），4.60 （dd，J = 11.4，5.3 Hz，1H，H-21），2.09，2.05 （s，3H，respectively，2 × $COCH_3$），1.29，1.01，0.98，0.95，0.86，0.84，0.82 （s，3H，respectively，7 × CH_3）；IR （KBr） ν：3437 （OH），2945，1726，1375，1252，1028，993 cm^{-1}.

Dehydration of tohogenol diacetate （**14**） *to* **6** $SOCl_2$（5 drops） was added to an ice-cooled solution of diacetate tohogenol （25 mg） in pyridine （2 mL），and the mixture was stirred for 4 h at room temperature. Work-up as the above and crystallization of the residue gave **6** （17 mg）. ^1H NMR and TLC of the product did not show the presence of *iso*-serratenediol diacetate.

Miyoshianol A （**1**） Colorless needles from $CHCl_3$-CH_3OH （1∶1），m.p. 247—249 ℃，$[\alpha]_D^{20}$ − 15.7 （*c* 0.12，C_5H_5N）；^1H and ^{13}C NMR data see Tables 1 and 2；IR （KBr） ν：3504，3408，2939，1720，1518，1463，1369，1182，989，752 cm^{-1}；EIMS *m/z* （%）：638 （$[M]^+$，0.7），620 （41），425 （55），407 （44），287 （11），196 （35），189 （39），189 （39），137 （100），95 （44）；HREIMS calcd for $C_{40}H_{62}O_6$ 638.4546，found 638.4527.

Miyoshianol B （**2**） White powders，m.p. 235—238 ℃，$[\alpha]_D^{20}$ − 19.3 （*c* 0.12，$CHCl_3$）；^1H and ^{13}C NMR data see Tables 1 and 2；IR （KBr） ν：3410，2939，1702，1666，1600，1516，1462，1385，1268，1157，1036，986 cm^{-1}；EIMS *m/z* （%）：648 （M^+，10），630 （14），455 （27），437 （12），220 （19），194 （51），177 （100），107 （45）；HREIMS calcd for $C_{40}H_{56}O_7$ 648.4026，found 648.4009.

Miyoshianol C （**3**） White powders，m.p. 240—243 ℃，$[\alpha]_D^{20}$ − 15.4 （*c* 0.17，$CHCl_3$）；^1H and ^{13}C NMR data see Tables 1 and 2；IR （KBr） ν：3427，2926，1699，1655，1603，1516，1464，1387，1269，1157，995，756 cm^{-1}；EIMS *m/z* （%）：648 （M^+，10），630 （12），454 （25），421 （20），177 （90），71 （65），57 （100）；HREIMS calcd for $C_{40}H_{56}O_7$ 648.4026，found 648.4044.

3-*O-acetyltohogenol* （**4**） Colorless needles from $CHCl_3$-CH_3OH （1∶1），m.p. 298—300 ℃，$[\alpha]_D^{20}$ − 7 （*c* 0.27，C_5H_5N）；^1H and ^{13}C NMR data see Tables 1 and 2；IR （KBr） ν：3433，2939，1720，1248，1030，993 cm^{-1}；EIMS *m/z* （%）：502 （M^+，9），484 （58），469 （47），442 （29），427 （49），409 （41），391 （37），189 （92），161 （47），135 （96），107 （100）.

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