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Lanceocrepidiasides A–F, glucosides of guaiane-type sesquiterpene from *Crepidiastrum lanceolatum*

Yoshio Takeda [a,b,*], Toshiya Masuda [a], Hiroyuki Morikawa [c], Hisako Ayabe [a], Eiji Hirata [d], Takakazu Shinzato [d], Mitsunori Aramoto [b], Hideaki Otsuka [c]

[a] *Faculty of Integrated Arts and Sciences, The University of Tokushima, 1-1 Minamijosanjima-cho, Tokushima 770-8502, Japan*
[b] *Tropical Biosphere Research Center, University of the Ryukyus, Taketomi, Yaeyama-Gun, Okinawa 907-1541, Japan*
[c] *Department of Pharmacognosy, Graduate School of Biomedical Sciences, Hiroshima University, 1-2-3 Kasumi, Minami-ku, Hiroshima 734-8551, Japan*
[d] *Faculty of Agriculture, University of the Ryukyus, 1 Senbaru, Nishihara-cho, Nakagami-gun, Okinawa 903-0213, Japan*

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Abstract

From the aerial parts of *Crepidiastrum lanceolatum*, six guaiane-type sesquiterpene glucosides, lanceocripidiasides A–F were isolated together with five known sesquiterpene glucosides, ixerin Y, crepidialanceosides A and B, and youngiasides A and D, two known megastigmane glucosides, icariside B_1 and corchoionoside A, and benzyl 6′-*O*-β-D-apiofuranosyl-β-D-glucopyranoside. Structures were elucidated by spectroscopic analyses.

Keywords: *Crepidiastrum lanceolatum*; Asteraceae; Sesquiterpene glucoside; Guaiane; Lanceocrepidiaside

1. Introduction

In the Okinawa Prefecture, Japan, *Crepidiastrum lanceolatum* (Asteraceae) (Hatusima and Amano, 1994) is used as a folk medicine to treat amoebic colitis, colitis, fever and swelling. The aerial parts of this plant are also used as garnishings with raw fishes (Tawada, 1972). This paper deals with the isolation and structure elucidation of six new glucosides of guaiane type sesquiterpenes, lanceocrepidiasides A–F (**1**–**6**), as well as other previously known metabolites, including compounds **7**–**11**. Previously, we had isolated two new sesquiterpene glucosides, crepidialanceosides A (**8**) and B (**9**) (Takeda et al., 2002) from the underground organs of the plant. In continuation of the studies on the constituents of this plant, we investigated the glycosidic constituents of the aerial parts of the plant.

2. Results and discussion

The EtOAc-soluble fraction of the MeOH extract was separated by repeated silica gel chromatography and finally by ODS-HPLC to give six sesquiterpene glucosides together with crepidialanceosides A (**8**) and B (**9**), and youngiaside D (**10**) (Adegawa et al., 1986). The *n*-BuOH soluble fraction was also separated by silica gel and reversed-phase silica gel chromatography, and finally by ODS-HPLC to give new sesquiterpene glucosides together with the known sesquiterpene glucosides, ixerin Y (**7**) (Ma et al., 1999), youngiaside A (**11**) (Adegawa et al., 1986), the megastigmane glucosides, icariside B_1 (Miyase et al., 1987) and corchoionoside A

* Corresponding author.
E-mail address: takeda@ias.tokushima-u.ac.jp (Y. Takeda).

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(Yoshikawa et al., 1997), and benzyl 6′-*O*-β-D-apiofuranosyl-β-D-glucopyranoside (Miyase et al., 1988).

Lanceocrepidiaside A (**1**), $[\alpha]_D$ ~0° (MeOH), was obtained as an amorphous powder whose elemental composition was determined as $C_{21}H_{30}O_9$ based on its negative-ion HR-FABMS. The ^1H and ^{13}C NMR spectra are very similar to those of youngiaside A (**11**) except for the absence of signals due to the *exo*-methylene group and the appearance of resonance corresponding to a secondary methyl group. Thus, lanceocrespidiaside A (**1**) was deduced to be the dihydro-derivative of youngioside A (**11**). Furthermore, $NaBH_4$ reduction of **11** gave **1**. Since the newly generated secondary methyl group generally takes an α-orientation when an α-methylene-γ-lactone group is reduced with $NaBH_4$ via 1,4-addition reaction (Nagumo et al., 1980; Corbella et al., 1974), the structure of lanceocrepidiaside A was assigned as shown in structure **1**.

Lanceocrepidiaside B (**2**), $[\alpha]_D$ +1.9° (MeOH), was obtained as an amorphous powder where molecular formula was assigned as $C_{29}H_{36}O_{11}$ based on its negative-ion HR-FABMS. The ^1H NMR spectrum was very similar to that of **1** except for the appearance of signals due to a *p*-hydroxy phenyl acetate moiety and the downfield shift of H_2-6′ signals. The ^{13}C NMR spectrum (Table 1) also showed the presence of a *p*-hydroxyphenyl acetate and 6-*O*-acylated glucose moieties (Garcia et al., 1989). Based on the above mentioned data, lanceocrepidiaside B was deduced to be 6′-*O*-*p*-hydroxyphenyl acetate of lanceocrepidiaside A (**1**).

Lanceocrepidiaside C (**3**), $[\alpha]_D$ +29.8° (MeOH), has the same molecular formula, $C_{29}H_{34}O_{11}$ as that of crepidialanceoside A (**8**). Based on the analyses of ^1H and ^{13}C NMR spectra, this compound also contained the same aglycone, and β-glucopyranosyl and *p*-hydroxyphenyl acetate moieties in the structure as that of crepidialanceoside A (**8**). The stereochemistry of the aglycone part was supported by the results of phase sensitive NOESY, the results of which are summarized in Fig. 1. The location of the glycosidic linkage was deduced to be on *O*-8, since cross peaks were observed between C-8 (δ 78.7) and the anomeric proton (δ 5.05) in the HMBC spectrum. The configuration of the glycosidic linkage is β as judged from the coupling constant (J = 7.7 Hz) of the anomeric proton. The *p*-hydroxyphenylacetyl moiety was deduced to be located at *O*-15, since the proton signals due to H_2-15 resonated downfield, compared to those (δ 4.81 and 4.91) in lanceocrepidiaside A (**1**). Thus, the structure of lanceocrepidiaside C was elucidated as shown in structure **3**.

Lanceocrepidiaside D (**4**), $[\alpha]_D$ −14.0° (MeOH), has a molecular formula, $C_{29}H_{32}O_{11}$ based on its negative-ion HR-FABMS. The ^1H and ^{13}C NMR spectra of the aglycone part were essentially the same as those of crepidiaside A (**12**) (Adegawa et al., 1985). The differences in the NMR spectra were the appearance of the signals due to

Table 1
^{13}C NMR spectroscopic data (C_5D_5N) of **1**–**6**

Atom	1	2	3	4	5	6
1	136.1	136.1	136.3	131.7	131.7	82.3
2	38.5	38.5	37.2	195.0	195.1	209.6
3	127.9	127.8	128.8	134.5	134.4	128.3
4	142.2	142.1	139.9	169.3	169.7	176.5
5	52.0	52.2	52.6	50.1	49.8	58.5
6	85.4	85.4	82.5	84.0	83.7	82.3
7	47.0	47.0	57.7	52.5	55.6	45.3
8	34.1	34.1	78.7	24.3	25.8	25.1
9	71.7	71.7	44.9	37.1	37.5	27.8
10	135.0	135.0	127.6	152.7	152.9	39.6
11	41.3	41.3	138.1	139.6	41.3	140.1
12	179.0	178.7	169.9	169.0	177.4	169.7
13	12.2	12.3	131.1	118.4	12.2	120.0
14	22.4	22.4	22.7	21.5	21.3	14.7
15	68.4	68.3	63.9	68.9	68.9	68.8
1′	103.3	103.3	105.8	104.2	104.3	104.4
2′	75.0	74.9	75.3	75.1	75.1	75.0
3′	78.3	78.1	78.7	78.3	78.3	78.2
4′	71.5	71.5	71.6	71.4	71.4	71.3
5′	78.1	75.0	78.4	75.3	75.3	75.2
6′	62.5	65.1	62.7	64.9	64.9	64.9
1″		125.4	125.4	125.4	125.4	125.3
2″, 6″		131.1	131.1	131.2	131.2	131.2
3″, 5″		116.2	116.3	116.3	116.3	116.3
4″		157.7	157.9	157.9	158.0	157.9
7″		40.5	40.8	40.4	40.4	40.4
8″		172.6	171.9	172.4	172.4	172.4

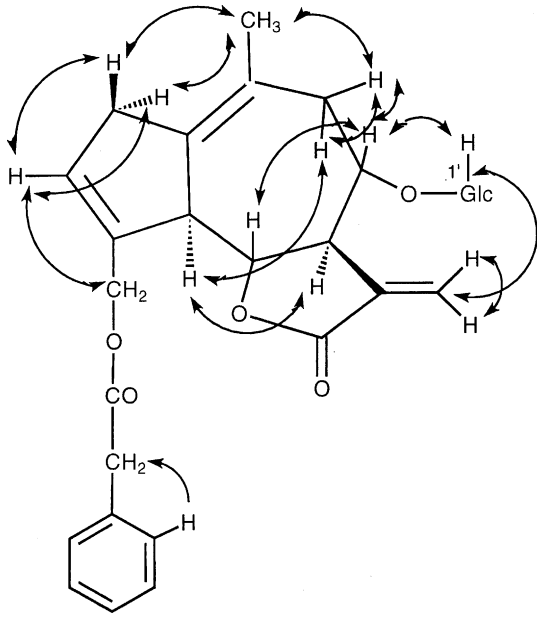


Fig. 1. The results of phase-sensitive NOESY for lanceorepidiaside C (**3**).

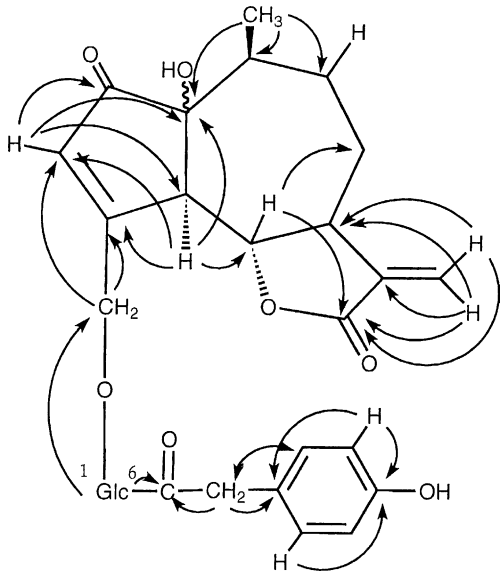


Fig. 2. The results of HMBC spectrum for lanceorepidiaside F (**6**).

a *p*-hydroxyphenylacetate moiety and a 6-*O*-acylated β-glucopyranosyl residue. Thus, the structure of lanceocrepidiaside D was elucidated as shown in structure **4**.

Lanceocrepidiaside E (**5**), $[\alpha]_D$ −24.1° (MeOH), was assigned the molecular formula, $C_{29}H_{34}O_{11}$, which is two mass units more than that of lanceocrepidiaside D (**4**) based on its negative-ion HR-FABMS. In the ^1H and ^{13}C NMR spectra, the signals due to an *exo*-methylene group as was observed in **4**, were absent, with resonance due to a secondary methyl group being present instead. Considering that the ^{13}C NMR signals due to aglycone portion were essentially the same as those of crepidiaside C (**13**) (Adegawa et al., 1985), the structure of lanceocrepidiaside E is assigned as **5**, which corresponds to the dihydro-derivative of lanceocrepidiaside D (**4**).

Lanceocrepidiaside F (**6**), $[\alpha]_D$ +70.2° (MeOH), was also obtained as an amorphous powder and the results of negative-ion HR-FABMS indicated the elemental composition to be $C_{29}H_{34}O_{12}$ which is 18 mass units more than that of lanceocrepidiaside D (**4**). Intensive analyses of NMR spectra including ^1H–^1H COSY and HSQC data suggested that lanceocrepidiaside F has a structure **6**, which might be formed formally via addition of water to the structure of lanceocrepidiaside D (**4**), since signals arising from tetra-substituted double bond which was observed in **4** disappeared in **6** in the ^{13}C NMR spectrum and instead signals due to a quaternary carbon atom having an oxygen atom and a secondary methyl group were observed in the ^1H and ^{13}C NMR spectra. The presumption was supported by the results of HMBC spectrum, which are summarized in Fig. 2. The stereochemistry except for C-1 was confirmed as shown based on the observation of the cross peaks between H_3-14 and H-6, and H-5 and H-7 in the phase-sensitive NOESY. Thus, the structure of lanceocrepidiaside F was elucidated as shown in structure **6**.

3. Experimental

3.1. General experimental procedures

Optical rotations were measured on a JASCO DIP-360 polarimeter. FT-IR and UV spectra were recorded on Horiba FT-710 and JASCO V-530SR spectrophotometers, respectively. ^1H and ^{13}C NMR spectra were recorded on JEOL EX-400 and a α-400 spectrometers (400 and 100 MHz, respectively) with tetramethylsilane (TMS) as internal standard. HR-FABMS analyses were carried out on a JEOL SX-102 mass spectrometer with PEG-400 or -600 as the calibration matrix. For purification, the following were used; silica gel 60 (Merck, 230–400 mesh), $75C_{18}$-OPN (NacaLai Tesque, Kyoto), packed column for HPLC [Cosmosil $5C_{18}$AR (20 × 250 mm), detection, 210 nm; solvent, mixture of MeOH and H_2O, 6 ml/min] and silica gel 60 F_{254} TLC plates (Merck, 0.25 mm in thickness).

3.2. Plant material

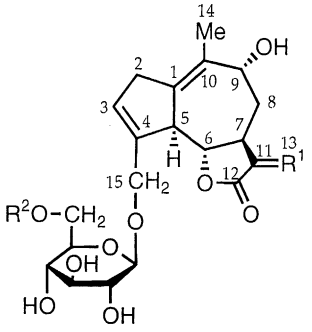
Aerial parts of *C. lanceolatum* (Houtt.) Nakai were collected in July, 1999, in Kunigami-son, Kunigami-gun, Okinawa Prefecture, Japan. A specimen was authenticated by one (T.S.) of the authors and a voucher herbarium specimen (99-CL-Okinawa 0708) was deposited in the Herbarium of the Department of

Pharmacognosy, Graduate School of Biomedical Sciences, Hiroshima University.

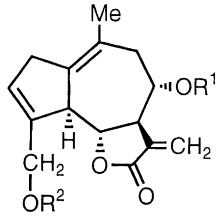
3.3. Extraction and isolation

Dried aerial parts (5.0 kg) of *C. lanceolatum* were extracted with MeOH (54 l) at room temperature for 2 weeks. The extraction was repeated once. The combined MeOH extracts were concentrated in vacuo. The residue was dissolved in MeOH–H_2O (9:1), (1.5 l) and the solution was washed with *n*-hexane The (1 l × 3). The MeOH–H_2O (9:1) OH layer was concentrated in vacuo, will the resulting residue suspended in H_2O (1 l) and extracted with EtOAc (1 l × 3) and *n*-BuOH saturated with H_20 (1 l × 3), successively. The EtOAc and *n*-BuOH layers were individually concentrated in vacuo to give residues (38.2 and 44.6 g, respectively).

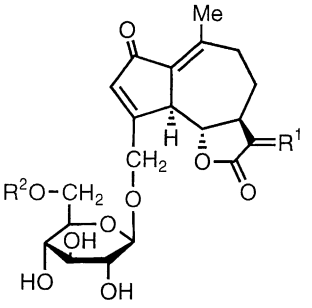
The residue obtained from the EtOAc layer was applied to the silica gel column (1 kg) eluted with 6 l each of $CHCl_3$, $CHCl_3$–MeOH (97:3), $CHCl_3$–MeOH (19:1), $CHCl_3$–MeOH (9:1), $CHCl_3$–MeOH (22:3), $CHCl_3$–MeOH (17:3) and $CHCl_3$–MeOH (4:1), respectively,



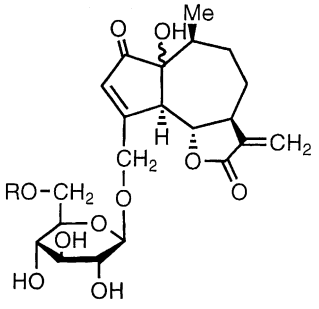
(1) R^1=α-Me, β-H ; R^2=H
(2) R^1=α-Me, β-H ; R^2=PHPAA
(10) R^1=CH_2 ; R^2=PHPAA
(11) R^1=CH_2 ; R^2=H



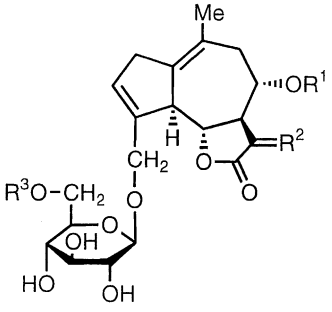
(3) R^1=Glc ; R^2=PHPAA



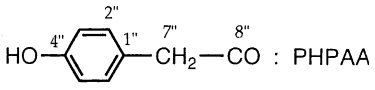
(4) R^1=CH_2 ; R^2=PHPAA
(5) R^1=α-Me, β-H ; R^2=PHPAA
(12) R^1=CH_2 ; R^2=H



(6) R=PHPAA



(7) R^1=H ; R^2=CH_2 ; R^3=H
(8) R^1=H ; R^2=CH_2 ; R^3=PHPAA
(9) R^1=H ; R^2=α-Me, β-H ; R^3=PHPAA
(13) R^1=R^3=H ; R^2=α-Me, β-H



PHPAA

while collecting 500 ml fractions. Fractions 44–48 gave a residue (1.35 g) which was separated by silica gel CC with $CHCl_3$–MeOH eluant containing increasing amounts of MeOH at first. Fractions which showed R_f value around 0.42 (silica gel TLC, solvent: $CHCl_3$–MeOH 4:1) were combined and dried (754 mg), with the latter purified by HPLC (solvent; MeOH–H_2O 1:1) to give **4** (28.2 mg), **5** (16.2 mg) and **6** (32.1 mg), respectively. Fractions 49–59 gave a residue (3.25 g) which was subjected to silica gel CC with a $CHCl_3$–MeOH eluant with increasing amounts of MeOH. Fractions which showed R_f value around 0.36 (silica gel TLC, solvent: as above) were combined to give, after solvent evaporation, a residue (1.20 g) which was purified further by HPLC (conditions as above) to give **2** (5.3 mg), **3** (4.7 mg), **8** (175 mg), **9** (34.0 mg) and **10** (193 mg).

The residue obtained from the *n*-BuOH layer was applied to over silica gel (1 kg), column eluted with 6 l each of $CHCl_3$, $CHCl_3$–MeOH (97:3), $CHCl_3$–MeOH (19:1), $CHCl_3$–MeOH (93:7), $CHCl_3$–MeOH (9:1), $CHCl_3$–MeOH (22:3), $CHCl_3$–MeOH (17:3), $CHCl_3$–MeOH (4:1) and $CHCl_3$–MeOH (7:3) while collecting 500 ml fractions. Fractions 52–70, after solvent removal, gave a residue (6.64 g) which was separated by silica gel chromatography with $CHCl_3$–MeOH as eluent with increasing amounts of MeOH. Fractions which showed R_f value ca. 0.5 (silica gel TLC, solvent: $CHCl_3$–MeOH–H_2O 15:6:1) were collected and evaporated in vacuo to give a residue (1.43 g), and was further separated by HPLC (solvent, MeOH–H_2O 2:3 and then MeOH–H_2O 3:7) to give **1** (17.5 mg), icariside B_1 (46.1 mg), corchoionoside A (5.1 mg), 7 (33.1 mg) and 11 (147 mg). The residue (4.10 g) from fractions 87–98 was subjected to chromatography over 75 C_{18}-OPN with H_2O–MeOH as eluent [Linear gradient 0–60% MeOH (each 1.5 l)], 12 ml fractions being collected. Fractions 131–143 gave a residue (108 mg) which was finally purified by HPLC (solvent MeOH-H_2O 1:3) to give benzyl 6′-*O*-β-D-apiofuranosyl-β-D-glucopyranoside (13.5 mg).

Known compounds isolated were identified by comparisons of the spectral data with those reported.

3.4. Lanceocrepidiaside A (*1*)

$[\alpha]_{D^{26}} = \sim 0°$ (MeOH, *c* 0.90). IR ν_{max} (film) cm^{-1}: 3396, 1757, 1643, 1171, 1077, 1043. ^1H NMR (C_5D_5N): δ 1.13 (3H, *d*, *J* = 7.0 Hz, H-13), 1.52 (1H, *br.t*, *J* = 12.8 Hz, H_a-8), 1.73 (3H, *d*, *J* = 1.7 Hz, H-14), 2.16 (1H, *ddd*, *J* = 12.8, 5.6, 2.9 Hz, H_b-8), 2.35 (1H, *qd*, *J* = 7.0, 6.0 Hz, H-12), 2.87 (1H, *m*, H-7), 2.88 (1H, *br.d*, *J* = 21.6 Hz, H_a-2), 3.04 (1H, *br.d*, *J* = 21.6 Hz, H_b-2), 3.57 (1H, *m*, H-5′), 3.71 (1H, *t*, *J* = 10.3 Hz, H-6), 4.04 (1H, *dd*, *J* = 7.7, 8.8 Hz, H-2′), 4.18 (1H, *t*, *J* = 8.8 Hz, H-4′), 4.23 (1H, *t*, *J* = 8.8 Hz, H-3′), 4.25 (1H, *br.d*, *J* = 10.3 Hz, H-5), 4.32 (1H, *dd*, *J* = 11.9, 5.4 Hz, H_a-6′), 4.42 (1H, *br.d*, *J* = 4.8 Hz, H-9), 4.48 (1H, *dd*, *J* = 11.9, 2.5 Hz, H_b-6′), 4.81 (1H, *br.d*, *J* = 13.9 Hz, H_a-15), 4.88 (1H, *d*, *J* = 7.7 Hz, H-1′), 4.91 (1H, *br.d*, *J* = 13.9 Hz, H_b-15), 6.15 (1H, *br.s*, H-3). For ^{13}C NMR spectra, see; Table 1. HR-FABMS *m/z*: 425.1799 $[M - H]^-$; found for $C_{21}H_{29}O_9$; required *m/z*: 425.1812.

3.5. Lanceocrepidiaside B (*2*)

$[\alpha]_{D^{26}} = +1.9°$ (MeOH, *c* 0.57). UV λ (MeOH) nm ($\log\varepsilon$); 277 (3.65). IR ν_{max} (film) cm^{-1}: 3393, 1746, 1739, 1651, 1616, 1517, 1227, 1077, 1052. ^1H NMR (C_5D_5N): δ 1.12 (3H, d, *J* = 6.8 Hz, H-13), 1.50 (1H, *t*, *J* = 13.1 Hz, H_a-8), 1.71 (3H, *br.s*, H-14), 2.14 (1H, *ddd*, *J* = 13.1, 5.4, 2.7 Hz, H_b-8), 2.32 (1H, *qd*, *J* = 6.8, 6.0 Hz, H-12), 2.86 (1H, *br.d*, *J* = 21.6 Hz, H_a-2), 2.89 (1H, *m*, H-7), 3.05 (1H, *br.d*, *J* = 21.6 Hz, H_b-2), 3.72 (1H, *t*, *J* = 10.2 Hz, H-6), 3.77 (2H, s, H-7″), 3.98–4.08 (H-2′, H-4′, H-5′), 4.20 (1H, *t*, *J* = 8.8 Hz, H-3′), 4.28 (1H, *br.d*, *J* = 10.2 Hz, H-5), 4.41 (1H, *d*, *J* = 5.4 Hz, H-9), 4.77 (1H, *dd*, *J* = 11.6, 6.1 Hz, H_a-6′), 4.88 (1H, d, *J* = 7.9 Hz, H-1′), 4.91 (2H, *br.s*, H-15), 4.98 (1H, *br.d*, *J* = 11.6 Hz, H_b-6′), 7.15 (2H, *d*, *J* = 8.5 Hz, H-3″, H-5″), 7.35 (2H, *d*, *J* = 8.5 Hz, H-2″, H-6″). For ^{13}C NMR spectra, see; Table 1. HR-FABMS *m/z*: 559.2200 $[M - H]^-$; found for $C_{29}H_{35}O_{11}$; required *m/z*: 559.2179.

3.6. Lanceocrepidiaside C (*3*)

$[\alpha]_{D^{26}} = +29.8°$ (MeOH, *c* 0.24). UV λ (MeOH) nm ($\log\varepsilon$): 277 (3.79). IR ν_{max} (film) cm^{-1}: 3367, 1765, 1734, 1649, 1616, 1595, 1515, 1259, 1154, 1076, 964. ^1H NMR (C_5D_5N): δ 1.78 (3H, *br.s*, H-14). 2.56 (1H, *br.t*, *J* = 12.3 Hz, H_a-9), 2.80 (1H, *br.d*, *J* = 20.9 Hz, H_a-2), 2.97 (1H, *br.d*, *J* = 20.9 Hz, H_b-2), 3.23 (1H, *m*, H-7), 3.26 (1H, *dd*, *J* = 12.3, 1.9 Hz, H_b-9), 3.53 (1H, *br.d*, *J* = 9.7 Hz, H-5), 3.59 (1H, *t*, *J* = 9.7 Hz, H-6), 3.76 (2H, *s*, H-7″), 3.87 (1 H, *m*, H-8), 4.00 (1H, *m*, H-5′), 4.06 (1H, *dd*, *J* = 8.8, 7.7 Hz, H-2′), 4.18 (1H, *t*, *J* = 8.8 Hz, H-4′), 4.25 (1H, *t*, *J* = 8.8 Hz, H-3′), 4.34 (1H, *dd*, *J* = 11.6, 5.7 Hz, H_a-6′), 4.54 (1H, *dd*, *J* = 11.6, 2.4 Hz, H_b-6′), 5.02 (1H, *br.d*, *J* = 14.5 Hz, H_a-15), 5.05 (1H, *d*, *J* = 7.7 Hz, H-1′), 5.12 (1H, *br.d*, *J* = 14.5 Hz, H_b-15), 5.84 (1H, *br.s*, H-3), 6.47 (1H, *d*, *J* = 2.2 Hz, H_a-13), 7.20 (2H, *d*, *J* = 8.4 Hz, H-3″, H-5″), 7.34 (1H, *d*, *J* = 2.2 Hz, H_b-13), 7.37 (2H, *d*, *J* = 8.4 Hz, H-2″, H-6″). For ^{13}C NMR spectra, see Table 1. HR-FABMS *m/z*: 557.2018 $[M - H]^-$; found for $C_{29}H_{33}O_{11}$; required *m/z*: 557.2033.

3.7. Lanceocrepidiaside D (*4*)

$[\alpha]_{D^{26}} = -14.0°$ (MeOH, *c* 0.08). UV λ (MeOH) nm ($\log\varepsilon$): 222 (4.07), 255 (4.07). IR ν_{max} (film) cm^{-1}: 3355, 1761, 1739, 1676, 1616, 1416, 1446, 1253, 1078,

1022. ^{1}H NMR (C_5D_5N): δ 1.14 (1H, *q*, *J* = 12.7 Hz, H_a-8), 1.90 (1H, *br.d*, *J* = 12.7 Hz, H_b-8), 2.10 (1H, *dd*, *J* = 13.8, 5.9 Hz, H_a-9), 2.31 (1H, *t*, *J* = 13.8 Hz, H_b-9), 2.46 (3H, *br.s*, H-14), 2.78 (1H, *m*, H-7), 3.45 (1H, *t*, *J* = 10.3 Hz, H-6), 3.63 (1H, *br.d*, *J* = 10.3 Hz, H-5), 3.81 (2H, *s*, H-7″), 4.02 (1H, *m*, H-5′), 4.07–4.12 (2H, H-2′, H-4′), 4.22 (1H, t, *J* = 8.8 Hz, H-3′) 4.79 (1H, *dd*, *J* = 11.7, 6.4 Hz, H_a-6′). 4.91 (1H, *d*, *J* = 7.3 Hz, H-1′), 4.98 (1H, *br.d*, *J* = 17.3 Hz, H_a-15), 5.01 (1H, *br.d*, *J* = 11.7 Hz, H_b-6′), 5.28 (1H, *br.d*, *J* = 17.3 Hz, H_b-15), 5.36 (1H, *d*, *J* = 2.9 Hz, H_a-13), 6.17 (1H, *d*, *J* = 2.9 Hz, H_b-13), 6.99 (1H, *br.s*, H-3), 7.12 (2H, *d*, *J* = 8.3 Hz, H-3″, H-5″), 7.37 (2H, *d*, *J* = 8.3 Hz, H-2″, H-6″). For ^{13}C NMR spectra, see: Table 1. HR-FABMS *m*/*z*: 555.1833 $[M - H]^-$; found for $C_{29}H_{31}O_{11}$; required *m*/*z*: 555.1866.

3.8. Lanceocrepidiaside E (*5*)

$[\alpha]_{D^{26}} = -24.1^\circ$ (MeOH, *c* 0.80). UV λ (MeOH) nm (log ε): 228 (4.08), 254.5 (4.12). IR ν_{max} (film) cm^{-1}: 3367, 1762, 1740, 1676, 1616, 1516, 1446, 1274, 1165, 1122. ^{1}H NMR (C_5D_5N): δ ca. 1.1 (overlapped, Ha-8), 1.14 (3H, *d*, *J* = 6.8 Hz, H-13), 1.70 (1H, *m*, H_b-8), 1.86 (1H, *m*, H-7), 2.08 (1H, *dd*, *J* = 14.2, 5.9 Hz, Ha-9), 2.22–2.30 (2H, H_b-9, H-12), 2.46 (3H, *br.s*, H-14), 3.45 (1H, *t*, *J* = 9.8 Hz, H-6), 3.54 (1H, *br.d*, *J* = 9.8 Hz, H-5), 3.81 (2H, *s*, H-7″), 4.02 (1H, *m*, H-5′), 4.08-4.14 (2H, H-2′, H-4′), 4.23 (1H, *t*, *J* = *8.8* Hz, H-3′), 4.80 (1H, *dd*, *J* = 11.7, 5.9 Hz, Ha-6′), 4.93 (1H, *d*, *J* = 7.8 Hz, H-1′), 4.98 (1H, *br.d*, *J* = 17.4 Hz, Ha-15), 5.02 (1H, *br.d*, *J* = 11.7 Hz, H_b-6′), 5.27 (1H, *br.d*, *J* = 17.4 Hz, H_b-15), 7.02 (1H, *br.s*, H-3), 7.13 (2H, *d*, *J* = 8.3 Hz, H-3″, H-5″), 7.37 (2H, *d*, *J* = 8.3 Hz, H-2″, H-6″). For ^{13}C NMR spectra, see: Table 1. HR-FABMS *m*/*z*: 557.2024 $[M - H]^-$; found for $C_{29}H_{33}O_{11}$; required *m*/*z*: 557.2023.

3.9. Lanceocrepidiaside F (*6*)

$[\alpha]_{D^{26}} = +70.2^\circ$ (MeOH, *c* 0.61). UV λ (MeOH) nm (log ε): 224 (4.20), 278 (3.60), 282 (3.58). IR ν_{max} (film) cm^{-1}: 3380, 1704, 1614, 1590, 1516, 1448, 1230, 1078. ^{1}H NMR (C_5D_5N): δ 0.78 (3H, *d*, *J* = 7.5 Hz, H-14), 1.39–1.51 (2H, Ha-8, Ha-9), 1.93 (1H, *br.d*. *J* = 12.6 Hz, H_b-8), 2.59–2.65 (2H, H_b-9, H-10), 3.16 (1H, *m*, H-7), 3.48 (1H, *dd*, *J* = 10.6, 1.6 Hz, H-5), 3.80 (2H, *s*, H-7″), 3.98 (1H, *m*, H-5′), 4.05 (1H, *t*, *J* = 8.6 Hz, H-4′), 4.09 (1H, *dd*, *J* = 7.6, 8.6 Hz, H-2′), 4.19 (1H, *t*, *J* = 8.6 Hz, H-3′), 4.55 (1H, *dd*, *J* = 10.6, 9.3 Hz, H-6′), 4.75 (1H, *dd*, *J* = 11.7, 6.1 Hz, H-6′), 4.92 (1H, *dd*, *J* = 11.7, 1.9 Hz, H_b-6′), 4.96 (1H, *d*, *J* = 7.6 Hz, H-1′), 5.08 (1H, *br.d*, *J* = 18.7 Hz, H a-15), 5.19 (1H, *br.d*, *J* = 18.7 Hz, H_b-15), 5.51 (1H, *d*, *J* = 3.0 Hz, Ha-13), 6.28 (1H, *d*, *J* = 3.0 Hz, H_b-13), 6.92 (1H, *dd*, *J* = 3.8, 1.7 Hz, H-3), 7.12 (2H, *d*, *J* = 8.5 Hz, H-3″, H-5″), 7.37 (2H, *d*, *J* = 8.5 Hz, H-2″, H-6″). For ^{13}C NMR spectra, see: Table 1. HR-FABMS *m*/*z*: 573.1944 $[M - H]^-$; found for $C_{29}H_{33}O_{12}$; required *m*/*z*: 573.1972.

3.10. $NaBH_4$ reduction of youngiaside A (*11*)

Youngiaside A (**11**) (23.0 mg) dissolved in MeOH (1 ml) was reduced by $NaBH_4$ (33 mg) under stirring for 10 min in an ice-bath. After acidifying the solution with AcOH, the mixture was concentrated in vacuo to give a residue which was purified over silica gel (5 g) with $CHCl_3$–MeOH with increasing amounts of MeOH as elements. Fractions eluted with 10–12% MeOH in $CHCl_3$ gave, on evaporation, dihydroyoungiaside A (11.1 mg) which was identical ($[\alpha]_D$, ^{1}H and ^{13}C NMR) with natural lanceocrepidiaside A (**1**).

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