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ALANGICADINOSIDES A–E: SESQUITERPENE GLYCOSIDES FROM LEAVES OF *ALANGIUM PREMNIFOLIUM*

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Key Word Index—*Alangium premnifolium*; Alangiaceae; cadinane; sesquiterpene glycoside; alangicadinosides A–E.

Abstract—From leaves of *Alangium premnifolium*, harvested on Okinawa island, Japan, five glycosides of cadinane derivatives, alangicadinosides A–E, were isolated. Their structures were determined mainly from spectroscopic evidence.

INTRODUCTION

In a previous investigation of an Alangiaceous plant, *Alangium platanifolium* var. *trilobum*, several glycosides were isolated [1–3]. During the course of our studies on the genus *Alangium*, we examined the constituents of leaves of *Alangium premnifolium* Ohwi collected on Okinawa island, Japan, [4] and isolated five new sesquiterpene glycosides; alangicadinosides A–E. This paper deals with the structural elucidation of the new compounds.

RESULTS AND DISCUSSION

Air-dried leaves of *Alangium premnifolium* were extracted with methanol. The methanol extract was separated by solvent partition, and the *n*-BuOH-soluble fraction thus obtained was used for further separation by highly porous synthetic resin (Diaion HP-20) and silica gel column chromatography, droplet counter-current chromatography (DCCC) and reversed-phase open column chromatography and preparative HPLC.

Alangicadinoside A (**1**), $[\alpha]_D$ − 30.5°, was obtained as an amorphous powder, whose elemental composition was established as $C_{27}H_{42}O_{13}$ by negative-ion HR-FAB mass spectrometry. The ^{13}C NMR spectrum showed the presence of an aromatic ring, two methyl groups (one of which must be on the aromatic ring from the chemical shift δ2.30 in the ^1H NMR spectrum), an isopropyl group, a methylene carbon, and a methine carbon, which must have a hydroxyl function from its deshielded chemical shift (δ76.9). The remaining 12 signals were attributed to those of two units of β-glucopyranose [δ_C 103.5 with δ_H 4.43 (J = 8 Hz) and δ_C 107.9 with δ_H 4.45 (J = 8 Hz)]. The aromatic carbon signals consisted of five singlets, two of which were substituted by hydroxyl groups. The ^1H–^1H COSY spectrum revealed the connectivity of all proton atoms on the saturated ring system, and combination with the ^{13}C–^1H COSY spectrum facilitated the assignment of all the carbon atoms. The disposition of an aromatic proton, and two hydroxyl and methyl groups, and the positions to which the saturated ring was connected were determined by precise inspection of the long-range ^{13}C–^1H COSY spectrum (J = 7.5 Hz). The correlation of H-5 and C-7 indicated that the isopropyl group must be located close to the aromatic proton, and the correlations of C-3 and H-5, and C-5 and H_3-14 revealed the disposition of all substituents, as shown in structure **1**. This structure is biosynthetically in accordance with the isoprene rule and the skeleton is called a cadinane, or more strictly a calamenene. Other correlations observed were reasonably explained and allowed the unequivocal assignment of the aromatic carbon signals (see **1** in Fig. 1).

There were three hydroxyl groups to which two β-glucopyranoses could be attached. In the NOE experiments, irradiation of the H_3-14 signals affected the anomeric proton signal, δ4.45 (H-1′). A significant NOE enhancement of the signal at δ4.43 (H-1″), came from irradiation of δ4.16 (H-9). Thus, the hydroxyl groups, to which the β-glucopyranoses were attached, were concluded to be at the C-3 and C-9 positions. Therefore, the structure of alangicadinoside A is depicted as **1**. As to the stereochemistry, the relative relationships of the three substituents on the saturated carbon atoms were

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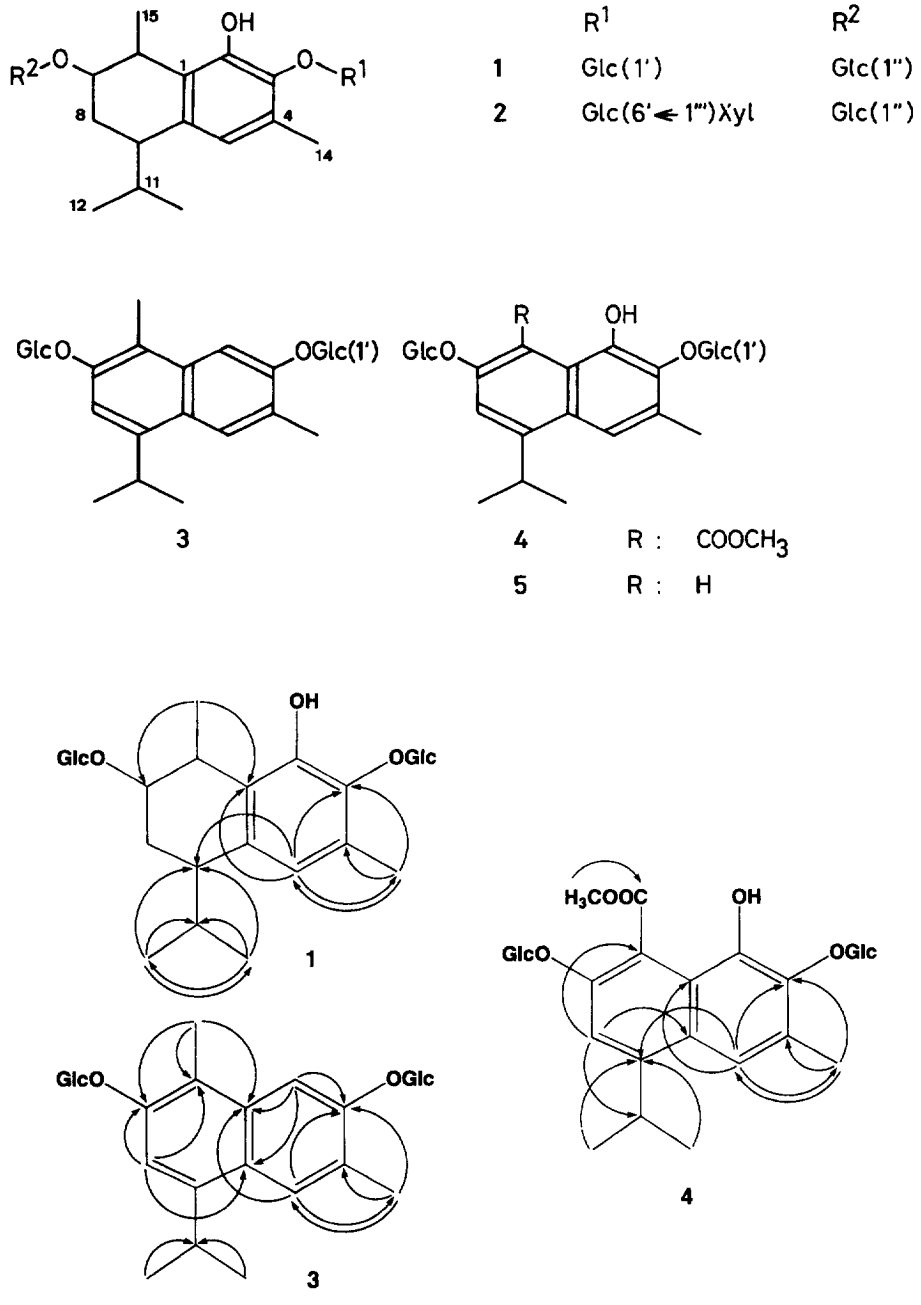

Fig. 1. The selected diagnostic C–H long-range correlations (J = 7.5 Hz) of alangicadinosides A (**1**), C (**3**) and D (**4**) obtained from the ^{13}C–^{1}H long-range COSY spectrum. The arrowheads indicate carbon atoms and the tails indicate protons.

expected to be as follows. The proton signal resonating at δ4.16 was assigned as that of the C-9 position and coupled as *dt* (J = 4 and 13 Hz). The triplet coupling constant with 13 Hz indicated that the proton at the C-10 position and the axial proton at the C-8 position form a dihedral angle of nearly 180° with the proton at the C-9 position. Thus, the methyl and hydroxyl groups were in the equatorial orientation. The NOE enhancement of the signal intensity of H-11 (1.9%), on irradiation at H-9, implied that the isopropyl moiety must be oriented in the axial position. However, to account for the coupling constant between H-7 and H-8ax (J = 7 Hz), a skewed conformation is required to make the isopropyl group in the pseudo-axial orientation.

Alangicadinoside B (**2**), $[\alpha]_D$ − 55.5°, was obtained as an amorphous powder, whose molecular composition, $C_{32}H_{50}O_{17}$, showed a five-carbon excess compared with alangicadinoside A. The ^{13}C and ^{1}H NMR spectra showed that the aglycone portion was the same as that of alangicadinoside A, and the three signals at δ_C 103.8

Table 1. ^{13}C NMR data for alangicadinosides A–E (**1**–**5**) (100 MHz, CD_3OD)

C	1	2	3*	4	5
1	129.3	130.3	135.0	122.9	127.5a
2	147.7	147.5	108.5	145.0	145.3
3	143.3	143.4	155.7	142.6	141.5
4	130.2	130.3	126.5	132.0	130.6
5	122.4	122.6	125.3	116.4	115.9b
6	136.4	136.5	124.0	127.7	127.2a
7	44.6	44.6	143.5	149.1	147.0
8	24.1	24.1	113.2	114.5	115.8b
9	76.9	77.2	153.6	152.5	155.8
10	34.0	34.1	118.3	117.2	104.7
11	35.9	35.9	28.8	30.2	29.8
12	19.3	19.3	23.7	23.7	23.8
13	22.4	22.4	23.8	23.8	23.9
14	17.2	17.2	17.4	18.3	18.4
15	14.6	14.8	11.5	172.6	
CH_3O–				53.1	
Glucose at 3-*O*					
1′	107.9	107.8	104.1	108.0	108.2
2′	75.5	75.4a	75.3	75.5	75.6
3′	78.3a	78.3b	79.2a	78.6a	78.5c
4′	71.7b	71.7c	71.6b	71.5b	71.4d
5′	78.0a	78.0b	78.91a	78.1a	78.21c
6′	62.8c	62.8	62.7c	62.7c	62.50e
Glucose at 9-*O*					
1″	103.5	103.8	103.0	103.9	102.6
2″	75.3	75.3a	75.1	75.2	75.1
3″	78.4a	78.4b	78.91a	78.4a	78.21c
4″	71.2b	71.7c	71.55b	71.1b	71.2d
5″	78.1a	78.0b	78.87a	78.0a	78.15c
6″	62.5c	70.1	62.6c	62.4c	62.45e
Xylose					
1‴		105.5			
2‴		75.5a			
3‴		77.6			
4‴		71.2c			
5‴		66.9			

*In pyridine-d_5.

Signals with the same letters in each column may be interchangeable.

[with δ_H4.43 (J = 8 Hz)], 105.5 [with δ_H4.27 (J = 7 Hz)), and 107.8 (with δ_H4.46 (J = 8 Hz)] were expected to be anomeric carbon signals of sugar moieties, indicating that alangicadinoside B was a triglycoside. Two signals, appearing at δ_C62.8 and 66.9, had two protons each and were assigned to those of the C-6 position of β-glucopyranose and the C-5 position of β-xylopyranose, respectively. GLC analysis of the sugar portion of **2** revealed that it contained a glucose moiety and a xylose moiety in a ratio 2:1. Thus, the remaining triplet signal at δ_C70.1 should be due to that of the C-6 position of β-glucopyranose, to which the xylose moiety is attached. As the ^{13}C and ^1H NMR chemical shifts of alangicadinosides A and B were essentially the same, the two sugar units must be located at the C-3 and C-9 positions. Even precise inspection of the ^1H–^1H COSY spectrum of **2** to determine which position had the diglycoside unit was unsuccessful because of many overlapped sugar ring protons. Therefore, ^1H–^1H correlation was performed using the undeca-acetate (**2a**). First, in the NOE experiments, the enhancement of the H-9 signal (3.2%) on irradiation of the anomeric proton at δ4.69 enabled us to assign it to the glucose at the C-9 position. Second, from the H–H COSY spectrum of the acetate, this anomeric proton was found to be correlated with the protons at δ4.69 and δ4.24, which were expected to be the C-6 position of either glucose units from the coupling pattern. As one set of protons at the C-6 position of another glucose unit appeared at δ3.51 and δ3.81, the protons in question were expected to be affected by acylation induced downfield shifts. Thus, the diglycoside is located at the hydroxyl group at the C-3 position and the unsubstituted glucose must be placed on that at the C-9 position.

Alangicadinosides A (**1**) and B (**2**) showed essentially the same Cotton effects in their CD spectra, therefore their three chiral centres must have the same absolute configuration, however, they remain to be determined.

Alangicadinoside C (**3**), $[\alpha]_D$ −37.9°, was obtained as needles, whose elemental composition analysed for $C_{27}H_{38}O_{12}$. The ^{13}C NMR spectrum indicated the presence of 10 aromatic carbon signals with two oxygen functions and five aliphatics: four methyl and one methine signals. The remaining 12 signals were assigned to two sets of β-glucopyranose moieties, which were the same as alangicadinoside A (**1**). By comparison with the skeleta of the aforementioned compounds, alangicadinoside C (**3**) probably had a fully aromatized ring system, such as a naphthalene skeleton, instead of the tetralin skeleton in alangicadinoside A (**1**). The disposition of one hydroxyl and other functional groups on the naphthalene skeleton may be similar to that in alangicadinosides A and B. This was confirmed by means of two-dimensional NMR spectroscopy, especially the long-range ^{13}C–^1H COSY spectrum (see **3** in Fig. 1). Three aromatic proton signals appeared as singlets, which was expected from the established disposition of functional groups. These results indicated structure **3** for alangicadinoside C.

Alangicadinoside D (**4**), $[\alpha]_D$ −45.0°, was obtained as an amorphous powder. The ^{13}C and ^1H NMR spectra indicated the presence of carbomethoxyl groups and the composition, $C_{28}H_{38}H_{15}$, analysed by HR-FAB mass spectrometry, indicated that one of the methyl groups in alangicadinoside A (**1**) was oxidized to carboxylic acid, which had then been methylated. The aromatic methyl carbon, possessed crossed peaks with the proton at the C-5 position in the long-range ^{13}C–^1H COSY spectrum (see **4** in Fig. 1). The isopropyl methyl signals were apparent in the ^1H NMR spectrum. Hence, the structure of the aglycone portion of alangicadinoside D (**4**) was established as shown. NOE experiments indicated that two glucoses were linked to the hydroxyl groups at the C-3 and C-9 positions, which was similar to that in alangicadinosides A, B and C.

Alangicadinoside E (**5**), $[\alpha]_D$ − 53.1°, was obtained as crystals, mp 215–218°, and its elemental composition was determined as $C_{26}H_{36}O_{13}$. The ^{13}C NMR spectrum indicated that **5** also had a naphthalene skeleton with two oxygen functions. The ^1H NMR spectrum showed the presence of three aromatic protons, two (δ7.15 and 7.61) of which were *m*-coupled (J = 2 Hz) to each other. As the proton resonating at δ7.15 was determined to be at the C-8 position in the NOE experiment, the other signal must be placed at the C-10 position. This means that the C-15 methyl group was oxidized to carboxylic acid. This was then methylated to form alangicadinoside D (**4**), whereas it was lost by decarboxylation to complete the biosynthesis of alangicadinoside E (**5**). The positions of sugar moieties were also determined in the NOE experiments. Thus, the structure of alangicadinoside E was established as **5**.

Some cadinane derivatives have been found in plant sources. The liverwort, *Heteroscyphus planus*, produces cadinane derivatives [5], and a Malvaceous plant, *Azanza garckeana*, contains azanone A [6], which has an *o*-naphthoquinone structure. Diol structures, probably derived from the aglycone of alangicadinoside A through aromatization and hydrolysis, were easily oxidized to *o*-quinone. In *Alangium premnifolium*, 2,3-dihydroxyl or 3-monohydroxyl derivatives, endogenously formed, were once glucosylated at the C-3 positions, and these may be diverted from further oxidation to an *o*-quinone skeleton.

EXPERIMENTAL

General. Mp uncorr.; ^1H and ^{13}C NMR at 400 MHz and 100 MHz, respectively. EI-MS: 70 eV; The DCCC was equipped with 500 columns (Φ = 2 mm, l = 40 cm). The ascending method was used with $CHCl_3$–MeOH–H_2O–*n*-PrOH (9:12:8:2), and 5 g frs were collected and numbered according to the elution of mobile phase. Prep. HPLC was performed with ODS (Inertsil, GL Science, Tokyo, 20 mm × 250 mm column) with aq. MeOH (6 ml min^{-1}).

Plant material. Leaves of *A. premnifolium* were collected at Nakagami-gun, Okinawa in August (1990). The plant was identified by one of the authors (A.T.) and a voucher specimen (AP-90-Okinawa) was deposited in the Herbarium of Institute of Pharmaceutical Sciences, Hiroshima University School of Medicine.

Isolation procedure. Air-dried leaves of *A. premnifolium* (5.72 kg) was extracted with MeOH (30 l × 3). The MeOH extract was concd to about 2.5 l and 150 ml H_2O and 350 ml MeOH added to give 95% aq. MeOH. This soln was extracted with 3 l of *n*-hexane (200 g) and then concd. The concte was suspended in 1.5 l of H_2O and then extracted with EtOAc (1 l × 2, 52.1 g) and *n*-BuOH (1.5 l. and 1 l., 139 g), successively. The *n*-BuOH soluble fr. (138 g) was separated by highly porous synthetic resin, Diaion HP-20 (Mitsubishikasei Co. Ltd, Tokyo) (70 mm × 650 mm column) with stepwise increases of MeOH contents in H_2O [20% (6 l.), 40% (8 l.), 60% (10 l.), 80% (10 l.) MeOH in H_2O and MeOH (8 l)], frs of 2 l. being collected. The residue (32.6 g) of 40% MeOH eluate was subjected to silica gel CC (600 g) with increasing amounts of MeOH in $CHCl_3$ [$CHCl_3$ (3 l.), $CHCl_3$–MeOH (39:1, 6 l), (19:1, 6 l), (37:3, 6 l), (9:1, 9 l.), (7:1, 9 l.), (17:3, 6 l.), (4:1, 6 l.), (3:1, 3 l.), and (7:3, 3 l.)], frs of 500 ml were collected. The residue (1.38 g) of the 15% MeOH eluate was separated by reversed-phase open CC (RPCC) [ODS (Cosmosil), 50 mm × 250 mm column], 10% MeOH (1.5 l) → 70% MeOH (1.5 l), linear gradient, frs of 10 g collected. The residue (67 mg) of frs 212–221 was purified by DCCC, followed by prep. HPLC (MeOH–H_2O, 9:11) of the frs 28–34 (26 mg) gave 13 mg of alangicadinoside A (**1**).

The residue (121 mg) of frs 199–211 of RPCC was purified by DCCC (fractions 19–23) and prep. HPLC (MeOH–H_2O, 9:11) to give 10 mg of alangicadinoside B (**2**). The purification of the DCCC frs 27–30 (17 mg) by prep. HPLC yielded 4.9 mg of alangicadinoside E (**5**) as needles.

The residue (178 mg) of frs 185–198 of RPCC was purified by DCCC (fractions 22–30) and Sephadex LH-20 CC (20 mm × 130 cm, MeOH, frs of 10 g being collected). From frs 40–45, 9 mg of alangicadinoside C (**3**) was crystallized. Purification of the mother liquor by prep. HPLC (MeOH–H_2O, 7:13) gave further amounts of **3** (3 mg) and 12 mg of alangicadinoside D (**4**).

Alangicadinoside A (**1**). Amorphous powder, $[\alpha]_D^{23}$ − 30.5° (MeOH; *c* 0.79), UV λ_{max}^{MeOH} nm (log ε): 209 (4.35), 223sh (3.96), 280 (3.10); ^{13}C NMR: see Table 1; ^1H NMR (CD_3OD): δ0.78 (3H, *d*, J = 7 Hz, H_3 on δ_C 19.3), 1.05 (3H, *d*, J = 7 Hz, H_3 on δ_C 22.4), 1.11 (3H, *d*, J = 7 Hz, H_3-15), 1.87 (H, *dt*, J = 8, 13 Hz, H-8ax), 2.00 (H, *br dd*, J = 4, 13 Hz, H-8eq), 2.11 (H, *m*, 11-H), 2.30 (3H, *s*, H_3-14), 2.75 (H, *br t*, J = 6 Hz, H-7), ≈ 3.35 (H-10), 3.70 (H, *dd*, J = 5, 12 Hz, H-6′a or 6″a), 3.74 (H, *dd*, J = 5, 12 Hz, H-6″a or 6′a), 3.85 (2H, *dd*, J = 2, 12 Hz, H-6′b and 6″b), 4.16 (H, *dt*, J = 4, 13 Hz, H-9), 4.43 (H, *d*, J = 8 Hz, H-1″), 4.45 (H, *d*, J = 8 Hz, H-1′), 6.50 (H, *s*, H-5); CD λ nm ($\Delta\varepsilon$): 220 (0.00), 234 (− 3.43), 247 (− 0.16), 279 (− 2.14) (MeOH, *c* 0.00472); HR-FAB-MS (negative centroid) *m/z*: 573.2561 ($C_{27}H_{41}O_{13}$ requires 573.2546).

Alangicadinoside B (**2**). Amorphous powder; $[\alpha]_D^{23}$ − 55.5° (MeOH; *c* 0.54), UV λ_{max}^{MeOH} nm (log ε): 208 (4.51), 223sh (3.94), 279 (3.05); ^{13}C NMR: see Table 1; ^1H NMR (CD_3OD): δ0.78 (3H, *d*, J = 7 Hz, on δ_C 19.3, H_3-12 or H_3-13), 1.06 (3H, *d*, J = 7 Hz, on δ_C 22.4, H_3-13 or 12), 1.11 (3H, *d*, J = 7 Hz, H_3-15), 1.88 (H, *dt*, J = 7, 13 Hz, H-8ax), 2.00 (H, *br dd*, J = 4, 13 Hz, H-8eq), 2.09 (H, *sept. d*, J = 7, 8 Hz, H-11), 2.29 (H, 3H, *s*, H_3-14), 2.74 (H, *t*, J = 6 Hz, H-7), 3.20 (H, *dd*, J = 10, 11, H-5‴a). 3.23 (H, *dd*, J = 8, 9 Hz, H-2″), 3.25 (H, *dd*, J = 7, 9 Hz, H-2‴), 3.34 (H, *t*, J = 9 Hz, H-3″), 3.35 (H, *m*, H-10), 3.50 (H, *dd*, J = 8, 9 Hz), 3.72 (H, *dd*, J = 5, 12 Hz, H-6′a or 6″a), 3.77 (H, *dd*, J = 5, 11 Hz, H-6″a or 6′a), 3.85 (H, *dd*, J = 2, 12 Hz, H-6′b or 6″b), 3.87 (H, *dd*, J = 5, 11 Hz, H-5‴b), 4.10 (H, *dd*, J = 2, 11 Hz, H-6″b or 6′b), 4.16 (H, *dt*, J = 4, 13 Hz, H-9), 4.27 (H, *d*, J = 7 Hz, H-1‴), 4.43 (H, *d*, J = 8 Hz, H-1″), 4.46 (H, *d*, J = 8 Hz, H-1′), 6.51 (H, *s*,

H-5); CD λ nm ($\Delta\varepsilon$): 211 (0.00), 217 (− 0.33), 234 (− 3.41), 249 (− 0.20), 279 (− 2.46) (MeOH, *c* 0.00324); HR-FAB-MS (negative centroid) *m/z*: 705.3006 ($C_{32}H_{49}O_{17}$ requires 705.2970).

Alangicadinoside C (**3**). Crystals (MeOH), mp 174–177°; $[\alpha]_D^{23}$ − 37.9° (pyridine, *c* 0.66). UV λ_{max}^{MeOH} nm (log ε): 220inf (4.76), 239 (5.07), 290 (3.98), 331 (3.48); ^{13}C NMR: see Table 1; ^{1}H NMR (pyridine-d_5): δ1.34 (3H, *d*, *J* = 7 Hz, on δ_C 23.7, H_3-12 or H_3-13), 1.41 (3H, *d*, *J* = 7 Hz, on δ_C 23.8, H_3-13 or H_3-12), 2.63 (3H, *s*, H_3-14), 2.92 (3H, *s*, H_3-15), ≈ 4.1 [*m*, one of the signals on δ_C 78.9 (H-5′ or 5″)], 4.23 (H, *ddd*, *J* = 2, 5, 8 Hz, H-5″ or 5′), 3.68 (H, *septet*, *J* = 7 Hz, H-11), 4.58 (H, *dd*, *J* = 2, 12 Hz, H-6′b or 6″b), 4.62 (H, *dd*, *J* = 2, 12 Hz, H-6″b or 6′b), 5.62 (H, *d*, *J* = 7 Hz, H-1′), 5.83 (H, *d*, *J* = 7 Hz, H-1″), 7.83 (H, *s*, H-8), 8.01 (H, *s*, H-5), 8.18 (H, *s*, H-2); HR-FAB-MS (negative centroid) *m/z*: 553.2292 ($C_{27}H_{37}O_{12}$ requires 553.2284).

Alangicadinoside D (**4**). Amorphous powder. $[\alpha]_D^{23}$ − 45.0° (MeOH: *c* 0.81); UV λ_{max}^{MeOH} nm (log ε): 219 (4.45), 245 (4.62), 306 (3.69); ^{13}C NMR: see Table 1; ^{1}H NMR (CD_3OD): δ 1.36 (3H, *d*, *J* = 7 Hz, H_3-12 or H_3-13), 1.38 (3H, *d*, *J* = 7 Hz, H_3-13 or H_3-12), 2.54 (3H, *s*, H_3-14), 3.55 (H, *dd*, *J* = 8, 9 Hz), 3.68 (H, *septet*. *J* = 7 Hz, H-11), 3.70 (H, *dd*, *J* = 5, 12 Hz, H-6′a or 6″a), 3.75 (H, *d*, *J* = 5, 12 Hz, H-6″a or 6′a), 3.86 (2H, *dd*, *J* = 2, 12 Hz, H-6′b and 6″b), 3.90 (3H, *s*, –COO$\underline{H}_3$), 4.60 (H, *d*, *J* = 8 Hz, H-1′), 4.93 (H, *d*, *J* = 8 Hz, H-1″), 7.41 (H, *s*, H-8), 7.45 (H, *s*, H-5); HR-FAB-MS (negative centroid) *m/z*: 613.2101 ($C_{28}H_{37}O_{15}$ requires 613.2132).

Alangicadinoside E (**5**). Crystals (MeOH), mp 215–218°, $[\alpha]_D^{23}$ − 53.1° (MeOH, *c* 0.32); UV λ_{max}^{MeOH} nm (log ε): 222sh (4.44), 240 (4.58), 290 (3.62), 333 (3.17); ^{13}C NMR: see Table 1; ^{1}H NMR (CD_3OD): δ1.34 (3H, *d*, *J* = 7 Hz, H_3-12 or H_3-13), 1.35 (3H, *d*, *J* = 7 Hz, H_3-12 or H_3-13), 2.52 (3H, *s*, H-14), 3.57 (H, *dd*, *J* = 8, 9 Hz), 3.64 (H, *septet*, *J* = 7 Hz, H-11), 3.76 (2H, *dd*, *J* = 5, 12 Hz, H-6′a and 6″a), 3.87 (H, *dd*, *J* = 2, 12 Hz, H-6′b or 6″b), 3.92 (H, *dd*, *J* = 2, 12 Hz, H-6″b or 6′b), 4.60 (H, *d*, *J* = 8 Hz, H-1′), 5.03 (H, *d*, *J* = 8 Hz, H-1″), 7.15 (H, *d*, *J* = 2 Hz, H-8), 7.35 (H, *s*, H-5), 7.61 (H, *d*, *J* = 2 Hz, H-10); HR-FAB-MS (negative centroid) *m/z*: 555.2089 ($C_{26}H_{35}O_{13}$ requires 555.2078).

Alangicadinoside B undeca-acetate (**2a**). A small amount of **2** (4.1 mg) was acetylated with a mixture of Ac_2O (one drop) and pyridine (one drop) for 18 hr at 20°. The reagents were evapd under a stream of N_2 and the product purified by prep. TLC (precoated silica gel plate, Merck GF_{254}, 0.25 mm thick, 5 cm × 10 cm, developed for 10 cm with benzene–Me_2CO, 5:1, eluted with $CHCl_3$–MeOH, 9:1) to give 4.4 mg (65%) of alangicadinoside B undeca-acetate. ^{1}H NMR ($CDCl_3$): δ0.75 (3H, *d*, *J* = 7 Hz, H_3-12 or H_3-13), 0.98 (3H, *d*, *J* = 6 Hz, H_3-15), 1.06 (3H, *d*, *J* = 7 Hz, H_3-13 or 12), 1.74 (H, *dt*, *J* = 8, 13 Hz, H-8ax), 1.86 (H, *br d*, *J* = 11 Hz, H-8eq), 2.01 (3H, *s*), 2.017 (3H, *s*), 2.022 (6H, *s*), 2.03 (3H, *s*), 2.05 (6H, *s*), 2.06 (3H, *s*), 2.07 (3H, *s*), 2.08 (3H, *s*, C$\underline{H}_3$CO– × 10 on aliphatic OH), 2.15 (H, *m*, H-11), 2.24 (3H, *s*, H_3-14), 2.35 (3H, *s*, C$\underline{H}_3$CO– on phenolic OH), 2.82 (H, *t*-like, H-7), 3.14 (H, *m*, H-10), 3.29 (H, *dd*, *J* = 8, 12 Hz, H-5‴a), 3.51 (H, *dd*, *J* = 6, 10 Hz, H-6′a), 3.57 (*m*, H-5′), 3.72 (H, *ddd*, *J* = 3, 5, 10 Hz, H-5″), 3.82 (H, *dd*, *J* = 2, 10 Hz, H-6′b), 4.08 (H, *dd*, *J* = 5, 12 Hz, H-5‴b), ≈ 4.1 (H, *m*, H-9), 4.16 (H, *dd*, *J* = 2, 12 Hz, H-6″a), 4.24 (H, *dd*, *J* = 5, 12 Hz, H-6″b), 4.43 (H, *d*, *J* = 6 Hz, H-1‴), 4.69 (H, *d*, *J* = 8 Hz, H-1″), 4.81 (H, *dd*, *J* = 6, 8 Hz, H-2‴), 4.88 (H, *dt*, *J* = 5, 8 Hz, H-4‴), 5.04 (H, *dd*, *J* = 8, 10 Hz, H-2″), 5.09 (H, *t*, *J* = 8 Hz, H-3‴), 5.10 (H, *t*, *J* = 10 Hz, H-4″), 5.12 (H, *t*, *J* = 10 Hz, H-4′), 5.15 ~ 5.20 (3H, H-1′, 2′ and 3′), 5.26 (H, *t*, *J* = 10 Hz, H-3″), 6.92 (H, *s*, H-5); FAB-MS (*m*-nitrobenzyl alcohol) *m/z*: 1167 $[M + H]^+$, 1189 $[M + Na]^+$ (+ NaI), 1205 $[M + K]^+$ (+ KI); EI-MS *m/z* (rel. int.): 622 (2), 580 (2), 547 (5) [Xyl $(OAc)_3$Glu$(OAc)_3$ oxonium ion]$^+$, 331 (8) [Glu$(OAc)_4$ oxonium ion]$^+$, 259 (85) [Xyl$(OAc)_3$ oxonium ion]$^+$, 199 (39), 189 (17), 169 (21), 157 (43), 139 (43), 43 (100).

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