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Sesquiterpene Glycosides from *Crepidiastrum keiskeanum* NAKAI

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Five new guaiane-type sesquiterpene glycosides have been isolated from *Crepidiastrum keiskeanum* NAKAI (Compositae). Their structures were elucidated on the basis of spectral data and several chemical transformations.

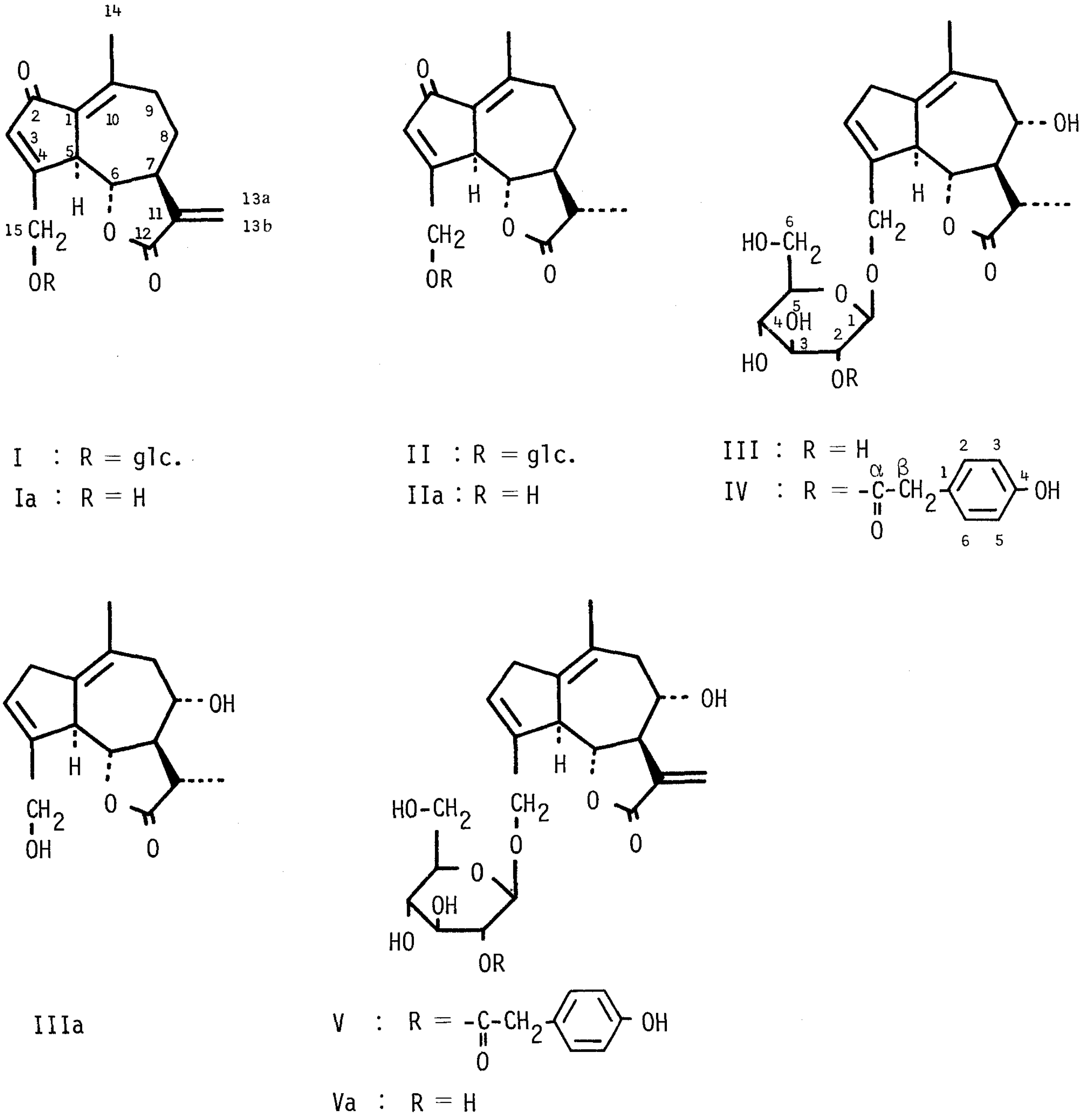
Keywords——*Crepidiastrum keiskeanum*; Compositae; sesquiterpene glycoside; sesquiterpene lactone; crepidiaside A; crepidiaside B; crepidiaside C; crepidiaside D; crepidiaside E

In connection with a study on the sesquiterpene glycosides of some plants in Compositae, we have also investigated *Crepidiastrum keiskeanum* NAKAI (syn. *Lactuca keiskeana* MAKINO) and isolated five new guaianolide-type sesquiterpene glycosides, crepidiasides A—E. Their structures were elucidated on the basis of spectroscopic studies and some chemical transformations.

Crepidiaside A (I): $C_{21}H_{26}O_9 \cdot H_2O$, $[\alpha]_D$ $-34.5°$. Its infrared (IR) spectrum showed hydroxyl (3420 cm^{-1}), γ-lactone (1765 cm^{-1}), and α,β-unsaturated carbonyl group (1680 cm^{-1}) absorptions. The ultraviolet (UV) spectrum showed an absorption maximum at 253 nm (α,β-unsaturated carbonyl). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum showed two doublet signals at δ 5.35 (1H, d, $J=3.1$ Hz) and 6.15 (1H, d, $J=3.2$ Hz), characteristic of exocyclic methylene protons of the α-methylene-γ-lactone grouping common in sesquiterpene lactones. Furthermore, a vinyl methyl signal at δ 2.45 (3H, br s) and an olefinic proton signal at δ 6.90 (1H, br s) were observed. These two signals were shifted downfield compared with those of common sesquiterpenes,[1] presumably due to the deshielding effect of a conjugated carbonyl, as with the C-2 carbonyl of lactucin.[2] In the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum, twenty-one signals were observed, including six signals due to a glucopyranosyl moiety. Two carbonyl signals were observed at δ 169.1 (unsaturated lactone) and 194.9 (unsaturated ketone).

Acid hydrolysis of I afforded glucose, and enzymatic hydrolysis with crude hesperidinase afforded an aglycone (Ia), mp 150—153 °C. The mass spectrum (MS) of Ia showed a molecular ion peak at m/z 260 in agreement with the molecular formula $C_{15}H_{16}O_4$. The IR spectrum showed hydroxyl (3430 cm^{-1}), γ-lactone (1765 cm^{-1}), and α,β-unsaturated carbonyl group (1670 cm^{-1}) absorptions. The ^{1}H-NMR spectrum showed two doublet signals at δ 5.50 (1H, d, $J=3.1$ Hz) and 6.19 (1H, d, $J=3.2$ Hz), hydroxymethyl signals at δ 4.59 (1H, br d, $J=18$ Hz) and 4.87 (1H, br d, $J=18$ Hz), and an olefinic proton signal at δ 6.45 (1H, br s). These signals were identical with those reported for 8-deoxylactucin.[2a,3] Thus, the structure of Ia was finally established by comparison (mp, IR, ^{1}H-NMR, MS) with the data for 8-deoxylactucin. We concluded that crepidiaside A is a sesquiterpene glucoside having the structure I. The anomeric structure of I was determined to be β from the $J_{H_1-H_2}$ value (7 Hz).

Crepidiaside B (II): $C_{21}H_{28}O_9$, mp 237—240 °C. $[\alpha]_D$ $-62.5°$. The IR spectrum showed



I : R = glc.
Ia : R = H

II : R = glc.
IIa : R = H

III : R = H
IV : R = $-\mathrm{C(=O)}-CH_2-C_6H_4-OH$

IIIa

V : R = $-\mathrm{C(=O)}-CH_2-C_6H_4-OH$
Va : R = H

Chart 1

hydroxyl ($3430\,cm^{-1}$), γ-lactone ($1770\,cm^{-1}$) and α,β-unsaturated carbonyl group ($1680\,cm^{-1}$) absorptions. The UV spectrum showed an absorption maximum at 253 nm (α,β-unsaturated carbonyl). The ^1H-NMR spectrum was similar to that of I except for the appearance of a methyl signal at δ 1.15 (3H, d, $J=6$ Hz) instead of two doublet signals due to exomethylene protons. A comparison of the ^{13}C-NMR spectrum of II with that of I showed a downfield shift of 8.1 ppm at C-12 (lactone carbonyl), suggesting that the exocyclic methylene at the γ-lactone ring had been converted to a methyl group.

Acid hydrolysis of II afforded glucose and enzymatic hyrolysis afforded an aglycone (IIa), which melted at 77 °C, and after solidification, melted again at 167—170 °C. The MS of IIa showed a molecular ion peak at m/z 262 in agreement with the molecular formula $C_{15}H_{18}O_4$. The ^1H-NMR spectrum showed a doublet methyl signal at δ 1.26 (3H, d, $J=7$ Hz), a vinyl methyl signal at δ 2.44 (3H, br s), hydroxymethyl signals at δ 4.55 (1H, br d, $J=18$ Hz) and 4.83 (1H, br d, $J=18$ Hz), and an olefinic proton signal at δ 6.43 (1H, br s). We determined the configuration of the C-13 methyl group at the γ-lactone to be α on the basis of Narayanan's rule.[4] The methyl group of IIa showed an upfield shift of 0.27 ppm in benzene-d_6 relative to chloroform-d_1 solution (Table III). These data were identical with those previously

Table I. ^{1}H-NMR Chemical Shifts and Coupling Constants

Proton No.	I	II	III	IV	V
Aglycone moiety					
3	6.90 (1H, br s)	6.89 (1H, br s)	6.10 (1H, br s)	5.99 (1H, br s)	5.98 (1H, br s)
13a	5.35 (1H, d, J=3.1 Hz)	1.15 (3H, d, J=6 Hz)	1.59 (3H, d, J=7 Hz)	1.66 (3H, d, J=7 Hz)	6.32 (1H, br s)
13b	6.15 (1H, d, J=3.2 Hz)				6.55 (1H, br s)
14	2.45 (3H, br s)	2.44 (3H, br s)	1.62 (3H, br s)	1.61 (3H, br s)	1.60 (3H, br s)
Sugar moiety					
1	4.92 (1H, d, J=7 Hz)	4.88 (1H, d, J=7 Hz)	4.91 (1H, d, J=7 Hz)	4.88 (1H, d, J=8 Hz)	4.90 (1H, d, J=8 Hz)
p-Hydroxyphenylacetic acid moiety					
β				3.78 (2H, s)	3.79 (2H, s)
2,6				7.34 (2H, d, J=8 Hz)	7.35 (2H, d, J=8 Hz)
3,5				7.12 (2H, d, J=8 Hz)	7.14 (2H, d, J=8 Hz)

Run at 89.55 MHz in pyridine-d_5 solution.

Table II. ^{13}C-NMR Chemical Shifts

Carbon No.	I	II	III	IV	V
Aglycone moiety					
1	131.8	131.7	136.5	136.3	136.9
2	194.9	195.0	37.5	37.5	37.5
3	134.6	134.4	129.0	127.5	127.8
4	169.1	169.5	142.2	141.5	141.3
5	50.1	49.8	52.3	52.8	53.0
6	84.1	83.8	82.5	82.2	82.5
7	52.6	55.6	62.9	62.4	58.9
8	24.4	25.9	70.4	70.3	68.8
9	37.2	37.5	46.5	46.4	46.6
10	152.5	152.8	126.9	126.8	126.6
11	139.7	41.3	42.2	42.1	139.8
12	169.1	177.2	178.5	178.4	169.9
13	118.2	12.2	16.1	16.1	121.3
14	21.6	21.4	23.0	23.0	23.0
15	68.8	68.8	68.2	69.0	69.0
Sugar moiety					
1	104.2	104.1	103.2	101.5	101.5
2	75.1	75.0	75.1	75.6	75.6
3	78.5	78.3	78.6	75.9	76.0
4	71.7	71.5	71.8	71.8	72.0
5	78.3	78.1	78.2	78.1	78.3
6	62.8	62.6	62.5	62.4	62.5
p-Hydroxyphenylacetic acid moiety					
α				171.3	171.4
β				41.0	41.0
1				125.3	125.4
2,6				130.8	131.0
3,5				116.2	116.2
4				157.7	157.8

Run at 22.5 MHz in pyridine-d_5 solution.

Table III. ^{1}H-NMR Chemical Shifts and Coupling Constants

Proton No.	Ia[a]	IIa[a]	IIa[b]	IIIa[c]
2,2′				3.03 (2H, br t, $J=20$ Hz)
3	6.45 (1H, br s)	6.43 (1H, br s)	6.59 (1H, br s)	5.85 (1H, br s)
5	3.65 (m)	3.62 (m)	2.88 (m)	3.47 (1H, br d, $J=10$ Hz)
6	3.65 (m)	3.62 (m)	2.88 (m)	3.63 (1H, t, $J=10$ Hz)
7				2.00 (1H, dt, $J=12$; 10 Hz)
8				3.60 (1H, dt, $J=10$; 2 Hz)
9α				2.53 (overlapped)
9β				2.17 (1H, dd, $J=14$; 2 Hz)
11				2.53 (overlapped)
13a	5.50 (1H, d, $J=3.1$ Hz)	1.26 (3H, d, $J=7$ Hz)	0.99 (3H, d, $J=7$ Hz)	1.42 (3H, d, $J=7$ Hz)
13b	6.19 (1H, d, $J=3.2$ Hz)			
14	2.46 (3H, br s)	2.44 (3H, br s)	2.46 (3H, br s)	1.74 (3H, br s)
15	4.59 (1H, br d, $J=18$ Hz)	4.55 (1H, br d, $J=18$ Hz)	4.33 (1H, br d, $J=18$ Hz)	4.34 (2H, br t, $J=16$ Hz)
15′	4.87 (1H, br d, $J=18$ Hz)	4.83 (1H, br d, $J=18$ Hz)	4.72 (1H, br d, $J=18$ Hz)	

[a] Run at 89.55 MHz in $CDCl_3$ solution. [b] Run at 89.55 MHz in C_6D_6 solution. [c] Run at 399.65 MHz in $CDCl_3$ solution.

published for jacquinelin.[2a,5] Thus, the structure of IIa was finally established by comparison (mp, ^{1}H-NMR, MS) with the data for jacquinelin. We concluded that crepidiaside B has the structure II.

Crepidiaside C (III): $C_{21}H_{30}O_9 \cdot 1/2H_2O$, $[\alpha]_D$ -65.1 °, mp 125—130 °C. The IR spectrum showed hydroxyl (3450 cm^{-1}) and γ-lactone ring (1760 cm^{-1}) absorptions. However, the UV spectrum did not show a characteristic absorption band near 253 nm (α,β-unsaturated carbonyl). The ^{1}H-NMR spectrum showed a doublet methyl signal at δ 1.59 (3H, d, $J=7$ Hz), a vinyl methyl signal at δ 1.62 (3H, br s) and an olefinic proton signal at δ 6.10 (1H, br s). A comparison of the ^{1}H-NMR spectrum of III with that of II showed upfield shifts at a vinyl methyl signal (Δ 0.82 ppm) and an olefinic proton signal (Δ 0.79 ppm). These results led us to presume that an α,β-unsaturated carbonyl group was lacking in III. A doublet methyl signal at δ 1.59 (3H, d, $J=7$ Hz) was shifted downfield by 0.44 ppm compared with that of II. This is characteristic of an α-oriented C-13 methyl group in an 8α-hydroxy-sesquiterpene lactone.[1]

Acid hydrolysis of III afforded glucose and enzymatic hydrolysis afforded an aglycone (IIIa). The MS of IIIa showed a molecular ion peak at m/z 264 in agreement with the molecular formula $C_{15}H_{20}O_4$. The high resolution ^{1}H-NMR spectrum showed a doublet methyl signal at δ 1.42 (3H, d, $J=7$ Hz), a vinyl methyl signal at δ 1.74 (3H, br s), a hydroxymethyl signal at δ 4.34 (2H, br t, $J=16$ Hz) and an olefinic proton signal at δ 5.85 (1H, br s). Decoupling experiments showed that the olefinic proton signal at δ 5.85 was coupled with the hydroxymethyl signal at δ 4.34. Furthermore, coupling constants among H-5, H-6, H-7 and H-8 were 10 Hz, and the coupling constant between H-7 and H-11 was 12 Hz. Thus, these protons are in anti-diaxial relationships. In the ^{13}C-NMR spectrum of III, C-15 (δ 68.2) was shifted downfield in comparison with common hydroxymethyl groups, indicating that the glycosidic position was at C-15. If the assumption is made that the absolute configuration of the C-7 side chain is as shown (as in all other known sesquiterpene lactones having authenticated stereochemistry), the structure of crepidiaside C can be concluded to be III.

Crepidiaside D (IV): $C_{29}H_{36}O_{11} \cdot H_2O$, $[\alpha]_D$ -40.1 °. The IR spectrum showed hydroxyl (3425 cm^{-1}) and γ-lactone ring (1755 cm^{-1}) absorptions. The UV spectrum showed an absorption maximum at 277 nm. The ^{1}H-NMR spectrum was similar to that of III except for the additional presence of A_2B_2 type signals in the aromatic region, and a methylene signal at δ 3.78 (2H, s).

Acid hydrolysis of IV afforded glucose. Treatment of IV with 2% sodium hydroxide afforded *p*-hydroxyphenylacetic acid and III. A comparison of the glucose signals in the ^{13}C-NMR spectrum of IV with those of III showed upfield shifts of 1.7 and 2.7 ppm at C-1 and C-3, respectively, and a downfield shift of 0.5 ppm at C-2, so we concluded that *p*-hydroxyphenylacetic acid is esterified at C-2 of the glucose moiety. Thus, crepidiaside D was assigned the structure IV.

Crepidiaside E (V): $C_{29}H_{34}O_{11} \cdot H_2O$, $[\alpha]_D$ −22.2°. The IR spectrum showed hydroxyl (3425 cm^{-1}) and γ-lactone ring (1750 cm^{-1}) absorptions. The UV spectrum showed an absorption maximum at 277 nm. The ^{1}H-NMR spectrum was similar to that of IV except for the appearance of exocyclic methylene signals at δ 6.32 (1H, br s) and 6.55 (1H, br s), instead of a doublet methyl signal. Thus, this compound has an exocyclic α-methylene-γ-lactone ring. Acid hydrolysis of V afforded glucose. Treatment of V with 2% sodium hydroxide afforded *p*-hydroxyphenylacetic acid.

When an α-methylene-γ-lactone is reduced with $NaBH_4$, the reduction product generally has an α-oriented methyl group.[6,7] When V was treated with $NaBH_4$, it afforded the sole product IV [based on IR, ^{1}H-NMR, and high-performance liquid chromatography (HPLC)]. This result also supported the view that III and IV have an α-oriented methyl group at C-11. Thus, crepidiaside E was assigned the structure V.

Experimental

Melting points were determined on a Yanaco MP-500 micromelting point apparatus and are uncorrected. Optical rotations were determined with a JASCO DIP-140 digital polarimeter. Circular dichroism (CD) spectra were recorded with a JASCO J-20A automatic recording spectropolarimeter. IR spectra were taken on a JASCO A-202 infrared spectrophotometer and UV spectra on a Shimadzu UV-360 recording spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on JEOL FX 90Q (89.55 and 22.5 MHz, respectively) and JEOL GX-400 (399.65 MHz) spectrometers. Chemical shifts are given on the δ (ppm) scale with tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; m, multiplet; br, broad). Gas chromatography (GC) was run on a Hitachi K 53 gas chromatograph. HPLC was run on a Kyowa Seimitsu model K 880 instrument.

Isolation——Air-dried whole plants (2.3 kg) of *C. keiskeanum* collected in autumn 1983, in Tokushima, Japan, were extracted twice with methanol under reflux. The extract was concentrated under reduced pressure and the residue was suspended in water. This suspension was extracted with ether and *n*-butanol to give gums, 105 and 90 g, respectively. The *n*-butanol extract was chromatographed repeatedly on a silica gel column, mainly with a chloroform–methanol system so as to give the following sesquiterpene glycosides.

Crepidiaside A (I)——Amorphous powder (9 mg), $[\alpha]_D^{17}$ −34.5° (c=0.58, MeOH). *Anal.* Calcd for $C_{21}H_{26}O_9 \cdot H_2O$: C, 57.27; H, 6.41. Found: C, 57.28; H, 6.14. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3420, 1765, 1680, 1635, 1618. UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 253 (4.15). CD (c=0.15, MeOH) [θ] (nm): −2614 (273). ^{1}H- and ^{13}C-NMR: Tables I, II.

Crepidiaside B (II)——Colorless needles (86 mg), mp 237—240 °C (dec., MeOH). $[\alpha]_D^{17}$ −62.5° (c=0.32, MeOH). *Anal.* Calcd for $C_{21}H_{28}O_9$: C, 59.43; H, 6.65. Found: C, 59.25; H, 6.60. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3430, 1770, 1680, 1635, 1618. UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 253 (4.15). ^{1}H- and ^{13}C-NMR: Tables I, II.

Crepidiaside C (III)——Colorless needles (33 mg), mp 125—130 °C (dec., MeOH). $[\alpha]_D^{25}$ −65.1° (c=0.53, MeOH). *Anal.* Calcd for $C_{21}H_{30}O_9 \cdot 1/2H_2O$: C, 57.92; H, 7.18. Found: C, 57.84; H, 7.00. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3450, 1760, 1628. ^{1}H- and ^{13}C-NMR: Tables I, II

Crepidiaside D (IV)——Amorphous powder (59 mg), $[\alpha]_D^{22}$ −40.1° (c=0.71, MeOH). *Anal.* Calcd for $C_{29}H_{36}O_{11} \cdot H_2O$: C, 60.20; H, 6.62. Found: C, 60.12; H, 6.38. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3425, 1755, 1643, 1620, 1603, 1523. UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 277 (3.33), 282 (3.29). ^{1}H- and ^{13}C-NMR: Tables I, II.

Crepidiaside E (V)——Amorphous powder (25 mg), $[\alpha]_D^{22}$ −22.2° (c=0.63, MeOH). *Anal.* Calcd for $C_{29}H_{34}O_{11} \cdot H_2O$: C, 60.41; H, 6.29. Found: C, 60.45; H, 6.07. IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3425, 1750, 1640, 1616, 1600, 1520. UV $\lambda_{\max}^{\mathrm{MeOH}}$ nm (log ε): 277 (3.16), 282 (3.09). CD (c=0.11, MeOH) [θ] (nm): +1887 (265). ^{1}H- and ^{13}C-NMR: Tables I, II.

Enzymatic Hydrolysis of Crepidiaside A (I)——Crepidiaside A (I) (50 mg) was dissolved in water (2 ml) and stirred with crude hesperidinase (40 mg) for 2 h at 37 °C. After being diluted with water, the mixture was passed through an Amberlite XAD-2 column, which was washed with water. The methanol eluate was purified by silica gel column chromatography and preparative HPLC to give 8-deoxylactucin (Ia) (9 mg), as colorless needles, mp 150—153 °C (dec., hexane–methylene chloride). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3430, 1765, 1670, 1610, 1255, 1135, 990, 980. MS m/z: 260 (M$^+$, 100), 242 (10), 214 (36), 189 (34), 185 (38), 159 (61). ^{1}H-NMR ($CDCl_3$): Table III.

Enzymatic Hydrolysis of Crepidiaside B (II)——Crepidiaside B (II) (6 mg) was dissolved in water (0.5 ml) and stirred with crude hesperidinase (6 mg) for 2 h at 37 °C, then the reaction mixture was extracted with ethyl acetate 4 times. The ethyl acetate extract gave jacquinelin (IIa) (4 mg) as colorless needles after recrystallization from ethyl acetate–benzene, mp 77 °C and 167—170 °C. MS *m/z*: 262 (M^+, 100), 244 (9), 233 (12), 231 (11), 216 (21), 205 (12), 189 (78), 188 (53), 161 (49), 159 (91). ^{1}H-NMR ($CDCl_3$): Table III.

Enzymatic Hydrolysis of Crepidiaside C (III)——Crepidiaside C (III) (10 mg) was dissolved in water (1 ml) and stirred with crude hesperidinase (10 mg) for 4 h at 37 °C. After being diluted with water, the mixture was passed through an Amberlite XAD-2 column, which was washed with water. The methanol eluate was purified by silica gel column chromatography to give the aglycone (IIIa) (1 mg) as an amorphous powder. MS *m/z*: 264 (M^+, 17), 246 ($M^+ - H_2O$, 38), 217 (19), 173 (32), 143 (49), 131 (40), 119 (71), 106 (61). ^{1}H-NMR ($CDCl_3$): Table III.

Saponification of Crepidiasides D (IV) and E (V)——A solution of crepidiaside D (IV) (*ca.* 0.1 mg) in aqueous 2% NaOH (0.1 ml) was stirred for 1 h at room temperature under a nitrogen atmosphere. The solution was acidified with diluted HCl and extracted with *n*-butanol. The extract was concentrated to give *p*-hydroxyphenylacetic acid, and III. Crepidiaside E (V) was saponified in a similar manner to give *p*-hydroxyphenylacetic acid and Va, which were detected by HPLC. HPLC conditions: TSK GEL LS-410AK, 4 mm × 30 cm; eluent, H_2O–CH_3CN (83 : 17); detector, UV 220 nm; t_R, 3.8 min (*p*-hydroxyphenylacetic acid), 11.6 min (III), 18.8 min (Va).

Reduction of Crepidiaside E (V)——Crepidiaside E (V) (4 mg) was dissolved in methanol (3 drops) and stirred with $NaBH_4$ (5 mg) for 10 min at 0 °C. The solution was acidified with diluted HCl followed by extraction with *n*-butanol 5 times. The *n*-butanol layer was washed with water and concentrated to give IV (4 mg). IR ν_{max}^{KBr} cm^{-1}: 3425, 1755, 1643, 1620, 1603, 1523. ^{1}H-NMR (pyridine-d_5): Table I.

Acid Hydrolysis of Crepidiaside A—E——A solution of a glycoside (*ca.* 0.1 mg) in 10% H_2SO_4 (2 drops) was heated in a boiling water bath for 30 min. The solution was passed through an Amberlite IR-45 column and concentrated to give a residue, which was reduced with $NaBH_4$ (*ca.* 1 mg) for 1 h at room temperature. The reaction mixture was passed through an Amberlite IR-120 column and concentrated to dryness. Boric acid was removed by distillation with methanol and the residue was acetylated with acetic anhydride (1 drop) and pyridine (1 drop) at 100 °C for 1 h. The reagents were evaporated off *in vacuo*. Glucitol acetate was detected by GC. GC conditions: column 1.5% OV-17, 3 mm × 1 m; column temperature, 230 °C; carrier gas, N_2; t_R, 3.5 min.

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