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Studies on Sesquiterpene Glycosides from *Crepis japonica* BENTH.

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Nine new guaianolide-type glycosides, crepisides A(II), B(III), C(IV), D(V), E(VI), F(VII), G(VIII), H(IX) and I(X), have been isolated from *Crepis japonica* BENTH., together with a known glycoside, glucozaluzanin C (I). The structures of II—X were established on the basis of chemical and spectral data.

Keywords——*Crepis japonica*; Compositae; sesquiterpene glycoside; guaianolide; crepiside

As a part of our studies on sesquiterpene glycosides from Compositae plants, we now report the isolation and structural elucidation of nine new guaianolide-type glycosides, crepisides A—I, together with a known glycoside, glucozaluzanin C (I), which were isolated from the methanol extract of *Crepis japonica* BENTH. (syn. *Youngia japonica* DC). The structures of these compounds were determined on the basis of chemical transformations and spectroscopic studies.

Glucozaluzanin C (I); $C_{21}H_{28}O_8 \cdot 1/2H_2O$, mp 104—106 °C, was isolated as a main component of this plant and identified by direct comparison [thin layer chromatography (TLC), proton nuclear magnetic resonance (^{1}H-NMR), mixed mp] with an authentic sample.[1]

Crepiside A (II), $C_{29}H_{34}O_{10} \cdot 1/2H_2O$, $[\alpha]_D$ +12.3° was obtained as an amorphous powder. Its ultraviolet (UV) spectrum showed absorption maxima at 278 (3.29) and 285 (sh 3.23) nm. The ^{1}H-NMR spectrum exhibited three exomethylene signals at δ 5.38, 6.22 (H_2-13); 4,85, 5.07 (H_2-14); 5.53, 5.79 (H_2-15), like those of glucozaluzanin C (I), as well as A_2B_2 type signals at δ 7.12 and 7.32 (J=9 Hz) and a singlet signal at δ 3.72 (2H) which were due to a *p*-hydroxyphenylacetic acid moiety.[2] On saponification, glucozaluzanin C (I) and *p*-hydroxyphenylacetic acid were obtained, while acid hydrolysis gave glucose as the sugar moiety. In the carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum, C-6 (δ 64.9) of glucose was shifted downfield by 1.8 ppm and C-5 (δ 75.1) of glucose was shifted upfield by 3.2 ppm[3] compared with those of I. These data led us to conclude the structure of crepiside A to be II.

Crepiside B (III), $C_{29}H_{34}O_{10} \cdot 1/2H_2O$, $[\alpha]_D$ −6.7° was obtained as amorphous powder. Its ^{1}H-NMR spectrum was very similar to that of II. On saponification, I and *p*-hydroxyphenylacetic acid were obtained, as in the case of II. Acid hydrolysis gave glucose as the sugar moiety. In the ^{13}C-NMR spectrum, C-4 (δ 72.9) of glucose was shifted downfield by 0.9 ppm, compared with that of I, while C-3 (δ 75.6) and C-5 (δ 75.4) of glucose were shifted upfield by 3.0 and 2.9 ppm, respectively.[3] From these data the structure of crepiside B was decided to be III.

Crepiside C (IV), $C_{21}H_{28}O_9$, mp 213—216 °C, $[\alpha]_D$ +24.0° was obtained as colorless needles. Its ^{1}H-NMR spectrum showed the presence of a vinyl methyl group at δ 1.92 (3H, br s) and two exomethylene groups at δ 5.07, 5.45 (1H, each s), and 5.69 (1H, d, J=3.1 Hz), 6.49 (1H, d, J=3.4 Hz). These two doublet signals are characteristic of exocyclic α-methylene-γ-lactone,[4] and judging from these chemical shifts, this compound was assumed to have a β-

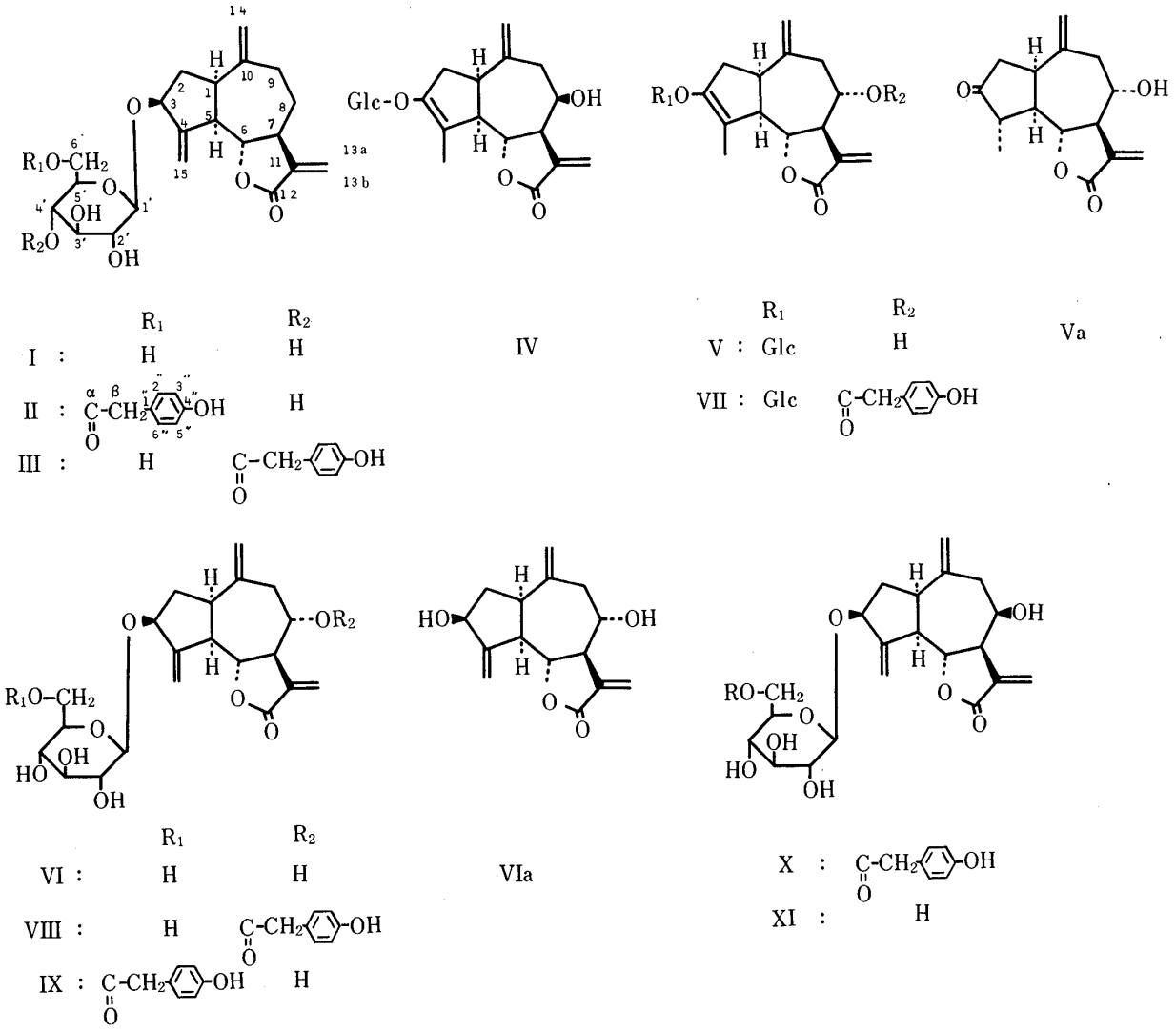

Chart 1

hydroxyl group at C-8.[5] Acid hydrolysis gave glucose as the sugar moiety. The ^{13}C-NMR spectrum showed an anomeric carbon signal at δ 101.8, which was assigned to C-1 of enol-type glucoside. From these data, the structure of this compound was assumed to be IV, and this was confirmed by direct comparison (^{1}H- and ^{13}C-NMR) with a saponification product of ixerin S which had been isolated from *Ixeris stolonifera* A. GRAY by our group.[6]

Crepiside D (V), $C_{21}H_{28}O_9 \cdot H_2O$, $[\alpha]_D$ +51.5° was obtained as an amorphous powder. The circular dichroism (CD) spectrum showed a negative Cotton effect $[\theta]_{273}$ −646. This compound gave spectral data similar to those of IV, but in the ^{1}H-NMR spectrum H-13a (δ 6.39) was shifted downfield by 0.70 ppm compared with that of crepiside C (IV), which has a β-hydroxyl group at C-8, and H-13a and H-13b were both observed as multiplets while those of IV were observed as doublets. These two differences indicated that V has an α-hydroxyl group at C-8.[7] Acid hydrolysis of V afforded glucose as the sugar moiety, while enzymatic hydrolysis of V with crude hesperidinase afforded a ketonic aglycone Va, $C_{15}H_{18}O_4$, mp 198—201 °C, through an unisolable enol intermediate. Compound Va was identical with grosheimin[5,8] based on comparisons of mp and ^{1}H-NMR spectrum. Thus, the structure of crepiside D was deduced to be V. The stereochemistry of the anomeric center was decided on the basis of the $J_{H_{1'}-H_{2'}}$ coupling constant (8 Hz).

Crepiside E (VI), $C_{21}H_{28}O_9 \cdot H_2O$, $[\alpha]_D$ +12.9° was obtained as an amorphous powder. The ^{1}H-NMR spectrum exhibited three exomethylene signals at δ 5.06, 5.12 (1H, each s); 5.56,

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

Proton No.	I	II	III	IV	V
13a	5.38 (1H, d, J=3.3 Hz)	5.38 (1H, d, J=3.1 Hz)	5.37 (1H, d, J=3.0 Hz)	5.69 (1H, d, J=3.1 Hz)	6.39 (1H, m)
13b	6.22 (1H, d, J=3.3 Hz)	6.22 (1H, d, J=3.3 Hz)	6.20 (1H, d, J=3.3 Hz)	6.49 (1H, d, J=3.4 Hz)	6.51 (1H, m)
14	4.85 (1H, s)	4.85 (1H, s)	4.82 (1H, s)	5.07 (1H, s)	5.01 (1H, s)
	5.02 (1H, s)	5.07 (1H, s)	5.00 (1H, s)	5.45 (1H, s)	5.24 (1H, s)
15	5.51 (1H, br s)	5.53 (1H, br s)	5.50 (1H, br s)	1.92 (3H, br s)	1.96 (3H, br s)
	5.83 (1H, br s)	5.79 (1H, br s)	5.78 (1H, br s)		
1′			4.96 (1H, d, J=7 Hz)	5.30 (1H, d, J=7 Hz)	5.28 (1H, d, J=8 Hz)
β		3.72 (2H, s)	3.73 (2H, s)		
2″, 6″		7.32 (2H, d, J=9 Hz)	7.29 (2H, d, J=9 Hz)		
3″, 5″		7.12 (2H, d, J=9 Hz)	7.08 (2H, d, J=9 Hz)		

Proton No.	VI	VII	VIII	IX	X
13a	6.40 (2H, m)	5.53 (1H, m)	5.48 (1H, br d, J=3.2 Hz)	6.40 (2H, m)	5.69 (1H, d, J=3.1 Hz)
13b		6.17 (1H, m)	6.16 (1H, br d, J=3.4 Hz)		6.50 (1H, d, J=3.3 Hz)
14	5.06 (1H, s)	4.89 (1H, s)	4.82 (1H, s)	5.08 (1H, s)	4.98 (1H, s)
	5.12 (1H, s)	5.17 (1H, s)	5.08 (1H, s)	5.17 (1H, s)	5.26 (1H, s)
15	5.56 (1H, br s)	1.94 (3H, br s)	5.54 (1H, br s)	5.57 (1H, br s)	5.62 (1H, br s)
	5.75 (1H, br s)		5.69 (1H, br s)	5.72 (1H, br s)	5.85 (1H, br s)
β		3.80 (2H, s)	3.80 (2H, s)	3.73 (2H, s)	3.74 (2H, s)
2″, 6″		7.40 (2H, d, J=8 Hz)	7.40 (2H, d, J=8 Hz)	7.32 (2H, d, J=8 Hz)	7.34 (2H, d, J=8 Hz)
3″, 5″		7.20 (2H, d, J=8 Hz)	7.20 (2H, d, J=8 Hz)	7.12 (2H, d, J=8 Hz)	7.13 (2H, d, J=8 Hz)

Run at 89.55 MHz in pyridine-d_5 solution.

TABLE II. ^{13}C-NMR Chemical Shifts and Coupling Constants

Carbon No.	II	III	IV	V	VI	VII	VIII	IX	X
Aglycone moiety									
1	45.0[a]	45.0[b]	45.7	44.7[e]	45.9	45.2	46.3	46.1	45.2
2	38.3	38.0	35.6	34.8	38.4	34.7	38.4	38.5	38.6
3	80.8	80.5	151.2	153.4	80.5	151.4	80.2	80.9	81.1
4	150.4	150.1	112.3	112.9	150.0	112.9	149.5	149.8	151.0
5	50.5	50.6	54.1[d]	54.2[f]	52.0[g]	54.3	52.4	52.1	50.7[i]
6	83.6	83.3	80.3	81.7	78.9	81.2	78.6	79.0	78.1[j]
7	45.2[a]	45.3[b]	50.0[d]	51.4[f]	51.2[g]	47.5	47.3	51.3	49.9[i]
8	30.7	30.6	65.9	72.8	72.2	74.8[h]	74.6	72.2	66.0
9	34.2	33.9	43.2	45.0[e]	42.9	41.2	36.9	43.1	44.0
10	148.9	148.8	144.9	144.7	144.3	143.3	143.2	144.5	145.0
11	141.0	141.1	137.8	139.7	140.4	138.2	139.0	140.5	137.7
12	169.7	169.9	170.2	170.1	170.0	169.2	169.1	170.0	170.1
13	119.1	119.1	120.7	121.1	121.7	121.8	121.2	121.7	121.0
14	114.0	114.0	115.8	115.7	116.2	117.3	117.5	116.3	116.2
15	112.5	112.9	11.6	12.1	114.3	12.2	115.1	114.5	112.0
Sugar moiety									
1′	104.0	103.5	101.8	102.0	103.3 (157 Hz)	102.1	102.8	103.4	104.5
2′	75.1	75.9[c]	74.9	74.9	75.2	75.0[h]	75.1	75.1	75.0
3′	78.2	75.6[c]	78.4	78.6	78.5	78.7	78.2	78.3	78.5[j]
4′	71.6	72.9	71.4	71.5	71.8	71.6	71.9	71.7	71.6
5′	75.1	75.4[c]	78.4	78.5	78.1	78.6	78.2	75.1	75.0
6′	64.9	62.1	62.5	62.6	62.9	62.6	63.0	65.0	64.9
p-Hydroxyphenylacetic acid moiety									
α	171.9	171.6				171.2	171.3	172.0	171.9
β	40.6	40.8				41.2	41.1	40.7	40.6
1″	125.2	125.1				125.6	124.8	125.3	125.3
2″, 6″	130.8	130.8				131.0	130.9	130.9	130.8
3″, 5″	116.2	116.2				116.5	116.5	116.3	116.2
4″	157.8	157.8				158.3	158.2	157.9	157.8

Run at 22.5 MHz in pyridine-d_5 solution. *a*—*j*) Assignments may be interchanged in each column.

5.75 (1H, each br s); 6.40 (2H, m). H-13a (δ 6.40) was shifted downfield by 0.70 ppm compared with that of 8-epidesacylcynaropicrin glucoside,[6] which had a β-hydroxyl group at C-8. Thus, VI has an α-hydroxyl group at C-8 for the same reason as in the case of V. Enzymatic hydrolysis of VI gave VIa as an aglycone, whose mass spectrum (MS) showed a molecular ion peak at *m/z* 262, in agreement with the molecular formula $C_{15}H_{18}O_4$. The ^{1}H-NMR spectrum of VIa was superimposable on that of desacylcynaropicrin.[9] The stereochemistry of the anomeric center was deduced from the $J_{C_{1'}-H_{1'}}$ coupling constant (157 Hz).[10] From these data, the structure of crepiside E was deduced to be VI.

Crepiside F (VII), $C_{29}H_{34}O_{11}\cdot H_2O$, $[\alpha]_D$ +68.3° was obtained as an amorphous powder. Its UV spectrum showed absorption maxima at 277 (3.35) and 285 (sh 3.29) nm. The ^{1}H-NMR spectrum was very similar to that of crepiside D (V) except for signals due to *p*-hydroxyphenylacetic acid [δ 3.80 (2H, s); 7.20, 7.40 (2H, each d, J=8 Hz)]. On saponification, grosheimin (Va), *p*-hydroxyphenylacetic acid and a trace of crepiside D (V) were obtained, while acid hydrolysis gave glucose as the sugar moiety. In the ^{13}C-NMR spectrum, C-8 (δ 74.8) was shifted downfield by 2.0 ppm while C-7 (δ 47.5) and C-9 (δ 41.2) were shifted upfield by 3.9 and 3.8 ppm, respectively, compared with those of V. These data indicated that

p-hydroxyphenylacetic acid was esterified at C-8. Therefore the structure of crepiside F was deduced to be VII.

Crepiside G (VIII), $C_{29}H_{34}O_{11} \cdot 3/2H_2O$, $[\alpha]_D$ +41.3° and crepiside H (IX), $C_{29}H_{34}O_{11}$ H_2O, $[\alpha]_D$ +22.9° were both obtained as amorphous powder, and gave crepiside E (VI) and *p*-hydroxyphenylacetic acid on saponification. In the ^{13}C-NMR spectrum of VIII, C-8 (δ 74.6) was shifted downfield by 2.4 ppm, while C-7 (δ 47.3) and C-9 (δ 36.9) were shifted upfield by 3.9 and 6.0 ppm, respectively, compared with those of VI. Furthermore, H-13a (δ 5.48) was shifted upfield by 0.92 ppm in the ^{1}H-NMR spectrum of VIII. These two NMR spectral differences suggested that the structure of crepiside G could be assigned as VIII. On the other hand, in the ^{13}C-NMR spectrum of IX, C-6 (δ 65.0) of glucose was shifted downfield by 2.1 ppm, while C-5 (δ 75.1) of glucose was shifted upfield by 3.0 ppm. These data led us to conclude the structure of crepiside H to be IX.

Crepiside I (X), $C_{29}H_{34}O_{11} \cdot H_2O$, $[\alpha]_D$ −22.6° was obtained as an amorphous powder. Its UV spectrum showed absorption maxima at 278 (3.38) and 285 (sh 3.33) nm. On saponification, 8-epidesacylcynaropicrin glucoside (XI) and *p*-hydroxyphenylacetic acid were obtained. In the ^{13}C-NMR spectrum of X, C-6 (δ 64.9) of glucose was shifted downfield by 2.0 ppm, while C-5 (δ 75.0) of glucose was shifted upfield by 3.0 ppm compared with those of XI. Thus, the structure of crepiside I was deduced to be X.

These ten glycosides have closely related structures and taste strongly bitter.

Experimental

Melting points were taken on a Yanaco MP-500 micromelting point apparatus and are uncorrected. Optical rotations were determined with a JASCO DIP-140 digital polarimeter. Infrared (IR) spectra were run on a JASCO A-202 IR spectrometer and UV spectra on a Shimadzu UV-360 recording spectrophotometer. MS were measured on a JEOL JMS-D 100 mass spectrometer. CD spectrum was recorded on a JASCO J-20A spectropolarimeter. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL FX-90Q NMR spectrometer (89.55 and 22.5 MHz, respectively). Chemical shifts are given on the δ scale with tetramethylsilane as an internal standard (s, singlet; d, doublet; t, triplet; m, multiplet; br, broad). Gas chromatography (GC) was done on a Hitachi K 53 gas chromatograph. High-performance liquid chromatography (HPLC) was done on a Kyowa Seimitsu model K 880 instrument.

Isolation——Air-dried whole plant of *C. japonica* (700 g) was 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, successively. After repeated chromatography of the *n*-butanol layer (17 g) on Silica gel 60 with a chloroform–methanol system and HPLC with a water–acetonitrile system, ten sesquiterpene glycosides were isolated.

Glucozaluzanin C (I)——Recrystallized from water as colorless needles (450 mg), mp 104—106 °C. *Anal.* Calcd for $C_{21}H_{28}O_8 \cdot 1/2H_2O$: C, 60.42; H, 7.00. Found: C, 60.66; H, 6.71. IR ν_{max}^{KBr} cm^{-1}: 3430, 1755, 1660, 1635. ^{1}H-NMR and ^{13}C-NMR: Tables I, II.

Crepiside A (II)——Amorphous powder (50 mg). $[\alpha]_D^{20}$ +12.3° (c=0.65, pyridine). *Anal.* Calcd for $C_{29}H_{34}O_{10} \cdot 1/2H_2O$: C, 63.15; H, 6.40. Found: C, 63.11; H, 6.48. IR ν_{max}^{KBr} cm^{-1}: 3450, 1745, 1660, 1640, 1618, 1522, 1265, 1075. UV λ_{max}^{MeOH} nm (log ε): 278 (3.29), 285 (sh 3.23). ^{1}H-NMR and ^{13}C-NMR: Tables I, II.

Crepiside B (III)——Amorphous powder (20 mg). $[\alpha]_D^{18}$ −6.7° (c=0.52, methanol). *Anal.* Calcd for $C_{29}H_{34}O_{10} \cdot 1/2H_2O$: C, 63.15; H, 6.40. Found: C, 63.03; H, 6.37. IR ν_{max}^{KBr} cm^{-1}: 3430, 1760, 1745, 1660, 1640, 1615, 1520, 1260, 1145, 1080, 1020. UV λ_{max}^{MeOH} nm (log ε): 277 (3.20), 284 (sh 3.14). ^{1}H-NMR and ^{13}C-NMR: Tables I, II.

Crepiside C (IV)——Recrystallized from methanol as colorless needles (70 mg), mp 213—216 °C, $[\alpha]_D^{20}$ +24.0° (c=1.56, methanol). *Anal.* Calcd for $C_{21}H_{28}O_9$: C, 59.42; H, 6.65. Found: C, 59.21; H, 6.61. IR ν_{max}^{KBr} cm^{-1}: 3500, 1740, 1695, 1660, 1642, 1322, 1250, 1115, 1080, 1060, 1038, 995. ^{1}H-NMR and ^{13}C-NMR: Tables I, II.

Crepiside D (V)——Amorphous powder (200 mg). $[\alpha]_D^{20}$ +51.5° (c=0.68, methanol). *Anal.* Calcd for $C_{21}H_{28}O_9 \cdot H_2O$: C, 57.01; H, 6.83. Found: C, 56.90; H, 6.80. IR ν_{max}^{KBr} cm^{-1}: 3430, 1750, 1695, 1660, 1640, 1070, 1035. CD (c=0.42, methanol) [θ] (nm): −646 (273). ^{1}H-NMR and ^{13}C-NMR: Tables I, II.

Crepiside E (VI)——Amorphous powder (100 mg). $[\alpha]_D^{20}$ +12.9° (c=0.62, methanol). *Anal.* Calcd for $C_{21}H_{28}O_9 \cdot H_2O$: C, 57.01; H, 6.83. Found: C, 57.26; H, 6.64. IR ν_{max}^{KBr} cm^{-1}: 3430, 1750, 1660, 1640, 1070, 1040. ^{1}H-NMR and ^{13}C-NMR: Tables I, II.

Crepiside F (VII)——Amorphous powder (10 mg). $[\alpha]_D^{20}$ +68.3° (c=0.41, methanol). *Anal.* Calcd for $C_{29}H_{34}O_{11} \cdot H_2O$: C, 60.41; H, 6.29. Found: C, 60.42; H, 6.32. IR ν_{max}^{KBr} cm^{-1}: 3430, 1760, 1745, 1700, 1660, 1640, 1618,

1522, 1265, 1075. UV λ_{max}^{MeOH} nm (log ε): 277 (3.35), 285 (sh 3.29). ^{1}H-NMR and ^{13}C-NMR: Tables I, II.

Crepiside G (VIII)——Amorphous powder (12 mg). $[\alpha]_D^{20}$ +41.3° (c=0.40, methanol). *Anal.* Calcd for $C_{29}H_{34}O_{11} \cdot 3/2H_2O$: C, 59.48; H, 6.37. Found: C, 59.65; H, 6.37. IR ν_{max}^{KBr} cm^{-1}: 3450, *ca.* 1760, 1745, 1660, 1642, 1618, 1522, 1270, 1075, 1015. UV λ_{max}^{MeOH} nm (log ε): 277 (3.23), 285 (sh 3.15). ^{1}H-NMR and ^{13}C-NMR: Tables I, II.

Crepiside H (IX)——Amorphous powder (15 mg). $[\alpha]_D^{20}$ +22.9° (c=0.83, methanol). *Anal.* Calcd for $C_{29}H_{34}O_{11} \cdot H_2O$: C, 60.41; H, 6.22. Found: C, 60.71; H, 6.29. IR ν_{max}^{KBr} cm^{-1}: 3430, 1745, 1660, 1640, 1618, 1522, 1075. UV λ_{max}^{MeOH} nm (log ε): 278 (3.34), 285 (sh 3.31). ^{1}H-NMR and ^{13}C-NMR: Tables I, II.

Crepiside I (X)——Amorphous powder (15 mg). $[\alpha]_D^{29}$ −22.6° (c=0.31, methanol). *Anal.* Calcd for $C_{29}H_{34}O_{11} \cdot H_2O$: C, 60.41; H, 6.29. Found: C, 60.66; H, 6.19. IR ν_{max}^{KBr} cm^{-1}: 3450, 1745, 1660, 1640, 1620, 1522, 1075. UV λ_{max}^{MeOH} nm (log ε): 278 (3.38), 285 (sh 3.33). ^{1}H-NMR and ^{13}C-NMR: Tables I, II.

Enzymatic Hydrolysis of Crepiside D (V)——A solution of crepiside D (V) (23 mg) in water (1 ml) was treated with crude hesperidinase (20 mg) at 37 °C for 3 h. The reaction mixture was passed through an Amberlite XAD-2 column and the absorbed material was eluted with methanol. The methanol eluate was purified by silica gel column chromatography with benzene–acetone (92 : 8) to give grosheimin as an aglycone Va (4 mg). Colorless needles from chloroform–methanol, mp 198—201 °C (lit. mp 199—200 °C).[8] IR ν_{max}^{KBr} cm^{-1}: 3430, 1740, 1650, 1070. MS m/z: 262 (M^+, 5), 244 ($M^+ - 18$, 17), 166 (13), 165 (18), 137 (35), 136 (35), 69 (100). ^{1}H-NMR ($CDCl_3$) δ: 1.28 (3H, d, J=7 Hz, H_3-15), 4.00 (1H, t, J=9 Hz, H-6), 4.85; 5.09 (1H each, s, H-14), 6.33 (1H, dd, J=3.1; 1 Hz, H-13a), 6.37 (1H, dd, J=3.2; 1 Hz, H-13b). ^{13}C-NMR ($CDCl_3$) δ: 15.0, 40.4, 43.1, 47.0, 47.8, 49.6, 51.5, 73.3, 82.0, 115.7, 125.3, 136.8, 143.3, 169.5, 218.2.

Enzymatic Hydrolysis of Crepiside E (VI)——Crepiside E (VI) (23 mg) was hydrolyzed in the same way as V. Desacylcynaropicrin (VIa)[9] was obtained as an amorphous powder (7 mg) as the aglycone of VI. IR ν_{max}^{KBr} cm^{-1}: 3430, 1755, 1635, 900. MS m/z: 262 (M^+, 8). ^{1}H-NMR ($CDCl_3$) δ: 3.95 (1H, m, H-8), 4.16 (1H, t, J=10 Hz, H-6), 4.56 (1H, br t, J=8 Hz, H-3), 4.98; 5.13 (1H, each, br s, H-14), 5.34; 5.48 (1H each, br s, H-15), 6.16 (1H, m, H-13a), 6.26 (1H, m, H-13b). ^{13}C-NMR (pyridine-d_5) δ: 39.9 (C-2), 44.1 (C-9), 45.1 (C-1), 50.9; 51.4 (C-5, C-7), 72.4 (C-8), 73.4 (C-3), 79.7 (C-6), 110.7 (C-15), 115.9 (C-14), 122.1 (C-13), 140.1 (C-11), 144.6 (C-10), 154.8 (C-4), 170.0 (C-12).

Saponification of Crepisides A (II), B (III), F (VII), G (VIII), H (IX) and I (X)——A solution of a glycoside (*ca.* 0.1 mg in aqueous 2% NaOH solution (2 drops) 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 desacyl compounds (I from II and III; X from XI; VI from VIII and IX; V, Va from VII), which were detected by HPLC. Conditions: column, TSK GEL LS-410 AK, 4 mm × 30 cm; flow, 1.5 ml/min; detector, UV 220 nm; solvent, (1): H_2O–CH_3CN (75 : 25); t_R 2.5 min (*p*-hydroxyphenylacetic acid), 10.2 min (I); solvent, (2): H_2O–CH_3CN (83 : 17); t_R 3.2 min (*p*-hydroxyphenylacetic acid), 6.5 min (V), 6.7 min (VI), 11.6 min (XI), 23.6 min (Va).

Acid Hydrolysis of Crepisides A (II), B (III), C (IV), D (V), E (VI), F (VII), G (VIII), H (IX) and I (X)——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 IRA-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 the eluate was concentrated to dryness. Boric acid was removed by co-distillation with methanol and the residue was acetylated with acetic anhydride and pyridine (1 drop each) at 100 °C for 1 h. The reagents were evaporated off *in vacuo*. From each glycoside, glucitol acetate was detected by GC. Conditions; column, 1.5% OV-17, 3 mm × 1 m; column temperature, 220 °C; carrier gas, N_2; t_R 6.5 min.

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