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FOUR NEW IRIDOID GLUCOSIDE *p*-COUMAROYL ESTERS FROM *AJUGA DECUMBENS*

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Key Word Index—*Ajuga decumbens*; Labiatae; decumbesides; galiridoside *p*-coumaroyl ester; 8-acetylharpagide *p*-coumaroyl ester; reptoside; 8-acetylharpagide; structure elucidation.

Abstract—From the methanolic extract of the dried whole plant of *Ajuga decumbens*, four new iridoid glucoside *cis*- and *trans*-*p*-coumaroyl esters, decumbeside A (**1**), B (**2**), C (**7**) and D (**8**) were isolated together with the known reptoside (**6**) and 8-acetylharpagide (**9**). The structures of the new compounds have been elucidated on the basis of spectroscopic and chemical evidence.

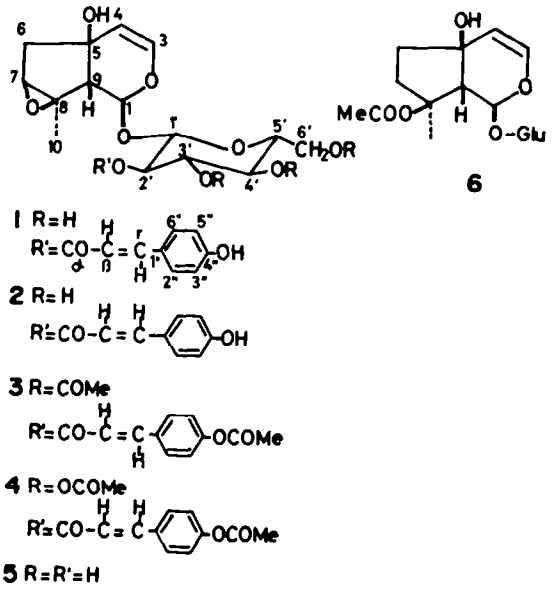
INTRODUCTION

Ajuga decumbens is widely distributed in East Asia and it has been used as remedy for sore throat and alleviating fever in folk medicine. In the course of our studies on the biologically active substances from the Labiatae, we investigated the constituents of the titled plant and isolated four new iridoid glucoside *p*-coumaroyl esters, together with the known reptoside (**6**) [1] and 8-acetylharpagide (**9**) [2, 3]. The present paper describes the structure elucidation of the new compounds.

RESULTS AND DISCUSSION

A methanolic extract of the whole plant of *A. decumbens* was fractionated as described in the Experimental section. From the ethyl acetate soluble fraction, the new compounds, decumbeside A (**1**), B (**2**), C (**7**) and D (**8**) were isolated by a combination of silica gel chromatography and reversed phase HPLC. From the *n*-butanol soluble fraction, 8-acetylharpagide (**9**) was isolated as a major constituent together with minor component, reptoside (**6**).

Decumbeside A (**1**), $C_{24}H_{28}O_{11} \cdot 3/2\ H_2O$, $[\alpha]_D$ −60° (MeOH), was obtained as an amorphous powder. The ^1H NMR spectrum (C_5D_5N) of **1** (see Experimental) was strongly reminiscent of that reported [4] for galiridoside (**5**) and in addition contained signals arising from a *trans*-*p*-coumaroyl moiety [δ6.63 and 7.98 (each 1H, *d*, *J* = 16 Hz)] (double bond), and 7.17 and 7.55 (each 2H, *d*, *J* = 8.5 Hz) (1,4-disubstituted benzene ring). The ^{13}C NMR spectrum of **1** (Table 1) showed the presence of a methyl, a methylene, a methine, two methines having an oxygen function, and an acetalic carbon and a disubstituted double bond besides the signals due to a sugar moiety and a *trans*-*p*-coumaroyl group. Acetylation of decumbeside A (**1**) with a mixture of acetic anhydride and pyridine gave the tetraacetate (**3**), in the ^1H NMR spectrum of which signals due to three alcoholic and a phenolic acetoxy groups were observed.



On the basis of the above mentioned spectral data, decumbeside A was presumed to have a structure in which galiridoside (**5**) is esterified by a *trans*-*p*-coumaroyl group at the sugar portion. This speculation was supported by the close similarity of the ^{13}C NMR spectrum of **1** with that [5] of galiridoside (**5**) except for the signals due to sugar and *p*-coumaroyl portions and confirmed from the fact that mild alkaline hydrolysis of **1** gave galiridoside (**5**) [4]. The location of the *trans*-*p*-coumaroyl group was presumed to be at C-2′ from the comparisons of ^{13}C NMR spectra of **1** and **5**, since the anomeric carbon in **1** resonated at 1.7 ppm higher field than that of **5** and could be confirmed by ^1H spin–spin decoupling experiments. Namely, the signal at δ5.44 assignable to C-1′-H was collapsed to a singlet on irradiation at δ5.66 which

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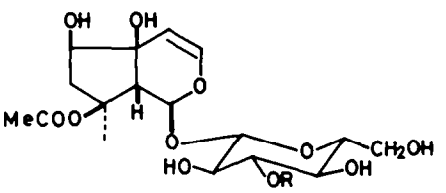
Table 1. ^{13}C NMR Data (δ)* of decumbeside A (1), B (2), C (7), D (8), galiridoside (5), and 8-acetylharpagide (9)

Carbons	1	2	5†	7	8	9
1	94.9	95.3	95.3	94.5	94.4	94.5
3	141.2	141.4	141.7	143.7	143.7	143.7
4	110.6	110.1	109.6	106.8	106.8	106.8
5	76.9	76.7	76.6	73.2	73.2	73.2
6	43.7	43.7	44.4	77.9	77.9[e]	78.0
7	64.1	64.0	64.2	46.0	46.0	46.0
8	67.1	67.0	67.3	88.4	88.4	88.5
9	54.6	54.5	54.5	55.4	55.4	55.5
10	17.1	17.3	17.6	22.5	22.4	22.5
1′	97.9	97.9	99.6	99.7	99.7	99.8
2′	75.7[c]	75.6[d]	74.8	72.9	72.8	74.5
3′	75.1[c]	74.8[d]	78.5	78.4	78.0[e]	77.6
4′	71.7	71.8	71.8	69.8	69.7	71.6
5′	78.5	78.4	77.9	77.5	77.5	77.6
6′	62.8	62.7	63.0	62.5	62.4	62.8
α	169.2	167.0		168.9	167.9	
β	115.3	115.8		115.4	116.9	
γ	147.3	145.5		146.5	144.4	
1″	127.1	127.7		127.1	127.5	
2″	131.2	133.8		131.0	133.4	
3″	116.9	115.8		116.7	115.7	
4″	161.3	160.0		161.0	159.7	
5″	116.9	115.8		116.7	115.7	
6″	131.2	133.8		131.0	133.4	
AcO				22.2	22.1	22.2
				173.1	173.1	173.2

*Solvent CD_3OD.
†Data from ref. [5].
[c-e] may be exchanged.

was assigned to the proton on the carbon having the *p*-coumaroyloxy group. On the basis of these findings, the structure of decumbeside A was elucidated as galiridoside 2′-*trans*-*p*-coumaroyl ester (**1**).

Decumbeside B (**2**), $[\alpha]_D$ −13° (MeOH) was obtained as an amorphous powder and has the same molecular formula as **1** on the basis of its FAB mass spectrum. The ^{1}H NMR spectrum (C_5D_5N) of **2** (see Experimental) is very similar to that of **1**. The difference in the ^{1}H NMR spectrum of **2** and **1** is the appearence of signals due to a *cis*-*p*-coumaroyl group [δ6.05 and 6.93 (each 1H, *d*, J = 13 Hz), and 7.15 and 8.12 (each 2H, *d*, J = 8.5 Hz)] in **2** instead of those arising from the *trans*-*p*-coumaroyl group in **1**. Irradiation at δ6.93, an NOE (18%) was observed for the signal at δ6.05, indicating a *cis*-arrangement of the double bond. Acetylation of **2** gave the tetraacetate (**4**). Accordingly, the structure of decumbeside B was presumed to be galiridoside *cis*-*p*-coumaroyl ester. The location of the *cis*-*p*-coumaroyl group was suggested to be at C-2′ from the upfield shift of the anomeric carbon (δ97.9) in the ^{13}C NMR spectrum and was confirmed from the fact that the signal at δ5.44 arising from the anomeric proton collapsed to a singlet on irradiation of the signal at δ5.62 (1H, *dd*, J = 8.5 and 8.5 Hz) assignable to the proton attached on the carbon having the *cis*-*p*-coumaroyloxy group. On the basis of these findings, the structure of decumbeside B was elucidated as galiridoside 2′-*cis*-*p*-coumaroyl ester (**2**).



7 R = CO-C(H)=C(H)--OH

8 R = CO-C(H)=C(H)--OH

9 R = H

Decumbeside C (**7**), $C_{26}H_{32}O_{13} \cdot 3/2H_2O$, $[\alpha]_D$ −108° (MeOH), was obtained as an amorphous powder. The ^{1}H NMR spectrum (CD_3OD) (see Experimental) was strongly reminiscent of that of 8-acetylharpagide (**9**) and in addition contained signals due to a *trans*-*p*-coumaroyl group [δ6.393 and 7.66 (each 1H, *d*, J = 16 Hz), and 6.80 and 7.47 (each 2H, *d*, J = 8.5 Hz)]. The ^{13}C NMR spectrum (CD_3OD) of **7** showed the presence of a methyl, a methylene, a methine, a secondary carbinyl carbon, two quarternary carbons having an oxygen function, a disubstituted double bond and an acetalic carbon in addition to the signals due to a *trans*-*p*-coumaroyl group and a sugar moiety. These spectral data suggest that decumbeside C (**7**) might be the *trans*-*p*-coumaroyl ester of 8-acetylharpagide (**9**) which was isolated at the same time. In fact, the ^{13}C NMR signals assignable to the aglycone portion were identical to those of **9** and partial hydrolysis of decumbeside C (**7**) with NaOH gave **9** as one of the products. The location of the *p*-coumaroyl group was elucidated to be at C-3′ from the results of the spin–spin decoupling experiments. On irradiation at δ4.72 (C-1′-H), the signal at δ3.41 (1H, J = 10 and 8 Hz) collapsed to a doublet (J = 10 Hz), leading to the assignment of this signal to C-2′-H. This signal also collapsed to a doublet (J = 8 Hz) on irradiation at δ5.07 which was assigned to the proton on the carbon having a *trans*-*p*-coumaroyloxy group. This assignment was further supported by the fact that the signal assignable to C-4′ resonated in a 1.9 ppm higher field compared to that of **9** in the ^{13}C NMR spectrum. On the basis of these findings, the structure of decumbeside C was elucidated as 8-acetylharpagide 3′-*trans*-*p*-coumaroyl ester (**7**).

Decumbeside D (**8**), $[\alpha]_D$ −158° (MeOH) was obtained as an amorphous powder. The spectral data of decumbeside D (**8**) were very similar to those of **7** except for the presence of a *cis*-*p*-coumaroyl group [δ5.83 and 6.86 (each 1H, *d*, J = 13 Hz), and 6.74 and 7.64 (each 2H, *d*, J = 8.5 Hz)] instead of a *trans*-*p*-coumaroyl group in **7** in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum of **8** is almost identical to that of **7** except for the above mentioned differences. On the basis of these spectral data, the structure of decumbeside D could be represented as 8-acetylharpagide 3′-*cis*-*p*-coumaroyl ester (**8**).

EXPERIMENTAL

General. ^{1}H NMR: 200 MHz; ^{13}C NMR: 50 MHz. Unless otherwise noted TMS was used as int. standard.

Plant material. The plant was collected in the suburbs of Tokushima city, Japan in April, 1985 and identified by Dr K. Murakami of this Faculty. A voucher specimen (Y. Takeda No. 1) is deposited in the herbarium of this Faculty.

Isolation. Dried whole plant of *A. decumbens* Thunb. (3.6 kg) was extd with MeOH (30 l) for 3 weeks at room temp. The extract was concd *in vacuo*. The residue was partitioned between 90% MeOH (1.9 l) and *n*-hexane (total 3.6 l). The 90% MeOH layer was concd *in vacuo* and the residue suspended in H_2O (1 l). The suspension was extd with EtOAc (800 ml × 3) and then with *n*-BuOH (800 ml × 3). After washing with H_2O, the EtOAc extract was dried and evapd *in vacuo* to give a residue (22.5 g). The *n*-BuOH extract gave a residue (61 g) on evapn.

The EtOAc fraction was chromatographed on a silica gel column (1 kg) with $CHCl_3$–MeOH as eluant with increasing MeOH content. A fraction (1.7 g) eluted with $CHCl_3$–MeOH (93:7) was rechromatographed on a smaller column (Kiesel gel PF_{254}, 60 g) using the same solvent and collecting 8 ml fractions. Fraction Nos 67–84 were combined and evapd *in vacuo* to give a residue (264 mg) which was sepd by prep. HPLC [column: M & S Pack C-18B, 20 id × 250 mm; solvent: H_2O–MeOH 1:1; flow rate: 7.5 ml/min; detection 210 nm) to give a mixture (71 mg) of decumbeside C (7) and D (8). The mixture was further sepd by prep. HPLC (column: as above; solvent: H_2O–MeOH 3:2; flow rate: 6.5 ml; detection: 240 nm) to give 7 (37.9 mg) and 8 (16.9 mg).

Decumbeside C (7). Amorphous powder $[\alpha]_D^{29}$ −108° (MeOH, *c* 0.50); UV λ_{max}^{MeOH} nm (ε): 227 (11546) and 312 (22927) IR ν_{max}^{KBr}: 3750–3050, 1725, 1710, 1660, 1630, 1610, 1520, 1270, 1240, 1175 and 840 cm^{-1}; ^1H NMR (CD_3OD): δ 1.46 (3H, *s*, 10-H_3), 1.94 (1H, *dd*, *J* = 15 and 4.5 Hz, 7α-H), 2.02 (3H, *s*, OAc), 2.18 (1H, *d*, *J* = 15 Hz, 7β-H), 2.86 (1H, *br s*, 9-H), 3.41 (1H, *dd*, *J* = 10 and 8 Hz, 2'-H), 3.54 (1H, *dd*, *J* = 10 and 9 Hz, 4'-H), 3.72 (1H, *d*, *J* = 4.5 Hz, 6-H), 3.65–3.77 (1H), 3.91 (1H, *dd*, *J* = 12 and 2 Hz, 6'-H), 4.72 (1H, *d*, *J* = 8 Hz, 1'-H), 4.91 (1H, *dd*, *J* = 1.5 and 6.5 Hz, 4-H), 5.07 (1H, *dd*, *J* = 10 and 9 Hz, 3'-H), 6.09 (1H, *br s*, 1-H), 6.391 (1H, *d*, *J* = 6.5 Hz, 3-H), 6.393 and 7.66 (each 1H, *d*, *J* = 16 Hz, *trans*-double bond), 6.80 and 7.47 (each 2H, *d*, *J* = 8.5 Hz, 1,4-disubstituted benzene); ^{13}C NMR (CD_3OD): see Table 1; FAB-MS *m/z*: 575 $[M+Na]^+$ (+NaI) and 591 $[M+K]^+$ (+KI) (Found: C, 53.77; H, 5.83. $C_{26}H_{32}O_{13}\cdot 3/2\ H_2O$ requires: C, 53.88; H, 6.09%).

Decumbeside D (8). Amorphous powder, $[\alpha]_D^{29}$ −158° (MeOH, *c* 0.53); UV λ_{max}^{MeOH} nm (ε): 224 (9424) and 307 (12738); IR ν_{max}^{KBr}: 3700–3100, 1725, 1710, 1650, 1630, 1610, 1515, 1270, 1240, 1170, and 830 cm^{-1}; ^1H NMR (CD_3OD): δ 1.46 (3H, *s*, 10-H_3), 1.94 (1H, *dd*, *J* = 4.5 and 15 Hz, 7α-H), 2.17 (1H, *d*, *J* = 15 Hz, 7β-H), 2.86 (1H, *br s*, 9-H), 3.70–3.76 (2H, *m*, 6-H + 1H), 3.90 (1H, *dd*, *J* = 12 and 2 Hz, 6'-H_1), 4.70 (1H, *d*, *J* = 8 Hz, 1'-H), 4.91 (1H, *dd*, *J* = 6.5 and 1.5 Hz, 4-H), 5.06 (1H, *dd*, *J* = 9 and 9 Hz, 3'-H), 5.83 and 6.86 (each 1H, *d*, *J* = 13 Hz, *cis*-double bond), 6.08 (1H, *d*, *J* = 1 Hz, 1-H), 6.39 (1H, *d*, *J* = 6.5 Hz, 3-H), and 6.74 and 7.64 (each 2H, *d*, *J* = 8.5 Hz, 1,4-disubstituted benzene); ^{13}C NMR: See Table 1; FAB-MS *m/z*: $[M+Na]^+$ (+NaI) and 591 $[M+K]^+$ (+KI).

Fraction Nos 85–102 were combined and evapd *in vacuo* to give a residue (255 mg) which was sepd by prep. HPLC (column: as above; solvent: H_2O–MeOH 1:1; flow rate 7.5 ml/min; detection: 210 nm). From the faster eluate decumbeside A (1) (45.1 mg) was obtained. Decumbeside B (2) (28.7 mg) was obtained from the slower eluate.

Decumbeside A (1). Amorphous powder, $[\alpha]_D^{26}$ −60° (MeOH, *c* 0.52); UV λ_{max} nm (ε): 228 (9083) and 315 (17163); IR ν_{max}^{KBr} 3700–3000, 1700, 1650, 1630, 1605, 1515, 1270, 1240, 1175, 960, 860, and 825 cm^{-1}; ^1H NMR (CD_3OD): δ 1.43 (3H, *s*, 10-H_3), 1.97 (2H, *br s*, 6-H_2), 2.27 (1H, *d*, *J* = 5 Hz, 9-H), 3.21 (1H, *br s*, 7-H), 3.70 (2H, *m*), 3.94 (1H, *d*, *J* = 11.5 Hz, 6'-H_1), 5.50 (1H, *d*, *J* = 5 Hz, 1-H), 6.21 (1H, *d*, *J* = 6.5 Hz, 3-H), 6.36 and 7.65 (each 1H, *d*, *J* = 16 Hz, *trans*-double bond), and 6.81 and 7.48 (each 2H, *d*, *J* = 8.5 Hz, 1,4-disubstituted benzene); (C_5D_5N): δ 1.36 (3H, *s*, 10-H_3), 1.98 (1H, *dd*, *J* = 14 and 2.5 Hz, 6-H_1), 2.23 (1H, *d*, *J* = 14 Hz, 6-H_1), 2.74 (1H, *br d*, *J* = 4 Hz, 9-H), 3.10 (1H, *d*, *J* = 2.5 Hz, 7-H), 5.01 (1H, *dd*, *J* = 6 and 1 Hz, 4-H), 5.44 (1H, *d*, *J* = 8.5 Hz, 1'-H), 5.66 (1H, *dd*, *J* = 8.5 and 8.5 Hz, 2'-H), 5.79 (1H, *d*, *J* = 4 Hz, 1-H), 6.41 (1H, *d*, *J* = 6 Hz, 3-H), 6.63 and 7.98 (each 1H, *d*, *J* = 16 Hz, *trans*-double bond), and 7.17 and 7.55 (each 2H, *d*, *J* = 8.5 Hz, 1,4-disubstituted benzene); ^{13}C NMR: see Table 1; FAB-MS *m/z* 515 $[M+Na]^+$ (+NaI) and 531 $[M+K]^+$ (+KI) (Found: C, 55.59; H, 5.91. $C_{24}H_{28}O_{11}\cdot 3/2\ H_2O$ requires: C, 55.49; H, 6.02%).

Decumbeside B (2). Amorphous powder, $[\alpha]_D^{26}$ −13° (MeOH, *c* 0.59); UV λ_{max}^{MeOH} nm (ε): 225 (9212) and 312 (14371); IR ν_{max}^{KBr}: 3700–3000, 1710, 1650, 1630, 1605, 1515, 1280, 1280, 1240, 1180, 960, 860, and 825 cm^{-1}; ^1H NMR (CD_3OD): δ 1.47 (3H, *s*, 10-H_3), 1.99 (2H, *br s*, 6-H_2), 2.24 (1H, *d*, *J* = 6 Hz, 9-H), 3.26 (1H, *br s*, 7-H), 3.63 (2H, *m*), 3.94 (1H, *d*, *J* = 11.5 Hz, 6'-H_1), 5.42 (1H, *d*, *J* = 6 Hz, 1-H), 5.81 and 6.89 (each 1H, *d*, *J* = 13 Hz, *cis*-double bond), 6.25 (1H, *d*, *J* = 6.5 Hz, 3-H), and 6.75 and 7.65 (each 2H, *d*, *J* = 8.5 Hz, 1,4-disubstituted benzene); (C_5D_5N): δ 1.44 (3H, *s*, 10-H_3), 1.90 (1H, *dd*, *J* = 14 and 2.5 Hz, 6α-H), 2.20 (1H, *d*, *J* = 14 Hz, 6β-H), 2.70 (1H, *br d*, *J* = 4 Hz, 9-H), 3.10 (1H, *d*, *J* = 2.5 Hz, 7-H), 5.03 (1H, *dd*, *J* = 6 and 1 Hz, 4-H), 5.44 (1H, *d*, *J* = 8.5 Hz, 1'-H), 5.62 (1H, *dd*, *J* = 8.5 and 8.5 Hz, 2'-H), 5.71 (1H, *d*, *J* = 4 Hz, 1-H), 6.05 and 6.93 (each 1H, *d*, *J* = 13 Hz, *cis*-double bond), 6.45 (1H, *d*, *J* = 6 Hz, 3-H), and 7.15 and 8.12 (each 2H, *d*, *J* = 8.5 Hz, 1,4-disubstituted benzene); ^{13}C NMR: see Table 1; FAB-MS *m/z*: 515 $[M+Na]^+$ (+NaI) and 531 $[M+K]^+$ (+KI).

An aliquot (3 g) of the residue from the *n*-BuOH sol portion was subjected to silica gel chromatography (Kiesel gel PF_{254}; 60 g) with $CHCl_3$–MeOH (22:3) as eluant collecting 7 ml fractions. The residue from Fr. Nos 36–40 was purified by repeated silica gel chromatography to give reptoside (6) (9.7 mg) as an amorphous powder. $[\alpha]_D^{23}$ −80° (MeOH, *c* 1.0); IR ν_{max}^{KBr}: 3400, 2930, 1710, 1370, 1235, 1070, and 840 cm^{-1}; ^1H NMR (CD_3OD): δ 1.47 (3H, *s*, 10-H_3), 1.62–1.71 (2H, *m*), 1.97–2.11 (2H, *m*), 2.02 (3H, *s*, OAc), 2.63 (1H, *br s*, 9-H), 4.75 (1H, *d*, *J* = 8 Hz, 1'-H), 4.95 (1H, *dd*, *J* = 6.5 and 1.5 Hz, 4-H), 5.91 (1H, *d*, *J* = 1 Hz, 1-H) and 6.36 (1H, *d J* = 6.5 Hz, 3-H); FAB-MS *m/z*: 413[M + Na]$^+$ (+NaI). Fraction Nos 46–88 were combined and the solvent was removed *in vacuo* to give 8-acetylharpagide (9) (756 mg) as an amorphous powder. $[\alpha]_D^{20}$ −117° (MeOH, *c* 1.0); IR ν_{max}^{KBr}: 3400, 2900, 1700, 1650, 1370, 1240, 1070, and 960 cm^{-1}; ^1H NMR (CD_3OD) δ: 1.45 (3H, *s*, 10-H_3), 1.95 (1 H, *dd*, *J* = 15 and 4.5 Hz, 7α-H), 2.01 (3H, *s*, OAc), 2.17 (1 H, *d*, *J* = 15 Hz, 7β-H), 2.85 (1 H, *br s*, 9-H), 3.71 (1 H, *d*. *J* = 4.5 Hz, 6-H), 3.89 (1 H, *dd*, *J* = 12 and 1.5 Hz, 6'-H_1), 4.59 (1 H, *d*, *J* = 8 Hz, 1'-H), 4.91 (1 H, *dd*, *J* = 6.5 and 1 Hz, 4-H), 6.07 (1 H, *d*, *J* = 1 Hz, 1-H) and 6.38 (1 H, *d*, *J* = 6.5 Hz, 3-H); FAB-MS *m/z*: 407 $[M+1]^+$ and 445 $[M+K]^+$. Reptoside (6) and 8-O-acetylharpagide (9) were identified on the basis of comparisons of spectral data with those reported.

Decumbeside A tetracetate (3). Acetylation of decumbeside A (1) with Ac_2O–pyridine gave the tetraacetate (3) as an amorphous powder. IR $\nu_{max}^{CHCl_3}$: 3500, 1750, 1650 (sh), 1635, 1600, 1505, and 1240 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.47 (3 H, *s*, 10-H_3), 1.99, 2.05, and 2.11 (each 3H, *s*, 3 × alcoholic OAc), 2.32 (3H, *s*, phenolic OAc), 2.42 (1H, *d*, *J* = 5.5 Hz, 9-H), 3.26 (2H, *br s*, 7-H + OH), 3.77 (1H, *m*, 5'-H), 4.21 (1H, *dd*, *J* = 12.5 and 2.5 Hz, 6'-H_1), 4.30 (1H, *dd*, *J* = 12.5 and 4 Hz, 6'-H_1) 4.83 (1H, *dd*, *J* = 6.5 and 0.5 Hz, 4-H), 4.94 (1H, *d*, *J* = 8 Hz, 1'-H), 5.10–5.42 (4H), 6.14 (1H, *d*, *J* = 6 Hz, 3-H), 6.35 and 7.70 (each 1H, *d*, *J* = 16 Hz, *trans*-double bond), and 7.14 and 7.56 (each 2H, *d*, *J* = 8.5 Hz,

1,4-disubstituted benzene); FAB-MS *m/z*: 683 $[M+Na]^+$ (+NaI) and 699 $[M+K]^+$ (+KI).

Hydrolysis of decumbeside A (1). To a soln of decumbeside A (1) (12.7 mg) in MeOH (3 ml), 1 N NaOH aq soln (3 drops) was added. After 3 hr at room temp., the reaction mixture was neutralized with Amberlite IR-120B (H-form). The ion exchange resin was removed and the filtrate evapd *in vacuo*. The residue was purified by prep. TLC (silica gel; solvent: $CHCl_3$–MeOH 7:3) to give galiridoside (5) (5.4 mg) as a syrup. $[\alpha]_D^{30}$ −70° (MeOH, *c* 0.23); IR ν_{max} (film on NaCl plate): 3400 (*br*), 1660, 1080, 1030, 890 and 815 cm^{-1}; ^1H NMR* (D_2O): δ1.53 (3H, *s*, 10-H_3), 2.12 (1H, *d*, *J* = 15 Hz, 7-H_1), 2.23 (1H, *dd*, *J* = 15 and 2 Hz, 7-H_1), 2.43 (1H, *d*, *J* = 6 Hz, 9-H), 3.54 (1H, *br s*, 7-H), 3.74 (1H, *dd*, *J* = 12.5 and 5 Hz, 6'-H), 3.94 (1H, *dd*, *J* = 12.5 and 2 Hz), 4.78 (DOH), 4.82 (1H, *d*, *J* = 7.5 Hz, 1'-H), 5.05 (1H, *dd*, *J* = 6 and 0.5 Hz, 4-H), 5.48 (1H, *d*, *J* = 6 Hz, 1-H) and 6.42 (1H, *d*, *J* = 6 Hz, 3-H); FAB-MS *m/z*: 369 $[M+Na]^+$ (+NaI) and 385 $[M+K]^+$ (+KI). This sample was identified as galiridoside (5) by comparisons of spectral data.

Decumbeside B tetraacetate (4). Acetylation of decumbeside B (2) with Ac_2O–pyridine gave the tetraacetate (4) as an amorphous powder. IR $\nu_{max}^{CHCl_3}$: 3500, 1755, 1655, 1630, 1600, 1505 and 1230 cm^{-1}; ^1H NMR ($CDCl_3$): δ1.49 (3H, *s*, 10-H_3), 1.97, 2.03 and 2.09 (each 3H, *s*, 3 × alcoholic OAc), 2.31 (3H, *s*, phenolic OAc), 2.34 (1H, *d*, *J* = 5 Hz, 9-H), 3.18 (1H, *s*, OH), 3.32 (1H, *br s*, 7-H), 3.73 (1H, *m*, 5'-H), 4.23 (2H, *m*, 6'-H_2), 4.86 (1H, *d*, *J* = 6 Hz, 4-H), 4.91 (1H, *d*, *J* = 8 Hz, 1'-H), 5.04–5.30 (4H), 5.89 and 6.98 (each 1H, *d*, *J* = 13 Hz, *cis*-double bond), 6.20 (1H, *d*, *J* = 6 Hz, 3-H), and 7.10 and 7.68 (each 2H, *d*, *J* = 8.5 Hz, 1,4-disubstituted benzene); FAB-MS *m/z*: 683 $[M+Na]^+$ (+NaI) and 699 $[M+K]^+$ (+KI).

Partial hydrolysis of decumbeside C (7). To a soln of decumbeside C (7) (15.9 mg) in MeOH (3 ml), 1 N NaOH aq soln (1 drop) was added. After 2 hr at room temp., the reaction mixture was neutralized with Amberlite IR-120B (H-form). The ion exchange resin was removed and the filtrate concd *in vacuo*. The residue was sepd by prep. TLC (silica gel; solvent: $CHCl_3$–MeOH 7:3) to give 8-acetylharpagide (9) (4.3 mg), $[\alpha]_D^{30}$ −112° (MeOH, *c* 0.21), as a syrup [FAB-MS *m/z*: 429 $[M+Na]^+$ (+NaI) and 445 $[M+K]^+$ (+KI)], which was identical with an authentic sample in all respects.

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*TSP [3-trimethylsilyl)-propionic acid-d_4-sodium salt] was used as an external standard and the spectrum was measured at 26°.

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