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FOUR IRIDOIDS FROM *RANDIA CANTHIOIDES**

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Key Word Index—*Randia canthioides*; Rubiaceae; iridoid glucosides; iridoid; 10-dehydrogardenoside; dimeric 10-dehydrogardenoside; randioside; deacetylasperulosidic acid methyl ester aglycone.

Abstract—Four new iridoids, 10-dehydrogardenoside, dimeric 10-dehydrogardenoside, randioside and deacetylasperulosidic acid methyl ester aglycone, have been isolated together with three known iridoid glucosides, gardenoside, deacetylasperulosidic acid methyl ester and scandoside methyl ester, from *Randia canthioides*. It is conceivable that dimeric 10-dehydrogardenoside could be an artefact formed during the isolation process.

INTRODUCTION

As a part of the studies on iridoid glucosides of plants of the Rubiaceae [1, 2], we have examined the constituents of *Randia canthioides* Champ. *ex* Benth. (Japanese name: Shimamisaonoki).

This paper describes the structure elucidation of four new iridoids isolated along with three known iridoid glucosides from this plant.

RESULTS AND DISCUSSION

The MeOH extract of twigs and leaves of *Randia canthioides* was diluted with H_2O and washed with C_6H_6. The H_2O-soluble portion was fractionated by a combination of charcoal chromatography, droplet counter-current chromatography (DCCC) and Si gel chromatography (see Experimental), giving 10-dehydrogardenoside (**1**), dimeric 10-dehydrogardenoside (**2**), randioside (**3**) and deacetylasperulosidic acid methyl ester aglycone (**4**), along with three known iridoid glucosides: gardenoside (**5**), deacetylasperulosidic acid methyl ester (**6**) and scanoside methyl ester (**7**).

10-*Dehydrogardenoside* (**1**) *and dimeric* 10-*dehydrogardenoside* (**2**)

Because of the lability, as well as a low content of 10-dehydrogardenoside (**1**), this compound was purified with difficulty as its acetate (**8**). The ^{1}H NMR spectrum of the pentaacetate (**8**) showed signals for five acetoxy groups at δ 1.92–2.14, a singlet for the 11-carbomethoxy group at 3.77, a doublet (J = 2.0 Hz) for the C-1 proton at 5.60, a broad singlet for the C-3 proton characteristic of iridoids at 7.30 and a singlet for an aldehyde group at 9.44. In addition, it showed an AB part of an ABX system at 6.03 (*dd*, $J_{7,6}$ = 7.0 Hz, $J_{7,5}$ = 2.0 Hz) and 6.63 (*dd*, $J_{6,7}$ = 7.0 Hz, $J_{6,5}$ = 3.0 Hz), which is characteristic of gardenoside (**5**) or monotropein (**9**) type compounds. These data indicated that **1** is a 10-dehydro derivative of gardenoside (**5**) or monotropein methyl ester (**10**). Furthermore, the smooth conversion of **1** into its pentaacetate suggested the β-orientation of the 8-hydroxy group on the less hindered convex face of the iridoid skeleton. This was also supported by the structure of the dimeric compound **2** described below.

Dimeric 10-dehydrogardenoside (**2**) was obtained as hygroscopic colourless needles, mp 168–170°, $C_{34}H_{44}O_{22}.2H_2O$, $[\alpha]_D$ −113.9° (H_2O). It showed in the IR spectrum (KBr) bands for OH groups (3350 cm^{-1}) and a conjugated ester (1680 and 1630 cm^{-1}). In the ^{1}H NMR spectrum (200 MHz), signals very similar in coupling patterns to those of the protons in gardenoside–monotropein type compounds appeared in pairs as follows: δ5.74 (*dd*, $J_{7,6}$ = 6.0 Hz, $J_{7,5}$ = 2.0 Hz) and 5.84 (*dd*, $J_{7,6}$ = 6.4 Hz, $J_{7,5}$ = 1.0 Hz, C-7 and C-7′ protons); 6.40 (*dd*, $J_{6,7}$ = 6.0 Hz, $J_{6,5}$ = 3.0 Hz) and 6.46 (*dd*, $J_{6,7}$ = 6.4 Hz, $J_{6,5}$ = 3.2 Hz, C-6 and C-6′ protons); 7.46 and 7.50 (each *br s*, C-3 and C-3′ protons). In addition, the signals for the proton on the C-10 of the acetal moiety and that on C-10′ of the hemiacetal portion were at 5.23 and 5.58 (each *s*), respectively. The ^{1}H NMR spectrum (200 MHz) of the acetate (**11**) showed signals for nine OAc groups. In addition, the signal for the C-10′ proton shifted considerably downfield (0.84 ppm), whereas that for the C-10 proton moved slightly upfield (0.15 ppm) relative to the corresponding frequencies in the free glucoside (**2**). These data indicated that the aglycone moiety of **11** had only one

*Part 43 in the series "Studies on Monoterpene Glucosides and Related Natural Products". For Part 42 see Inoue, K., Takeda, Y., Tanahashi, T. and Inouye, H. *Chem. Pharm. Bull. (Tokyo)* (1981) **29**, 981.

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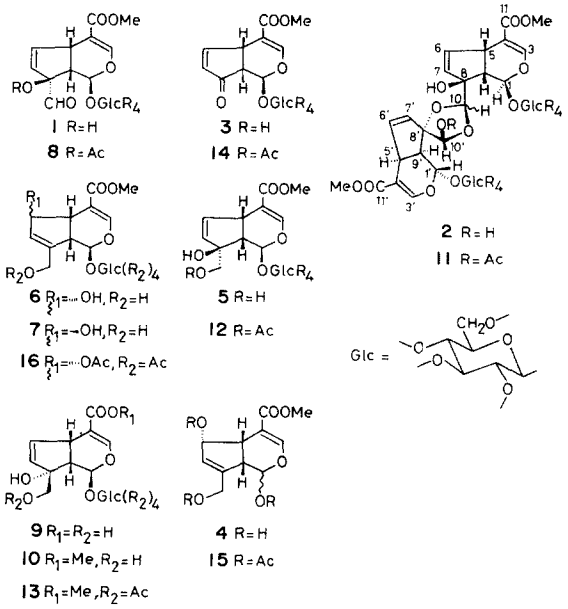

acetoxy group at the C-10′ position. In view of the absence of monotropein type compounds in this plant, the dimeric compound was presumed to have the structure **2** formed from two units of 10-dehydrogardenoside (**1**) through C–O bond formations between the 8′-hydroxy and 10-aldehyde groups as well as the 10′-aldehyde and the 10-aldehyde groups. The ^{13}C NMR spectrum (Table 1) agreed with this structure. Furthermore, the chemical shifts of C-9 and C-9′ of **11** were in accordance with the corresponding frequencies of gardenoside pentaacetate (**12**) rather than those of monotropein methyl ester pentaacetate (**13**) [3]. This fact suggested a gardenoside type substance constituting the dimeric compound (**2**). In fact, a D_2O soln of **2**, when set aside at room temperature for 1 hr, showed in the ^1H NMR spectrum a very weak signal of an aldehyde proton at δ9.38 which was considered to originate from a partially liberated monomer. This D_2O solution afforded, on addition of $NaBH_4$, a reduction product in a low yield, which on acetylation gave rise to gardenoside pentaacetate (**12**). Thus, the absolute configuration of all chiral centres in the dimeric compound (**2**) except for that of C-10 and C-10′ was elucidated. Furthermore, the presence of NOE (*ca* 16%) between the C-10′ and C-1′ protons as well as the absence of that between the C-10′ and C-7′ protons in the acetate (**11**) indicated the *S*-configuration at the C-10′ position. However, the orientation of the C-10 remained unclarified owing to the absence of NOEs between the corresponding protons of the counterpart. Since the configuration of the C-10′ of the original glucoside (**1**) is expected to be the same as that of the acetate (**11**), the absolute structure of **2** except for the stereochemistry of C-10 was thus established.* It is conceivable that **2** could be an artefact formed during the isolation process.

Randioside (**3**)

Randioside (**3**) was obtained as a hygroscopic white powder, $C_{16}H_{20}O_{10}.H_2O$, $[\alpha]_D$ −29.4° (MeOH). It showed in the IR spectrum (KBr) bands for hydroxy groups (3350 cm^{-1}) and a conjugated ester (1700 and 1640 cm^{-1}). The ^1H NMR spectrum (100 MHz) of the tetraacetate (**14**) showed signals for acetoxy groups (δ1.95–2.12), the 11-carbomethoxy group (3.78) and the C-1 proton (5.85, *d*, J = 1.2 Hz), as well as signals comprising an AMX system at 3.99 (*m*, $J_{5,9}$ = 7.5 Hz, $J_{5,6}$ = 3.0 Hz, $J_{5,7}$ = 1.8 Hz, $J_{5,3}$ = 1.0 Hz), 6.18 (*dd*, $J_{7,6}$ = 5.6 Hz, $J_{7,5}$ = 1.8 Hz) and 7.98 (*dd*, $J_{6,7}$ = 5.6 Hz, $J_{6,5}$ = 3.0 Hz), whose coupling patterns are similar to those of the protons on C-5, C-7 and C-6 of gardenoside–monotropein type compounds. In view of a significant downfield shift of the C-6 proton signal of **3** relative to the corresponding frequencies observed for the other similar compounds, randioside tetraacetate was assumed to have structure **14**. Indeed, it was found to be identical with the compound (mp 129–131°) obtained during the study on the transformation of geniposide into plumieride [4]. Furthermore, Jones oxidation of gardenoside (**5**) followed by acetylation also yielded the same compound. Thus, the absolute structure of randioside tetraacetate (**14**) and hence, that of randioside (**3**) was established.

Deacetylasperulosidic acid methyl ester aglycone (**4**)

Compound **4**, a trace constituent, was purified as its triacetate. The acetate (**15**) showed IR ($CHCl_3$) bands for a conjugated ester at 1720 and 1640 cm^{-1} characteristic of iridoids. The ^1H NMR spectrum of **15**

*According to a personal communication, Dr. S. R. Jensen and his group of Technical University of Denmark also isolated compounds **1** and **2** from *Stylidium* plants.

Table 1. ^{13}C NMR spectral data* for the glucoside acetates, **11**, **12** and **13**

Compound	C-1	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	COOMe
11	92.7	149.4	111.5	37.2	128.9	136.0	84.3	49.9	94.1	166.5	51.3
	(*d*)	(*d*)	(*s*)	(*d*)	(*d*)	(*d*)	(*s*)	(*d*)	(*d*)	(*s*)	(*q*)
	92.9	149.5	111.7		133.5	138.8	96.1	51.7	105.7	166.6	
	(*d*)	(*d*)	(*s*)		(*d*)	(*d*)	(*s*)	(*d*)	(*d*)	(*s*)	
12	95.5	149.2	111.1	37.3	133.8	135.3	83.5	50.9	67.9	166.4	51.4
	(*d*)	(*d*)	(*s*)	(*d*)	(*d*)	(*d*)	(*s*)	(*d*)	(*t*)	(*s*)	(*q*)
13	96.3	149.8	110.8	37.8	131.6	137.6	83.5	45.0	68.1	166.4	51.3
	(*d*)	(*d*)	(*s*)	(*d*)	(*d*)	(*d*)	(*s*)	(*d*)	(*t*)	(*s*)	(*q*)

*Off-resonance patterns are given in parentheses.
All compounds have additional signals arising from the glucose moiety.

showed five-proton signals at δ3.19 ($J_{5,9}$ = 8.0 Hz, $J_{5,6}$ = 6.4 Hz, $J_{5,3}$ = 2.0 Hz), 4.68 (*br s*), 5.73 (*dd*, $J_{6,5}$ = 6.4 Hz, $J_{6,7}$ = 3.0 Hz) and 6.15 (*br s*). These chemical shifts and coupling patterns are very similar to those of the protons on C-5, C-10, C-6 and C-7 of methyl deacetylasperulosidate hexaacetate (**16**), respectively. In addition, signals for three acetoxy groups (1.94–2.17), the 11-carbomethoxy group (3.71), the C-1 proton (5.68, *d*, *J* = 10.0 Hz) and the C-3 proton (7.57, *d*, *J* = 2.0 Hz) were found in this spectrum. The low field shift of the C-1 proton was explained by the presence of an acetoxy group at C-1. From these findings, **15** was assumed to be a triacetate of deacetylasperulosidic acid methyl ester aglycone. Therefore, deacetylasperulosidic acid methyl ester (**6**) was submitted to enzymatic hydrolysis with β-glucosidase under mild conditions, giving an aglycone, which, on acetylation, afforded the substance identical with **15** in all respects. The absolute structure of **4** was thus established.

The genus *Randia*, like *Gardenia*, is taxonomically referred to the tribe Gardenieae. In earlier works Briggs and Nicholls [5] as well as Kooiman [6] have reported that species of *Randia* failed to give positive reactions for asperuloside-type compounds. However, the present work showing the occurrence of deacetylasperulosidic acid methyl ester (**6**) and its aglycone (**4**) has provided chemotaxonomic evidence for the genus *Tandia* belonging to the tribe Gardenieae.

EXPERIMENTAL

General procedures. All mps are uncorr. Unless otherwise noted, ^{1}H NMR spectra were recorded at 60 MHz, and ^{13}C NMR spectra at 20 MHz. TMS was used in $CDCl_3$, whereas DSS was used in D_2O as the int. standard. Chemical shifts are given in δ (ppm) relative to the int. standard. CC was carried out using activated charcoal or Si gel. Si gel 60 GF_{254} was employed for TLC, and spots were visualized by exposure to I_2 vapour or by spraying with an anisaldehyde–H_2SO_4 reagent (anisaldehyde 0.5 ml, conc H_2SO_4 0.5 ml, 95% EtOH 9.0 ml and a few drops of AcOH) followed by heating. Si gel 60 PF_{254} was used for PLC (20 × 20 cm, 1 mm in thickness) and bands were detected under UV light (254 nm). DCCC was carried out by the use of an apparatus consisting of Pyrex glass tubes (120 cm × 3.4 mm) and Teflon tubes (140 cm × 1.1 mm) [7]. *n*-BuOH–EtOH–H_2O (4:1:5) was used as the solvent system, and the upper phase was moved in the ascending manner. HPLC was conducted under the following conditions: column, LS-410 K (30 cm × 4.0 mm) (reversed-phase): solvent, 30% MeOH–H_2O; flow rate, 0.7 ml/min; detector, UV (230 and 254 nm).

Plant material. Randia canthioides was collected in Ishigaki Island (Okinawa Pref.) in December 1978. Plant material was identified by Mr. G. Murata of Faculty of Science, Kyoto University. Voucher specimen of *Randia canthioides* (S. Uesato and I. Kawamura, No. 1) has been deposited in the Herbarium of the Institute of Botany, Faculty of Science, Kyoto University (KYO), Kitashirakawa-oiwake-cho, Sakyo-ku, Kyoto 606, Japan.

Isolation of iridoids from Randia canthioides. *Expt A.* Dry leaves with twigs (1.2 kg) of *R. canthioides* were extracted with boiling MeOH (20 l. × 4) for 20 min. After concn of the combined extracts *in vacuo*, the residue was diluted with H_2O (3 l.). Insoluble materials were filtered off and washed with H_2O (2 l.). The combined filtrate and washings were rinsed with C_6H_6 (1 l. × 2) and concd *in vacuo* to *ca* 3.5 l. This soln was transferred to a charcoal (500 g) column and eluted using MeOH–H_2O as eluent with an increasing MeOH content to afford the following eluates: 50% MeOH (Chr 1–1), 60% MeOH (Chr 1–2), 70% MeOH (Chr 1–3), 80% MeOH (Chr 1–4) and 100% MeOH (Chr 1–5). On concn, Chr 1–1, 1–2 and 1–3 gave gardenoside (**5**) (11.5 g), deacetylasperulosidic acid methyl ester (**6**) (2.7 g) and scandoside methyl ester (**7**) (0.3 g), respectively. The residue (1.7 g) from Chr 1–4 was subjected to DCCC. Fractions showing a major peak at (R_t) 11.5 min on HPLC were combined and concd *in vacuo* to give a residue (132 mg) (Chr 2–1). The residue (0.9 g) from Chr 1–5 was also submitted to DCCC, and fractions showing a major peak at R_t 11.5 min on HPLC were combined and concd *in vacuo* to furnish a residue (47 mg) (Chr 3–1), whereas fractions showing a major peak at R_t 15.0 min gave a residue (232 mg) (Chr 3–2). Next, Chr 2–1 and Chr 3–1 (total 179 mg) were combined and subjected to prep. TLC (3 developments) with $CHCl_3$–MeOH (85:15) as eluant. The major band was scraped off and extracted with $CHCl_3$–MeOH (8:2). Evaporation of the extract gave a colourless oily residue (51 mg), an aliquot (27 mg) of which was acetylated with Ac_2O–pyridine (each 0.5 ml) by the usual method. The product was purified by prep. TLC (9 developments) with $CHCl_3$–MeOH (99.5 : 0.5) as eluant to afford the aglycone triacetate (**15**) of methyl deacetylasperulosidate (21.4 mg) as a colourless oil. $[\alpha]_D^{14}$ + 118.0° ($CHCl_3$; *c* 1.00); UV λ_{max}^{MeOH} nm (log ε): 234 (3.81); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1720, 1640; ^{1}H NMR ($CDCl_3$): δ1.94–2.17 (3 × OCOMe), 2.75 (*dd*, *J* = 10.0, 8.0 Hz, 9-H), 3.19 (*ddd*, *J* = 8.0, 6.4, 2.0 Hz, 5-H), 3.71 (*s*, COOMe), 4.68 (*br s*, 10-H_2), 5.68 (*d*, *J* = 10.0 Hz, 1-H), 5.73 (*dd*, *J* = 6.4, 3.0 Hz, 6-H), 6.15 (*br s*, 7-H), 7.57 (*d*, *J* = 2.0 Hz, 3-H); MS: M^+ 368.1129, $C_{17}H_{20}O_9$ requires: 368.1107. Chr 3–2 (232 mg) was submitted to prep. TLC (3 developments) with $CHCl_3$–MeOH (75 : 25) as eluant. Of the two major bands, the less-polar one gave randioside (**3**) (14 mg) as a hygroscopic white powder, whereas the more-polar one afforded, after recrystallization from MeOH, dimeric 10-dehydrogardenoside (**2**) (31 mg) as hygroscopic colourless needles, mp 168–170°. Randioside (**3**), $[\alpha]_D^{17}$ − 29.4° (MeOH; *c* 0.20); UV λ_{max}^{MeOH} nm (log ε): 217 (4.13); IR ν_{max}^{KBr} cm^{-1}: 3350, 1700, 1640, 1580; ^{1}H NMR (D_2O): δ3.80 (*s*, COOMe), 5.68 (*d*, *J* = 3.0 Hz, 1-H), 6.28 (*dd*, *J* = 6.0, 2.0 Hz, 7-H), 7.45 (*d*, *J* = 1.4 Hz, 3-H), 8.08 (*dd*, *J* = 6.0, 3.0 Hz, 6-H). (Found: C, 49.47; H, 5.74. $C_{16}H_{20}O_{10}.H_2O$ requires: C, 49.23; H, 5.68%.) Dimeric 10-dehydrogardenoside (**2**), $[\alpha]_D^{13}$ −113.9° (H_2O; *c* 0.36); UV λ_{max}^{MeOH} nm (log ε): 235 (4.30); IR ν_{max}^{KBr} cm^{-1}: 3350, 1680, 1630; ^{1}H NMR (200 MHs, D_2O): δ2.77 (*dd*, *J* = 8.0, 2.0 Hz) and 2.99 (*dd*, *J* = 9.2, 1.2 Hz) (9- and 9′-H), 3.77 (*s*, 2 × COOMe), 5.23 and 5.58 (each *s*) (10- and 10′-H), 5.74 (*dd*, *J* = 6.0, 2.0 Hz) and 5.84 (*dd*, *J* = 6.4, 1.0 Hz (7- and 7′-H), 5.87 (*d*, *J* = 2.0 Hz) and 5.94 (*d*, *J* = 1.2 Hz) (1- and 1′-H), 6.40 (*dd*, *J* = 6.0, 3.0 Hz) and 6.46 (*dd*, *J* = 6.4, 3.2 Hz) (6- and 6′-H), 7.46 and 7.50 (each *br s*, 3- and 3′-H). (Found: C, 48.70; H, 6.05. $C_{34}H_{44}O_{22}.2H_2O$ requires: C, 48.57; H, 5.75%.)

Expt B. Fresh leaves (0.6 kg) of *R. canthioides* were worked up in the same way as described above, giving a conc aq. extract, which was transferred to a charcoal (300 g) column and eluted successively with H_2O, 50% MeOH, 70% MeOH and 100% MeOH. After concn of the 70% MeOH eluate, an aliquot (0.51 g) of the residue (3.49 g) was acetylated in the usual way and the product was purified by chromatography on Si gel (40 g) with Et_2O as

eluant to yield 10-dehydrogardenoside pentaacetate (**8**)* (16 mg), besides the aglycone triacetate (**15**) (4 mg) of methyl deacetylasperulosidate (**6**), deacetylasperulosidic acid methyl ester hexaacetate (**16**) (50 mg), the hexaacetate (15 mg) of scandoside methyl ester (**7**) and gardenoside pentaacetate (**12**) (390 mg). The residue (0.43 g) from the 100% MeOH eluate was subjected to DCCC in the same way as in expt A to afford dimeric 10-dehydrogardenoside (**2**) (8 mg) and randioside (**3**) (3 mg), respectively. 10-Dehydrogardenoside pentaacetate (**8**), a white powder, ^{1}H NMR ($CDCl_3$): δ 1.92–2.14 (5 × OCOMe), 3.07 (*dd*, J = 9.5, 2.0 Hz, 9-H), 3.77 (*s*, COOMe), 5.60 (*d*, J = 2.0 Hz, 1-H), 6.03 (*dd*, J = 7.0, 2.0 Hz, 7-H), 6.63 (*dd*, J = 7.0, 3.0 Hz, 6-H), 7.30 (*br s*, 3-H), 9.44 (*s*, 10-H).

Acetylation of randioside (**3**). Randioside (**3**) (10.0 mg) was acetylated with Ac_2O–pyridine (each 0.2 ml) by the usual method and the product was recrystallized from EtOH to give randioside tetraacetate (**14**) (7.2 mg) as colourless needles, mp 129–131°. $[\alpha]_D^{30}$ −56.8° ($CHCl_3$; *c* 0.56); UV λ_{max}^{MeOH} nm (log ε): 217 (4.27); IR ν_{max}^{KBr} cm^{-1}: 1740, 1700, 1640, 1580; ^{1}H NMR (100 MHz, $CDCl_3$): δ1.95–2.12 (4 × OCOMe), 3.03 (*dd*, J = 7.5, 1.2 Hz, 9-H), 3.78 (*s*, COOMe), 3.99 (*m*, 5-H), 5.85 (*d*, J = 1.2 Hz, 1-H), 6.18 (*dd*, J = 5.6, 1.8 Hz, 7-H), 7.28 (*d*, J = 1.0 Hz, 3-H), 7.98 (*dd*, J = 5.6, 3.0 Hz, 6-H). (Found: C, 53.10; H, 5.18. $C_{24}H_{28}O_{14}$ requires: C, 53.34; H, 5.22%.)

Acetylation of dimeric 10-dehydrogardenoside (**2**). Dimeric 10-dehydrogardenoside (**2**) (21.4 mg) was acetylated and the product was subjected to prep. TLC (two developments) with $CHCl_3$–MeOH (98:2) as eluant. The major band gave a residue (25.2 mg), which was recrystallized from EtOH to afford dimeric 10-dehydrogardenoside nonaacetate (**11**) (16.5 mg) as colourless needles, mp 183–185°, $[\alpha]_D^{18}$ −110.5° ($CHCl_3$; *c* 0.61); UV λ_{max}^{MeOH} nm (log ε): 235 (4.28); IR ν_{max}^{KBr} cm^{-1}: 1740, 1700, 1640; ^{1}H NMR (200 MHz, $CDCl_3$): δ1.89–2.11 (9 × OCOMe), 2.77 (*d*, J = 10.0 Hz) and 2.98 (*dd*, J = 10.0, 1.5 Hz) (9- and 9′-H), 3.70 and 3.71 (each *s*, COOMe), 5.08 and 6.42 (each *s*, 10- and 10′-H), 5.64 (*dd*, J = 5.5, 2.0 Hz) and 5.71 (*dd*, J = 5.5, 1.5 Hz) (7- and 7′-H), 5.85 (*br s*) and 6.06 (deformed *d*) (1- and 1′-H), 6.32 (*dd*, J = 5.5, 3.0 Hz) and 6.36 (*dd*, J = 5.5, 3.0 Hz) (6- and 6′-H), 7.31 (*d*, J = 1.5 Hz) and 7.33 (*d*, J = 1.5 Hz) (3- and 3′-H). (Found: C, 52.97; H, 5.08. $C_{52}H_{62}O_{31}$ requires: C, 52.79; H, 5.28%.)

Conversion of dimeric 10-dehydrogardenoside (**2**) *into gardenoside pentaacetate* (**12**). Dimeric 10-dehydrogardenoside (**2**) (7.0 mg) was dissolved in D_2O (0.3 ml) and set aside for 1 hr at room temp. This soln showed in the ^{1}H NMR spectrum a very weak signal at δ9.38 (*s*) due to the 10-aldehyde group. To this soln was added $NaBH_4$ (10 mg) and the reaction mixture was stirred for 1.5 hr under ice cooling. After neutralization with Amberlite IR-120 (H^+-form), the solvent was removed *in vacuo*. The residue (6.1 mg) was acetylated in the usual way and the product was submitted to prep. TLC (two developments) with $CHCl_3$–MeOH (98:2) as eluant. Of the two major bands, the more-polar one afforded a white powder (1.4 mg). $[\alpha]_D^{16}$ −98.0° ($CHCl_3$; *c* 0.12); ^{1}H NMR (100 MHz, $CDCl_3$: δ1.91–2.11 (5 × OCOMe), 2.76 (*dd*, J = 8.8, 2.0 Hz, 9-H), 3.71 (*s*, COOMe), 4.10–4.27 (10-H_2 and 6′-H_2), 5.64 (*d*, J = 2.0 Hz, 1-H), 5.67 (*dd*, J = 6.0, 2.0 Hz, 7-H), 6.24 (*dd*, J = 6.0, 3.0 Hz, 6-H), 7.30 (*d*, J = 1.5 Hz, 3-H). This compound was found to be identical with the pentaacetate (**12**) of gardenoside (**5**) isolated from the plant. On the other hand, from the less polar band, dimeric 10-dehydrogardenoside nonaacetate (**11**) (2.6 mg) was recovered.

Conversion of gardenoside (**5**) *into randioside tetraacetate* (**14**). Jones reagent (10.5 ml) diluted 1:6 with Me_2CO was added to a soln of **5** (316 mg) in MeOH–Me_2CO (2:7) (27 ml) over a period of *ca* 10 min under ice cooling. After stirring for a further 20 min under ice cooling, the mixture was neutralized with 0.1 N methanolic $Ba(OH)_2$ and the insoluble materials were filtered off. Concn of the filtrate *in vacuo* gave a residue consisting of organic and inorganic materials, which was chromatographed on a charcoal column (1.5 g), eluting successively with H_2O (500 ml) and MeOH (800 ml). After concn of the MeOH eluate, the residue (246 mg) was subjected to prep. TLC (six developments) with $CHCl_3$–MeOH (9:1) as eluant. Of the three major bands, the most-polar one was scraped off and extracted with $CHCl_3$–MeOH (9:1). Evaporation of the extract *in vacuo* afforded a white powder (33.7 mg), which was acetylated and the product was recrystallized from EtOH to give colourless needles (23.0 mg), mp 129–131°. $[\alpha]_D^{14}$ −51.5° ($CHCl_3$; *c* 1.09). (Found: C, 53.12; H, 5.52. Calc. for $C_{24}H_{28}O_{14}$: C, 53.34;H, 5.22%.) This compound was found to be identical with the tetraacetate (**14**) of randioside (**3**) isolated from the plant. The remaining two major bands recovered from the prep. TLC were not examined.

Conversion of deacetylasperulosidic acid methyl ester (**6**) *into the corresponding aglycone acetate* (**15**). β-Glucosidase (emulsin prepared from almonds) (80 mg) was added to a soln of **6** (180 mg) in H_2O (5 ml). After standing for 4.5 hr at 23°, the mixture was extracted with EtOAc (25 ml × 8), and the combined extracts were dried and evaporated *in vacuo*. (Under the usual hydrolysis conditions with acetate buffer, pH 4.9, at 37°, the resulting aglycone underwent decomposition.) The residue (71.6 mg) was acetylated and the product was subjected to prep. TLC (9 developments) with $CHCl_3$–MeOH (99.5:0.5) as eluant, yielding a colourless oil (38.7 mg). $[\alpha]_D^{16}$ +114.8° ($CHCl_3$; *c* 0.55); MS: M^+ 368.1107. Calc. for $C_{17}H_{20}O_9$, 368.1107. This compound was found to be identical with the triacetate (**15**) of deacetylasperulosidic acid methyl ester aglycone (**4**) isolated from the plant.

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*The failure to detect compound **8** or the free compound (**1**) in Experiment A might be attributable to decomposition caused by air-drying of the fresh leaves.

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