Phytochemistry, 1974, Vol. 13, pp. 2219 to 2224. Pergamon Press. Printed in England.

TWO NEW IRIDOID GLUCOSIDES FROM *GARDENIA JASMINOIDES* FRUITS*

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(*Received* 7 *February* 1974)

Key Word Index—*Gardenia jasminoides*; Rubiaceae; iridoid glucosides; structures.

Abstract—From the fruits of *Gardenia jasminoides* which have been employed as Chinese crude drug "Shan-zhi-i", two further new iridoid glucosides, gardoside (8,10-dehydrologanic acid) and scandoside methyl ester have been isolated and their structures have been established.

INTRODUCTION

FROM ancient times the fruit of *Gardenia jasminoides* Ellis forma *grandiflora* [L.] Makino (Rubiaceae) ("Shan-zhi-i" in Chinese) has been used as a drug for its antiphlogistic effect. Gardenoside, shanzhiside and deacetylasperulosidic acid methyl ester were isolated from fruits and leaves of this plant by our group.[1–3] Almost simultaneously, from fruits of the same plant geniposide (**4**) and genipin gentiobioside were isolated by Taguchi's group.[1,3] It was recently found by Kuwano *et al.*[4] that of these glucosides, geniposide (**4**) is a purgative.

This paper describes the structural elucidation of two further new iridoid glucosides of this plant.

RESULTS AND DISCUSSION

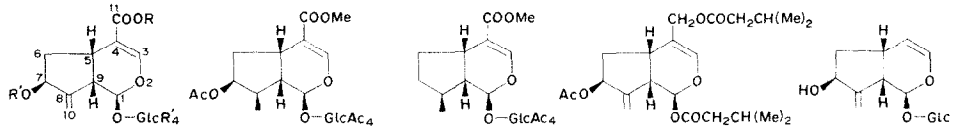
The concentrated methanolic extract of *G. jasminoides* furits was diluted with water, washed with ethyl acetate and evaporated. The residue was fractionated as described in the Experimental and two new iridoid glucosides and geniposidic acid were isolated along with the known gardenoside, shanzhiside, deacetylasperulosidic acid methyl ester, geniposide and genipin gentiobioside.

Gardoside (**1**) was obtained as a powder, $C_{16}H_{22}O_{10}.H_2O$. The NMR spectrum (in D_2O) of **1** showed a two proton signal at δ 5·39 which seems to be due to a terminal olefinic group besides the signal at δ 7·33 assignable to C-3 proton. Acetylation of **1** gave a penta-acetate (**5**), $C_{26}H_{32}O_{15}$, which showed NMR signals due to five acetyl groups (δ 1·99–2·09).

* (a) Part XXVI in the series "Studies on Monoterpene Glucosides and Related Natural Products". For Part XXV see INOUYE, H., UEDA, S., UESATO, S., SHINGU, T., THIES, P. W., KUCABA, W. and CORDERO, H., *Tetrahedron* In press. (b) Also Part II in the series "On the Constituents of *Gardenia* species". For Part I see INOUYE, H., TAKEDA, Y., SAITO, S., NISHIMURA, H. and SAKURAGI, R. (1974) *Yakugakuzasshi* **94,** 577.

[1] INOUYE, H., SAITO, S., TAGUCHI, H. and ENDO, T. (1969) *Tetrahedron Letters*, 2347.
[2] INOUYE, H., SAITO, S. and SHINGU, T. (1970) *Tetrahedron Letters*, 3581.
[3] ENDO, T. and TAGUCHI, H. (1973) *Chem. & Pharm. Bull. (Tokyo)* **21,** 2684.
[4] YAMAUCHI, K., SAKURAGI, R., KUWANO, S. and INOUYE, H. (1974) *Planta Medica* **24,** In press.

Methylation of **5** giving the pentaacetate methyl ester (**6**), $C_{27}H_{34}O_{15}$, followed by catalytic hydrogenation over Pd–C afforded two reduction products. **7**, $C_{27}H_{36}O_{15}$, m.p. 139–140° and **8**, $C_{25}H_{34}O_{13}$, m.p. 113–114·5°. The NMR spectrum of **7** showed signals of a secondary methyl group (δ 1·03, *d*, *J* 7·0 Hz) and five acetyl groups (δ 1·95–2·01), while that of **8** revealed the presence of a secondary methyl group (δ 1·07, *d*, *J* 7·0 Hz) in addition to four acetyl groups (δ 1·93–2·09). From m.mps, IR and NMR data, **7** and **8** were found to be loganin pentaacetate and deoxyloganin tetraacetate, respectively.



(**1**) R = R' = H
(**5**) R = H; R' = —COMe
(**6**) R = CH_3; R' = —COMe

(**7**) (**8**) (**17**) (**18**)

The structure of gardoside as (**1**) was also confirmed by chemical transformation of geniposide (**4**) into gardoside pentaacetate methyl ester (**6**). On Jones oxidation followed by acetylation, geniposide (**4**) was converted to 10-dehydrogeniposide tetraacetate (**9**), $C_{25}H_{30}O_{14}$. This substance was reduced with $NaBH_4$ to alcohol (**10**), $C_{25}H_{32}O_{14}$, which was oxidized with *m*-chloroperbenzoic acid to give two isomeric epoxides **11** and **12** having the same composition, $C_{25}H_{32}O_{15}$. The configurations of their oxiran ring were inferred by the NMR spectral analysis, comparison being made to data on the corresponding 10-deoxy derivatives **13** and **14**.*[5] Namely, the C-3 proton signal of **13** having a β-oriented oxiran ring appeared at δ 7·38, while the parallel signal of **14** of opposite configuration arose at δ 7·25. The appearance of the C-3 proton signal of **11** and **12** at δ 7·43 and 7·25, respectively, lead to the conclusion that the configuration of the oxiran portion of **11** and **12** are β and α, respectively. Oxidation of β-epoxide (**11**) with a mixture of DMSO and Ac_2O, or CrO_3-pyridine complex gave 7,8-β-epoxy-10-dehydrogeniposide tetraacetate (**15**), $C_{25}H_{30}O_{15}$, which was treated with hydrazine monohydrate and AcOH in anhydrous methanol[6] to give gardoside 2',3',4',6'-tetraacetate methyl ester (**16**). This was acetylated in the usual way to give gardoside pentaacetate methyl ester (**6**).

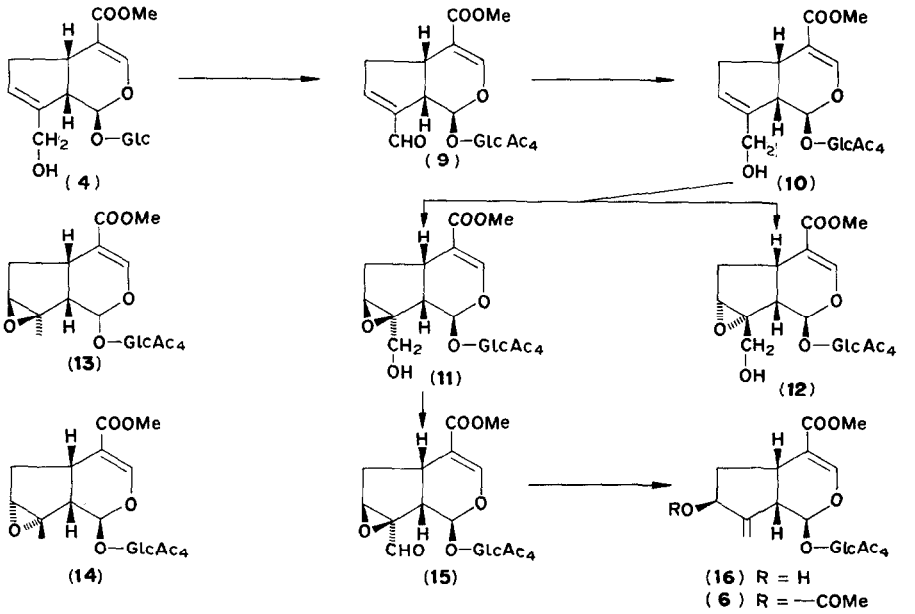
Taking into account the fact that gardoside (**1**) is an iridoid of an unusual type in having an exo double bond at C-8 and a hydroxy group at C-7 on the cyclopentane ring and that it co-occurs with geniposide (**4**), it might be considered that this glucoside (**1**) could be biosynthesized by an allylic rearrangement of **4**. The following known iridoids have the same structural characteristics: 8,10-deoxydihydrovaltrate (**17**) from *Valeriana wallichii* DC.[7] and antirride (**18**) from *Antirrhinum* species[8] and *Linaria japonica* Miq.[9]

Substance **2**, $C_{16}H_{22}O_{10}.H_2O$, was obtained as a powder, whose pentaacetate (**19**), $C_{26}H_{32}O_{15}$, shows NMR signals at δ 4·73, 5·87 and 7·55 assignable to C-10, C-7 and C-3 protons, respectively, in addition to the signals of five acetyl groups at δ 2·02–2·08. This

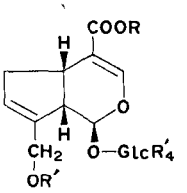
* See footnote on p. 2219.

[5] INOUYE, H., YOSHIDA, T., TOBITA, S. and OKIGAWA, M. (1970) *Tetrahedron* **26**, 3905.
[6] KLEIN, E. and OHLOFF, G. (1963) *Tetrahedron* **19**, 1091.
[7] THIES, P. W. (1968) *Tetrahedron* **24**, 313.
[8] SCARPATI, M. L. and GUISO, M. (1969) *Gazz. Chim. Ital.* **99**, 807.
[9] KITAGAWA, I., TANI, T., AKITA, K. and YOSIOKA, I. (1973) *Chem. & Pharm. Bull. (Tokyo)* **21**, 1978.

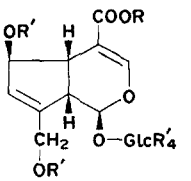
spectrum is very similar to that of geniposide pentaacetate (**20**) except for the absence of the signal due to a carbomethoxy group. The crystalline pentaacetate methyl ester, $C_{27}H_{34}O_{15}$, m.p. 134–135°, derived from **19** was actually identified with an authentic sample of geniposide pentaacetate (**20**). Substance **2** was thus found to be geniposidic acid, which has recently been isolated[10] from *Genipa americana* L. which is taxonomically closely related to *G. jasminoides*.



SCHEME 1



(**2**) R = R′ = H
(**4**) R = Me; R′ = H
(**19**) R = H; R′ = —COMe
(**20**) R = Me; R′ = —COMe



(**3**) R = Me; R′ = H
(**21**) R = Me; R′ = —COMe
(**22**) R = H; R′ = —COMe
(**23**) R = R′ = H

Substance **3**, $C_{17}H_{24}O_{11}.2\,H_2O$ is a powder, which was acetylated to give hexaacetate (**21**), $C_{29}H_{36}O_{17}$. The NMR spectrum of **21** shows signals at δ 4·75, 5·54, 5·88 and 7·39 due to C-10, C-6, C-7 and C-3 protons, respectively, besides the signals at δ 1·96–2·10 and 3·72 due to six acetyl groups and a carbomethoxy group. As the NMR spectrum of **21** closely resembles that of scandoside hexaacetate (**22**) except for the appearance of the signal of carbomethoxy group at δ 3·72, substance **3** was presumed to be scandoside methyl

[10] GUARNACCIA, R., MADYASTHA, K. M., TEGTMEYER, E. and COSCIA, C. J. (1972) *Tetrahedron Letters*, 5125.

ester. This was then verified by the identification of **21** with an authentic sample of scandoside hexaacetate methyl ester which was derived from scandoside (**23**).[11] Substance **3** is thus scandoside methyl ester, the eighth iridoid glucoside to be characterized from the fruit of *G. jasminoides*.

EXPERIMENTAL

General procedures. All m.ps were uncorrected. TLC was carried out on silica gel G and the spots were visualized by exposure to iodine vapour or spraying with anisaldehyde (0·5 ml), conc H_2SO_4 (0·5 ml), AcOH (few drops) and 95% EtOH (9 ml) and then heating. Column chromatography was carried out using carbon or silica gel as adsorbents.

Isolation procedure. Dried fruits of *G. jasminoides* (5 kg) collected in Kochi prefecture (Japan) were extracted with 10 l. MeOH (× 3) under reflux. The MeOH extracts were combined and conc. *in vacuo*. The residue was dissolved in H_2O (3 l.) and the insoluble material was removed by filtration through celite. The filtrate was washed with EtOAc (3 × 1·5 l.) and conc. *in vacuo* to about 1 l. This soln was then chromatographed on a charcoal–celite (1:1) column and eluted with H_2O–MeOH with increasing MeOH content. The fraction eluted with H_2O–MeOH (3:2) was evaporated *in vacuo*. When the residue was chromatographed on silica gel (600 g) eluted with $CHCl_3$–MeOH with increasing MeOH content, geniposide (**4**), scandoside methyl ester (**3**) (1·2 g), deacetylasperulosidic acid methyl ester, gardenoside, geniposidic acid (**2**) (0·9 g), genipin gentiobioside, gardoside (**1**) (0·7 g) and shanzhiside were eluted successively.

Gardoside (**1**) $[\alpha]_D^{22}$ −33·6° (*c* = 0·40, MeOH); UV: λ_{max}^{MeOH} 235·5 nm (log ε 3·98); IR: ν_{max}^{KBr} 3300, 1675, 1625 cm^{-1}; NMR (D_2O): δ 5·39 (2H, *s*, C-10H), 5·53 (1H, *d*, *J* 3·0 Hz, C-1H), 7·33 (1H, *s*, C-3H). (Found: C, 49·04; H, 5·98. $C_{16}H_{22}O_{10}.H_2O$ requires: C, 48·97; H, 6·18%).

Scandoside methyl ester (**3**) $[\alpha]_D^{24}$ −56·11° (*c* = 2·42, MeOH); UV: λ_{max}^{MeOH} 238 nm (log ε 3·89); IR ν_{max}^{Nujol} 1695, 1635 cm^{-1}; NMR (D_2O): δ 3·75 (3H, *s*, $COOCH_3$), 4·31 (2H, diffused *s*, C-10H), 5·38 (1H, *d*, *J* 4·5 Hz, C-1H), 5·86 (1H, *m*, C-7H), 7·50 (1H, *d*, *J* 1·0 Hz, C-3H). (Found: C, 46·55; H, 6·59. $C_{17}H_{24}O_{11}.2H_2O$ requires: C, 46·36; H, 6·41%).

Gardoside pentaacetate (**5**). **1** (0·2 g) was acetylated (Ac_2O-pyridine) to give the pentaacetate (**5**) (0·15 g) as needles ex EtOH, m.p. 209–211°. $[\alpha]_D^{22}$ −54·4° (*c* = 0·57, $CHCl_3$), UV: λ_{max}^{MeOH} 233 nm (log ε 3·97); IR: ν_{max}^{KBr} 1745, 1720, 1694, 1642 cm^{-1}; NMR ($CDCl_3$): δ 1·99–2·09 (5 × OCOMe), 3·05 (2H, *m*, C-6H), 7·50 (1H, *s*, C-3H). (Found: C, 53·16; H, 5·57. $C_{26}H_{32}O_{15}$ requires: C, 53·42; H, 5·52%).

Gardoside pentaacetate methyl ester (**6**). A methanolic soln of **5** (0·05 g) was treated with excess ethereal CH_2N_2 to give gardoside pentaacetate methyl ester (**6**) (0·039 g) as needles ex EtOH, m.p. 110–111·5° $[\alpha]_D^{22}$ −75·0° (*c* = 0·68, $CHCl_3$); UV: λ_{max}^{MeOH} 235 nm (log ε 4·04); IR: ν_{max}^{KBr} 1746, 1730 (*sh*), 1700, 1640 cm^{-1}; NMR ($CDCl_3$): δ 1·95–2·10 (5 × OCOMe), 3·07 (2H, *m*, C-6H), 3·73 (3H, *s*, COOMe), 7·39 (1H, *d*, *J* 1·0 Hz, C-3H). (Found: C, 54·29; H, 5·65. $C_{27}H_{34}O_{15}$ requires: C, 54·18, H, 5·73%).

Catalytic hydrogenation of gardoside pentaacetate methyl ester (**6**). A soln of **6** (0·09 g) in MeOH (20 ml) was hydrogenated until the absorption of hydrogen had ceased in the presence of Pd–C catalyst prepared from 5% $PdCl_2$ and charcoal (0·1 g). The catalyst was filtered off and the solvent was removed *in vacuo* and the residue was chromatographed on silica gel (15 g) with Et_2O as eluent. The faster eluate was conc. *in vacuo* and the residue was recrystallized from EtOH to give **8** (0·039 g) as needles, m.p. 113–114·5°. IR: ν_{max}^{KBr} 1743, 1700, 1632 cm^{-1}; NMR ($CDCl_3$): δ 1·07 (3H, *d*, *J* 7·0 Hz, C-10H), 1·93–2·09 (4 × OCOMe). (Found: C, 55·24; H, 6·28. Calc. for $C_{25}H_{34}O_{13}$: C, 55·35; H, 6·32%). This sample was identified with an authentic sample of deoxyloganin tetraacetate by m.m.p. and comparisons of IR (Nujol) and NMR ($CDCl_3$) spectra. The slower eluate was concentrated *in vacuo*. The residue was recrystallized from EtOH to give **7** (0·019 g) as needles, m.p. 139–140°. $[\alpha]_D^{26}$ −74·0° (*c* = 1·01, $CHCl_3$); IR: ν_{max}^{KBr} 1753, 1733, 1690, 1643 cm^{-1}; NMR ($CDCl_3$): δ 1·03 (3H, *d*, *J* 7·0 Hz, C-10H), 1·95–2·10 (5 × OCOMe (Found: C, 54·07; H, 5·96. Calc. for $C_{27}H_{36}O_{15}$: C, 54·00; H, 6·04%). This substance was identified with an authentic sample of loganin pentaacetate by m.m.p. and comparisons of IR (Nujol) and NMR ($CDCl_3$) spectra.

10-*Dehydrogeniposide tetraacetate* (**9**). A solution of **4** (0·3 g) in Me_2CO (80 ml) was stirred with Jones reagent[12] (0·9 ml) for 5 min under cooling. MeOH (3 ml) was added to the reaction mixture and the soln was neutralized with methanolic $Ba(OH)_2$ soln. The insoluble material was filtered off and the filtrate was conc. *in vacuo* to dryness. The residue was acetylated and the product was purified by chromatography on silica gel (20 g) with Et_2O as eluent and recrystallized from a mixture of Et_2O–petrol. to give **9** (0·1 g) as needles, m.p. 130–131°. $[\alpha]_D^{25}$ +17·72° (*c* = 0·79, $CHCl_3$); UV: λ_{max}^{MeOH} 227·5 nm (log ε 3·77); IR ν_{max}^{KBr} 1755, 1705, 1680, 1640 cm^{-1}; NMR ($CDCl_3$): δ 1·92–2·14 (4 × OCOMe), 3·69 (3H, *s*, COOMe), 6·13 (1H, *d*, *J* 2·0 Hz, C-1H), 6·93 (1H, *m*, C-7H), 7·34 (1H, *s*, C-3H), 9·77 (1H, *s*, C-10H). (Found: C, 54·32; H, 5·72. $C_{25}H_{30}O_{14}$ requires: C, 54·15; H, 5·45%).

[11] INOUYE, H., INOUYE, S., SHIMOKAWA, N. and OKIGAWA, M. (1969) *Chem. & Pharm. Bull. (Tokyo)* **17**, 1942.

[12] MEINWALD, J., CRANDALL, J. and HYMANS, W. E. (1973) *Organic Synthesis* (BAUMGARTEN, H. E., ed.), coll. Vol. 5, pp. 866–868, Wiley, New York.

Geniposide 2',3',4',6'-tetraacetate (**10**). To a soln of **9** (0·201 g) in dioxane (20 ml) was added $NaBH_4$ (0·04 g) in H_2O (1·5 ml). After stirring for 30 min at room temp., AcOH was added and the solvent was evaporated *in vacuo*. The residue was extracted with $CHCl_3$, washed with H_2O and dried. The soln was evaporated *in vacuo*. The residue was recrystallized from aq. EtOH to give **10** (0·17 g) as needles, m.p. 117–119°. $[\alpha]_D^{28}$ + 6·10° (*c* = 0·85, $CHCl_3$); IR: ν_{max}^{KBr} 3450, 1750, 1705, 1640 cm^{-1}; NMR ($CDCl_3$): δ 2·02–2·08 (4 × OCOMe), 3·73 (3H, *s*, COOMe), 4·26 (4H, *m*, C-10H and C-6'H), 5·82 (1H, *m*, C-7H), 7·45 (1H, *d*, *J* 1·0 Hz, C-3H). (Found: C, 53·85; H, 6·01. $C_{25}H_{32}O_{14}$ requires: C, 53·96; H, 5·80%).

Epoxidation of geniposide 2',3',4',6'-tetraacetate (**10**). To a solution of **10** (0·337 g) in anhyd. CH_2Cl_2 (7 ml) was added *m*-chloroperbenzoic acid (0·15 g) and the mixture was allowed to stand at room temp. overnight. The soln was washed with 1 N NaOH and then with H_2O, dried and evaporated to give a residue (0·325 g). The residue was chromatographed on silica gel (25 g) using Et_2O as eluent and 5 ml fractions of eluate were collected. Evaporation of the combined fractions No. 19–28 gave **11** (0·152 g) as a powder. $[\alpha]_D^{20}$ −47·25° (*c* = 0·65, $CHCl_3$); IR: ν_{max}^{KBr} 3500, 1750, 1705, 1640 cm^{-1}; NMR ($CDCl_3$): δ 2·02–2·08 (4 × OCOMe), 3·48 (1H, diffused *s*, C-7H), 3·72 (3H, *s*, COOMe), 3·97 (2H, *d*, *J* 9·0 Hz, C-10H), 7·43 (1H, *d*, *J* 1·0 Hz, C-3H). (Found: C, 52·15; H, 5·79. $C_{25}H_{32}O_{15}$ requires: C, 52·45; H, 5·63%). Fr. Nos. 30–35 gave a residue (0·04 g) which was recrystallized from EtOH to give **12** as needles, m.p. 157–158°. $[\alpha]_D^{26}$ −81·13° (*c* = 0·85, $CHCl_3$); IR: ν_{max}^{KBr} 3500–3200, 1745, 1697, 1645 cm^{-1}; NMR ($CDCl_3$): δ 1·89–2·11 (4 × OCOMe), 3·44 (1H, diffused *s*, C-7H), 3·69 (3H, *s*, COOMe), 3·93 (2H, *d*, *J* 5·0 Hz, C-10H), 5·81 (1H, *d*, *J* 2·0 Hz, C-1H), 7·25 (1H, *d*, *J* 1·0 Hz, C-3H). (Found: C, 52·33; H, 5·63. $C_{25}H_{32}O_{15}$ requires: C, 52·45; H, 5·63%).

7,8-*β*-*Epoxy*-10-*dehydrogeniposide tetraacetate* (**15**). (a) To a soln of **11** (0·302 g) in DMSO (6 ml) was added Ac_2O (1 ml) and the mixture was allowed to stand at room temperature for 22 hr. The reaction mixture was diluted with H_2O and extracted with $CHCl_3$. The combined $CHCl_3$ extracts were dried and evaporated. The residue was purified by chromatography on silica gel (20 g) with Et_2O as eluent and recrystallized from a mixture of Et_2O and petrol. to give **15** (0·101 g) as needles, m.p. 169–171°. $[\alpha]_D^{22}$ +7·61° (*c* = 1·16, $CHCl_3$); IR: ν_{max}^{KBr} 1745, 1700, 1635 cm^{-1}; NMR ($CDCl_3$): δ 2·03–2·08 (4 × OCOMe), 3·73 (3H, *s*, COOMe), 3·81 (1H, diffused *s*, C-7H), 7·46 (1H, *d*, *J* 1·0 Hz, C-3H), 10·05 (1H, *s*, C-10H). (Found: C, 52·33; H, 5·20. $C_{25}H_{30}O_{15}$ requires: C, 52·63; H, 5·30%). (b) To a solution of **11** (0·370 g) in anhyd. CH_2Cl_2 (20 ml) was added a soln of CrO_3–pyridine (1·5 g) in anhyd. CH_2Cl_2 (10 ml) and the mixture was stirred at room temp. for 1 hr. The resulting ppts were filtered off and the filtrate was washed with 1 N HCl, 5% aq. $NaHCO_3$ and H_2O, successively. The CH_2Cl_2 soln was dried and evaporated. The residue (0·258 g) was purified by chromatography on silica gel (30 g) using Et_2O as eluent. The purified residue was recrystallized from a mixture of Et_2O and petrol. to give **15** (0·200 g) as needles.

Gardoside 2',3',4',6'-tetraacetate methyl ester (**16**). To a solution of **15** (0·1 g) in anhyd. MeOH (2·7 ml) were added $NH_2NH_2.H_2O$ (0·025 ml) and HOAc (0·002 ml) with ice cooling and the reaction mixture was stirred for 30 min. This soln was diluted and extracted with $CHCl_3$. The $CHCl_3$ extract was dried and evaporated. The residue (0·08 g) was purified by chromatography on silica gel (10 g) using Et_2O as eluent and was recrystallized from a mixture of Et_2O and petrol. to give **16** (0·04 g) as needles, m.p. 150–152°. $[\alpha]_D^{23}$ +2·38° (*c* = 0·38, $CHCl_3$); IR: ν_{max}^{KBr} 3550–3250, 1745, 1710, 1700, 1640 cm^{-1}; NMR ($CDCl_3$): δ 1·93–2·09 (4 × OCOMe), 3·71 (3H, *s*, COOMe), 7·38 (1H, *d*, *J* 1·0 Hz, C-3H). (Found: C, 53·79; H, 5·81. $C_{25}H_{32}O_{14}$ requires: C, 53·96; H, 5·80%).

Acetylation of **16** *to gardoside pentaacetate methyl ester* (**6**). **16** (0·04 g) was acetylated to give **6** (0·03 g) as needles ex EtOH, m.p. 110–111·5°. $[\alpha]_D^{25}$ −82·19° (*c* = 0·39, $CHCl_3$); IR: ν_{max}^{KBr} 1746, 1730 (*sh*), 1700, 1640 cm^{-1}; NMR ($CDCl_3$): δ 1·93–2·08 (5 × OCOMe), 3·71 (3H, *s*, COOMe), 7·37 (1H, *d*, *J* 1·0 Hz, C-3H). (Found: C, 54·39; H, 5·50. Calc. for $C_{27}H_{34}O_{15}$: C, 54·18; H, 5·73%). This substance was identified with an authentic sample of gardoside pentaacetate methyl ester (**6**) by m.m.p. and comparisons of IR (KBr) and NMR ($CDCl_3$) spectra.

Acetylation of geniposidic acid (**2**). **2** (0·35 g) was acetylated to give pentaacetate (**19**) (0·40 g) as a powder, $[\alpha]_D^{23}$ +14·9° (*c* = 1·61, $CHCl_3$), UV: λ_{max}^{MeOH} 235 nm (log ϵ 4·01); IR: $\nu_{max}^{CHCl_3}$ 1750, 1680, 1630 cm^{-1}; NMR ($CDCl_3$): δ 2·02–2·08 (5 × OCOMe), 4·73 (2H, diffused *s*, C-10H), 5·87 (1H, *m*, C-7H), 7·55 (1H, *s*, C-3H). (Found: C, 53·20; H, 5·40. Calc. for $C_{26}H_{32}O_{15}$: C, 53·43; H, 5·52%).

Methylation of geniposidic acid pentaacetate (**19**). A methanolic soln of **19** (0·07 g) was methylated with an ethereal CH_2N_2. The reaction product was recrystallized from EtOH to give **20** (0·05 g) as needles, m.p. 134–135°. $[\alpha]_D^{25}$ +2·4° (*c* = 1·17, $CHCl_3$), UV: λ_{max}^{MeOH} 237 nm (log ϵ 4·01); IR: ν_{max}^{KBr} 1745, 1705, 1640 cm^{-1}; NMR ($CDCl_3$): δ 1·98–2·08 (5 × OCOMe), 3·72 (3H, *s*, COOMe); 4·70 (2H, diffused *s*, C-10H), 5·83 (1H, *m*, C-7H). 7·42 (1H, *d*, *J* 1·0 Hz, C-3H). (Found: C, 53·88; H, 5·63. Calc. for $C_{27}H_{34}O_{15}$: C, 54·18; H, 5·73%). **20** thus obtained was identified with an authentic sample of geniposide pentaacetate by m.m.p. and comparisons of IR (KBr) and NMR ($CDCl_3$) spectra.

Acetylation of scandoside methyl ester (**3**). **3** (0·06 g) was acetylated to give **21** (0·06 g) as needles ex EtOH, m.p. 132–134°. $[\alpha]_D^{33}$ −87·6° (*c* = 1·01, $CHCl_3$); UV: λ_{max}^{MeOH} 234 nm (log ϵ 3·61); IR: ν_{max}^{KBr} 1740, 1700, 1640 cm^{-1}; NMR ($CDCl_3$): δ 1·96–2·10 (6 × OCOMe), 3·72 (3H, *s*, COOMe), 5·54 (1H, *m*, C-6H), 5·88 (1H, *m*, C-7H), 7·39 (1H, *s*, C-3H). (Found: C, 53·07; H, 5·47. Calc. for $C_{29}H_{36}O_{17}$: C, 53·05; H, 5·52%). Substance **21** was identified with an authentic sample of scandoside hexaacetate methyl ester by m.m.p. and comparisons of IR (Nujol) and NMR ($CDCl_3$) spectra.

Acknowledgements—This work was partly supported by a grant for scientific research from the Ministry of Education. The authors are grateful to Prof. T. Sawada of Kyoto College of Pharmacy and to Prof. S. Kuwano of

Mukogawa Women's University for their kind gift of plant material. We are also indebted to Dr. K. Kitamura and Mrs. M. Uobe for measurements of NMR spectra and to members of the Microanalytical Centre of this University for microanalyses.