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ABELIOSIDES A AND B, SECOIRIDOID GLUCOSIDES FROM *ABELIA GRANDIFLORA**

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Key Word Index—*Abelia grandiflora; A. spathulata, A. serrata*; Caprifoliaceae; secoiridoid glucoside; abelioside A; abelioside B; structure elucidation; 2-D NMR.

Abstract—Two new secoiridoid glucosides, abeliosides A and B, were isolated along with cantleyoside and sylvestroside II from *Abelia grandiflora*. On the basis of spectral and chemical evidence, these new glucosides were identified as esters of secologanic acid or secologanolic acid with an iridoid lactone which may arise from loganin. Cantleyoside was also isolated from *A. spathulata* and *A. serrata*.

INTRODUCTION

Abelia grandiflora (Rndre) Rehd., a half-evergreen plant, is a hybrid from *A. chinensis* R. Br. and *A. uniflora* R. Br., both native to China, and now cultivated as a garden plant.

In the course of investigation of secoiridoid glucosides of plants of Genus *Abelia* (Caprifoliaceae), we have isolated from this plant the two new secoiridoid glucosides, abeliosides A (**1**) and B (**2**), along with two known glucosides, cantleyoside (**3**) and sylvestroside II (**4**). In contrast, we have isolated only **3** from *A. spathulata* Sieb. et Zucc. and *A. serrata* Sieb. et Zucc. which are native to Japan.

The glucosides **1** and **2** have the 'bis-iridoid structure' in which secologanic acid (**6**) or secologanolic acid (**7**) is esterified to the hydroxy group at C-7′ of an iridoid lactone as are **3** and **4** from *Cantleya* [1], *Scabiosa* [2] and *Dipsacus* [3] plants. This paper describes the structure elucidation of these new glucosides.

RESULTS AND DISCUSSION

The water soluble portion of fresh leaves of *A. grandiflora* was fractionated by charcoal chromatography, silica gel column chromatography and preparative TLC to give two new glucosides, abeliosides A (**1**) and B (**2**), along with two known glucosides, cantleyoside (**3**) and sylvestroside II (**4**).

Abelioside A (**1**) was obtained as a hygroscopic white powder, $C_{25}H_{34}O_{12} \cdot 1/2H_2O$, $[\alpha]_D - 38°$ (methanol). It showed a UV maximum at 236 nm (log ε4.02) and IR absorptions at 3400–3300 (OH groups), 1720 (ester and aldehyde) and 1690 and 1620 cm^{-1} (conjugated ester). The ^1H NMR spectrum of **1** showed signals at δ2.53 (*dd* (*br*), J = 17.5, 8 Hz, $-CH_2CHO$), 2.7–3.0 ($-CH_2CHO$), 5.24 and 5.26 (*d* (*br*), J = 18 Hz; *d* (*br*), J = 9 Hz, $-CH=CH_2$), 5.51 (*d*, J = 6.5 Hz, $-O-CH-O$), 5.66 (*dt*, J = 18, 9 Hz, $-CH=CH_2$), 7.53 (*s*, $-C=CH-$), 9.70 (*s* (*br*), –CHO), closely similar to those of secologanin (**8**), indicating the presence of the partial structure **A**. In addition, the signals due to a secondary methyl group (δ1.03, *d*, J = 6.5 Hz) and three pairs of geminal coupled methylenes (δ1.45, *ddd*, J = 14, 10, 4 Hz and 2.12 *d* (*br*), J = 14, 8 Hz; δ2.38, *dd*, J = 15, 4 Hz and 2.7–3.0, and δ4.21, *dd*, J = 12, 3.5 Hz and 4.43, *dd*, J = 12, 4Hz) were observed. These signals were found to be coupled with four methine protons in the carbon chain **B** by decoupling experiments. These findings, together with the composition of **1** led us to assume a partial structure **C** for the non-secologanin moiety.

Acetylation of **1** gave the tetraacetate **9**, colourless needles, $C_{33}H_{42}O_{16} \cdot H_2O$, mp 170–172°C, $[\alpha]_D - 41°$ (chloroform). Its ^1H and ^{13}C NMR spectra (*vide infra*) also supported the structure **1** for abelioside A, consisting of the secologanic acid (**6**) moiety and the partial structure **C**.

As glucoside **1** was easily acetalized by passage through a silica gel column with methanol–dichloromethane to afford a stable methyl acetal (**10**), $C_{27}H_{40}O_{13} \cdot 1/2H_2O$, the acetal was subjected to further chemical reactions in order to establish the stereochemistry of the partial structure **C**. Alkaline hydrolysis of **10** with methanolic sodium hydroxide yielded three products, **11**, **12** and **13**. Compound **11**, colourless needles, $C_{28}H_{44}O_{14} \cdot 1/2H_2O$, mp 198–200°, showed no UV maximum at 236 nm and no IR bands at 1690 and 1620 cm^{-1}, unlike compound **10**. Furthermore, the ^1H NMR spectrum of **11** lacked the signal due to the C-3 olefinic proton of **10**, but showed a methoxy signal at δ3.51 (*s*). Thus, **11** was deduced to be the 3,4-dihydro-3-methoxy derivative of **10** (the stereochemistry at C-3 and C-4 is not yet defined). Compound **12** was converted through methylation and acetylation to methyl

*Part 54 in the series "Studies on Monoterpene Glucosides and Related Natural Products". For Part 53 see Inoue, K., Tanahashi, T. and Inouye, H. (1985) *Phytochemistry* **24**, 1299.

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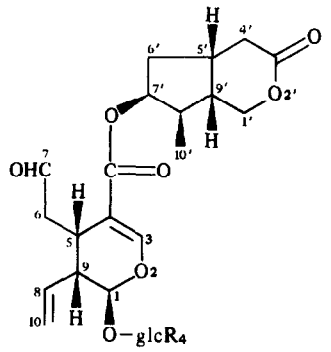

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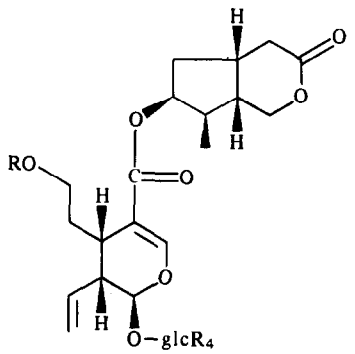
9 R = Ac



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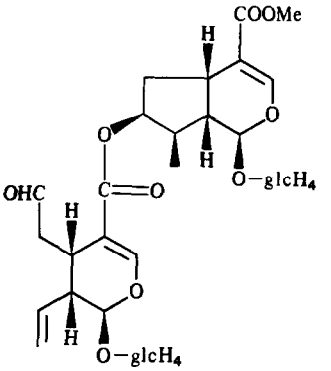
22 R = Ac



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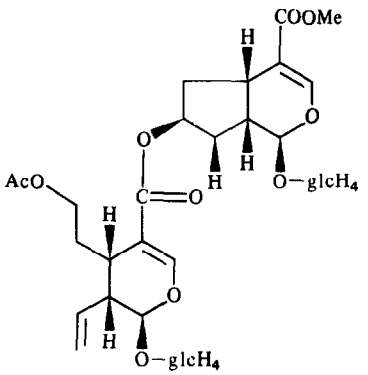

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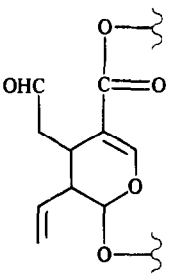
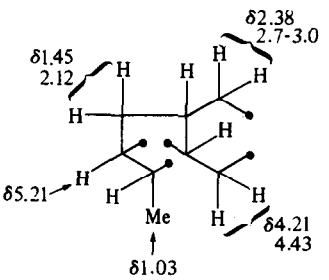
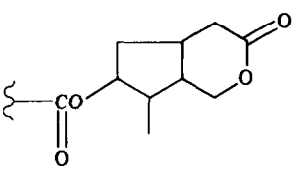


A



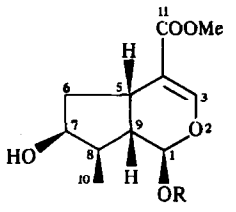
B



C

ester acetate **14**, $C_{28}H_{42}O_{16}$, the NMR spectrum of which lacked the signals due to the partial structure **C** and instead showed a methyl ester signal at δ3.68. Compound **14** was identified with 3,4-dihydro-3-methoxysecologanin methyl acetal tetraacetate derived from secologanin tetraacetate (**15**) by treating successively with hydrochloric acid–methanol, sodium hydroxide–methanol, diazomethane and acetic anhydride–pyridine. Compound **13**, colourless prisms, $C_9H_{14}O_3$, mp 101–102.5°, $[\alpha]_D$ +133°C (chloroform), showed IR absorptions at 3400 (OH group) and 1730 (δ-lactone) cm^{-1}. Its ^1H NMR spectrum exhibited a broad triplet (δ4.14, J = 3.5 Hz) due to a C-7 proton and a series of signals attributed to the partial structure **C**. In particular the signals for the C-5, 8 and 9 methine protons, which were overlapped with signals originated from the secologanin moiety in the spectrum of **1**, were clearly observed at δ2.95 (*m*), 1.93 (*m*), and 2.16 (*tt*, J = 9, 4 Hz). On acetylation, **13** gave the monoacetate **16**, whose C-7 proton resonates nearly at the same field as do those of **1** and **10**. Therefore, it follows that glucoside **1** consists of secologanic acid (**6**) and lactone **13**, which are joined through an ester bond between the carboxy group of **6** and the hydroxy group of **13**.

The absolute structure of **13** was established in the following way. Aglucone **17** obtained by β-glucosidase-catalysed hydrolysis of loganin (**5**) was reduced with sodium borohydride to afford three reduction products. The two major products, **18** and **19**, were separated as their diacetates **20** and **21**, each having $C_{14}H_{20}O_6$. The structures of these acetates were elucidated by detailed ^1H NMR analyses (see Experimental). The minor one,



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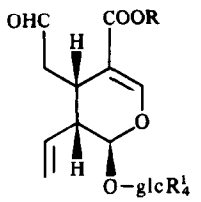
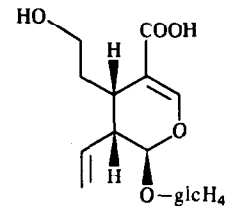
17 R = H



6 R = R^1 = H
8 R = Me, R^1 = H
15 R = Me, R^1 = Ac



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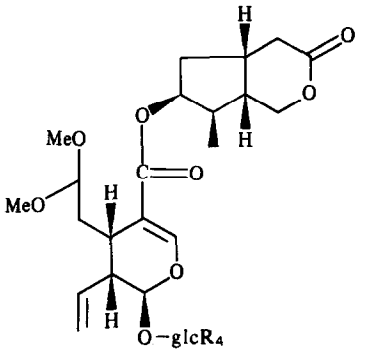
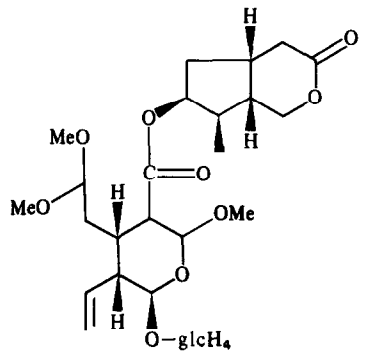


10 R = H
23 R = Ac



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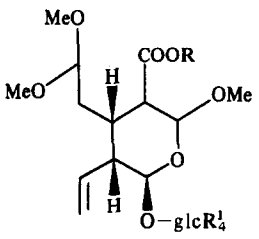
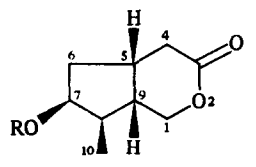
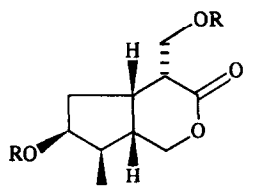


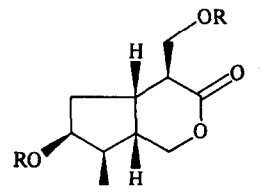
12 R = R^1 = H
14 R = Me, R^1 = Ac



13 R = H
16 R = Ac



18 R = H
20 R = Ac



19 R = H
21 R = Ac

colourless prisms, $C_9H_{14}O_3$, mp 101–103°C, $[\alpha]_D$ + 131° (chloroform), was identified with lactone **13** obtained by degradation of **10**. Therefore, the absolute structure of lactone **13** was established, and the structure of abelioside A is represented by **1**.

Abelioside B (**2**)*, a minor component, was isolated as the pentaacetate (**22**), colourless needles, $C_{35}H_{46}O_{17}$, mp 211–213°, $[\alpha]_D$ − 38° (chloroform)†. The IR and ^{1}H NMR spectra of **22** were similar to those of **9** except that the C-7 aldehyde proton in **9** was replaced by the acetoxy group in **22**. Therefore, this glucoside was presumed to be the 7-alcoholic congener of abelioside A (**1**). In fact, the acetate **22** was identical with the acetate prepared from **9** by sodium borohydride reduction and acetylation. The absolute structure of abelioside B was thus determined as **2**.

Subsequently, in order to analyse the ^{13}C NMR spectra of **9** and **22**, the ^{1}H–^{13}C shift correlated NMR spectrum of abelioside A methyl acetal tetraacetate (**23**) was inspected as a model compound (Fig. 1). The chemical shifts of all the carbons were determined by correlation with the proton chemical shifts assigned by the detailed decoupling experiments. Noticeably, three acetal (C-1, C-7 and C-1″), five methine (C-5, C-9, C-5′, C-8′ and C-9′) and three methylene carbons (C-6, C-4′ and C-6′) were exactly

*In the course of the preparation of the manuscript, it was brought to our attention that Drs. S. R. Jensen and B. J. Nielsen (personal communication) of the Technical University of Denmark had isolated from *A. chinensis* two compounds which they considered to be abelioside B and its 7-acetate congener in addition to cantleyoside and sylvestroside II.

†The ^{1}H NMR spectrum of the crude fraction containing abelioside B (**2**) did not show acetyl methyl signals, indicating that **2** has no acetyl group.

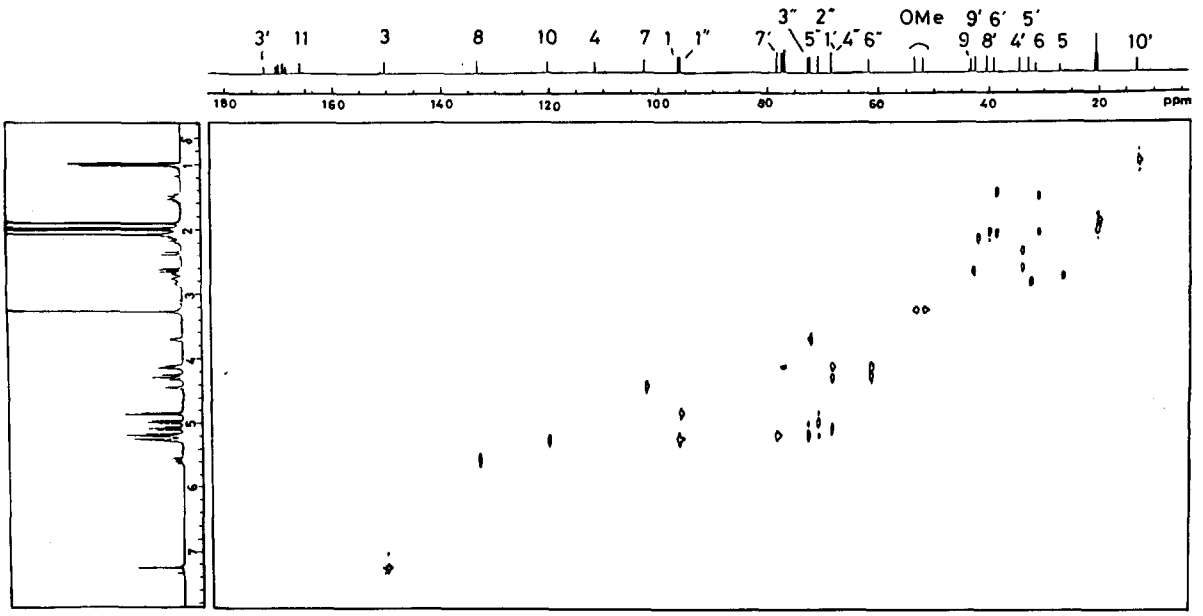


Fig. 1. ^{1}H–^{13}C shift correlated spectrum of abelioside A methyl acetal tetraacetate.

assigned. Based on these assignments, the ^{13}C NMR spectra of **9** and **22** (Table 1) were analysed. These data also supported the proposed structures **9** and **22**.

In view of the coexistence of **3** and **4** in *A. grandiflora* and of the same stereostructure of lactone **13** as that of loganin (**5**), the lactone moiety of **1** and **2** is assumed to be biosynthesized from loganin (**5**), formed via iridodial, through hydrolysis to aglucone **17** and modification to **13**. Elucidation of the biosynthetic pathway of **13** is an intriguing problem remaining to be studied.

EXPERIMENTAL

General procedures. Mps: uncorr; ^{1}H and ^{13}C NMR: 200 and 50.3 MHz, respectively, ^{1}H–^{13}C shift correlated spectrum recorded at 400 (^{1}H) and 100.4 (^{13}C) MHz, TMS was used in $CDCl_3$ and DSS in D_2O as the internal standard; GC: activated charcoal (Wako) and silica gel (Mallinckrodt); TLC and PLC: Kieselgel 60 F_{254} (0.25 and 0.5 mm in thickness, respectively), spots and bands detected under UV light (245 nm) and eluted with MeOH–CH_2Cl_2 (1:9).

Plant material. Abelia grandiflora (Rndre) Rehd. was collected at Kasugai City, Aichi Prefecture in June. A voucher specimen (H. Inouye, No. 6) 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. *A. spathulata* Sieb. et Zucc. and *A. serrata* Sieb. et Zucc. were collected at the Kyoto Herbal Garden of Takeda Chemical Industries Ltd. in September.

Isolation of secoiridoid glucosides from A. grandiflora. Fresh leaves (2.2 kg) were extracted with hot H_2O (6 l. × 3) and the combined extracts were concd *in vacuo* to 1 l. After filtration, the soln was washed with EtOAc (300 ml × 2) and the H_2O layer was transferred to a charcoal (350 g) column and eluted successively with H_2O–EtOH (19:1, 8 l.), (7:3, 3 l.; Fr. I), (1:1, 5 l.; Fr. II), (3:7, 12 l.; Fr. III, IV and V) and (1:9, 3 l.; Fr. VI).

Fr. IV (6.57 g) was chromatographed on silica gel (200 g) and eluted with MeOH–CH_2Cl_2 (1:19, 1.5 l.; fractions 1–13), (1:9, 2.5 l.; fractions 14–35), (13:17, 1.5 l.; fractions 36–46), and (1:4, 1 l.; fractions 47–54). An aliquot (126 mg) of fractions 21–25 (1036 mg) was subjected to prep. TLC with MeOH–$CHCl_3$ (13:17). The band around R_f 0.63 gave abelioside A methyl acetal (**10**) (37 mg) as a white powder. $[\alpha]_D^{22}$ −39° (*c* = 1.0, MeOH); UV λ_{max}^{EtOH} nm (log ε): 235 (4.02); IR ν_{max}^{KBr} cm^{-1}: 3400, 1730, 1690, 1630; ^{1}H NMR: δ 1.08 (3H, *d*, *J* = 6.5 Hz, 10'-H_3), 1.53 (1H, *ddd*, *J* = 14, 10, 4 Hz, 6'-H), 1.85–1.95 (2H, *m*, 6-H_2), 2.13 (1H, *m*, 8'-H), 2.22 (1H, *d* (*br*), *J* = 14, 8 Hz, 6'-H), 2.35 (1H, *m*, 9'-H), 2.50 (1H, *dd*, *J* = 15, 4 Hz, 4'-H), 2.76 (1H, *m*, 9-H), 2.85 (1H, *dd*, *J* = 15, 7 Hz, 4'-H), 2.9–3.0 (2H, *m*, 5- and 5'-H), 3.30 and 3.32 (each 3H, *s*, OMe), 4.35 (1H, *dd*, *J* = 11.5, 3.5 Hz, 1'-H), 4.52 (1H, *dd*, *J* = 11.5, 4 Hz, 1'-H), 4.61 (1H, *dd*, *J* = 7, 4.5 Hz, 7-H), 4.87 (1H, *d*, *J* = 8 Hz, 1"-H), 5.22 (1H, *t* (*br*), *J* = 3.5 Hz, 7'-H), 5.39 (1H, *d* (*br*), *J* = 9 Hz, 10-H), 5.42 (1H, *d* (*br*), *J* = 18 Hz, 10-H), 5.62 (1H, *d*, *J* = 6.5 Hz, 1-H), 5.80 (1H, *dt*, *J* = 18, 9 Hz, 8-H), 7.54 (1H, *s*, 3-H). [Found: C, 55.89; H, 7.00. $C_{27}H_{40}O_{13}\cdot 1/2H_2O$ requires: C, 55.76; H, 7.10%.]

The combined fractions 26–28 (430 mg) were chromatographed on prep. TLC with MeOH–$CHCl_3$ (3:17), repeatedly. Of two main bands, the less polar gave **10** (56 mg), while the more polar one afforded abelioside A (**1**) (205 mg) as a white powder, $[\alpha]_D^{22}$ −38° (*c* = 1.3, MeOH); UV λ_{max}^{EtOH} nm (log ε): 236 (4.01); IR ν_{max}^{KBr} cm^{-1}: 3400–3300, 1720, 1690, 1620; ^{1}H NMR: δ 1.03 (3H, *d*, *J* = 6.5 Hz, 10'-H_3), 1.45 (1H, *ddd*, *J* = 14, 10, 4 Hz, 6'-H), 2.12 (1H, *d* (*br*), *J* = 14, 8 Hz, 6'-H), 2.0–2.3 (2H, *m*, 8'- and 9'-H), 2.38 (1H, *dd*, *J* = 15, 4 Hz, 4'-H), 2.53 (1H, *dd* (*br*), *J* = 17.5, 8 Hz, 6-H), 2.7–3.0 (4H, *m*, 6-, 9-, 4'- and 5'-H), 3.2–3.5 (1H, *m*, 5-H, overlapped with glucose protons), 3.67 (1H, *dd*, *J* = 12, 5 Hz, 6"-H), 3.91 (1H, *d* (*br*), *J* = 12 Hz, 6"-H), 4.21 (1H, *dd*, *J* = 11.5, 3.5 Hz, 1'-H), 4.43 (1H, *dd*, *J* = 11.5, 4 Hz, 1'-H), 4.69 (1H, *d*, *J* = 8 Hz, 1"-H), 5.21 (1H, *t* (*br*), *J* = 3.5 Hz, 7'-H), 5.25 (1H, *d* (*br*), *J* = 9 Hz, 10-H), 5.26 (1H, *d* (*br*), *J* = 18 Hz, 10-H), 5.51 (1H, *d*, *J* = 6.5 Hz, 1-H), 5.66 (1H, *dt*, *J* = 18, 9 Hz, 8-H), 7.53 (1H, *s*, 3-H), 9.70 (1H, *s* (*br*), $W_{1/2}$ = 3 Hz, CHO). [Found: C, 56.26: H, 6.53. $C_{25}H_{34}O_{12}\cdot 1/2H_2O$ requires: C, 56.07; H, 6.59%.]

Fractions 40–46 (400 mg) were subjected to PLC (MeOH–$CHCl_3$ (1:4), multiple development). The most mobile major band gave a residue (88 mg), which, after acetylation was purified by PLC with Me_2CO–$CHCl_3$ (1:9) to give a solid.

Table 1. ^{13}C NMR data of abelioside A tetraacetate (**9**), abelioside B pentaacetate (**22**), and abelioside A methyl acetal tetraacetate (**23**) ($CDCl_3$)

C	23	9	22
1	96.3 *d*	95.9 *d*	96.3 *d*
3	150.3 *d*	151.1 *d*	150.8 *d*
4	111.5 *s*	109.7 *s*	111.0 *s*
5	27.0 *d*	25.5 *d*	27.6 *d*
6	31.4 *t*	43.4 *t*	27.5 *t*
7	102.5 *d*	200.3 *d*	62.1 *t*
8	133.2 *d*	132.3 *d*	132.6 *d*
9	43.3 *d*	43.7 *d*	42.9 *d*
10	120.1 *t*	121.2 *t*	120.4 *t*
11	166.0 *s*	165.8 *s*	166.0 *s*
1′	68.2 *t*	68.1 *t*	68.2 *t*
3′	172.7 *s*	172.8 *s*	172.8 *s*
4′	34.3 *t*	34.4 *t*	34.4 *t*
5′	32.7 *d*	32.8 *d*	32.8 *d*
6′	39.1 *t*	39.1 *t*	39.1 *t*
7′	78.2 *d*	78.4 *d*	78.4 *d*
8′	40.4 *d*	40.5 *d*	40.4 *d*
9′	42.4 *d*	42.5 *d*	42.5 *d*
10′	13.0 *q*	13.1 *q*	13.1 *q*
1″	96.0 *d*	95.9 *d*	96.0 *d*
2″	70.6 *d*	70.7 *d*	70.6 *d*
3″	72.4 *d*	72.3 *d*	72.4 *d*
4″	68.2 *d*	68.1 *d*	68.2 *d*
5″	72.2 *d*	72.3 *d*	72.2 *d*
6″	61.7 *t*	61.6 *t*	61.6 *t*
OCH_3	51.6, 53.4 *q*		
$COCH_3$	20.6, 20.5 × 2, 20.3	20.4, 20.7 × 3	20.4, 20.6 × 2, 20.7
$COCH_3$	168.7, 169.2, 170.1, 170.5	168.9, 169.4, 170.4, 170.6	168.9, 169.4 × 2, 170.7, 171.1

Recrystallization from EtOH afforded abelioside B pentaacetate (**22**) (31 mg) as colourless needles, mp 211–213°; $[\alpha]_D^{22} - 38°$ (c = 0.5, $CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 232 (4.02); IR ν_{max}^{KBr} cm^{-1}: 1750, 1700, 1620, 1240; ^1H NMR: δ1.05 (3H, *d*, J = 6.5 Hz, 10′-H_3), 1.95, 2.02, 2.04, 2.06 and 2.12 (each 3H, *s*, OAc), 2.42 (1H, *dd*, J = 15, 4 Hz, 4′-H), 2.6–3.0 (4H, 5-, 9-, 4′- and 5′-H), 4.0–4.3 (4H, 7-H_2, 1′- and 6″-H), 4.31 (1H, *dd*, J = 12, 4 Hz, 6″-H), 4.35 (1H, *dd*, J = 11.5, 4 Hz, 1′-H), 4.90 (1H, *d*, J = 8 Hz, 1″-H), 5.03 (1H, *dd*, J = 9, 8 Hz, 2″-H), 5.13 (1H, *t*, J = 9 Hz, 4″-H), 5.2–5.4 (5H, 1-, 7′- and 3″-H, 10-H_2), 5.60 (1H, *dt*, J = 18, 9 Hz, 8-H), 7.34 (1H, *d*, J = 1.5 Hz, 3-H). [Found: C, 56.80; H, 6.25. $C_{35}H_{46}O_{17}$ requires: C, 56.90; H, 6.28%.]

An aliquot (85 mg) of fractions 47–51 (606 mg) was subjected to PLC (MeOH–$CHCl_3$ (1:4), multiple development). Of two main bands, the more polar and less polar gave residues (19 mg) and (39 mg), respectively. The former was acetylated and the product was further purified by prep. TLC with Me_2CO–$CHCl_3$ (1:19) to give a solid. Recrystallization from EtOH afforded colourless needles (14 mg), mp 144–146°, $[\alpha]_D^{22} - 90°$ (c = 0.3, $CHCl_3$), which were identified with the octaacetate of cantleyoside (**3**) [1–3] (mmp, IR, ^1H NMR). The latter residue (39 mg) presumably containing the methyl acetal of cantleyoside (**3**) octaacetate was not examined in further details.

A part (200 mg) of Fr. V (4.84 g) was subjected to PLC (MeOH–$CHCl_3$ (1:4), multiple development) to give a residue (18 mg). The ^1H NMR spectrum of crude sylvestroside II (**4**) clearly showed a singlet at δ2.01 (3H, *s*, OAc) and signals at δ4.0–4.15 (2H, *m*, $-CH_2OAc$). Thus, **4** was confirmed to have a primary acetoxy group. Acetylation and PLC with Me_2CO–$CHCl_3$ (1:19) afforded two acetates (5 mg and 3 mg). The former one, on recrystallization, gave colourless needles, mp 158–160° (from EtOH), which were identified with the nona-acetate of sylvestroside II (**4**) [3] (mmp, IR, ^1H NMR). The latter residue was found to be octaacetate of **3**.

Isolation of cantleyoside (**3**) *from* A. spathulata *and* A. serrata. (i) Fresh leaves (380 g) of *A. spathulata* were extracted with H_2O (2 l. × 3). The combined extracts were concd *in vacuo* to 200 ml, which was fractionated by charcoal (50 g) CC with H_2O (1 l.), H_2O–MeOH (4:1, 0.5 l.), (1:1, 0.5 l.), and MeOH (2 l.) as the eluent. An aliquot (580 mg) of the MeOH fraction (3.28 g) was acetylated and the product was purified by prep. TLC with Me_2CO–$CHCl_3$ (1:19) by developing repeatedly to yield cantleyoside octaacetate (17 mg). (ii) Fresh leaves (460 g) of *A. serrata* were extracted with hot H_2O (2 l. × 3) and the combined extracts were worked up in the same way as above. An aliquot (540 mg) of the MeOH fraction (2.15 g) was acetylated and the product was purified by PLC in the same way as above to yield cantleyoside octaacetate (6 mg).

Acetylation of abelioside A (**1**). Glucoside **1** (50 mg) was acetylated and the product was recrystallized from EtOH to give the tetraacetate (**9**) (32 mg) as colourless needles, mp 170–172° $[\alpha]_D^{22} - 41°$ (c = 0.5, $CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 233 (4.00); IR ν_{max}^{KBr} cm^{-1}: 1740–1730, 1700, 1620; ^1H NMR: δ1.02 (3H, *d*, J = 6.5 Hz, 10′-H_3), 1.52 (1H, *ddd*, J = 14, 10, 4 Hz, 6′-H), 1.9–2.2 (3H, 6′-, 8′- and 9′-H), 1.93, 2.02, 2.04 and 2.11 (each 3H, *s*, OAc), 2.40 (1H, *dd*, J = 15, 7 Hz, 4′-H), 2.47 (1H, *dd* (*br*), J = 17.5, 8 Hz,

6-H), 2.67 (1H, *dd*, J = 15, 7 Hz, 4'-H), 2.86 (1H, *ddd*, J = 17.5, 5.5, 1.5 Hz, 6-H), 2.7–2.9 (2H, 9- and 5'-H), 3.31 (1H, *m*, 5-H), 3.75 (1H, *m*, 5''-H), 4.16 (2H, *dd*, J = 12, 3 Hz, 1'- and 6''-H), 4.29 (1H, *dd*, J = 12, 4.5 Hz, 6''-H), 4.32 (1H, *dd*, J = 12, 3.5 Hz, 1'-H), 4.90 (1H, *d*, J = 8 Hz, 1''-H), 5.03 (1H, *dd*, J = 9, 8 Hz, 2''-H), 5.12 (1H, *t*, J = 9 Hz, 4''-H), 5.2–5.4 (5H, 1-, 7'- and 3''-H, 10-H_2), 5.51 (1H, *dt*, J = 18, 9 Hz, 8-H), 7.38 (1H, *d*, J = 2 Hz, 3-H), 9.72 (1H, *s* (*br*), $W_{1/2}$ = 3 Hz, CHO). [Found: C, 56.54; H, 6.13. $C_{33}H_{42}O_{15}\cdot H_2O$ requires: C, 56.30; H, 6.16%.]

Alkaline hydrolysis of abelioside A methyl acetal (**10**). To a soln of methyl acetal (**10**) (26 mg) in MeOH (2 ml) was added 1 M NaOH (1 ml) and the soln was refluxed for 24 hr. After neutralization with amberlite–IR 120 (H^+-form), the reaction mixture was filtered and the filtrate was concd. The residue was separated by prep. TLC (MeOH–$CHCl_3$ (1:4), multiple development) into three bands. The residue from the least polar band was recrystallized from Et_2O to give lactone **13** (4 mg) as colourless prisms, mp 101–102.5°; $[\alpha]_D^{22}$ + 133° (c = 0.4, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1730; ^1H NMR: δ1.08 (3H, *d*, J = 6.5 Hz, 10-H_3), 1.42 (1H, *ddd*, J = 14, 10, 4 Hz, 6-H), 1.93 (1H, *m*, 8-H), 2.06 (1H, *dd* (*br*), J = 14, 8 Hz, 6-H), 2.16 (1H, *tt*, J = 9, 4 Hz, 9-H), 2.36 (1H, *dd*, J = 15, 3.5 Hz, 4-H), 2.65 (1H, *dd*, J = 15, 7 Hz, 4-H), 2.95 (1H, *m*, 5-H), 4.14 (1H, *t* (*br*), J = 3.5 Hz, 7-H), 4.16 (1H, *dd*, J = 11.5, 3.5 Hz, 1-H), 4.32 (1H, *dd*, J = 11.5, 4 Hz, 1-H); MS m/z: 170 $[M]^+$, 152, 139, 126, 111, 81, 69, 55; High resolution MS: Found 170.0960. $C_9H_{14}O_3$ $[M]^+$ requires 170.0943.

The residue from the middle band was recrystallized from EtOH to afford 3,4-dihydro-3-methoxy-abelisoside A methyl acetal (**11**) (4 mg), mp 198–200° $[\alpha]_D^{22}$ + 12° (c = 0.8, MeOH); IR ν_{max}^{KBr} cm^{-1}: 3400–3300, 1720; ^1H NMR: δ1.04 (3H, *d*, J = 6.5 Hz, 10'-H_3), 3.34, 3.35 and 3.51 (each 3H, *s*, OMe), 4.30 (1H, *dd*, J = 11.5, 3.5 Hz, 1'-H), 4.47 (1H, *dd*, J = 11.5, 4 Hz, 1'-H), 4.55 (1H, *dd*, J = 8, 3.5 Hz, 7-H), 5.17 (1H, *d*, J = 7 Hz, 1-H), 5.20 (1H, *t* (*br*), J = 3.5 Hz, 7'-H), 5.34 (1H, *d* (*br*), J = 18 Hz, 10-H), 5.39 (1H, *d* (*br*), J = 9 Hz, 10-H), 5.87 (1H, *dt*, J = 18, 9 Hz, 8-H). [Found: C, 55.09; H, 7.26. $C_{28}H_{44}O_{14}\cdot 1/2\ H_2O$ requires: C, 54.80; H, 7.39%.]

The residue from the most polar band was methylated and acetylated and the acetate was purified by PLC (Me_2CO–$CHCl_3$ (1:19), multiple development). The main band gave 3,4-dihydro-3-methoxysecologanin methyl acetal tetraacetate (**14**) (3 mg) as a white powder. $[\alpha]_D^{22}$ − 43° (c = 0.9, $CHCl_3$); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740, 1240; ^1H NMR: δ1.36 (1H, *ddd*, J = 14, 7.5, 4 Hz, 6-H), 1.57 (1H, *ddd*, J = 14, 9, 4.5 Hz, 6-H), 2.02 (6H, *s*, OAc × 2), 2.09 and 2.11 (each 3H, OAc), 2.37 (1H, *m*, 5-H), 2.46 (1H, *d*, J = 8.5 Hz, 4-H), 2.53 (1H, *m*, 9-H), 3.25, 3.30 and 3.49 (each 3H, *s*, OMe), 3.68 (3H, *s*, COOMe), 3.74 (1H, *m*, 5'-H), 4.12 (1H, *dd*, J = 12, 2 Hz, 6'-H), 4.30 (1H, *dd*, J = 12, 5 Hz, 6'-H), 4.33 (1H, *dd*, J = 7.5, 4.5 Hz, 7-H), 4.84 (1H, *d*, J = 8.5 Hz, 3-H), 4.90 (1H, *d*, J = 8 Hz, 1'-H), 5.07–5.34 (6H, 1-, 2'-, 3'- and 4'-H, 10-H_2), 5.82 (1H, *dt*, J = 18, 9 Hz, 8-H). [Found: C, 53.27; H, 6.69. $C_{28}H_{42}O_{16}$ requires: C, 52.99; H, 6.67%.]

Conversion of secologanin tetraacetate (**15**) *into* 3,4-*dihydro*-3-*methoxysecologanin methyl acetal tetraacetate* (**14**). To a soln of **15** (50 mg) in MeOH (5 ml) was added two drops of 5% HCl and the soln was allowed to stand overnight. The reaction mixture was diluted with H_2O and extracted with $CHCl_3$ (5 ml × 3). The $CHCl_3$ layer was washed, dried and concd to a foamy residue, which was dissolved in MeOH (5 ml) and heated with 1 M NaOH (1 ml) for 10 hr. After cooling and neutralization with amberlite-IR 120 (H^+-form), the soln was concd. The residue was methylated and acetylated. The product was purified by prep. TLC (Me_2CO–$CHCl_3$, 1:19, multiple development) to yield the tetraacetate (10 mg) as a white powder, identical with **14** obtained by the degradation of **10**.

Acetylation of lactone **13**. Lactone **13** (2 mg) was acetylated and the product was recrystallized from Et_2O to give 7-acetyl-lactone (**16**) (1.5 mg) as colourless needles, mp 82–84°; ^1H NMR: δ1.02 (3H, *d*, J = 6.5 Hz, 10-H_3), 1.50 (1H, *ddd*, J = 14, 10, 3.5 Hz, 6-H), 2.0–2.3 (3H, 6-, 8- and 9-H), 2.17 (3H, *s*, OAc), 2.40 (1H, *dd*, J = 15, 3.5 Hz, 4-H), 2.66 (1H, *dd*, J = 15, 7 Hz, 4-H), 2.88 (1H, *m*, 5-H), 4.17 (1H, *dd*, J = 11.5, 3.5 Hz, 1-H), 4.33 (1H, *dd*, J = 11.5, 4 Hz, 1-H), 5.21 (1H, *t* (*br*), J = 3.5 Hz, 7-H); MS m/z: 212 $[M]^+$, 169, 151, 126, 111, 93, 81: High resolution MS: Found 212.1052. $C_{11}H_{16}O_4$ $[M]^+$ 212.1049.

Reduction of loganin aglucone (**17**) *with* $NaBH_4$. To a soln of aglucone **17** (162 mg) in MeOH (5 ml) was added $NaBH_4$ (42 mg) and the mixture was stirred for 1.5 hr at 55–60°. After decomposition of the excess $NaBH_4$ with Me_2CO (1 ml), the soln was neutralized with amberlite–IR 120 (H^+-form) and concd. The residue (150 mg) was chromatographed on a silica gel (20 g) column and eluted successively with MeOH–$CHCl_3$ (1:39, 50 ml; fractions 1–15), (1:19, 50 ml; fractions 16–30), and (1:9, 100 ml; fractions 31–58). The combined fractions 20–21 (25 mg) were subjected to PLC with MeOH–$CHCl_3$ (1:9) as an eluent. From the more polar band the starting material **17** was recovered, whereas the less polar band afforded a solid. The latter was recrystallized from Et_2O to furnish colourless prisms (2.5 mg), mp 99–101°, $[\alpha]_D^{22}$ + 131° (c = 0.1, $CHCl_3$), identical with **13**, obtained by degradation of **10** (mmp, IR, ^1H NMR). Fractions 27–43 (16 mg) were acetylated and the product was subjected to prep. TLC with Me_2CO–$CHCl_3$ (1:19) as an eluent. Of two major bands, the less polar band gave a solid, which was recrystallized from EtOH to give the diacetate **20** (4.2 mg) as colourless columns, while the more polar one gave the diacetate **21** (6.8 mg) as a colourless syrup. Diacetate **20**, mp 148–150.5°; $[\alpha]_D^{22}$ + 164° (c = 0.4, $CHCl_3$); ^1H NMR: δ1.03 (3H, *d*, J = 6.5 Hz, 10-H_3), 1.38 (1H, *ddd*, J = 14, 10, 4 Hz, 6-H), 2.00 (1H, *dd* (*br*), J = 14, 7.5 Hz, 6-H), 2.08 and 2.10 (each 3H, *s*, OAc), 2.23 (1H, *m*, 9-H), 2.1–2.2 (1H, *m*, 8-H), 2.9–3.1 (2H, *m*, 4- and 5-H), 4.08 (1H, *dd*, J = 12, 7 Hz, 11-H), 4.25 (1H, *d* (*br*), J = 12 Hz, 1-H), 4.50 (1H, *dd*, J = 12, 6 Hz, 11-H), 4.53 (1H, *dd*, J = 12, 3 Hz, 1-H), 5.21 (1H, *t* (*br*), J = 3.5 Hz, 7-H); MS m/z: 284 $[M]^+$, 224, 163, 120, 43; High resolution MS: Found 284.1300. $C_{14}H_{20}O_6$ $[M]^+$ 284.1260. Diacetate **21**, $[\alpha]_D^{22}$ − 6° (c = 0.6, $CHCl_3$); ^1H NMR: δ1.03 (3H, *d*, J = 6.5 Hz, 10-H_3), 1.68 (1H, *ddd*, J = 14, 10, 4 Hz, 6-H), 1.87 (1H, *m*, 8-H), 2.08 (6H, *s*, OAc × 2), 2.27 (1H, *dd* (*br*), J = 14, 7.5 Hz, 6-H), 2.3–2.5 (2H, 5- and 9-H), 2.64 (1H, *ddd*, J = 11, 6, 5 Hz, 4-H), 3.98 (1H, *t*, J = 11, 1-H), 4.24 (1H, *dd*, J = 11.5, 5 Hz, 11-H), 4.41 (1H, *dd*, J = 11.5, 6 Hz, 11-H), 4.43 (1H, *dd*, J = 11, 6 Hz, 1-H), 5.27 (1H, *t* (*br*), J = 3.5 Hz, 7-H); MS m/z: 284 $[M]^+$, 224, 163, 150, 93, 43; High resolution MS: Found 284.1250. $C_{14}H_{20}O_6$ $[M]^+$ 284.1260.

Conversion of abelioside A tetraacetate (**9**) *into abelioside B pentaacetate* (**22**). To a soln of the acetate **9** (5 mg) in MeOH (1 ml) was added $NaBH_4$ (1 mg) and the soln was stirred for 30 min at room temp. After decomposition of the excess $NaBH_4$ with Me_2CO (0.5 ml), the mixture was neutralized with amberlite–IR 120 (H^+-from) and concd. The residue was acetylated and the product was recrystallized from EtOH to give colourless needles, mp 211–213°, $[\alpha]_D^{22}$ − 41° (c = 0.3, $CHCl_3$), which were identified by comparison with an authentic specimen of abelioside B pentaacetate (**22**) (mmp, IR, ^1H NMR).

Acetylation of abelioside A methyl acetal (**10**). Glucoside **10** (50 mg) was acetylated and the product was recrystallized from Et_2O to give the tetraacetate **23** (38 mg) as colourless needles, mp 180–181.5°; $[\alpha]_D^{22}$ − 41° (c = 1.0, $CHCl_3$); UV λ_{max}^{EtOH} nm (log ε): 233 (4.05); IR ν_{max}^{KBr} cm^{-1}: 1750, 1700, 1630; ^1H NMR (400 MHz): δ1.01 (3H, *d*, J = 6.7 Hz, 10'-H_3), 1.49 (1H, *ddd*, J = 14.0, 10.0, 3.7 Hz, 6'-H), 1.54 (1H, *ddd*, J = 14.0, 9.1, 4.6 Hz, 6-H), 1.90, 1.97, 2.00 and 2.07 (each 3H, *s*, OAc), 1.9–2.1 (3H, 6-, 6'- and 8'-H), 2.18 (1H, *tt*, J = 10.0, 4 Hz, 9'-H), 2.36 (1H, *dd*, J = 15.2, 4.3 Hz, 4'-H),

2.62 (1H, *dd*, J = 15.2, 7.0 Hz, 4′-H), 2.68 (1H, *dt*, J = 9.3, 4.6 Hz, 9-H), 2.76 (1H, *m*, 5-H), 2.83 (1H, *m*, 5′-H), 3.27 (6H, *s*, OMe × 2), 3.70 (1H, *ddd*, J = 9.7, 4.6, 2.5 Hz, 5″-H), 4.12 (1H, *dd*, J = 12.2, 2.5 Hz, 6″-H), 4.13 (1H, *dd*, J = 11.6, 3.5 Hz, 1′-H), 4.26 (1H, *dd*, J = 12.2, 4.6 Hz, 6″-H), 4.30 (1H, *dd*, J = 11.6, 4.0 Hz, 1′-H), 4.40 (1H, *dd*, J = 7.3, 4.6 Hz, 7-H), 4.85 (1H, *d*, J = 7.9 Hz, 1″-H), 4.98 (1H, *dd*, J = 9.7, 7.9 Hz, 2″-H), 5.08 (1H, *t*, J = 9.7 Hz, 4″-H), 5.18 (1H, *t*, J = 9.7 Hz, 3″-H), 5.2–5.3 (4H, 1- and 7′-H, 10-H_2), 5.58 (1H, *dt*, J = 18.3, 9.3 Hz, 8-H), 7.25 (1H, *d*, J = 1.5 Hz, 3-H). [Found: C, 56.68; H, 6.53. $C_{35}H_{48}O_{17}$ requires: C, 56.75; H, 6.53%.]

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