Chemistry of Fijian Plants. V.[1] Constituents of *Fagraea gracilipes* A. GRAY

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Five new compounds were isolated from the heartwood of the Fijian tree *Fagraea gracilipes* A. GRAY in addition to methyl *p*-coumarate, methyl caffeate, methyl sinapate, and the secoiridoid glucoside sweroside. The new compounds have been identified as methyl syringate α-L-rhamnoside, (*Z*)-5-ethylidene-3,4,5,6-tetrahydro-*cis*-6,8-dimethoxy-1*H*,8*H*-pyrano[3,4-*c*]pyran-1-one, (*Z*)-5-ethylidene-3,4,5,6-tetrahydro-*trans*-6,8-dimethoxy-1*H*,8*H*-pyrano[3,4-*c*]pyran-1-one, 3-*O*-sinapoyl D-glucose and 3′-*O*-sinapoyl sweroside by spectroscopic methods, chemical conversion and X-ray analysis.

Keywords *Fagraea gracilipes*; Potaliaceae; secoiridoid acetal; secoiridoid glucoside; phenylpropanoid; ^{13}C-NMR; X-ray analysis

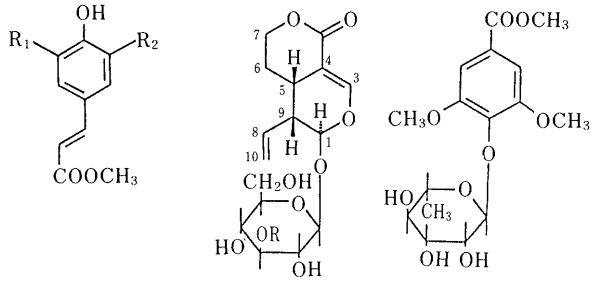
Fagraea gracilipes A. GRAY; the Fijian buabua, is a member of the family Potaliaceae and is a commercial native tree of Fiji. The durable timber is now in short supply and the cutting of trees with a girth of less than three feet has been prohibited in certain areas. As part of a continuing phytochemical study of Fijian plants[1] we report an examination of the constituents of the heartwood of *Fagraea gracilipes*.

Results and Discussion

In addition to methyl *p*-coumarate **1**, methyl caffeate **2**, methyl sinapate **3**, and the iridoid glucoside sweroside **4**, five new compounds **5**, **6**, **7**, **8** and **11** were isolated from *n*-hexane, ethyl acetate, and methanol extracts of the dried heartwood after multiple chromatography of fractions on silica gel or Sephadex LH-20.

Compound **6**, colorless plates, mp 87—90 °C, $[\alpha]_D^{20}$ −108° (c=1.0, MeOH), was formulated as $C_{16}H_{22}O_9$ from the molecular ion in the low-resolution mass spectrum (MS), and the proton nuclear magnetic resonance (^{1}H-NMR) and carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectra. The infrared (IR) spectrum (ν_{max}^{KBr} cm^{-1}: 1712, 1594, 1495) and ultraviolet (UV) spectrum [λ_{max}^{MeOH} nm (log ε): 215 (4.52), 266 (4.05)] showed absorptions due to an aromatic ester. The IR spectrum also showed strong absorptions due to hydroxy groups at 3355 and 1129 cm^{-1} suggesting that compound **6** was a glycoside. The ^{1}H-NMR spectrum of **6** (in CD_3OD) showed signals due to a carbomethoxy group at δ 3.89 (3H, s), two aromatic methoxy groups at δ 3.87 (6H, s), two aromatic protons at δ 7.31 (2H, s) and a glycosyl moiety at δ 1.21 (3H, d, J=7 Hz), 3.44 (1H, t, J=10 Hz), 3.90 (1H, dd, J=10 and 4 Hz), 4.14 (1H, dd, J=4 and 2 Hz), 4.24 (1H, dq, J=10 and 7 Hz) and 5.34 (1H, d, J=2 Hz). The ^{13}C-NMR spectrum of **6** (in CD_3OD) showed signals due to carbomethoxy carbons at δ 168.9 (s) and 53.6 (q), aromatic ring carbons at δ 108.5 (d, 2C), 127.9 (s), 140.8 (s) and 155.3 (s, 2C), two methoxy carbons at δ 57.4 (q, 2C), and glycosyl carbons at δ 18.7 (q), 72.1 (d), 72.8 (d), 73.0 (d), 74.5 (d) and 104.2 (d). These spectral data indicated that **6** was a glycoside of a phenol substituted symmetrically by one carbomethoxy and two methoxy groups.

On acid methanolysis, **6** gave methyl syringate and a methyl glycoside which on acid hydrolysis afforded L-rhamnose. Thus, the structure of **6** was determined as methyl syringate L-rhamnoside. The configuration at the anomeric carbon was assigned as α from a comparison



1 : R_1=R_2=H
2 : R_1=H, R_2=OH
3 : R_1=R_2=OCH_3
4 : R=H
5 : R=sinapoyl

6

Fig. 1

of the molecular rotation difference, $[M]_D$(glycoside)−$[M]_D$(aglycone)=−387°, with those of the anomeric methyl rhamnosides, $[M]_D$(α-anomer)−147°, $[M]_D$(β-anomer)+185°.[3]

Compound **7**, colorless prisms, mp 90—92 °C, was formulated as $C_{12}H_{16}O_5$ from the molecular ion (m/z 240.1016) in the high-resolution mass spectrum (HRMS). It showed signals of five sp^2 carbons at δ 119.8 (s), 130.6 (s), 133.9 (d), 143.9 (s) and 163.3 (s) in its ^{13}C-NMR spectrum (in CD_3OD). The latter signal was assigned as an ester carbonyl carbon on the basis of its chemical shift, 163.3, and from the IR spectrum of **7**, which showed absorption due to a carbonyl group at 1709 cm^{-1} but no absorption assignable to a hydroxy group. As **7** showed UV absorption at 272 nm, the five sp^2 carbons were considered to form a linear conjugated dienone system. In the ^{1}H-NMR spectrum of **7**, signals due to an olefinic methyl group at δ 1.90 (3H, d, J=7.3 Hz), an olefinic proton at δ 6.23 (1H, dq, J=1.2 and 7.3 Hz), two vicinal methylene groups at δ 2.55 (1H, dt, J=17.1 and 4.1 Hz), 2.66 (1H, dddd, J=17.1, 10.8, 6.0 and 1.6 Hz), and 4.40 (1H, dt, J=4.1 and 10.8 Hz), 4.45 (1H, ddd, J=10.8, 6.0 and 4.1 Hz), two methoxy groups at δ 3.59 (3H, s) and 3.65 (3H, s) and two methine protons at δ 5.46 (1H, d, J=1.6 Hz) and 5.48 (1H, d, J=1.2 Hz) were observed. As the olefinic methyl signal was coupled with the olefinic proton signal, J=7.3 Hz, they were judged to be attached to the same carbon, namely, to the terminal carbon of the conjugated system. Further, the deshielding of one of the methylene groups indicated that it was adjacent to oxygen and a non-protonated olefinic carbon. Thus, the partial structure A shown in Fig. 2 was deduced for **7**. The

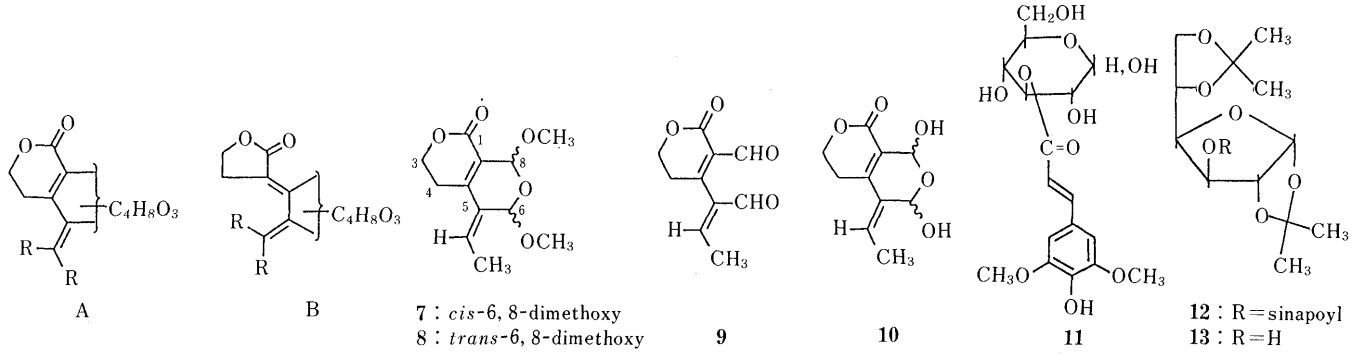


Fig. 2

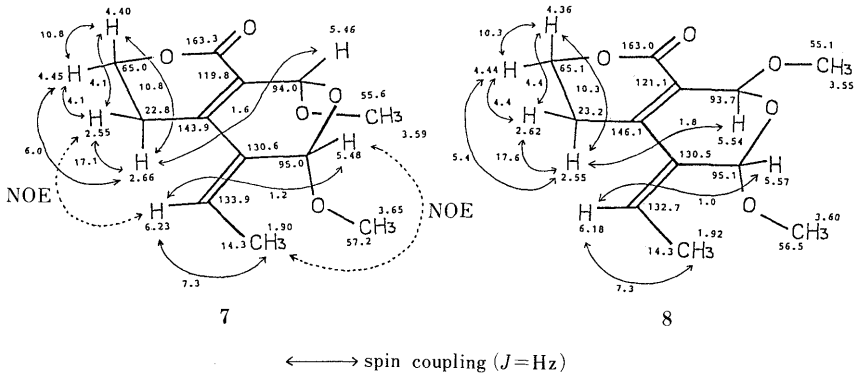


Fig. 3. ^{1}H- and ^{13}C-NMR Data (in $CDCl_3$)

possibility of a partial structure B was excluded since the IR absorption of the ester carbonyl for such a structure would be expected to appear at a much higher wave number[4] than that observed (1709 cm^{-1}). In order to accommodate two methoxy groups and an ether oxygen atom the remainder of the molecule had to be formulated as a cyclic diacetal system. The geometry of the methyl-substituted olefin bond was determined as *Z* from a nuclear Overhauser effect (NOE) correlation two-dimensional NMR spectrum (NOESY) in which NOE between the methyl group and an acetal proton (δ 5.48) and between the olefinic proton and one of the methylene protons at δ 2.55 was observed. Thus, the structure of **7** was determined as (*Z*)-5-ethylidene-3,4,5,6-tetrahydro-6,8-dimethoxy-1*H*,8*H*-pyrano[3,4-*c*]pyran-1-one, with the configuration at the acetal carbons remaining to be confirmed.

The final confirmation of the structure of **7** was carried out by X-ray analysis. Crystal data for **7** are as follows; triclinic, *a* 11.588 (2), *b* 12.209 (2), *c* 8.995 (33) Å, α 103.15 (3), β 106.46 (3), γ 90.06 (2)°, *U* 1185.50 $Å^3$, D_c (*Z*=4) 1.345 g cm^{-3}, *F* (000) 512, Z_r filtered MoK_α radiation λ 0.71069, μ 0.65 cm^{-1}, space group $P\bar{1}$, *T* 291 K.

Accurate unit cell data were obtained by a least-squares fit to the four-circle coordinates of 25 reflections. The unique data set was recorded on a Nonius CAD-4 diffractometer using $\omega/2\theta$ scans to a diffraction limit of 25°. Three standard reflections monitored throughout data collection, as a check on crystal movement or decomposition, showed no significant variation. The data were corrected for Lorentz and polarization effects and absorption corrections were considered unnecessary. In total, 4438 independent reflections were measured, of which 3216 exceeded 3σ (*I*) and were used for structure refinement.

The structure was solved using SHELXS-87[5] and refined using SHELX-76.[6] After initial isotropic refinement, all non-hydrogen atoms were assumed to exhibit anisotropic motion. Subsequent electron-density maps revealed the location of all hydrogen atoms and in subsequent least-squares cycles these were refined with fixed thermal parameters. Refinement converged to $R=0.039$ $R_W=0.049$ with weights $\omega=1.00/(\sigma^2(F)+0.003F^2)$. Computations were carried out on a micro-VAX computer for data correction and an IBM 3081 for structure solution and refinement. Material deposited comprises thermal parameters, hydrogen coordinates, bond angles and observed and calculated structure factors.

There are two independent molecules in the unit cell and the structure of one of these is depicted in Fig. 4. Atomic coordinates for non-hydrogen atoms and interatomic distances are given in Tables I and II. The two molecules are essentially identical, with close agreement between equivalent bond lengths. The structure confirms the relative stereochemistry at C(6) and C(8) and the positions of the double bonds, C(5)–C(11) and C(9)–C(10). The ring conformations are normal and all bond lengths fall within the normally expected ranges. Thus, the structure of **7** was established as (*Z*)-5-ethylidene-3,4,5,6-tetrahydro-*cis*-6,8-dimethoxy-1*H*,8*H*-pyrano[3,4-*c*]pyran-1-one.

Compound **8**, colorless syrup, was also formulated as $C_{12}H_{16}O_5$ from the molecular ion (*m/z* 240.1010) in the HRMS. It gave almost the same spectral data as those of **7**, indicating that it was an epimer of **7**. In acidic methanol solution, either **7** or **8** gave an equilibrium mixture of each compound in a ratio of 4:1. Therefore, the compounds could be formulated as epimers about one of the atoms of the cyclic acetal system. This means that **8** has a *trans*-

TABLE I. Atomic Coordinates for Compound **7**

	Molecule 1			Molecule 2		
	X/a	*Y/b*	*Z/c*	*X/a*	*Y/b*	*Z/c*
C(1)	0.4879 (2)	0.1767 (2)	−0.1881 (3)	0.0162 (2)	0.2435 (2)	−0.1818 (3)
O(1)	0.4061 (1)	0.2378 (1)	−0.2113 (2)	−0.1010 (2)	0.1793 (1)	−0.1972 (2)
O(2)	0.5067 (1)	0.1041 (1)	−0.3141 (2)	0.0047 (2)	0.2612 (1)	−0.3146 (2)
C(3)	0.6155 (2)	0.0427 (2)	−0.2867 (3)	0.1121 (2)	0.3308 (2)	−0.2954 (3)
C(4)	0.6332 (2)	−0.0062 (2)	−0.1435 (3)	0.1271 (2)	0.4346 (2)	−0.1640 (3)
C(5)	0.7014 (2)	0.0834 (2)	0.1599 (2)	0.2002 (2)	0.4656 (2)	0.1429 (3)
C(6)	0.7138 (2)	0.1934 (2)	0.2805 (3)	0.2133 (2)	0.4066 (2)	0.2759 (3)
O(7)	0.6026 (1)	0.2466 (1)	0.2583 (2)	0.1032 (1)	0.3471 (1)	0.2618 (2)
C(8)	0.5501 (2)	0.2673 (2)	0.1052 (2)	0.0501 (2)	0.2672 (2)	0.1153 (3)
C(9)	0.5661 (2)	0.1748 (2)	−0.0283 (2)	0.0624 (2)	0.3057 (2)	−0.0264 (3)
C(10)	0.6330 (2)	0.0867 (2)	−0.0021 (2)	0.1286 (2)	0.4003 (2)	0.0133 (3)
C(11)	0.7531 (2)	−0.0079 (2)	0.1990 (3)	0.2523 (2)	0.5678 (2)	0.1648 (3)
C(12)	0.8242 (3)	−0.0175 (2)	0.3604 (4)	0.3324 (3)	0.6382 (2)	0.3141 (4)
O(6)	0.8077 (1)	0.2592 (1)	0.2663 (2)	0.3090 (1)	0.3374 (1)	0.2744 (2)
C(13)	0.8407 (2)	0.3619 (2)	0.3852 (3)	0.3436 (3)	0.2865 (2)	0.4078 (3)
O(8)	0.5957 (1)	0.3706 (1)	0.0935 (2)	0.0995 (1)	0.1621 (1)	0.1135 (2)
C(14)	0.5484 (2)	0.4635 (2)	0.1791 (3)	0.0532 (3)	0.0985 (2)	0.2017 (4)

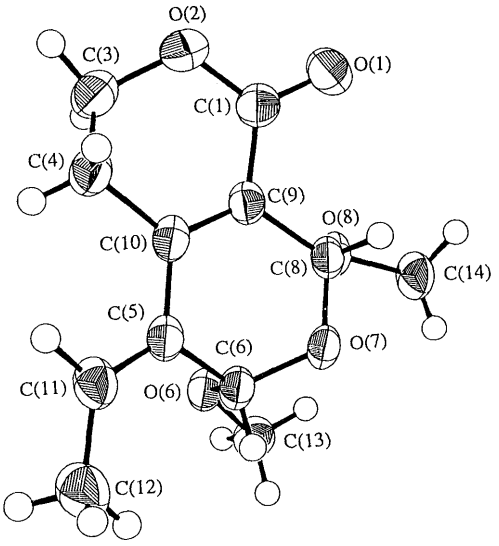


Fig. 4

TABLE II. Interatomic Distances for Compound **7**

	Molecule 1	Molecule 2
C(1)–O(1)	1.208 (2)	1.213 (5)
C(1)–O(2)	1.342 (3)	1.346 (3)
C(1)–C(9)	1.471 (3)	1.468 (3)
O(2)–C(3)	1.457 (3)	1.453 (3)
C(3)–C(4)	1.503 (3)	1.495 (4)
C(4)–C(10)	1.500 (3)	1.503 (3)
C(9)–C(10)	1.352 (3)	1.350 (3)
C(5)–C(10)	1.457 (3)	1.459 (3)
C(5)–C(6)	1.500 (3)	1.504 (3)
C(5)–C(11)	1.336 (3)	1.333 (3)
C(6)–O(7)	1.427 (2)	1.428 (2)
C(6)–O(6)	1.404 (2)	1.396 (2)
O(7)–C(8)	1.420 (2)	1.421 (3)
C(8)–C(9)	1.504 (3)	1.497 (3)
C(8)–O(8)	1.404 (2)	1.404 (2)
C(11)–C(12)	1.483 (3)	1.474 (3)
O(6)–C(13)	1.422 (3)	1.434 (3)
O(8)–C(14)	1.423 (3)	1.428 (3)

dimethoxy structure.

As neither **7** nor **8** showed optical activity, both were racemates. It is possible that they may be artifacts derived from a common dial **9** or a hemiacetal **10** during extraction. Compounds **1**, **2**, **3** and **6** may also exist in the deesterified form in the plant material.[7]

Compound **11**, colorless solid, $[\alpha]_D^{20}$ +20° (c=0.95, MeOH), possessed a UV spectrum [λ_{max}^{MeOH} nm (log ε): 224 (4.22), 237 (4.21), 328 (4.26)] similar to that of methyl sinapate (**3**). The ^{1}H-NMR spectrum of **11** (in CD_3OD) showed signals due to a sinapoyl group at δ 3.87 (6H, s), 6.45 (1H, d, J=16 Hz), 6.89 (2H, s) and 7.64 (1H, d, J=16 Hz) and a glycosyl group (which existed in an equilibrium between α- and β-anomers) at δ 4.62 (1H × 2/5, d, J=8 Hz), 5.05 (1H × 2/5, t, J=10 Hz), 5.18 (1H × 3/5, d, J=3 Hz), 5.34 (1H × 3/5, t, J=10 Hz) and 3.3—4.0 (5H). The signals at δ 4.62 and 5.18 were assigned to the anomeric protons and those at δ 5.05 and 5.34 to protons attached to the carbon bearing the sinapoyloxy group. The ^{13}C-NMR spectrum also showed signals due to a pair of anomers (see Experimental). This spectral data, together with a molecular ion peak at m/z 386 in the field desorption-mass spectrum (FD-MS), indicated that **11** was a sinapoyl ester of a hexose. In acidic acetone solution, **11** gave a di-*O*-isopropylidene derivative **12**, $[\alpha]_D^{20}$ −19° (c=1.0, $CHCl_3$), which, on alkaline methanolysis, afforded methyl sinapate (**3**) and 1,2; 5,6-di-*O*-isopropylidene D-glucose **13**, mp 112—114 °C, $[\alpha]_D^{20}$ −10° (c=0.1, $CHCl_3$).[8] Thus, the structure of **11** was determined as 3-*O*-sinapoyl D-glucose.

Compound **5**, colorless solid, $[\alpha]_D^{20}$ −136° (c=0.9, MeOH), was formulated as $C_{27}H_{32}O_{13}$ from the molecular ion (m/z 564) in the FD-MS and from the ^{1}H-NMR (32H) and ^{13}C-NMR (27C) spectra. The ^{1}H-NMR spectrum of **5** was similar to that of sweroside (**4**) except that one of the signals of the glucosyl moiety was observed at lower field, δ 5.08 (1H, t, J=8 Hz), and the spectrum showed additional signals assignable to a sinapoyl group. On alkaline methanolysis, **5** gave methyl sinapate (**3**) and sweroside (**4**). Thus, the structure of **5** was determined as a sinapoyl ester of sweroside.

The position of the sinapoyl group was deduced by comparison of the ^{13}C-NMR data of **5** with those of **4**. The

differences in the chemical shifts of their glucosyl moieties (δ_5–δ_4) are −0.2 (C-1′), −1.8 (C-2′), +0.6 (C-3′), −2.0 (C-4′), −0.5 (C-5′) and −0.4 (C-6′). These differences are considered to be caused by acylation at C-3′,[9] and their magnitudes are similar to those observed between the β-anomer of **11** and β-D-glucose,[10] *viz.* −0.1 (C-1), −1.7 (C-2), +1.1 (C-3), −1.8 (C-4), −0.3 (C-5) and −0.4 (C-6). Therefore, the structure of **5** was determined as 3′-*O*-sinapoyl sweroside.

Experimental

Melting points were determined with a Yanagimoto micromelting apparatus and are uncorrected. Optical rotations were taken with a JASCO DIP-360 automatic polarimeter. Gas-liquid chromatography (GLC) was run on a Shimadzu GC-4BM-PF gas chromatograph with a flame ionization detector using a capillary column (30 m × 0.25 mm i.d., WCOT, SE-30, Wako Pure Chemical). The ^{1}H-NMR and ^{13}C-NMR spectra were measured with a JEOL GSX-500 spectrometer and a Bruker WM-400 spectrometer. UV spectra were recorded on a Hitachi 323 spectrometer and IR spectra on a Shimadzu IR-460 spectrometer.

Isolation Procedure The dried heartwood of *Fagraea gracilipes* (132 g) was extracted (Soxlet) successively with *n*-hexane, EtOAc and MeOH. The hexane extract (3.5 g, 2.65%) contained long chain fatty esters which were not investigated further. The MeOH extract was evaporated under reduced pressure to yield a dark brown residue (7.0 g, 5.3%). A sample (2.7 g) was dissolved in a small amount of MeOH, mixed well with silica gel (5 g) and dried. The mixture was placed in a column of silica gel (60 g) and the column was eluted successively with $CHCl_3$, $CHCl_3$–EtOAc, EtOAc, EtOAc–MeOH and MeOH. Fractions eluted with $CHCl_3$ were rechromatographed on silica gel using benzene and $CHCl_3$ as eluents to yield methyl *p*-coumarate (**1**, 8 mg), methyl sinapate (**3**, 107 mg), compound **7** (34 mg) and compound **8** (7 mg). Fractions eluted with $CHCl_3$–EtOAc yielded methyl caffeate (**2**, 37 mg) and compound **6** (39 mg). Fractions eluted with EtOAc–MeOH were rechromatographed on silica gel using $CHCl_3$–MeOH mixtures as eluents to yield sweroside (**4**, 95 mg). The EtOAc extract was evaporated under reduced pressure to yield a dark brown residue (5.4 g, 4.1%). A sample (0.5 g) was subjected to droplet countercurrent chromatography (DCC). The apparatus consisted of 200 column units of glass tubing (2.4 mm i.d., 60 cm long) connected by Teflon tubing (0.5 mm i.d.). The solvent system used was $CHCl_3$–MeOH–H_2O (4:4:3), with the upper layer as the mobile and the lower layer as the stationary phase. The flow rate was 20 ml/h and fractions of 5 ml were taken in a fraction collector. Fractions 8 to 16, and 81 to 89 were rechromatographed on Sephadex LH-20 using MeOH as an eluent to yield compounds **5** (27 mg) and **11** (38 mg), respectively.

Sweroside (4) Colorless amorphous powder, $[\alpha]_D^{20}$ −207° (c=1.0, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3400, 2890, 1687, 1616, 1405, 1280, 1205, 1102, 1071, 1041, 1020, 984, 900, 840. UV λ_{max}^{MeOH} nm (log ε): 245 (3.97). ^{1}H-NMR (in CD_3OD) δ: 1.70 (1H, dq, J=4, 12 Hz, 7-H), 1.77 (1H, ddt, J=12, 5, 2 Hz, 7-H), 2.70 (1H, ddd, J=10, 6, 2 Hz, 9-H), 3.15 (1H, ddt, J=12, 2, 6 Hz, 5-H), 3.19 (1H, t, J=8 Hz, 2′-H), 3.27 (1H, t, J=8 Hz, 4′-H), 3.31 (1H, ddd, J=8, 6, 2 Hz, 5′-H), 3.37 (1H, t, J=8 Hz, 3′-H), 3.66 (1H, dd, J=12, 6 Hz, 6′-H), 3.89 (1H, dd, J=12, 2 Hz, 6′-H), 4.36 (1H, dt, J=2, 12 Hz, 7-H), 4.45 (1H, dq, J=12, 2 Hz, 7-H), 4.68 (1H, d, J=8 Hz, 1′-H), 5.27 (1H, dd, J=10, 2 Hz, 10-H), 5.31 (1H, dd, J=17, 2 Hz, 10-H), 5.55 (1H, dt, J=17, 10 Hz, 8-H), 5.55 (1H, d, J=2 Hz, 1-H), 7.59 (1H, d, J=2 Hz, 3-H). ^{13}C-NMR (in CD_3OD) δ: 26.2 (CH_2, C-6), 28.7 (CH, C-5), 44.1 (CH, C-9), 63.0 (CH_2, C-6′), 70.0 (CH_2, C-7), 71.8 (CH, C-4′), 75.0 (CH, C-2′), 78.2 (CH, C-5′), 78.7 (CH, C-3′), 98.3 (CH, C-1), 100.0 (CH, C-1′), 106.3 (C, C-4), 121.1 (CH_2, C-10), 133.6 (CH, C-8), 154.2 (CH, C-3), 168.8 (C, C=O). The properties and spectral data were in good agreement with those reported.[11]

3′-*O*-Sinapoyl Sweroside (Compound 5) Colorless solid, $[\alpha]_D^{20}$ −136° (c=0.9, MeOH). UV λ_{max}^{MeOH} nm (log ε): 241 (4.43), 329 (4.32). ^{1}H-NMR (in CD_3OD) δ: 1.69 (1H, dq, J=4, 12 Hz, 7-H), 1.76 (1H, ddt, J=12, 5, 2 Hz, 7-H), 2.71 (1H, ddd, J=10, 6, 2 Hz, 9-H), 3.13 (1H, ddt, J=12, 2, 6 Hz, 5-H), 3.43 (1H, t, J=8 Hz, 2′-H), 3.45 (1H, ddd, J=8, 6, 2 Hz, 5′-H), 3.55 (1H, t, J=8 Hz, 4′-H), 3.73 (1H, dd, J=12, 6 Hz, 6′-H), 3.87 (6H, s, OCH_3), 3.92 (1H, dd, J=12, 2 Hz, 6′-H), 4.34 (1H, dt, J=2, 12 Hz, 7-H), 4.43 (1H, dq, J=12, 2 Hz, 7-H), 4.82 (1H, d, J=8 Hz, 1′-H), 5.08 (1H, t, J=8 Hz, 3′-H), 5.28 (1H, dd, J=10, 2 Hz, 10-H), 5.31 (1H, dd, J=17, 2 Hz, 10-H), 5.55 (1H, dt, J=17, 10 Hz, 8-H), 5.56 (1H, d, J=2 Hz, 1-H), 6.45 (1H, d, J=16 Hz, S-8-H), 6.90 (2H, s, S-2,6-H), 7.60 (1H, d, J=2 Hz, 3-H), 7.64 (1H, d, J=16 Hz, S-7-H). ^{13}C-NMR (in CD_3OD) δ: 25.9 (CH_2, C-6), 28.5 (CH, C-5), 43.8 (CH, C-9), 56.9 (CH_3, OCH_3), 62.4 (CH_2, C-6′), 69.7 (CH_2, C-7), 69.8 (CH, C-4′), 73.2 (CH, C-2′), 78.2 (CH, C-5′), 78.8 (CH, C-3′), 98.1 (CH, C-1), 99.8 (CH, C-1′), 106.0 (C, C-4), 107.0 (CH, S-C-2,6), 116.2 (CH, S-C-8), 120.9 (CH_2, C-10), 126.7 (C, S-C-1), 133.3 (CH, C-8), 139.6 (C, S-C-4), 147.1 (S-C-7), 149.5 (C, S-C-3,5), 154.0 (CH, C-3), 168.4 (C, C=O), 168.9 (C, S-C-9). FD-MS m/z: 587 (M^++Na), 565 (M^++1), 564 (M^+).

Alkaline Methanolysis of Compound 5 A mixture of compound **5** (10 mg) and anhydrous Na_2CO_3 (200 mg) in MeOH (6 ml) was stirred under reflux for 45 min and filtered. The filtrate was evaporated and the residue was chromatographed on silica gel using a mixture of MeOH and $CHCl_3$ (1:4) as the eluent to give methyl sinapate (**3**, 2 mg) and sweroside (**4**, 3 mg). Methyl sinapate (**3**), colorless needles from MeOH, had mp 93—94 °C. The compound was identical with an authentic sample on direct comparison. Sweroside (**4**), a colorless amorphous powder, $[\alpha]_D^{20}$ −210° (c=0.2, MeOH), was identical with an authentic sample on direct comparison.

Methyl Syringate α-L-Rhamnoside (Compound 6) Colorless plates from acetone, mp 87—90°C, $[\alpha]_D^{20}$ −108° (c=1.0, MeOH). IR ν_{max}^{KBr} cm^{-1}: 3355, 2940, 1712, 1594, 1495, 1461, 1416, 1340, 1227, 1129, 1060, 1001, 970, 755. UV λ_{max}^{MeOH} nm (log ε): 215 (4.52), 266 (4.05). ^{1}H-NMR (in CD_3OD) δ: 1.21 (3H, d, J=7 Hz, 6′-H), 3.44 (1H, t, J=10 Hz, 4′-H), 3.87 (6H, s, OCH_3), 3.89 (3H, s, $COOCH_3$), 3.90 (1H, dd, J=10, 4 Hz, 3′-H), 4.14 (1H, dd, J=4, 2 Hz, 2′-H), 4.24 (1H, dq, J=10, 7 Hz, 5′-H), 5.34 (1H, d, J=2 Hz, 1′-H), 7.31 (2H, s, 2,6-H). ^{13}C-NMR (in CD_3OD) δ: 18.7 (CH_3, C-6′), 53.6 (CH_3, ester CH_3), 57.4 (CH_3 × 2, OCH_3), 72.1 (CH, C-5′), 72.8 (CH, C-3′), 73.0 (CH, C-2′), 74.5 (CH, C-4′), 104.2 (CH, C-1′), 108.5 (CH, C-2,6), 127.9 (C, C-1), 140.8 (C, C-4), 155.3 (C, C-3,5), 168.9 (C, C=O). FD-MS m/z: 358 (M^+), 211, 147.

Methanolysis of Compound 6 A solution of compound **6** (20 mg) in MeOH (10 ml) containing 5% HCl was heated under reflux for 2 h. The mixture was poured into ice-water, and extracted with EtOAc, then the extract was washed with water, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The residue was crystallized from EtOAc to give methyl syringate as colorless needles (6 mg), mp 111—112 °C. The product was identical with an authentic sample on direct comparison. The water layer from methanolysis was concentrated and hydrolyzed with 5% HCl solution (10 ml) under reflux for 2 h. The reaction mixture was evaporated and the residue was chromatographed on silica gel using $CHCl_3$ and MeOH as eluents to yield L-rhamnose (5 mg), $[\alpha]_D^{20}$ +6° (c=0.5, H_2O). The trimethylsilyl ether was identical with an authentic sample on GLC: t_R 4.4 and 5.3 min (column temperature 180 °C).

(*Z*)-5-Ethylidene-3,4,5,6-tetrahydro-*cis*-6,8-dimethoxy-1*H*,8*H*-pyrano[3,4-*c*]pyran-1-one (Compound 7) Colorless prisms from EtOAc, mp 90—92 °C. IR ν_{max}^{KBr} cm^{-1}: 3005, 2920, 1709, 1633, 1420, 1123, 1084, 985. UV λ_{max}^{MeOH} nm (log ε): 272 (4.31). ^{1}H-NMR (in $CDCl_3$) δ: 1.90 (3H, d, J=7.3 Hz), 2.55 (1H, dt, J=17.1, 4.1 Hz), 2.66 (1H, dddd, J=17.1, 10.8, 6.0, 1.6 Hz), 3.59 (3H, s), 3.65 (3H, s), 4.40 (1H, dt, J=4.1, 10.8 Hz), 4.45 (1H, ddd, J=10.8, 6.0, 4.1 Hz), 5.46 (1H, d, J=1.6 Hz), 5.48 (1H, d, J=1.2 Hz), 6.23 (1H, dq, J=1.2, 7.3 Hz). ^{13}C-NMR (in $CDCl_3$) δ: 14.3 (CH_3), 22.8 (CH_2), 56.6 (CH_3), 57.2 (CH_3), 65.0 (CH_2), 94.0 (CH), 95.0 (CH), 119.8 (C), 130.6 (C), 133.9 (CH), 143.9 (C), 163.3 (C). Assignments of these signals are shown in Fig. 3. HRMS: 240.1016. Calcd for $C_{12}H_{16}O_5$: 240.0997.

(*Z*)-5-Ethylidene-3,4,5,6-tetrahydro-*trans*-6,8-dimethoxy-1*H*,8*H*-pyrano[3,4-*c*]pyran-1-one (Compound 8) Colorless syrup. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3010, 2930, 1712, 1632, 1412, 1121, 1080, 1041, 981. UV λ_{max}^{MeOH} nm (log ε): 271 (4.23). ^{1}H-NMR (in $CDCl_3$) δ: 1.92 (3H, d, J=7.3 Hz), 2.55 (1H, dddd, J=17.6, 10.3, 5.4, 1.8 Hz), 2.62 (1H, dt, J=17.6, 4.4 Hz), 3.55 (3H, s), 3.60 (3H, s), 4.36 (1H, dt, J=4.4, 10.3 Hz), 4.44 (1H, ddd, J=10.3, 5.4, 4.4 Hz), 5.54 (1H, br s), 5.57 (1H, br s), 6.18 (1H, dq, J=1.0, 7.3 Hz). ^{13}C-NMR (in $CDCl_3$) δ: 14.3 (CH_3), 23.2 (CH_2), 55.1 (CH_3), 56.5 (CH_3), 65.1 (CH_2), 93.7 (CH), 95.1 (CH), 121.1 (C), 130.5 (C), 132.7 (CH), 146.1 (C), 163.0 (C). Assignments of these signals are shown in Fig. 3. MS m/z: 240 (M^+), 209 (M^+−OCH_3, base peak). HRMS: 240.1016. Calcd for $C_{12}H_{16}O_5$: 240.0997.

Epimerization of Compounds 7 and 8 Either **7** or **8** (2 mg) was dissolved in MeOH (2 ml) containing 1% H_2SO_4 and the solution was allowed to stand at room temperature. Thin layer chromatography (TLC) examination revealed the presence of an equilibrium mixture of **7** and **8** within 1 h in each case.

3-*O*-Sinapoyl D-Glucose (Compound 11) Colorless solid, $[\alpha]_D^{20}$ +20° (c=0.95, MeOH). UV λ_{max}^{MeOH} nm (log ε): 224 (4.22), 237 (4.21), 328 (4.26). ^{1}H-NMR (in CD_3OD) δ: 3.87 (6H, s, OCH_3), 3.3—4.0 (5H, G-2,4,5,6-H),

4.62 (1H × 2/5, d, J = 8 Hz, β-G-1-H), 5.05 (1H × 2/5, t, J = 10 Hz, β-G-3-H), 5.18 (1H × 3/5, d, J = 3 Hz, α-G-1-H), 5.34 (1H × 3/5, t, J = 10 Hz, α-G-3-H), 6.45 (1H, d, J = 16 Hz, S-8-H), 6.89 (2H, s, S-2,6-H), 7.64 (1H, d, J = 16 Hz, S-7-H). ^{13}C-NMR (in CD_3OD) δ: α-anomer, 94.0 (G-1), 72.3 (G-2), 77.1 (G-3), 70.0 (G-4), 72.9 (G-5), 62.4 (G-6), 126.8 (S-1), 106.9 (S-2,6), 149.4 (S-3,5), 139.5 (S-4), 146.9 (S-7), 116.5 (S-8), 169.3 (S-9), 56.9 (S-OCH_3), β-anomer, 98.2 (G-1), 74.7 (G-2), 79.2 (G-3), 70.0 (G-4), 77.9 (G-5), 62.6 (G-6), 126.8 (S-1), 106.9 (S-2,6), 149.4 (S-3,5), 139.5 (S-4), 147.0 (S-7), 116.3 (S-8), 169.0 (S-9), 56.9 (S-OCH_3). FD-MS m/z: 386 (M^+), 409 (M^+ + Na), 224 (sinapic acid).

1,2;5,6-Di-*O*-isopropylidene-3-*O*-sinapoyl D-Glucose (Compound 12) Compound **11** (25 mg) was dissolved in acetone (20 ml) containing a drop of concentrated H_2SO_4. The solution was allowed to stand at room temperature for 20 h and then poured into ice-water. The products were extracted with EtOAc. The extract was dried over anhydrous Na_2SO_4 and evaporated. The residue was chromatographed on silica gel using $CHCl_3$ as the eluent to give compound **12** (10 mg). Amorphous solid, $[\alpha]_D^{20}$ −19° (c = 1.0, $CHCl_3$). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3515, 2965, 1704, 1622, 1600, 1508, 1453, 1375, 1145, 1115, 1071, 1015. ^{1}H-NMR (in $CDCl_3$): 1.32, 1.43, 1.44, 1.55 (each 3H, s, isopropylidene CH_3), 3.93 (6H, s, OCH_3), 4.08 (1H, dd, J=9, 6 Hz, G-6-H), 4.12 (1H, dd, J=9, 6 Hz, G-6-H), 4.30 (1H, dd, J=8, 3 Hz, G-4-H), 4.32 (1H, dt, J=8, 6 Hz, G-5-H), 4.58 (1H, d, J=4 Hz, G-2-H), 5.40 (1H, d, J=3 Hz, G-3-H), 5.93 (1H, d, J=4 Hz, G-1-H), 6.30 (1H, d, J=16 Hz, S-8-H), 6.78 (2H, s, S-2,6-H), 7.62 (1H, d, J=16 Hz, S-7-H). MS m/z: 466 (M^+), 451, 408, 350, 307, 224, 207. HRMS: 466.1831. Calcd for $C_{23}H_{30}O_{10}$: 466.1836.

Alkaline Methanolysis of Compound 12 A mixture of compound **12** (7 mg) and anhydrous Na_2SO_4 (200 mg) in MeOH (6 ml) was stirred under reflux for 1 h. The mixture was poured into a cold 5% HCl solution and extracted with EtOAc. The extract was washed with water, dried over anhydrous Na_2SO_4, and then evaporated under reduced pressure. The residue was chromatographed on silica gel using a mixture of EtOAc and $CHCl_3$ (1:9) as the eluent to yield methyl sinapate (**3**, 1.5 mg) and 1,2;5,6-di-*O*-isopropylidene D-glucose (**13**, 2 mg). Methyl sinapate, colorless needles from MeOH, had mp 93—94 °C, and was identical with an authentic sample on direct comparison. 1,2;5,6-Di-*O*-isopropylidene D-glucose (compound **13**), colorless needles from *n*-hexane, mp 112—114 °C, $[\alpha]_D^{20}$ −10° (c = 0.1, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3415, 2985, 1376, 1246, 1220, 1160, 1119, 1091, 1065, 1031, 1006, 941, 885, 847, 783, 529. ^{1}H-NMR (in $CDCl_3$): 1.32, 1.37, 1.45, 1.50 (each 3H, s, isopropylidene CH_3), 2.59 (1H, d, J=4 Hz, OH), 3.99 (1H, dd, J=9, 6 Hz, 6-H), 4.07 (1H, dd, J=8, 3 Hz, 4-H), 4.17 (1H, dd, J=9, 6 Hz, 6-H), 4.32—4.37 (2H, m, 3,5-H), 4.54 (1H, d, J=4 Hz, 2-H), 5.95 (1H, d, J=4 Hz, 1-H). The compound was identical with an authentic sample prepared from D-glucose.[8]

References and Notes

1) Part IV: A. R. Lal, R. C. Cambie, P. S. Rutledge and P. D. Woodgate, *Phytochemistry*, **29**, 1925 (1990).
2) Visiting Professor, University of Auckland, New Zealand, 1988.
3) W. Klyne, "Determination of Organic Structures by Physical Methods," ed. by E. A. Braude and F. C. Nachod, Academic Press, New York, 1955, p. 73.
4) H. Zimmer, J. Rothe and J. M. Holbert, *J. Org. Chem.*, **25**, 1234 (1960).
5) G. M. Sheldrick, SHELXS-86, Institut für Anorganish Chemie, Universität Göttingen, Germany, 1986.
6) G. M. Sheldrick, SHELX-76, University Chemical Laboratory, Cambridge, England, 1976.
7) Though compounds **1**, **2**, **3**, **6**, **7** and **8** are soluble in EtOAc, none of them was detected in the EtOAc extract. This evidence favors the possibility that they are artifacts.
8) O. T. Schmidt, *Methods Carbohydrate Chem.*, **2**, 318 (1963).
9) K. R. Markham and V. M. Chari, "The Flavonoids: Advances in Research," ed. by J. B. Harborne and T. J. Mabry, Chapman and Hall, London, 1982, p. 44.
10) The ^{13}C chemical shifts of β-D-glucose in CD_3OD solution are as follows; 98.3 (C-1), 76.4 (C-2), 78.1 (C-3), 71.8 (C-4), 78.2 (C-5) and 63.0 (C-6).
11) H. Achenbach, C. Renner and I. Addae-Mensah, *Planta Medica*, **46**, 88 (1982); T. A. van Beek, P. P. Lankhorst, R. Verpoorte and A. Baerheim Svendsen, *ibid.*, **44**, 30 (1982).