Table 1. 400 MHz ^{1}H NMR methyl group chemical shifts of the C-24 epimeric C_{28} $\Delta^{5,22}$-sterols isolated from *Brassica juncea*

	C-18	C-19	C-21	C-26	C-27	C-28
22-Dehydrocampesterol (1)	0.692 (*s*)	1.009 (*s*)	1.001 (*d*, J = 6.35)	0.834 (*d*, J = 7.33)	0.817 (*d*, J = 6.83)	0.909 (*d*, J = 6.84)
Brassicasterol (2)	0.692 (*s*)	1.009 (*s*)	1.011 (*d*, J = 6.84)	0.833 (*d*, J = 6.35)	0.817 (*d*, J = 6.35)	0.909 (*d*, J = 6.84)

All chemical shifts given in δ-values from TMS; coupling constants in Hz.

were collected each time. GC was carried out on an OV-1 WCOT Si capillary column (0.25 mm i.d. × 50 m, 280°) and *RR*,s are given relative to cholesteryl acetate (1.000). ^{1}H NMR spectra were recorded at 400 MHz with a JEOL JNM FX-400 spectrometer, using $CDCl_3$ as solvent and TMS as an int. standard.

The $C_{28}\Delta^{5,22}$-steryl acetate mixture was obtained from the unsaponifiable matters of *B. juncea* seeds. Prep TLC, gave the sterols which were acetylated and further purified by $AgNO_3$–Si gel TLC as described previously [1].

22-Dehydrocampesterol (1). MS *m/z* (rel. int.): 398 $[M]^+$ (100), 383 (13), 380 (18), 365 (18), 355 (9), 337 (22), 300 (49), 271 (56), 255 (96), 213 (37). 1-acetate: 380 $[M - HOAc]^+$ (100), 365 (9), 337 (10), 282 (9), 255 (62), 228 (11), 213 (16).

Brassicasterol (2). MS *m/z* (rel. int): 398 $[M]^+$ (100), 383 (16), 380 (19), 365 (18), 355 (11), 337 (28), 300 (56), 271 (65), 255 (94), 213 (34). 2-acetate: 380 $[M - HOAc]^+$ (100), 365 (9), 337 (10), 282 (9), 255 (61), 228 (11), 213 (15).

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A XYLOSYLGLUCOSIDE OF XANTHOXYLIN FROM *SAPIUM SEBIFERUM* ROOT BARK

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Key Word Index—*Sapium sebiferum*; Euphorbiaceae; root bark; moretenone; moretenol; xanthoxylin; sitosterol β-D-glucoside; 2-acetyl-3,5-dimethoxyphenyl-*O*-β-D-xylopyranosyl-(1–6)-β-D-glucopyranoside; ^{1}H NMR; ^{13}C NMR.

Abstract—Besides four known compounds, a new xylosylglucoside of xanthoxylin was isolated from the root bark of Chinese tallow tree, *Sapium sebiferum* and identified as 2-acetyl-3,5-dimethoxyphenyl-*O*-β-D-xylopyranosyl-(1–6)-β-D-glucopyranoside.

INTRODUCTION

Chinese tallow tree, *Sapium sebiferum* Roxb. is common in Nagasaki city as a roadside tree. Its root bark has been used [1] in China as a purgative and diuretic. Recently, it was reported [1] to be effective against *Schistosoma japonicum*. However, only xanthoxylin (2-hydroxy-4,6-dimethoxyacetophenone) has been isolated from the root bark [2] although some other constituents, such as

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friedelin, sitosterol and ellagic acid from leaves and moretenone, moretenol and sterols from stem have been reported [3]. The present paper describes the isolation and structure elucidation of a xylosylglucoside obtained from the root bark.

RESULTS AND DISCUSSION

The methanol extracts of the bark were fractionated with chloroform, ethyl acetate, and *n*-butanol successively. Moretenone, moretenol [4], xanthoxylin (**1**), and sitosterol-β-D-glucoside were obtained from the chloroform-soluble part. The *n*-butanol-soluble part yielded a xylosylglucoside (**2**), mp 188–190°, which afforded **1**, xylose and glucose on acid hydrolysis. Compound **2** gave a hexa-acetate **3** and a hexamethyl ether **4**. The mass spectra of **3** and **4** suggested the presence of a terminal xylose because their base peaks, observed at *m/z* 175 and 259, are assignable to xylose fragments. The ^{13}C NMR spectrum of **2** suggested a xylo-(1–6)-glucoside structure because two methylene carbon signals at δ 66.9 and 70.1 are assignable [5] to C-5 of xylose and glycosylated C-6 of glucose, respectively. Final confirmation was obtained by methanolysis of **4** foflowed by GC detection of **1**, methyl-2,3,4-tri-*O*-methyl-D-xylopyranoside, and methyl-2,3,4-tri-*O*-methyl-D-glucopyranoside. In the ^1H NMR spectrum of **4**, two anomeric proton signals observed at δ 4.20 and 4.80 are doublets ($J = 7.2$ Hz), suggesting β-configurations in both the sugar linkages. Therefore, the structure of the glycoside was deduced as 2-acetyl-3,5-dimethoxyphenyl-*O*-β-xylopyranosyl-(1–6)-β-D-glucopyranoside.

EXPERIMENTAL

General. Mps are uncorr. Shimazu GC-3BF gas chromatograph equipped with a column (2.1 m) of 10% SE-30 was used for GC. Kiesel gel 60 (Merck) and Kiesel gel 60 GF_{254} were used for CC and TLC, respectively.

Isolation. The fresh root bark (2 kg) of Chinese tallow tree collected in Oct. at Nagasaki was ground with MeOH and extracted × 3 at room temp. The resulting MeOH extracts (64 g) were fractionated with $CHCl_3$, EtOAc and *n*-BuOH, successively. The $CHCl_3$-soluble part (9 g) was separated by CC (Si gel) eluting with a mixture of *n*-hexane and EtOAc to give moretenone (152 mg), xanthoxylin (327 mg), moretenol (5.3 mg) and sitosterol-β-D-glucoside (53 mg). The *n*-BuOH-soluble part (16 g) was dissolved in H_2O and separated by CC (Amberite XAD-2) eluting with H_2O, H_2O–MeOH and MeOH, successively. The latter two fractions gave a xanthoxylin glycoside (290 mg) after a further CC (Si gel, $CHCl_3$–MeOH, 4:1).

Moretenone. Colourless needles from MeOH, mp 196–198°, MS *m/z* (rel. int.): 424 $[M]^+$ (90), 409 (98), 381 (16), 205 (100); ^1H NMR ($CDCl_3$): δ 0.70 (3H, *s*), 0.95, 1.03 (6H, *s* each), 1.08, 1.68 (3H, *s* each), 4.68 (2H, *br s*). (Found: C, 84.73; H, 11.43. $C_{30}H_{48}O$ requires. C, 84.84; H, 11.39%.)

Moretenol. Colourless scales from Me_2CO, mp 215–217°, MS *m/z* (rel. int.): 426 $[M]^+$ (80), 411 (28), 383 (15), 368 (48), 207 (100); ^1H NMR ($CDCl_3$): δ 0.69, 0.72, 0.83, 0.94 (3H, *s* each), 0.97 (6H, *s*), 1.67 (3H, *s*), 3.51 (1H, *s*), 3.84 (1H, *d*, $J = 2.7$ Hz), 4.68 (2H, *br s*). PCC oxidation gave moretenone (TLC, MS and ^1H NMR).

Xanthoxylin (**1**). Colourless needles from MeOH, mp 77–79°, ^1H NMR ($CDCl_3$): δ 2.59, 3.80, 3.83 (3H, *s* each), 5.88, 6.03 (1H, *d*, $J = 2$ Hz each), 13.92 (1H, *s*).

Xanthoxylin glycoside (**2**). Colourless needles from MeOH, mp 188–190°, $[\alpha]_D^{26}$ −41.7° (pyridine; 0.5%); UV λ_{max}^{EtOH} (ε) nm: 225 (14 520) and 273 (7570); IR ν_{max}^{nujol} cm^{-1}: 1645, 1600, 815, 800; ^1H NMR (d_5-pyridine): δ 2.74, 3.64, 3.79 (3H, *s* each), 5.52 (1H, *d*, $J = 7.2$ Hz), 6.33, 7.02 (1 H, *d*, $J = 1.8$ Hz each); ^{13}C NMR (d_5-pyridine): δ 32.9 *q*, 55.7 *q*, 55.9 *q*, 66.9 *t*, 70.1 *t*, 71.0 *d*, 71.3 *d*, 74.7 *d*, 74.8 *d*, 77.5 *d*, 78.0 *d*, 78.3 *d*, 93.8 *d*, 95.7 *d*, 103.5 *d*, 105.8 *d*, 116.1 *s*, 157.1 *s*, 158.4 *s*, 162.8 *s*, 201.0 *s*. (Found: C, 50.88; H, 6.20. $C_{21}H_{30}O_{13}$ requires C, 51.42; H, 6.17%.) Hexa-acetate of **2**: Compound **2** (50 mg) was acetylated with Ac_2O (2 ml) and pyridine (4 ml) and purified by CC (Si gel, *n*-hexane–EtOAc, 4:1) to give colourless plates (45 mg) from 50% MeOH, mp 128–130°, MS *m/z* (rel. int.): 742 $[M]^+$ (6.5), 684 (2.9), 548 (48), 368 (7.2), 331 (4.3), 317 (34), 280 (17), 259 (100, VI), 215 (14); ^1H NMR ($CDCl_3$): δ 1.66, 1.96, 2.01, 2.06, 2.06, 2.08, 2.40, 3.79, 3.82 (3H, *s* each), 3.2–3.6 (3H, *m*), 4.0–4.3 (3H, *m*), 4.52 (1H, *d*, $J = 6.3$ Hz), 4.8–5.3 (6H, *m*), 6.23, 6.32 (1H, *d*, $J = 1.8$ Hz each). (Found: C, 53.37; H, 5.88. $C_{33}H_{42}O_{19}$ requires: C, 53.37; H, 5.70%.)

Acid hydrolysis of **2**. A mixture of **2** (30 mg) and 3% H_2SO_4 (4 ml) was refluxed for 1.5 hr and extracted with $CHCl_3$ to give a solid (6.3 mg), which was identified with **1** (MS and ^1H NMR). The aq. layer was neutralized with $Ba(OH)_2$ and the filtrate separated from $BaSO_4$ was analysed by avicel TLC for detection of xylose (R_f: 0.47 and 0.34) and glucose (R_f: 0.39 and 0.23); solvents used: pyridine–EtOAc–HOAc–H_2O (36:36:7:21) and *n*-BuOH–HOAc–H_2O (3:1:1), respectively.

Methanolysis of the hexamethyl ether of **2**. Compound **2** (30 mg) in DMF (1 ml) was mixed with MeI (0.5 ml) and Ag_2O (1.3 g). The mixture, in a sealed tube, was kept at 37° for 6 hr and then left standing overnight at room temp. The reaction mixture was extracted with $CHCl_3$ and the $CHCl_3$-soluble part was once more methylated by the same way as above except for the use of BaO (800 mg) instead of Ag_2O [6]. The product was purified by CC (Si gel, *n*-hexane–EtOAc, 7:3) to give an oil (7.5 mg). MS *m/z* (rel. int.): 574 $[M]^+$ (3), 531 (3), 391 (20), 378 (34), 370 (48), 313 (26), 279 (26), 256 (23), 196 (64), 175 (100, V); ^1H NMR ($CDCl_3$): δ 2.47, 3.45, 3.47, 3.56, 3.56, 3.59, 3.63, 3.79, 3.79 (3H, *s* each), 4.20, 4.80 (1H, *d*, $J = 7.2$ Hz each), 6.15, 6.32 (1H, *d*, $J = 2.7$ Hz each). The methyl ether (3.5 mg) was mixed with 0.3 N HCl–MeOH (5 ml) and refluxed for 2 hr. The cooled soln was neutralized with Ag_2CO_3 and the filtrate was evaporated to dryness. The reaction product was dissolved in Me_2CO and subjected to GC for detection of the following compounds: methyl-2,3,4-tri-*O*-methyl-β-D-xylopyranoside, R_t 1.9 min; α-compound, R_t 2.4 min; methyl-2,3,4-tri-*O*-methyl-β-D-glucopyranoside, R_t 4.6 min; α-compound, R_t 5.2 min; xanthoxylin (**1**), R_t 10.8 min. Each compound was detected by co-chromatography with an authentic sample.

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