

The Structure and Synthesis of Sudachiin A, a New Flavone Glucoside from *Citrus Sudachi*

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Sudachiin A was isolated from the green peels of *Citrus sudachi* Hort. ex Shirai. This structure was deduced to be sudachitin 4'- β -D-glucoside by means of its spectra and degradation; this was confirmed by the synthesis of the one from sudachitin 7-benzyl ether and α -acetobromoglucose *via* several steps. 4',5,7-Trihydroxy-3',6,8-trimethoxyflavone 7-glucoside (sudachitin 7- β -D-glucoside), which was isolated from *Sideritis leucantha* Cavanilles, was also synthesized from sudachitin and α -acetobromoglucose in a similar manner.

In continuous investigations of the constituents in green peels of *Citrus sudachi* Hort. ex Shirai, we have already reported the isolation of several flavonoids, sudachitin (**1**),^{1,2)} demethoxysudachitin (**2**),³⁾ dinatin (**3**),⁴⁾ xanthomicrol (**4**),⁴⁾ 4',5,7-trihydroxy-3',6-dimethoxyflavone (**5**),⁴⁾ and 7-methylsudachitin (**6**).⁴⁾ In a recent preliminary communication⁵⁾ we reported the structure elucidation of sudachiin A (sudachitin 4'- β -D-glucoside) (**7**), a new flavone glucoside isolated from the same source. Recently, 4',5,7-trihydroxy-3',6,8-trimethoxyflavone 7-glucoside (sudachitin 7- β -D-glucoside) (**8**), one of the isomers of sudachiin A (**7**), was isolated from a whole plant of *Sideritis leucantha* Cavanilles by F. Tomas and E. Ferreres.⁶⁾ In the present paper we will describe the details of the structure elucidation of sudachiin A (**7**) and the synthesis of **7** and its isomer (**8**).

The methanol concentrate, obtained from fresh green peels, was washed with ether and then extracted with ethyl acetate. The extract, dissolved in methanol, was allowed to stand in a refrigerator to give precipitates, which were then removed by filtration. The resulting solution was concentrated and fractionated by column chromatography over polyamide. The yellow fraction eluted with methanol was subjected to repeated chromatography over polyamide to give a glycoside, named sudachiin A.

Sudachiin A, yellow needles (mp 211—213 °C, $[\alpha]_D$ -37.4° (0.5% aq NaOH)), was analyzed for C₂₄H₂₆O₁₃ (mol wt 522) by means of elemental analysis and CI-MS (m/z 523 (MH⁺)).⁷⁾ The glycoside, which was easily converted into a hexaacetate (**9**; mp 212—213 °C), was hydrolyzed with 5% sulfuric acid to sudachitin (4',5,7-trihydroxy-3',6,8-trimethoxyflavone) (**1**)^{1,2,8)} and D-glucose. In the UV spectrum of the glucoside, Band I (λ_{max} 337 nm) was shifted to 385 nm in the presence of sodium acetate, and its intensity was markedly lower than that of Band II⁹⁾ (Table 1). On the other hand, the exhaustive methylation of sudachiin A with diazomethane, followed by the hydrolysis of the resultant methyl ether, gave 4'-hydroxy-3',5,6,7,8-pentamethoxyflavone (sudachitin 5,7-dimethyl ether) (**10**; mp 145—146 °C).¹⁰⁾ Judging from the above results, sudachiin A seemed to be sudachitin 4'-D-glucoside (4',5,7-trihydroxy-3',6,8-trimethoxyflavone 4'-D-glucoside) (**7**).

The ¹H NMR spectrum of the hexaacetate (**9**) showed the presence of two phenolic acetoxy groups (δ 2.43 and 2.48) in the flavone nucleus and four acetoxy groups (δ 2.04 and 2.08, each 6H) in the sugar moiety (Table 2). The proton signals attributable to the sugar moiety at δ 4.1—4.3 and 5.0—5.4 were superimposable on those of cirsilineol 4'-tetra-O-acetyl- β -D-glucopyranoside.¹¹⁾ Consequently, sudachiin A (**7**) was shown to be sudachitin 4'- β -D-glucopyranoside; the structure of **7** was further confirmed by the following synthesis.

Sudachitin (**1**) was partially benzylated with benzyl chloride, potassium iodide, and aqueous potassium hydroxide in acetone-*N,N*-dimethylformamide (DMF) to give two monobenzyl ethers, **11** (mp 159—160 °C) and **12** (mp 177—178 °C), and 7,4'-dibenzyl ether (**13**; mp 126—127 °C) of **1** (Table 2), in yields of 40, 2, and 8% respectively. Each Band I of the UV spectra for the monobenzyl ethers in ethanol underwent a bathochromic shift upon the addition of aluminum chloride and sodium acetate (Table 1). In the UV spectra for **11** and **12** in the presence of sodium acetate, the magnitude (71 nm) of the Band I shift of **11** is much larger than that (40 nm) of **12**; furthermore, the intensity for the Band I of **11** is markedly greater than that for the Band II of **11**. These facts show that the two hydroxyl groups on **11** are located at the 5- and 4'-positions.^{4,9)} Therefore, the monobenzyl ethers, **11** and **12**, are the 7- and 4'-benzyl ethers of **1** respectively. Sudachitin 7-benzyl ether (**11**) was easily condensed with α -acetobromoglucose to give an O-acetylglucoside (**14**; mp 156—157 °C), which was subsequently debenzylated to sudachitin 4'-O-acetylglucoside (**15**; mp 196—197 °C; $[\alpha]_D$ -22.5° (CHCl₃)) with 10% palladium on charcoal. The hydrolysis of **15** with 5% aqueous sodium hydroxide gave the desired 4'- β -D-glucopyranoside (**7**; mp 211—213 °C; $[\alpha]_D$ -39.2° (0.5% aq NaOH)). The synthetic glucoside and its hexaacetate were found to be identical with natural sudachiin A and its hexaacetate respectively on the basis of a mixed-melting point determination and by IR, UV, and ¹H NMR spectral comparisons.

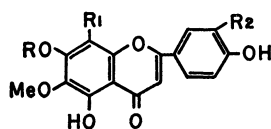
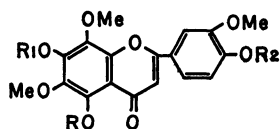
Sudachitin 7- β -D-glucopyranoside (**8**), one of the isomers of sudachiin A, was synthesized from sudachitin (**1**) and α -acetobromoglucose *via* the corresponding O-acetylglucoside by the same method as that described

TABLE 1. UV SPECTRAL DATA FOR SUDACHITIN DERIVATIVES^{a)}

Compd	λ_{max}/nm (log ϵ)					
	EtOH		EtOH-AlCl ₃		EtOH-NaOAc	
7 (Nat.)	284 (4.34)	337 (4.29)	298 (4.33)	354 (4.35)	283 (4.43)	385 (4.13)
7 (Syn.)	283 (4.38)	337 (4.32)	298 (4.34)	354 (4.35)	283 (4.45)	383 (4.13)
1	283 (4.29)	350 (4.24)	292 (4.21)	364 (4.36)	331 (4.06)	400 (4.18)
10	268 (4.22)	339 (4.40)			337 (4.17)	407 (4.25)
11	278 (4.27)	349 (4.36)	290 (4.26)	365 (4.41)	267 (4.32)	420 (4.53)
12	283 (4.31)	342 (4.36)	298 (4.28)	360 (4.37)	284 (4.43)	314 (4.24) 382 (4.16)
13	283 (4.32)	343 (4.40)	292 (4.29)	358 (4.41)		
14	284 (4.44)	332 (4.33)	301 (4.39)	349 (4.36)		
15	285 (4.49)	327 (4.29)	307 (4.51)	345 (4.33)	282 (4.56)	383 (4.15)
16	277 (4.22)	349 (4.34)	286 (4.19)	304 (4.14) 363 (4.35)	266 (4.24)	422 (4.40)
8 (Syn.)	279 (4.21)	348 (4.33)	287 (4.19)	303 sh (4.14) 364 (4.37)	266 (4.29)	422 (4.46)
8 (Nat.) ⁶⁾	272	344	278	300 sh 360 390 sh	268	410

a) sh: Shoulder.

above. The direct condensation of **1** with α -acetobromoglucose gave sudachitin 7- β -D-tetra-*O*-acetylglucopyranoside (**16**; mp 156—157 °C; $[\alpha]_D^{25} +25.4^\circ$ (CHCl₃)), which was then easily converted into a hexaacetate (**17**, mp 111—113 °C). The hydrolysis of **16** with 5% aqueous sodium hydroxide yielded the 7- β -D-glucopyranoside (**8**, mp 187—188 °C; $[\alpha]_D^{25} +58.9^\circ$ (0.5% aq NaOH)). The spectral data of the synthetic 7- β -D-glucoside were superimposable on those of 4',5,7-trihydroxy-3',6,8-trimethoxyflavone 7-glucoside (**8**).⁶⁾ The natural 7-glucoside (**8**) was shown to be sudachitin 7- β -D-glucopyranoside.



- | | |
|--|---|
| 1 R=R ₁ =R ₂ =H | 2 R=R ₂ =H, |
| 7 R=R ₁ =H, R ₂ =Glu. | R ₁ =OMe |
| 8 R=R ₂ =H, R ₁ =Glu. | 3 R=R ₁ =R ₂ =H |
| 9 R=R ₁ =Ac, | 4 R=Me, R ₁ =OMe, |
| R ₂ =Tetra- <i>O</i> -acetylglu. | R ₂ =H |
| 10 R=R ₁ =Me, R ₂ =H | 5 R=R ₁ =H, R ₂ =OMe |
| 11 R=R ₂ =H, | 6 R=Me, |
| R ₁ =C ₆ H ₅ CH ₂ | R ₁ =R ₂ =OMe |
| 12 R=R ₁ =H, | |
| R ₂ =C ₆ H ₅ CH ₂ | |
| 13 R=H, R ₁ = | |
| R ₂ =C ₆ H ₅ CH ₂ | |
| 14 R=H, R ₁ =C ₆ H ₅ CH ₂ , | |
| R ₂ =Tetra- <i>O</i> -acetylglu. | |
| 15 R=R ₁ =H, | |
| R ₂ =Tetra- <i>O</i> -acetylglu. | |
| 16 R=R ₂ =H, | |
| R ₁ =Tetra- <i>O</i> -acetylglu. | |
| 17 R=R ₂ =Ac, | |
| R ₁ =Tetra- <i>O</i> -acetylglu. | |

Experimental

All the melting points are uncorrected. The UV spectra were measured in ethanol with a Hitachi 215 spectrophotometer, and the ¹H NMR spectra were measured in CDCl₃ with a JEOL PS-100 spectrometer (100 MHz), with tetramethylsilane as the internal standard. The mass spectra

were obtained using a Shimadzu LKB-9000B mass spectrometer equipped with a chemical-ionization source. The operating conditions were as follows; ion source temp: 230—250 °C; electron energy: 140 eV; reactant gas pressure (isobutane): 0.3 Torr (1 Torr ≈ 133.322 Pa); emission current: 250 μ A. Polyamide (Wako polyamide C-200) was used for the column.

Isolation of Sudachiin A (7). Fresh green peels (8 kg) of *C. sudachi* collected at Tokushima Prefecture in August were extracted with methanol (*ca.* 20 l) for several days. The methanol solution was concentrated to *ca.* 2.5 l under reduced pressure below 30 °C. The concentrate was treated with hexane and then ether. The resulting water-soluble layer was concentrated to 1.5 l and then extracted thoroughly with ethyl acetate. The extract added to a small amount of methanol was allowed to stand in a refrigerator to give precipitates, which were then removed by filtration. The methanol solution was subjected to chromatographic purification on polyamide, using methanol as the eluent. The yellow eluate was repeatedly chromatographed on polyamide to yield **7** (0.96 g; 0.012%; mp 211—213 °C (yellow needles from methanol); $[\alpha]_D^{25} -37.4^\circ$ (0.5% aq NaOH, $c=0.31$). CI-MS (*i*-C₄H₁₀): m/z 523 (MH⁺, 0.5), 417 (2), 403 (4.5), 363 (7), 362 (14), 361 (AGL·H, 100), 360 (14), 163 (4.5), 145 (30), 127 (5.5). Found: C, 52.72; H, 5.15%. Calcd for C₂₄H₂₆O₁₃·1.5H₂O: C, 52.46; H, 5.32%.

Sudachiin A Hexaacetate (9). The glycoside (**7**) was converted into a hexaacetate (**9**) by an acetic anhydride-pyridine method. **9**; mp 212—213 °C (colorless needles from ethanol); $[\alpha]_D^{25} -21.6^\circ$ (CHCl₃, $c=0.31$). Found: C, 55.88; H, 4.66%. Calcd for C₃₆H₃₈O₁₉: C, 55.81; H, 4.94%.

Hydrolysis of Sudachiin A (7). A suspended mixture of **7** (101 mg) in 5% aq sulfuric acid (20 ml) was heated on a steam bath for 2 h under nitrogen. The precipitates thus separated were collected and recrystallized from aq ethanol to give an aglycone; mp 239—240 °C (yellow needles). Its acetate: mp 167—168 °C (colorless needles from ethanol). The aglycone and its acetate were identical with authentic sudachitin (4',5,7-trihydroxy-3',6,8-trimethoxyflavone) (**1**) and its acetate previously reported^{1,2,8)} respectively.

The aqueous solution remaining after the separation of the aglycone was neutralized with barium carbonate, filtered, and concentrated. The resulting syrupy compound was found to be identical with D-glucose by silica gel TLC. Its osazone: mp and mmp 200—202 °C.

4'-Hydroxy-3',5,6,7,8-pentamethoxyflavone (10) from Sudachiin

TABLE 2. ^1H NMR DATA FOR SUDACHITIN DERIVATIVES^{a)}

Compd	Solvent	Arom. H					OMe	OAc	Sugar moiety		CH ₂ C ₆ H ₅	OH
		C ₃ -H	C ₅ -H	C ₆ '-H	C ₂ '-H	C ₆ -H			OAc	Other H		
9	CDCl ₃	6.60 s	7.22 d	7.43 s	7.43 q	7.48 q	3.85 s (3H) 3.91 s (3H) 4.02 s (3H)	2.43 s (3H) 2.48 s (3H)	2.04 s (6H) 2.08 s (6H)	3.8—4.3 m (3H) 5.0—5.4 m (4H)		
15	CDCl ₃	6.59 s	7.20 d	7.43 s	7.48 q		3.90 s (3H) 3.98 s (3H) 4.01 s (3H)		2.05 s (6H) 2.09 s (6H)	3.7—4.3 m (3H) 5.0—5.4 m (4H)		6.4 b 12.67 bs
14	CDCl ₃	6.61 s	7.21 d	*	*		3.90 s (9H)		2.04 s (6H) 2.08 s (6H)	3.7—4.3 m (3H) 5.0—5.4 m (4H)	5.29 s (2H) 7.3—7.6 m (7H)	12.49 b
17	CDCl ₃	6.58 s	7.18 d	7.44 s	7.49 q		3.85 s (3H) 3.93 s (3H) 4.02 s (3H)	2.36 s (3H) 2.48 s (3H)	2.05 s (12H)	3.7—4.3 m (3H) 5.1—5.5 m (4H)		
16	CDCl ₃	6.56 s	7.00 d	7.35 d'	7.48 q		3.89 s (3H) 3.92 s (3H) 3.97 s (3H)		2.03 s (6H) 2.07 s (6H)	3.6—4.3 m (3H) 5.0—5.5 m (4H)		7.4 b 12.65 bs
10	CDCl ₃	6.60 s	7.06 d	7.43 d'	7.56 q		3.95 s (6H) 3.98 s (3H) 4.03 s (3H) 4.13 s (3H)					
11	DMSO	6.99 s	6.95 d	*	*		3.79 s (3H) 3.87 s (3H) 3.89 s (3H)				5.24 s (2H) 7.3—7.65 m (7H)	10.08 s 12.88 s
12	DMSO	6.96 s	7.20 d	7.57 s	7.61 q		3.75 s (3H) 3.86 s (6H)				5.16 s (2H) 7.3—7.5 m (5H)	12.85 s
13	DMSO	7.05 s	7.21 d	*	*		3.78 s (3H) 3.86 s (3H) 3.89 s (3H)				5.27 s (2H) 5.34 s (2H) 7.2—7.4 m (12H)	12.82 s

a) δ -Value: s, singlet; d, doublet ($J=8.5$ Hz); d', doublet ($J=2.5$ Hz); q, quartet ($J=8.5$, 2.5 Hz).

* Overlapped with the benzyl aromatic protons.

4 (7). A solution of **7** (206 mg) in ethanol was treated with an excess of diazomethane in ether. After standing at room temperature for 24 h, the mixture was evaporated under reduced pressure to dryness. The residue was heated at 100 °C with 5% sulfuric acid for 1 h, after which the mixture was worked up in the same manner as that described above to give precipitates, which were recrystallized from methanol as colorless needles **10** (83 mg); mp 145–146 °C. **10** was identical with the sample prepared by the method given in the literature.¹⁰⁾

Partial Benzoylation of Sudachitin (1). To a solution of **1** (1.5 g), benzyl chloride (0.8 g), and potassium iodide (0.83 g) in acetone–DMF (1:1) (60 ml), 1% aq potassium hydroxide (26 ml) was added. The reaction mixture was allowed to stand for 4 days at room temperature to give precipitates, which were then separated by filtration. Water was added to the filtrate, and the resulting precipitates were collected. The combined precipitates were recrystallized from methanol to recover sudachitin (**1**) (150 mg; 10%).

The mother liquor was evaporated, and the residue was chromatographed on silica gel with chloroform–ethyl acetate (5:1) to give three fractions. The first fraction was recrystallized from methanol–ethyl acetate to give sudachitin 4',7-dibenzyl ether as yellow needles (**13**) (188 mg; 8%); mp 126–127 °C. Found: C, 71.29; H, 5.45%. Calcd for C₃₂H₂₈O₈: C, 71.10; H, 5.22%.

The second fraction, which was a mixture of monobenzyl ethers, was separated into two components **11** and **12** by recrystallization from methanol–ethyl acetate and then by chromatography on silica gel with chloroform–ethyl acetate (5:1). Sudachitin 7-benzyl ether (**11**); yellow needles (755 mg; 40%), mp 159–160 °C. Found: C, 66.82; H, 4.99%. Calcd for C₂₅H₂₂O₈: C, 66.66; H, 4.92%.

Sudachitin 4'-benzyl ether (**12**); yellow needles (34 mg; 2%), mp 177–178 °C. Found: C, 66.46; H, 4.85%. Calcd for C₂₅H₂₂O₈: C, 66.66; H, 4.92%.

The third fraction was unchanged sudachitin (**1**) (250 mg; 17%).

7-Benzyl-4',5-dihydroxy-3',6,8-trimethoxyflavone 4'-Tetra-O-acetyl-β-D-glucopyranoside (14). To a solution of **11** (585 mg) and α-acetobromoglucose (1.1 g) in acetone–DMF (4:1) (25 ml), 2% aq potassium hydroxide (6 ml) was added.

The mixture was allowed to stand in a refrigerator for 1 week to give an O-acetylglucoside as yellow crystals, which were separated by filtration. To the filtrate, water was added. The separated precipitates were collected and then chromatographed on silica gel, using chloroform–ethyl acetate (5:1), to give unchanged **11** (190 mg; 32%) and the O-acetylglucoside. The combined O-acetylglucoside was recrystallized from methanol to give **14** as pale yellow needles (450 mg; 44%); mp 156–157 °C. Found: C, 60.12; H, 5.23%. Calcd for C₃₉H₄₀O₁₇: C, 60.00; H, 5.16%.

Sudachitin 4'-Tetra-O-acetyl-β-D-glucopyranoside (15). O-Acetylglucoside (**14**) (241 mg) was hydrogenated over 10% palladium on charcoal (80 mg) in a mixture of ethyl acetate (15 ml) and methanol (7 ml) until the uptake of hydrogen ceased. The catalyst was filtered off, and then the solvent was removed under reduced pressure. The residue was recrystallized from aq ethanol to give **15** as pale yellow needles (190 mg; 90%); mp 196–197 °C; [α]_D –22.5° (CHCl₃, c=0.196). Found: C, 54.45; H, 4.99%. Calcd for C₃₂H₃₄O₁₇·H₂O: C, 54.24; H, 5.12%.

Sudachitin 4'-β-D-Glucopyranoside Hexaacetate (Sudachiin A Hexaacetate) (9). Compound **15** was converted into the acetate **9** as colorless needles (mp 212–213 °C; undepressed on admixture with the natural sudachiin A hexaacetate.). The ¹H NMR spectrum of the acetate was also superimposable

on that of the acetate of sudachiin A.

Sudachitin 4'-β-D-Glucopyranoside (Sudachiin A) (7). A solution of **15** (98 mg) in 5% aq sodium hydroxide was heated at 50–60 °C for 5 min. The reaction mixture was then cooled and acidified with acetic acid. The resulting precipitates were separated and recrystallized from aq methanol as pale yellow needles (67 mg; 85%); mp 211–213 °C; [α]_D –39.2° (0.5% aq NaOH, c=0.204). Found: C, 52.50; H, 5.50%. Calcd for C₂₄H₂₆O₁₃·1.5H₂O: C, 52.46; H, 5.32%.

The synthetic glucoside was identified with natural sudachiin A on the basis of a mixed-melting point determination and by IR and UV spectral comparisons.

Sudachitin 7-Tetra-O-acetyl-β-D-glucopyranoside (16). To a solution of **1** (1.035 g) and α-acetobromoglucose (2.0 g) in acetone–DMF (2:1) (50 ml), 2% aq potassium hydroxide (8.8 ml) was added. The mixture was allowed to stand in a refrigerator for 5 d, and then the solvent was removed under reduced pressure. The residue was diluted with water and extracted with ethyl acetate. The extract was washed with water and dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The residue was chromatographed on polyamide (45 g), using methanol, to give **16** (710 mg; 36%), which was subsequently recrystallized from methanol; mp 156–157 °C (pale yellow needles); [α]_D +28.4° (CHCl₃, c=0.362). Found: C, 54.03; H, 5.42%. Calcd for C₃₂H₃₄O₁₇·H₂O: C, 54.24; H, 5.12%.

Sudachitin 7-β-D-Glucopyranoside Hexaacetate (17).

Compound **16** (70 mg) was acetylated by an acetic anhydride–pyridine method, and the acetate was chromatographed on silica gel with chloroform–ethyl acetate (5:1). The first fraction was dissolved in a small amount of methanol, and then water was added to give white precipitates (60 mg; 76%); mp 111–113 °C. Found: C, 55.52; H, 4.74%. Calcd for C₃₆H₃₈O₁₉: C, 55.81; H, 4.94%.

Sudachitin 7-β-D-Glucopyranoside (8). A solution of **16** (150 mg) in 5% aq sodium hydroxide was heated at 50–60 °C for 5 min. The reaction mixture was then cooled and acidified with acetic acid. The resulting semi-solids were separated and then chromatographed on silica gel, using ethyl methyl ketone (saturated water), to give **8** (91 mg; 80%), which was subsequently recrystallized from methanol; mp 187–188 °C (yellow needles, lit.⁹⁾ mp 185–187 °C; [α]_D +58.9 (0.5% aq NaOH, c=0.258). Found: C, 52.70; H, 5.53%. Calcd for C₂₄H₂₆O₁₃·1.5H₂O: C, 52.46; H, 5.32%.

The spectral data and mp of the synthetic glucoside were identical with those of natural 4',5,7-trihydroxy-3',6,8-trimethoxyflavone 7-glucoside.⁹⁾

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