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Tannins and Related Compounds. XXXIX.[1] Procyanidin C-Glucosides and an Acylated Flavan-3-ol Glucoside from the Barks of *Cinnamomum cassia* BLUME and *C. obtusifolium* NEES

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Along with procyanidins B-1 (**4**), B-2 (**5**), B-5 (**6**) and B-7 (**7**), and the doubly linked proanthocyanidin, A-2 (**8**), two new procyanidin glucosides have been isolated from the bark of *Cinnamomum cassia* BLUME (東興桂皮) (Lauraceae), and characterized as procyanidin B-2 8-*C*- and 6-*C*-*β*-D-glucopyranosides (**1** and **2**, respectively) on the basis of proton and carbon-13 nuclear magnetic resonance examinations and the results of thiolytic degradation. In addition, from the bark of *Cinnamomum obtusifolium* NEES (ベトナム桂皮), an acylated flavan-3-ol glucoside (**3**) has been isolated, together with the known proanthocyanidins B-1 (**4**), B-2 (**5**), B-5 (**6**) and A-2 (**8**). The structure of **3** has been established to be (+)-catechin 5-*O*-*β*-D-(2″-*O*-feruloyl-6″-*O*-*p*-coumaroyl)-glucopyranoside on the basis of chemical and spectral evidence.

Keywords——*Cinnamomum cassia*; *Cinnamomum obtusifolium*; Lauraceae; procyanidin glycoside; acylated flavan-3-ol glycoside; proanthocyanidin; tannin; thiolytic degradation

As a part of our systematic chemical studies on tannins and related compounds in *Cinnamomum* plants, we previously reported the isolation and characterization of several flavan-3-ol methyl ethers from the barks of *Cinnamomum cassia* BLUME (東興桂皮) and *C. obtusifolium* NEES (ベトナム桂皮).[2] Further examinations of these plant materials have now led to the isolation of two new procyanidin glucosides (**1** and **2**) and a new acylated flavan-3-ol glucoside (**3**), together with the known proanthocyanidins (**4**—**8**). In this paper we describe the isolation and characterization of these compounds.

The fraction previously obtained from the aqueous extract of the bark of *C. cassia* by Sephadex LH-20 chromatography,[2] was subjected to a combination of Sephadex LH-20, MCI-gel CHP 20P and Bondapak C_{18} chromatographies with various solvent systems to afford compounds **1**, **2** and **4**—**8**. Among them, compounds **4**—**8** were identified as procyanidins B-1,[3] B-2,[3] B-5[3] and B-7,[4] and the doubly-bonded proanthocyanidin, A-2,[3] respectively, by comparisons of their physical and spectral data with those of authentic samples. On the other hand, similar chromatographic separation of the fraction previously obtained from the bark of *C. obtusifolium*[2] gave compounds **3**—**6** and **8**.

Compound **1** gave an orange-red color with the anisaldehyde–sulfuric acid reagent (characteristic of proanthocyanidins). The proton nuclear magnetic resonance (^{1}H-NMR) spectrum revealed the presence of two flavan-3-ol units with a 5,7,3′,4′-tetrahydroxy substitution system (see Experimental). The appearance of a pair of singlet signals (δ 5.20 and 5.02) due to flavan H-2 suggested these units to possess epicatechin (2,3-*cis*) stereochemistry, while the one-proton singlet resonance (δ 4.76) due to H-4 indicated *β*-configuration of the interflavanoid linkage.[5] These observations were consistent with those in the case of 4,8-linked dimeric procyanidin, B-2 (**5**), or the alternative 4,6-linked isomer, B-5 (**6**). In addition, the occurrence of a sugar moiety was deduced from the anomeric proton resonance (δ 5.00, d, J=7 Hz) and also from the carbon nuclear magnetic resonance (^{13}C-NMR) spectral data

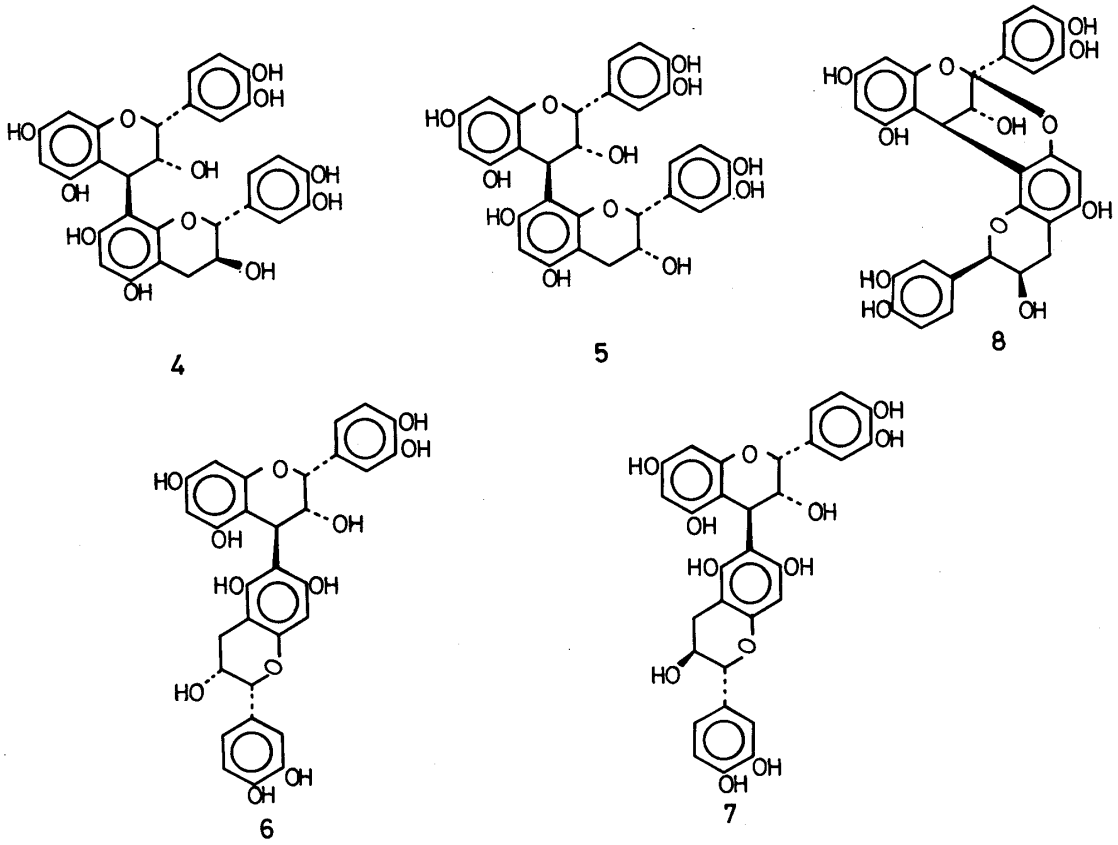

Chart 1

TABLE I. ^{13}C-NMR Spectral Data for Compounds **1**—**3** and **5** (δ Value)[a]

		1	2	5	3
	C-2	76.9	77.0	76.5	82.5
	C-3	73.0	72.9	72.7	66.7
	C-4	36.6	36.0	36.4	—[b]
	C-6	97.2	104.4	95.8[c]	96.7
	C-8	103.5	97.2	96.2[c]	97.9
	C-2″	78.6	79.0	78.8	
	C-3″	66.2	66.4	66.2	
	C-4″	—[b]	—[b]	—[b]	
	C-6″	97.2	96.6	96.9[c]	
	C-8″	107.1	107.4	106.7	
Sugar	C-1	76.6	76.9		102.7
	C-2	73.8	74.4		74.2
	C-3	79.1	79.0		75.0
	C-4	70.6	70.4		71.4
	C-5	81.4	81.9		75.3
	C-6	61.5	61.5		64.2

a) Measured in acetone-d_6. *b*) Overlapped with solvent signals. *c*) Assignments may be interchanged.

(Table I). Furthermore, the ^{13}C-NMR chemical shift (δ 76.6) of the anomeric signal suggested that compound **1** possesses a C-glycosidic nature.

To confirm the structure of compound **1**, the cleavage reaction of the interflavanoid linkage was attempted. Treatment of **1** with benzylmercaptan in the presence of acetic acid

yielded a flavan-3-ol shown to be identical with (−)-epicatechin (**9**) (formed from the lower unit), and a thioether (**10**) (formed from the upper unit), the latter being characterized as the 4-benzylthioether of (−)-epicatechin 8-*C*-*β*-D-glucopyranoside by ^{1}H-NMR analysis and by desulfurization with Raney nickel to give (−)-epicatechin 8-*C*-*β*-D-glucopyranoside (**11**).[1)]

The location of the interflavanoid linkage between these units was determined to be C(4)–C(8) on the basis of the ^{1}H-NMR chemical shifts (δ 5.02 and 4.38) for the respective H-2″ and H-3″, which were in good agreement with those (H-2″: δ 4.96 and H-3″: δ 4.31) of procyanidin B-2 (**5**) rather than those (H-2″: δ 4.84 and H-3″: δ 4.16) of procyanidin B-5 (**6**).[4)] From all these chemical and spectral data, compound **1** was characterized as procyanidin B-2 8-*C*-*β*-D-glucopyranoside.

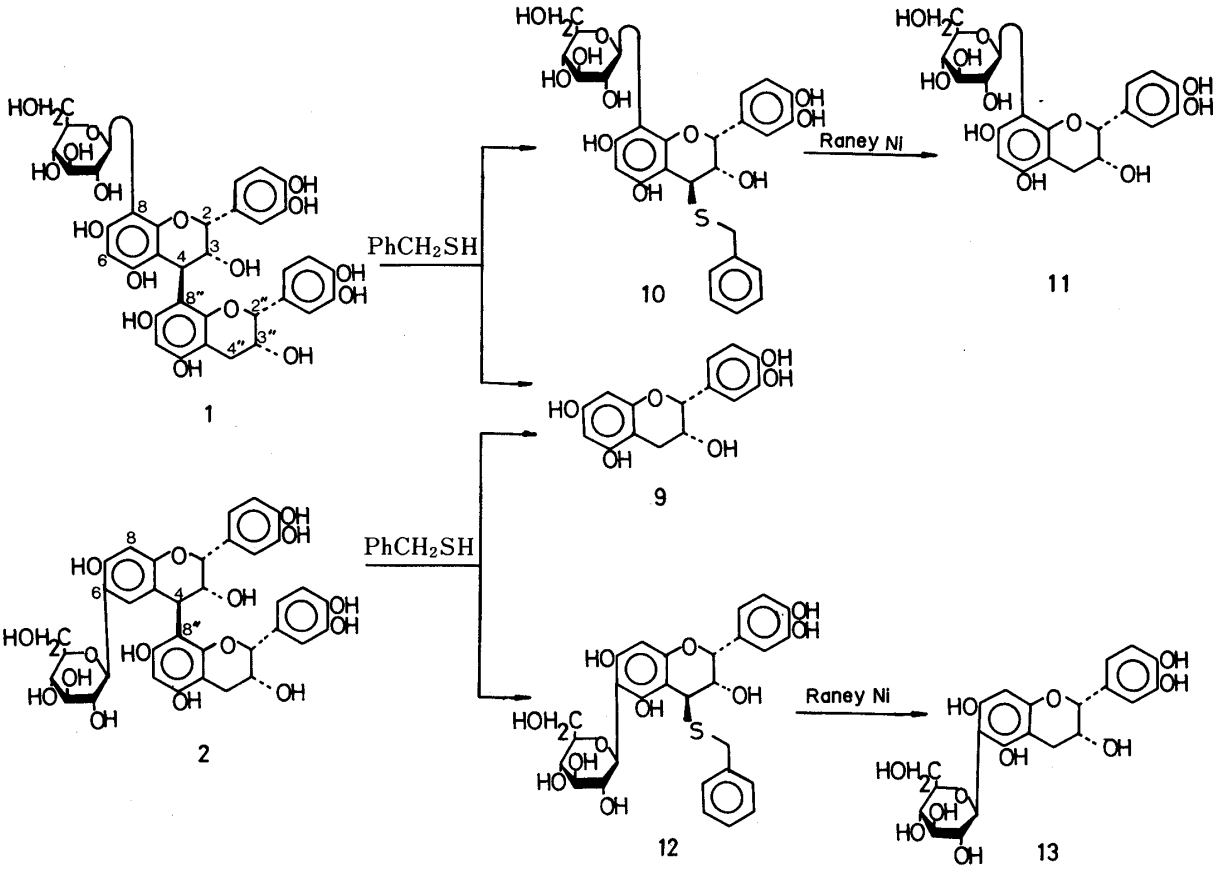

Chart 2

Compound **2** exhibited the same $(M+H)^+$ ion peak at *m/z* 741 as **1** in the fast atom bombardment mass spectrum (FAB-MS). The ^{1}H- and ^{13}C-NMR spectra were closely related to those of **1**, showing signals arising from two epicatechin units and a sugar moiety. The ^{13}C-NMR chemical shift (δ 76.9) of the anomeric signal indicated compound **2** to be a C-glycoside.

Thiolytic degradation similar to that described above led to the assignment of the structure. On treatment with benzylmercaptan, compound **2** afforded (−)-epicatechin (**9**) and a thioether (**12**), of which the latter was characterized as a 4-benzylthioether of (−)-epicatechin 6-*C*-*β*-D-glucopyranoside on the basis of ^{1}H- and ^{13}C-NMR examinations and the result of similar desulfurization with Raney nickel, giving (−)-epicatechin 6-*C*-*β*-D-glucopyranoside (**13**).[1)] The location of the interflavanoid linkage between these component units was concluded to be C(4)–C(8), since the chemical shifts (δ 4.96 and 4.31) for H-2″ and H-3″ were identical with those of procyanidin B-2 (**5**).[3)] Furthermore, the observation of a singlet at δ 4.88 due to H-4 indicated that the configuration of the interflavanoid linkage is *β*.

Accordingly, the structure of compound **2** was established as procyanidin B-2 6-*C*-*β*-D-glucopyranoside.

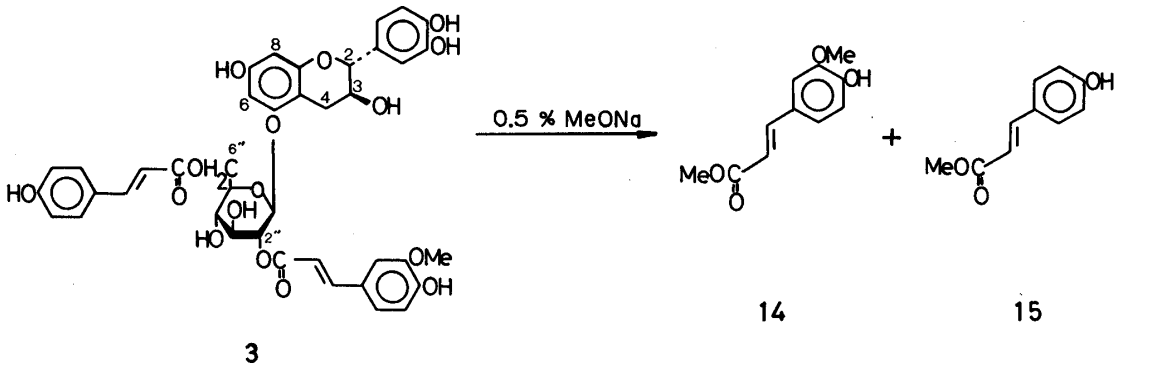

Chart 3

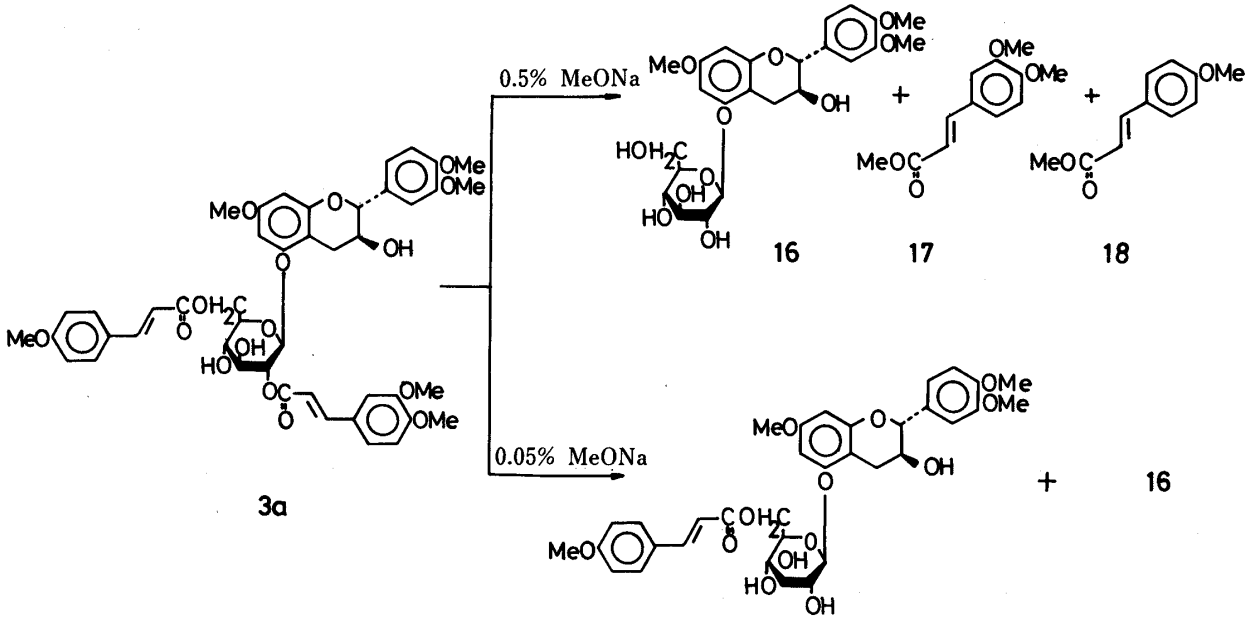

Chart 4

Compound **3** showed the $(M+H)^+$ ion peak at *m/z* 775 in the FAB-MS. The ^{13}C-NMR spectrum exhibited signals due to sugar carbons (Table I), and to flavan C-2 and C-3, the chemical shifts (δ 82.5 and 66.7) of the latter carbons being consistent with those (δ 82.7 and 67.5) of (+)-catechin (2,3-*trans*). In addition, the presence of two acyl groups in the molecule was confirmed by the ester carboxyl resonances at δ 168.1 and 167.7. On methanolysis with 0.5% sodium methoxide, **3** yielded a deeply colored mixture of products, from which two compounds were isolable, and they were characterized as methyl *p*-coumaroate (**15**) and methyl feruloate (**14**). On the other hand, similar methanolysis of the methyl ether (**3a**) prepared from **3** by methylation with anhydrous potassium carbonate and dimethyl sulfate, yielded a compound shown to be identical with 7,3′,4′-tri-*O*-methyl-(+)-catechin 5-*O*-*β*-D-glucopyranoside (**16**),[6] together with the two methyl esters (**17** and **18**).

The positions of the acyl groups in **3** were determined as follows. In the ^{1}H-NMR spectrum of **3a**, methine and methylene signals, shifted downfield (δ 5.48, t, J=7 Hz; δ 4.60, 2H, br s) by acylation, were observed. The methylene signals could be assigned to the glucose H-6. The assignment of the methine signal was achieved by means of spin-decoupling experiment. Upon irradiation of the anomeric signal (δ 5.13, d, J=7 Hz), the methine signal

changed into a doublet, thus permitting the assignment of this signal to the glucose H-2 proton. Next, in order to allocate each acyl group, partial methanolysis was attempted. Treatment of **3a** with 0.05% sodium methoxide in MeOH afforded a partial hydrolysate (**19**), together with the glucoside (**16**). The ^{1}H-NMR spectrum of **19** showed signals arising from a *p*-coumaroyl (δ 6.85, 7.56, each 2H, d, J=8 Hz), a catechin (δ 4.76, d, J=8 Hz, H-2), and a sugar moiety (δ 4.85, d, J=7 Hz, H-1), thus indicating that only the feruloyl ester was hydrolyzed. The appearance of the lowfield signals (δ 4.80, 2H) assignable to glucose H-6 confirmed that the *p*-coumaroyl ester is located at this position. Thus, it is evident that the feruloyl group exists at the glucose C-2 position. Consequently, the structure of compound **3** was established unequivocally to be (+)-catechin 5-*O*-β-D-(2″-*O*-feruloyl-6″-*O*-*p*-coumaroyl)-glucopyranoside.

Compounds **1** and **2** are the first examples of procyanidin glycosides to be isolated from a natural source.[7] Taking into consideration that the component units (flavan-3-ols) are believed to be formed biosynthetically from flavones, which occurs mostly as glycosides, it seems rather surprising that the glycosides of procyanidin have not hitherto been isolated. In addition, compound **3** is the first acylated flavan-3-ol glycoside to be isolated from a natural source.

Experimental

Melting points were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-4 digital polarimeter. ^{1}H- and ^{13}C-NMR spectra were taken with JEOL PS-100 and FX-100 machines. FD- and FAB-MS were recorded on a JEOL JMS DX-300 instrument. Column chromatography was carried out with Sephadex LH-20 (25—100 μ, Pharmacia Fine Chemical Co., Ltd.), Bondapak C_{18}/Porasil B (37—75 μ, Waters Associates, Inc.), MCI-gel CHP 20P (75—150 μ, Mitsubishi Chemical Industries, Ltd.) and Kieselgel 60 (70—230 mesh, Merck). Thin-layer chromatography (TLC) was performed on precoated Kieselgel 60 F_{254} plates (0.2 mm thick, Merck) with benzene–ethyl formate–formic acid (2 : 7 : 1 or 1 : 7 : 1) as a solvent system, and spots were detected by the use of anisaldehyde–sulfuric acid and ferric chloride reagent sprays.

Isolation——a) From the Bark of *Cinnamomum cassia*(東興桂皮): Fraction 2 (11 g), which had been previously obtained by Sephadex LH-20 chromatography of the aqueous extract of *C. cassia* (59 kg),[2] was rechromatographed over Sephadex LH-20. Elution with EtOH gave fractions 2-a (6 g) and 2-b (3 g). Fraction 2-a was repeatedly chromatographed over Sephadex LH-20 (60% aqueous MeOH) and Bondapak C_{18} (20% aqueous MeOH) to afford compounds **1** (43 mg), **2** (38 mg) **4** (18 mg) and **5** (3.3 g). Chromatography of fraction 2-b on MCI-gel CHP 20P with 30% aqueous MeOH gave compounds **6** (31 mg) and **7** (17 mg). Further elution with the same solvent, followed by crystallization, furnished compound **8** (72 mg).

b) From the Bark of *Cinnamomum obtusifolium*(ベトナム桂皮): Fraction 2 (10 g), obtained in a previous paper[2] from the aqueous acetone extract of *C. obtusifolium* (5 kg) was divided by Sephadex LH-20 chromatography (60% aqueous MeOH) into two fractions; fractions 2-a (5 g) and 2-b (1.5 g). Fraction 2-a was applied to an MCI-gel CHP 20P column, and this column was eluted with 30% aqueous MeOH to yield compounds **3** (105 mg), **4** (38 mg) and **5** (2.5 g). Fraction 2-b, after rechromatography on Sephadex LH-20 (EtOH) and MCI-gel CHP 20P (30% aqueous MeOH), afforded compounds **6** (21 mg) and **8** (35 mg).

Compound 1——An off-white amorphous powder, $[\alpha]_D^{21}$ +18.2° (c=1.0, acetone). *Anal.* Calcd for $C_{36}H_{36}O_{17}\cdot 2H_2O$: C, 55.66; H, 5.19. Found: C, 55.51; H, 5.31. FAB-MS *m/z*: 741 $(M+H)^+$. ^{1}H-NMR (acetone-d_6) δ: 2.84 (2H, m, H-4″), 3.92 (1H, s, H-3), 4.38 (1H, br s, H-3″), 4.76 (1H, s, H-4), 5.00 (1H, d, J=7 Hz, anomeric H), 5.02 (1H, s, H-2″), 5.20 (1H, s, H-2), 6.01, 6.04 (each 1H, s, H-6, 6″), 6.40—7.20 (6H in total, m, B-ring H). ^{13}C-NMR: Table I.

Thiolytic Degradation of 1——A mixture of **1** (30 mg), benzylmercaptan (1 ml) and acetic acid (1 ml) in EtOH (7 ml) was refluxed for 10 h with stirring. The reaction mixture was concentrated under reduced pressure, and the oily residue was chromatographed over Sephadex LH-20 (EtOH), affording (−)-epicatechin (**9**) (10 mg) and a thioether (**10**) (12 mg). **10**: an off-white amorphous powder, $[\alpha]_D^{24}$ +21.5° (c=1.1, acetone). *Anal.* Calcd for $C_{28}H_{30}O_{12}S\cdot H_2O$: C, 55.25; H, 5.30. Found: C, 55.50; H, 5.00. ^{1}H-NMR (acetone-d_6 + D_2O) δ: 3.98 (1H, d, J=2 Hz, H-3), 4.07 (2H, s, $-SCH_2-$), 4.17 (1H, d, J=2 Hz, H-4), 4.92 (1H, d, J=7 Hz, anomeric H), 5.40 (1H, s, H-2), 6.12 (1H, s, H-6), 6.70 (1H, dd, J=8, 2 Hz, H-6′), 6.82 (1H, d, J=8 Hz, H-4′), 7.21 (1H, d, J=2 Hz, H-2′), 7.24—7.60 (5H in total, m, aromatic H).

Desulfurization of 10——The thioether **10** (10 mg) in EtOH–acetic acid (9 : 1) (1 ml) was shaken at 50 °C with Raney nickel (W-4) for 30 min. After removal of the catalyst by filtration, the filtrate was concentrated to dryness

under reduced pressure. The residue was purified by Sephadex LH-20 chromatography (60% MeOH) to give the glucoside (**11**) (5 mg) as an off-white amorphous powder, $[\alpha]_D^{24}$ −33.5° (c=0.3, acetone). ^{1}H-NMR (acetone-d_6) δ: 2.85 (2H, m, H-4), 4.20 (1H, m, H-3), 4.92 (1H, d, J=7 Hz, anomeric H), 4.93 (1H, s, H-2), 6.08 (1H, s, H-6), 6.77 (1H, dd, J=7, 2 Hz, H-6′), 6.88 (1H, d, J=7 Hz, H-5′), 7.19 (1H, d, J=2 Hz, H-2′).

Compound 2——An off-white amorphous powder, $[\alpha]_D^{21}$ +12.5° (c=1.1, acetone). *Anal.* Calcd for $C_{36}H_{36}O_{17}\cdot 2H_2O$: C, 55.66; H, 5.19. Found: C, 55.75; H, 5.05. FAB-MS m/z: 741 $(M+H)^+$. ^{1}H-NMR (acetone-d_6) δ: 2.83 (2H, m, H-4″), 3.96 (1H, s, H-3), 4.31 (1H, br s, H-3″), 4.76 (1H, s, H-4), 4.87 (1H, d, J=7 Hz, anomeric H), 4.96 (1H, br s, H-2″), 5.16 (1H, s, H-2), 6.03 (2H, br s, H-8, 6″), 6.60—7.20 (6H in total, m, B-ring H). ^{13}C-NMR: Table I.

Thiolytic Degradation of 2——A mixture of **2** (30 mg), benzylmercaptan (1 ml) and acetic acid (1 ml) in EtOH (7 ml) was heated for 13 h with stirring. Work-up as described for **1** gave (−)-epicatechin (**9**) (8 mg) and a thioether (**12**) (15 mg). **12**: An off-white amorphous powder, $[\alpha]_D^{24}$ −11.2° (c=0.5, acetone). *Anal.* Calcd for $C_{28}H_{30}O_{12}S\cdot H_2O$: C, 55.25; H, 5.30. Found: C, 55.47; H, 5.22. ^{1}H-NMR (acetone-d_6 + D_2O) δ: 3.96 (1H, d, J=2 Hz, H-3), 4.05 (2H, s, $-SCH_2-$), 4.15 (1H, d, J=2 Hz, H-4), 4.90 (1H, d, J=7 Hz, anomeric H), 5.31 (1H, s, H-2), 6.02 (1H, s, H-8), 6.74 (1H, dd, J=8, 2 Hz, H-6′), 6.85 (1H, d, J=8 Hz, H-5′), 7.04 (1H, d, J=2 Hz, H-2′), 7.20—7.50 (5H in total, m, aromatic H).

Desulfurization of 12——The thioether **12** (10 mg) in EtOH–AcOH (9 : 1) (1 ml) was treated with Raney nickel at 50 °C for 30 min. The reaction mixture was worked up as before to furnish the glucoside (**13**) (5 mg) as an off-white amorphous powder, $[\alpha]_D^{24}$ +10.2° (c=0.3, acetone). ^{1}H-NMR (acetone-d_6) δ: 2.80 (2H, m, H-4), 4.23 (1H, m, H-3), 4.87 (1H, s, H-2), 4.95 (1H, d, J=7 Hz, anomeric H), 6.04 (1H, s, H-8), 6.90—7.10 (3H in total, m, H-2′,5′,6′).

Compound 3——An off-white amorphous powder, $[\alpha]_D^{22}$ −52.3° (c=1.1, acetone). *Anal.* Calcd for $C_{40}H_{38}O_{16}\cdot 2H_2O$: C, 67.53; H, 5.96. Found: C, 67.89; H, 6.07. FAB-MS m/z: 775 $(M+H)^+$. ^{1}H-NMR (acetone-d_6) δ: 2.40 (1H, dd, J=16, 8 Hz, H-4), 3.80 (3H, s, OMe), 4.32 (1H, dd, J=12, 4 Hz, glucose H-6), 4.48 (1H, d, J=8 Hz, H-2), 4.66 (1H, d, J=12 Hz, glucose H-6), 5.18 (2H, m, glucose H-1, 2), 6.00—7.90 (16H in total, m, aromatic and olefinic H). ^{13}C-NMR: Table I.

Methanolysis of 3——**3** (20 mg) was treated with sodium methoxide (15 mg) in MeOH (3 ml). (The color of the solution changed to red.) The reaction mixture was refluxed for 10 min. Neutralization with Dowex 50 WX (H^+ form) and evaporation of the solvent gave a solid, which was chromatographed over Sephadex LH-20 (80% aqueous MeOH) and silica gel [benzene–acetone (14 : 1)] to give methyl *p*-coumaroate (**15**) (1.5 mg) as colorless needles, mp 180—182 °C, and methyl feruloate (**14**) (2.1 mg) as colorless needles, mp 154—156 °C.

Methylation of 3——A mixture of **3** (85 mg), dimethyl sulfate (0.7 ml) and anhydrous potassium carbonate (1 g) in dry acetone (10 ml) was refluxed for 3 h with stirring. After removal of the inorganic salts by filtration, the filtrate was concentrated under reduced pressure, and the oily residue was chromatographed over silica gel. Elution with benzene–acetone (7 : 1) gave the methylate (**3a**) (73 mg) as colorless plates, mp 188 °C, $[\alpha]_D^{24}$ −55.2° (c=0.8, acetone). *Anal.* Calcd for $C_{45}H_{48}O_{16}\cdot H_2O$: C, 62.64; H, 5.84. Found: C, 62.33; H, 5.71. FD-MS m/z: 844 (M^+). ^{1}H-NMR ($CDCl_3$ + benzene-d_6) δ: 2.40—3.20 (2H, m, H-4), 3.40, 3.44, 3.57 (18H, each s, OMe × 6), 4.45 (1H, d, J=8 Hz, H-2), 4.60 (2H, br s, glucose H-6), 5.13 (1H, d, J=7 Hz, glucose H-1), 5.48 (1H, t, J=7 Hz, glucose H-2), 6.20—8.00 (16H in total, m, aromatic and olefinic H).

Methanolysis of 3a——A mixture of **3a** (30 mg) and sodium methoxide (15 mg) in MeOH (3 ml) was refluxed for 10 min. The reaction mixture was worked up as before to yield methyl *p*-methoxycinnamate (**18**) (2 mg) as colorless needles, mp 98 °C, methyl 3,4-dimethoxycinnamate (**17**) (2 mg) as colorless needles, mp 84 °C and 7,3′,4′-tri-*O*-methyl-(+)-catechin 5-*O*-β-D-glucopyranoside (**16**) (6 mg). **16**: Colorless needles, mp 213 °C, $[\alpha]_D^{24}$ −6.7° (c=0.3, MeOH). ^{1}H-NMR (DMSO-d_6) δ: 2.40—2.80 (2H, m, H-4), 3.68, 3.76 (9H, each s, OMe × 3), 4.65 (1H, d, J=8 Hz, H-2), 4.78 (1H, d, J=7 Hz, glucose H-1), 6.11 (1H, d, J=2 Hz, H-6), 6.32 (1H, d, J=2 Hz, H-8), 6.90—7.10 (3H in total, m, B-ring H). Compound **16** was identified by comparison of the spectral and physical data with those of an authentic sample.[6]

Partial Methanolysis of 3a——A mixture of **3a** (40 mg) and sodium methoxide (2 mg) in MeOH (4 ml) was left at room temperature for 12 h. Work-up as before afforded **16** (16 mg) and **19** (6 mg). **19**: Colorless needles, mp 204—203 °C, $[\alpha]_D^{24}$ −21.5° (c=0.3, MeOH). ^{1}H-NMR (DMSO-d_6 + D_2O) δ: 2.30—3.80 (2H, m, H-4), 3.71, 3.77 (9H, each s, OMe × 3), 4.76 (1H, d, J=8 Hz, H-2), 4.80 (2H, m, glucose H-6), 4.85 (1H, d, J=7 Hz, glucose H-1), 6.13 (1H, d, J=2 Hz, H-6), 6.32 (1H, d, J=16 Hz, *p*-coumaroyl H-β), 6.33 (1H, d, J=2 Hz, H-8), 6.85 (2H, d, J=8 Hz, *p*-coumaroyl H-3, 5), 6.90—7.00 (3H in total, m, H-2′,5′,6′), 7.53 (1H, d, J=16 Hz, *p*-coumaroyl H-α), 7.56 (2H, d, J=8 Hz, *p*-coumaroyl H-2, 6).

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