Phytochemistry, Vol. 26, No. 4, pp. 1167–1170, 1987.
Printed in Great Britain.

0031–9422/87 $3.00 + 0.00

FLAVAN-3-OL AND PROCYANIDIN GLYCOSIDES FROM *QUERCUS MIYAGII**

KANJI ISHIMARU, GEN-ICHIRO NONAKA and ITSUO NISHIOKA†

Faculty of Pharmaceutical Sciences, Kyushu University 62, 3-1-1 Maidashi, Higashi-ku, Fukuoka 812, Japan

(*Received* 14 *August* 1986)

Key Word Index—*Quercus miyagii*; Fagaceae; flavan-3-ol glycosides; procyanidin rhamnosides; catechin; tannin.

Abstract—A chemical examination of the leaves and bark of *Quercus miyagii* has led to the isolation and characterization of two flavan-3-ol glycosides and two procyanidin rhamnosides in which the sugar residue is located at C-3.

INTRODUCTION

Although flavan-3-ols are widely distributed in nature, accompanied almost invariably by condensed tannins, their glycosides are rarely found. In contrast, flavonoids, which are regarded as biosynthetic precursors of the flavan-3-ols, occur predominantly as glycosides. The sugar moieties in flavonoids are located non-regiospecifically. Glycosylation at C-3 is most common, however. As for the hitherto known flavan-3-ol glycosides [1–8], the locations of the sugar moieties are limited to the A- and B-rings (aromatic rings) except for three examples (epicatechin 3-*O*-β-D-glucopyranoside [7], catechin 3-*O*-α-L-rhamnopyranoside [8] and epicatechin 3-allopyranoside [9]). In continuing our systematic chemical studies on tannins and related compounds in fagaceous plants, we have now isolated, together with catechin (**5**) and several known proanthocyanidins (**6–12**), two flavan-3-ol glycosides (**1**, **2**) and two dimeric procyanidin glycosides (**3**, **4**) in which a sugar residue is present at the C-3 position, from the fresh leaf and bark of *Quercus miyagii* (Okinawa-urajirogashi in Japanese). Among the fagaceous plants so far investigated, this plant is unique in that large quantities of flavan-3-ol and procyanidin glycosides occur.

RESULTS AND DISCUSSION

The aqueous acetone extract of the fresh leaves of *Quercus miyagii* was applied to a combination of Sephadex LH-20 and MCI-gel CHP-20P chromatography with various solvent systems to afford compounds **1–11**. Among them, compounds **5–11** were identified as catechin (**5**), procyanidins B-1 (**6**) [10], B-3 (**7**) [10], B-6 (**8**) [11], B-7 (**9**) [11] and B-1 3″-*O*-gallate (**10**) [12] and gallocatechin-(4α-8)-catechin (**11**) [13] by comparison of their physical and spectral data with those of authentic samples. Extraction of the fresh bark of this plant with aqueous acetone, followed by similar chromatographic separation, gave compounds **1**, **3** and **5–10** and a trimeric procyanidin (**12**). Compound **12** was identified as epicatechin-(4β→8)-catechin-(4α→8)-catechin [13] by spectral comparison.

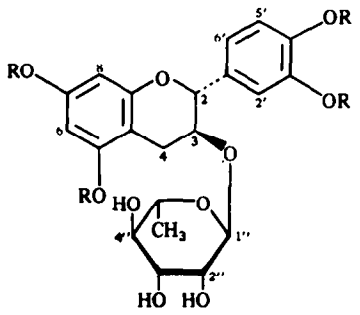
The ^{1}H and ^{13}C NMR spectra of compound **1** revealed the presence of a flavan-3-ol skeleton with 5,7,3′,4′-tetrahydroxy substitution. The appearance of a doublet at δ4.68 with J = 8 Hz, ascribable to the flavan 2-H, clearly indicated the *trans* configuration of C-2 and C-3. In addition, an anomeric proton resonance at δ4.36 (*br s*), as well as six aliphatic signals in the ^{13}C NMR spectrum (Table 1), showed the presence of a carbohydrate residue. On enzymatic hydrolysis with crude hesperidinase, **1** gave a carbohydrate and catechin (**5**). The sugar, after conversion into the osazone, was characterized as L-rhamnose. The location of the L-rhamnose moiety was presumed to be at C-3, since the ^{13}C NMR spectrum showed the lowfield shift of the C-3 signal (δ74.5) as compared with that (δ68.0) in **5**. This was further supported by the fact that methylation of **1** with diazomethane gave a tetramethyl ether (**1a**), which, on subsequent methanolysis with 0.5 N HCl–MeOH, afforded 5,7,3′,4′-tetra-*O*-methylcatechin (**5a**). The configuration of the anomeric carbon was determined to be α on the basis of the small coupling constant of the above-mentioned anomeric proton signal. Consequently, **1** was characterized as catechin 3-*O*-α-L-rhamnopyranoside. The occurrence of this compound in *Erythroxylum novogranatense* was previously reported [8], but it was not isolated free but as the acetate.

The ^{1}H and ^{13}C NMR spectra of compound **2** were similar to those of **1**, demonstrating the presence of a carbohydrate moiety and a flavan-3-ol skeleton. On enzymatic hydrolysis with crude hesperidinase, **2** gave catechin (**5**) and glucose. The location of the glucose moiety was determined to be at the C-3 position by ^{13}C NMR analysis which showed the C-3 signal (δ75.6) shifted downfield by 7.6 ppm as compared with that (δ68.0) in **5**. The configuration at the glucose C-1 position was concluded to be β on the basis of the J-value (8 Hz) of the anomeric proton signal (δ4.28) in the ^{1}H NMR spectrum of **2**. Thus, **2** was characterized as catechin 3-*O*-β-D-glucopyranoside.

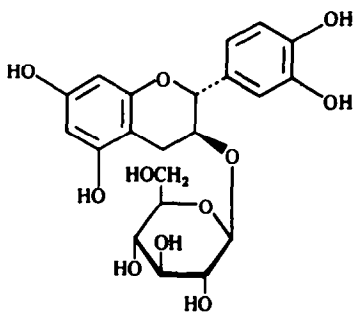
Compound **3**, obtained as a tan amorphous powder,

*Part 53 in the series "Tannins and Related Compounds". For Part 52 see Nonaka, G., Ishimaru, K., Watanabe, M., Nishioka, I., Yamauchi, T. and Wan, A. S. C., *Chem. Pharm. Bull.* (in press).

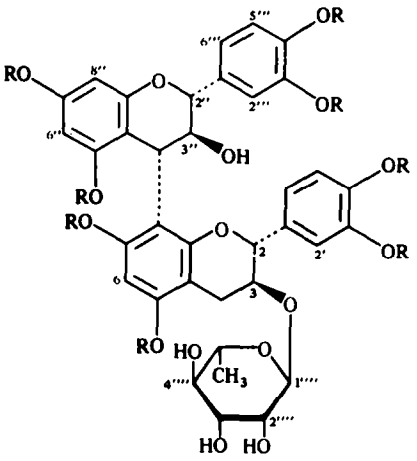
†To whom correspondence should be addressed.



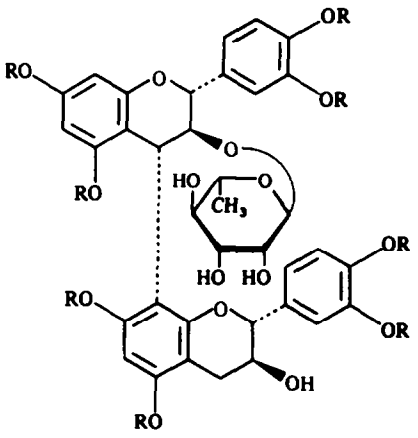
1 R = H
1a R = Me



2



3 R = H
3a R = Me



4 R = H
4a R = Me

gave an orange colour (characteristic of proanthocyanidins) with the anisaldehyde–H_2SO_4 reagent. The ^{1}H NMR spectrum of **3** revealed a complicated signal pattern due to rotational isomerism [11], and was closely related to that of **7**. The ^{13}C NMR spectrum of **3** showed the presence of a methylpentose moiety analogous to that of **1**. The negative FAB-MS with the prominent $[M-H]^-$ ion peak at *m/z* 723 confirmed the biflavanoid constitution as well as the existence of a methylpentose moiety. Methylation of **3** with dimethyl sulphate and anhydrous potassium carbonate in dry Me_2CO gave the octamethyl ether (**3a**), which on subsequent enzymatic hydrolysis with crude hesperidinase afforded 5,7,3′,4′,5″,7″,3‴,4‴-octa-*O*-methylprocyanidin B-3 (**7a**) and L-rhamnose. On the other hand, thiolytic degradation of **3** with benzylmercaptan in the presence of HOAc [11] yielded the 4-benzylthioether of catechin (**5b**) (formed from the upper unit) and **1** (from the lower unit). From these observations, **3** was concluded to be procyanidin B-3 3-*O*-α-L-rhamnopyranoside, i.e. catechin-(4α → 8)-catechin 3-*O*-α-L-rhamnopyranoside.

Compound **4** was also positive to the anisaldehyde–H_2SO_4 reagent. The ^{1}H and ^{13}C NMR spectra were closely correlated with those of **3**. Methylation of **4** with diazomethane gave the octamethyl ether (**4a**), which on similar hydrolysis with crude hesperidinase gave **7a** and L-rhamnose, while acid-catalysed thiolytic cleavage furnished the 4-benzylthioether of **1** (**1b**) (from the upper unit) and **5** (from the lower unit). Based on these results, the structure of **4** was established as procyanidin B-3 3″-*O*-α-L-rhamnopyranoside, i.e. 3-*O*-α-L-rhamnopyranosyl-catechin-(4α → 8)-catechin.

The accumulation of relatively large amounts of flavan-3-ol and procyanidin glycosides in this plant differs remarkably from those in other members of the Fagaceae which almost invariably contain free flavan-3-ols, linearly linked proanthocyanidins and/or hydrolysable tannins, especially ellagitannins.

This is the first reported isolation of dimeric procyanidin glycosides possessing the sugar residue at the flavan C-ring.

EXPERIMENTAL

Mps are uncorr. ^{1}H and ^{13}C NMR spectra were recorded at 100 and 25.05 MHz, respectively, with TMS as reference. TLC was performed on silica gel and Avicel SF cellulose, and spots were detected by spraying $FeCl_3$ or anisaldehyde–H_2SO_4 (for phenolics) and aniline hydrogen phthalate (for sugars) reagents. Plant material was collected at Amami-oshima, an island located in the West Pacific south of Japan. A voucher specimen is

Table 1. ^{13}C NMR spectral data of 1, 2 and 5*

	1†	2‡	5†
Aglycone moiety			
C-2	80.2	79.3	82.3
C-3	74.5	75.6	68.0
C-4	27.6	28.4	27.5
C-4a	100.2	100.0	100.2
C-5	157.0	156.9	156.7
C-6	95.4	95.3	95.0
C-7	157.6	157.4	157.1
C-8	96.4	96.4	95.9
C-8a	156.5	156.0	156.3
C-1′	131.6	131.7	131.5
C-2′	114.9	114.6	115.0
C-3′	145.6	145.6	145.2
C-4′	145.7	145.7	145.2
C-5′	115.8	116.0	115.4
C-6′	119.6	119.1	119.6
Sugar moiety			
C-1″	101.2	103.5	
C-2″	71.5	74.6	
C-3″	72.2	77.3	
C-4″	73.6	71.1	
C-5″	69.6	77.1	
C-6″	18.0	62.5	

*Run at 25.05 MHz with TMS as int. standard. Chemical shifts in δ-values (ppm).

†In Me_2CO-d_6 solution.

‡In Me_2CO-d_6 + D_2O solution.

deposited at the Herbarium, Faculty of Pharmaceutical Sciences, Kyushu University.

Extraction and isolation. (a) From the leaf of *Quercus miyagii*: fresh leaves (3.7 kg) were extracted × 4 at room temp. with 85% aq. Me_2CO. The combined extracts were concd under red. pres., and the ppt. was filtered off. After concn, the filtrate (*ca* 0.5 l) was subjected to CC over Sephadex LH-20 using H_2O with increasing amounts of MeOH to give 5 fractions; frs. 1 (2.4 g), 2 (2.9 g), 3 (5.5 g), 4 (6.1 g) and 5 (5.5 g). Fraction 1 was subjected to MCI-gel CHP-20P CC with H_2O–MeOH (1:0–6:4) to afford compounds **2** (21 mg) and **3** (37 mg). Chromatography of fr. 2 on MCI-gel CHP-20P (H_2O–MeOH) yielded **1** (29 mg) and **4** (22 mg). Fractions 3–5 were separately chromatographed over Sephadex LH-20 (60% MeOH, EtOH) and MCI-gel CHP-20P (H_2O–MeOH) to give **5** (200 mg), **6** (22 mg) and **7** (40 mg) (from fr. 3), **8** (118 mg) and **9** (22 mg) (from fr. 4) and **10** (40 mg) and **11** (40 mg) (from fr. 5). (b) From the bark of *Quercus miyagii*: fresh bark (3.2 kg) was chopped into small pieces and extracted × 4 at room temp. with 85% aq. Me_2CO. The combined extracts, after concn under red. pres. to *ca* 1.5 l., were subjected to Sephadex LH-20 CC using H_2O–MeOH (1:0–0:1) to afford 3 fractions; frs. 1 (8.1 g), 2 (20 g) and 3 (3.2 g). Fraction 1 was rechromatographed over MCI-gel CHP-20P [H_2O–MeOH (1:0–6:4)] and Sephadex LH-20 (EtOH, 60% aq. MeOH) to give **1** (5.6 g) and **12** (480 mg). Fractions 2 and 3 were separately purified by repeated chromatography using a variety of solvent systems (EtOH, H_2O–MeOH, etc.) to give **3** (1.1 g), **5** (10.2 g), **6** (61 mg) and **7** (2 g) (from fr. 2) and **8** (42 mg), **9** (144 mg) and **10** (144 mg) (from fr. 3).

Catechin 3-O-α-L-*rhamnopyranoside* (**1**). Colourless needles (H_2O), mp 259–261°, $[\alpha]_D^{28}$ −24.2° (Me_2CO; *c* 0.9). ^{1}H NMR (Me_2CO-d_6): δ 1.22 (3H, *d*, *J* = 5 Hz, Me-6″), 2.64 (1H, *dd*, *J* = 16, 8 Hz, H-4), 2.92 (1H, *dd*, *J* = 16, 4 Hz, H-4), 4.36 (1H, *br s*, anomeric H), 4.68 (1H, *d*, *J* = 8 Hz, H-2), 5.90, 6.04 (each 1H, *d*, *J* = 2 Hz, H-6 and -8), 6.7–7.0 (3H, *m*, B-ring H). ^{13}C NMR: see Table 1. (Found: C, 57.38; H, 5.59. $C_{21}H_{24}O_{10}$ requires: C, 57.79; H, 5.54%.)

Enzymatic hydrolysis of **1**. A soln of **1** (290 mg) in H_2O (16 ml) was incubated overnight with crude hesperidinase at 37°. The solvent was evaporated *in vacuo* and the residue treated with MeOH. The MeOH-soluble protion was subjected to CC over Sephadex LH-20 (60% aq. MeOH, EtOH) to afford a sugar (32 mg) and catechin (**5**) (86 mg). **5**: colourless needles, mp 177°, $[\alpha]_D^{23}$ + 10.1° (Me_2CO; *c* 1.2). The sugar (20 mg) was converted by treatment with phenylhydrazine (0.2 ml) and HOAc (0.4 ml) in H_2O (2 ml) into the osazone (9.6 mg), yellow needles, mp 184–188°, $[\alpha]_D^{23}$ + 47.6° (Me_2CO; *c* 0.3). IR ν_{KBr}^{max} cm^{-1}: 3400 (OH), 1600, 1490, 1250. This product was identified as L-rhamnosazone by direct comparison.

Methylation of **1**. A soln of **1** (607 mg) in MeOH was treated with an ethereal soln of CH_2N_2 at room temp. for 19 hr. The solvent was evaporated off, and the residue was purified by CC over silica gel (C_6H_6–EtOH 20:1–19:1) to furnish the tetramethyl ether (**1a**) (305 mg), an amorphous powder, $[\alpha]_D^{32}$ − 30.5° (Me_2CO; *c* 0.6) ^{1}H NMR ($CDCl_3$): δ 1.26 (3H, *d*, *J* = 5 Hz, Me-5″), 2.5–3.1 (2H, *m*, H-4), 3.72 (3H, *s*, OMe), 3.76 (3H, *s*, OMe), 3.84 (6H, *s*, OMe), 4.16 (1H, *br s*, anomeric H), 4.70 (1H, *d*, *J* = 8 Hz, H-2), 6.0–6.1 (2H, *m*, A-ring H), 6.7–7.0 (3H, *m*, B-ring H). (Found: C, 60.36; H, 6.66. $C_{25}H_{32}O_{10}$. 1/2 H_2O requires: C, 59.87; H, 6.63%.) EIMS *m/z* (rel. int.): 492 [M]$^+$ (12.7), 345 [M − rha]$^+$ (24.3), 328 (100). Methylation of **1** (280 mg) with Me_2SO_4 (2 ml) and anhydrous K_2CO_3 (1.1 g) in dry Me_2CO, followed by silica gel CC with C_6H_6–Me_2CO (1:0–1:1), afforded the 5,7,3′,4′-tetra-*O*-methyl, 2″,3″-isopropylidene derivative (178 mg), colourless needles (MeOH), mp 95°, $[\alpha]_D^{28}$ − 7.9° (Me_2CO; *c* 0.9). ^{1}H NMR ($CDCl_3$): δ 1.26 (3H, *d*, *J* = 5 Hz, Me-6″), 1.24, 1.44 (each 3H, *s*, C-Me), 2.5–3.1 (2H, *m*, H-4), 3.74, 3.78 (each 3H, *s*, OMe), 3.86 (6H, *s*, OMe), 4.44 (1H, *br s*, anomeric H), 4.76 (1H, *d*, *J* = 8 Hz, H-2), 6.08, 6.15 (each 1H, *d*, *J* = 2 Hz, H-6 and -8), 6.8–7.0 (3H, *m*, B-ring H). (Found: C, 62.72; H, 6.98. $C_{28}H_{36}O_{10}$ requires: C, 63.14; H, 6.81%.) FDMS *m/z* (rel. int.): 532 [M]$^+$ (100).

Acid hydrolysis of **1a**. A mixture of **1a** (32 mg) and 0.5 N MeOH–HCl (5 ml) was refluxed for 1.5 hr. The reaction mixture, after cooling, was subjected to CC over Sephadex LH-20 (60% MeOH) to afford 5,7,3′,4′-tetra-*O*-methylcatechin (12 mg), colourless needles (MeOH), mp 142–143°, $[\alpha]_D^{32}$ + 2.2° (Me_2CO; *c* 0.2).

Catechin 3-O-β-D-*glucopyranoside* (**2**). An amorphous powder, $[\alpha]_D^{23}$ − 13.2° (Me_2CO; *c* 0.4). ^{1}H NMR (Me_2CO-d_6 + D_2O): δ 2.6–2.9 (2H, *m*, H-4), 4.24 (1H, *d*, *J* = 6 Hz, H-3), 4.28 (1H, *d*, *J* = 8 Hz, anomeric H), 4.93 (1H, *d*, *J* = 6 Hz, H-2), 5.92, 6.04 (each 1H, *d*, *J* = 2 Hz, H-6 and -8), 6.7–7.0 (3H, *m*, B-ring H). (Found: C, 53.81; H, 6.04. $C_{21}H_{24}O_{11}$. H_2O requires: C, 53.61; H, 5.57%.) ^{13}C NMR: see Table 1.

Enzymatic hydrolysis of **2**. An aq. soln of **2** (10 mg) was treated overnight with crude hesperidinase at room temp. The reaction mixture was worked up as described for **1** to yield **5** (2 mg) and the sugar, the latter being identified as glucose by cellulose TLC (R_f: 0.39; solvent: BuOH–pyridine–H_2O, 6:4:3).

Procyanidin B-3 3-O-α-L-*rhamnopyranoside* (**3**). A tan amorphous powder, $[\alpha]_D^{32}$ − 203.0° (Me_2CO; *c* 0.8). ^{1}H NMR (Me_2CO-d_6 + D_2O): δ 1.16–1.24 (3H, *m*, Me-5‴) 2.5–2.9 (2H, *m*, H-4), 5.8–6.3 (3H, *m*, A-ring H), 6.4–7.1 (6H, *m*, B-ring H). ^{13}C NMR (Me_2CO-d_6 + D_2O): δ 18.0 ($C_{6‴}$), 26.1, 26.7 (C_4), 37.8 ($C_{4''}$), 69.6 ($C_{5‴}$), 79.0, 79.7 (C_3), 83.4 ($C_{2,2''}$). Complete assignments of the

^{1}H and ^{13}C NMR signals could not be made owing to the complicated signal pattern caused by rotational isomerism. (Found: C, 57.62; H, 5.63. $C_{36}H_{36}O_{16}$. 3/2 H_2O requires: C, 57.52; H, 5.23%.) Negative FABMS *m/z* (rel. int.): 723 $[M-H]^-$ (4.9).

Methylation of **3**. A soln of **3** (249 mg) in MeOH was treated with CH_2N_2 at room temp. for 12 hr. The solvent was evaporated off and the residue was CC over silica gel (C_6H_6–EtOH 20:1–9:1) to afford the octamethyl ether (**3a**) (80 mg), an amorphous powder, $[\alpha]_D^{32}$ −186.8° (Me_2CO; *c* 0.3). ^{1}H NMR ($CDCl_3$): δ 1.1–1.3 (3H, *m*, Me-5‴), 3.48, 3.68, 3.76, 3.80, 3.92 (24H in total, *s*, OMe), 6.0–7.1 (9H, *m*, A- and B-ring H). (Found: C, 61.63; H, 6.13. $C_{44}H_{52}O_{16}$. H_2O requires: C, 61.82; H, 6.37%.) EIMS *m/z* (rel. int.): 836 $[M]^+$ (74.7), 672 $[M-rha]^+$ (25.0), 625 (75.0).

Enzymatic hydrolysis of **3a**. A soln of **3a** (32 mg) in DMSO–H_2O (1:2) was incubated for 9 hr with crude hesperidinase at 37°. The reaction mixture was worked up as before to give L-rhamnose and 5,7,3′,4′,5″,7″,3‴,4‴-octa-*O*-methylprocyanidin B-3 (**7a**) (11 mg). **7a**: amorphous powder, $[\alpha]_D^{32}$ −213.2° (Me_2CO; *c* 0.6). ^{1}H NMR ($CDCl_3$): δ 3.44, 3.72, 3.80, 3.82, 3.84, 3.92 (24H in total, *s*, OMe), 5.9–7.1 (9H, *m*, A- and B-ring H). (Found: C, 63.45; H, 6.34. $C_{38}H_{42}O_{12}$. 3/2H_2O requires: C, 63.59; H, 6.32%.) EIMS *m/z* (rel. int.): 690 $[M]^+$ (100).

Thiolytic degradation of **3**. A mixture of **3** (88 mg), benzylmercaptan (2 ml) and HOAc (1 ml) in EtOH (10 ml) was heated under reflux for 7 hr with stirring. The reaction mixture was concd under red. pres., and the oily residue was subjected to Sephadex LH-20 CC with EtOH to afford **1** (23 mg) and the 4-benzylthioether (**5b**) (21 mg). **5b**: an amorphous powder, $[\alpha]_D^{32}$ +27.3° (Me_2CO; *c* 0.4). ^{1}H NMR (Me_2CO-d_6): δ 4.08 (2H, *s*, CH_2–S), 4.38 (1H, *d*, *J* = 4 Hz, H-4), 4.94 (1H, *d*, *J* = 9 Hz, H-2), 5.82, 6.02 (each 1H, *d*, *J* = 2 Hz, A-ring H), 6.8–7.0 (3H, *m*, B-ring H), 7.2–7.5 (5H, *m*, aromatic H).

Procyanidin B-3 3″-O-α-L-rhamnopyranoside (**4**). An amorphous powder, $[\alpha]_D^{22}$ −110.2° (Me_2CO; *c* 0.6). ^{1}H NMR (Me_2CO-d_6 + D_2O): δ 0.6–0.7 (3H, *m*, Me-5‴), 5.8–6.2 (3H, *m*, A-ring H), 6.5–7.4 (6H, *m*, B-ring H). ^{13}C NMR (Me_2CO-d_6 + D_2O): δ 17.6 ($C_{6\cdots}$), 36.4 ($C_{4\cdots}$), 69.2 ($C_{5\cdots}$), 71.5 ($C_{2\cdots}$), 72.2 ($C_{3\cdots}$), 73.7 ($C_{4\cdots}$), 100.0 ($C_{1\cdots}$). (Found: C, 58.24; H, 5.50. $C_{36}H_{36}O_{16}$. H_2O requires: C, 58.22; H, 5.16%.)

Methylation of **4**. A soln of **4** (50 mg) in MeOH was treated with CH_2N_2 at room temp. for 24 hr. The reaction mixture was worked up as described for **3** to afford the octamethyl ether (**4a**) (30 mg), as an amorphous powder, $[\alpha]_D^{24}$ −124.5° (Me_2CO; *c* 0.7). ^{1}H NMR ($CDCl_3$): δ 0.5–0.6 (3H, *m*, Me-5‴), 3.45, 3.68, 3.72, 3.76, 3.80, 3.84, 3.86, 3.88 (each 3H, *s*, OMe), 5.9–7.4 (9H, *m*, A- and B-ring H). (Found: C, 63.09; H, 6.57. $C_{44}H_{52}O_{16}$ requires: C, 63.15; H, 6.26%.)

Enzymatic hydrolysis of **4a**. A soln of **4a** (20 mg) in DMSO–H_2O (1:2) was incubated for 10 hr with crude hesperidinase at 37°. The reaction mixture was worked up as before to give L-rhamnose and **7a** (3 mg).

Thiolytic degradation of **4**. A mixture of **4** (75 mg), benzylmercaptan (2 ml) and HOAc (1 ml) in EtOH (10 ml) was refluxed for 24 hr. The reaction mixture was worked up as before to give catechin (**5**) (8 mg) and 4-benzylthioether of **1** (**1b**) (20 mg). **1b**: an amorphous powder, $[\alpha]_D^{17}$ +36.9° (Me_2CO; *c* 0.3). ^{1}H NMR (Me_2CO-d_6): δ 1.22 (3H, *d*, *J* = 5 Hz, Me-5″) 4.02 (1H, *br s*, anomeric H), 4.68 (1H, *d*, *J* = 4 Hz, H-4), 5.26 (1H, *d*, *J* = 9 Hz, H-2), 5.90, 6.08 (each 1H, *d*, *J* = 2 Hz, A-ring H), 6.7–7.2 (3H, *m*, *B*-ring H) 7.2–7.4 (5H, *m*, aromatic H).

Acknowledgements—The authors are grateful to Mr. H. Murata (Oshima-tsumugi Technical Center) for collecting plant material, and Dr. T. Tanaka (Sankyo Co., Ltd.) for provision of tannase. They are also indebted to Mr. Y. Tanaka, Miss K. Soeda and Mr. K. Isobe (Kyushu University) for measurements of ^{13}C NMR, ^{1}H NMR and MS, respectively, and to the staff of the Central Analysis Room of this University for microanalysis.

REFERENCES

1. Tschesche, R., Braun, T. M. and Sassen, W. V. (1980) *Phytochemistry* **19**, 1925.
2. Weinges, K. and Wild, R. (1970) *Justus Liebig's Ann. Chem.* **734**, 46.
3. Doskotch, R. W., Mikhail, A. A. and Chatterji, S. K. (1973) *Phytochemistry* **12**, 1153.
4. Takani, M., Nakano, M. and Takahashi, K. (1977) *Chem. Pharm. Bull.* **25**, 3388.
5. Nonaka, G., Ezaki, E., Hayashi, K. and Nishioka, I. (1983) *Phytochemistry* **22**, 1659.
6. Kashiwada, Y., Nonaka, G. and Nishioka, I. (1986) *Chem. Pharm. Bull.* **34**, 3208.
7. Morimoto, S., Nonaka, G. and Nishioka, I. (1986) *Chem. Pharm. Bull.* **34**, 633.
8. Bonefeld, M., Friedrich, H. and Kolodziej, H. (1986) *Phytochemistry* **25**, 1205.
9. Murakami, T., Wada, H., Tanaka, N., Kuraishi, T., Saiki, Y. and Chen, C. (1985) *Yakugaku Zasshi* **105**, 649.
10. Weinges, K., Göritz, K. and Nader, F. (1968) *Justus Liebig's Ann. Chem.* **715**, 164.
11. Thompson, R. S., Jacques, D., Haslam, E. and Tanner, R. J. N. (1972) *J. Chem. Soc. Perkin Trans.* 1 1387.
12. Nonaka, G., Miwa, N. and Nishioka, I. (1982) *Phytochemistry* **21**, 429.
13. Foo, L. Y. and Porter, L. J. (1978) *J. Chem. Soc. Perkin Trans.* 1 1186.
14. Hsu, F. L., Nonaka, G. and Nishioka, I. (1985) *Chem. Pharm. Bull.* **33**, 3293.