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Phenolic Glucosides from Inner Bark of Shirakamba Birch, *Betula platyphylla* Sukatchev var. *japonica* Hara

—Six phenolic glucosides containing a new glucoside 4'-hydroxy-3'-methoxyphenol-ß-D-[6-*O*-(4"-hydroxy-3",5"-dimethoxylbenzoate)]- glucopyranoside—

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Abstract

Alcoholic extracts obtained from the inner bark of shirakamba birch, *Betula platyphylla* Sukatchev var. *japonica* Hara were further investigated. A new phenolic glucoside 4'-hydroxy-3'-methoxyphenol-ß-D-[6-*O*-(4"-hydroxy-3",5"-dimethoxylbenzoate)]-glucopyranoside along with five known phenolic compounds was isolated. The structures of the isolated compounds were determined on the basis of spectroscopic studies.

Key Words: *Betula*, birch, 4'-hydroxy-3'-methoxyphenol-ß-D-[6-*O*-(4"-hydroxy-3",5"-dimethoxylbenzoate)]-glucopyranoside, 3,4,5-trimethoxyphenyl- ß -D-glucopyranoside, platyphyllenone, platyphylloside, betuloside, catechin

Introduction

Shirakamba birch (*Betula platyphylla* Sukatchev var. *japonica* Hara) is a tall deciduous tree that grows on Hokkaido and Honshu islands in Japan (Shibuya and Igarashi 1995). It has not been widely used in Japan except as pulp chip and chopstick production from its wood. However, in Europe, birch flowers and leaves have been utilized as herbal tea. The production of herbal tea has started in Bifuka, Hokkaido, Jappan since 1995 (Terazawa 1995). Traditionally, extractives from the leaves have been expected to be a source of compounds that increase the activity of the anti-oxidative defense of human blood plasma (Drozdova *et al.* 1995). Chemical constituents of the birch leaves have been investigated to be isolated as rhamnosides of lignans (Shen *et al.* 1999-a), glucosides of *p*-hydroquinone derivatives (Shen *et al.* 1999-b), gluocosides of sesquiterpenoids (Shen *et al* . 2001) and glycosides of flavonoids (Shen *et al.* 2000; Fuchino *et al.* 1995). The inner bark and leaves of shirakamba birch contains a large amount of phenolic glycosides, including salidroside, betuloside and platyphylloside (Terazawa *et al.* 1984). It was found later that platyphylloside has an inhibitory effect on ruminant digestibility *in vitro* (Sunnerheim *et al* . 1988).

In this paper, we report the isolation of six phenolic glucosides including a new phenolic glucoside 4'-hydroxy-3'-methoxyphenol-ß-D-[6-*O*-(4"- hydroxy- 3",5"- dimethoxyl- benzoate)]-glucopyranoside from the inner bark of shirakamba birch.

Material and Methods

Material

Fresh inner bark of shirakamba birch (*Betula platyphylla* Sukatchev var. *japonica* Hara) was collected in July 1998 at the Nakagawa Experiment Station of Hokkaido University Forestry.

Extraction and Isolation

Extraction: The fresh inner bark (2.51 kg) of shirakamba birch (*Betula platyphylla* Sukatchev var. *japonica* Hara) was cut into small sections and extracted with 95% ethanol (EtOH) at room temperatures for 2 weeks. The EtOH extracts were concentrated under reduced pressure to give syrup (170g). The syrup (26g) was mixed with silica-gel (1:2) and dried under reduced pressure to remove the solvent and water.

Chromatography: The dried cake was impregnated sufficiently with the developing solvent (ethyl acetate (EtOAc) saturated with water) before charging it on a silica-gel (Wakogel C-200) column. Each fraction was collected in 300 ml portion. The eluents were monitored by TLC (CMW: $CHCl_3$/MeOH/H_2O, 40:10:1, v/v), and the fractions containing the same compounds were combined. Three fractions of F1, F2 and F3 were obtained. Chromatographic purification of the each fraction was carried out until each compound became pure on TLC (CMW).

Purification of F1: The fraction F1 (0.33g) containing compound 1 was subjected to a silica-gel column and eluted with a developing solvent ($CHCl_3$/MeOH/H_2O 80:10:1, v/v). Each 15 ml eluent

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was collected as a fraction and the fractions containing the same compounds were combined. Purification of F1-1 containing mainly compound 1 was carried out until compound 1 became pure on TLC (CMW).

Purification of F2: The fraction F2 (0.68g) was subjected to a silica-gel column and eluted with a developing solvent ($CHCl_3$/MeOH/H_2O, 60:10:1, v/v). Each 15 ml eluent was collected as a fraction and the fractions containing the same compounds were combined. Purification of F2-1 containing compound 2 , F2-2 containing compound 3 and F2-3 containing compound 4, was carried out until each compound became pure on TLC (CMW).

Purification of F3: Fraction F3 (0.48g) was subjected to a silica-gel column and eluted with a developing solvent ($CHCl_3$/MeOH/H_2O, 50:10:1, v/v). Each 15 ml eluent was collected as a fraction and the fractions containing the same compounds were combined. Purification of F3-1 containing compound 5 and F3-2 containing compound 6 was carried out until each compound became pure on TLC (CMW).

Instrumental Analyses

Spectra were obtained with the following instruments: NMR: a Bruker AM-500FT-NMR spectrometer and a JEOL JNM-EX 270 FT-NMR system; FD-MS and EI-MS: a JEOL JMS01SG-2, mass spectromer and a JMS-DX-300 mass spectrometer, respectively. Melting points were measured with a Yanagimoto Micro Melting Apparatus. Optical rotatory was measured with a JASCO Digital Polarmeter DIP-360.

Physico-chemical properties of the isolated compounds

Structures of the compounds 1- 6 are shown in Fig.1.

Compound 1

((+)-3,3',4',5,7-pentahydroxyflavan ((+)- catechin)) was positive to DSA.. TLC (AEAW): Rf 0.68. (Yield: 91.6mg). FD-MS *m/z* : 290 $[M]^+$. EI-HR-MS *m/z* : 290.0789 $[M]^+$ (calcd. for $C_{15}H_{14}O_6$: 290.0790); EI-MS *m/z* (rel. int.): 290 (43.21), 139 (100), 123 (35.55), 107 (6.53); ^{1}H-NMR (ppm, CD_3COCD_3): δ 6.85 (1H, *d*, *J* = 2.0 Hz), 6.74 (1H, *s*), 6.73 (1H, *dd*, *J* = 2.4, 3.0 Hz), 5.98 (1H, *d*, *J* = 2.4 Hz), 5.84 (1H, *s*), 4.53 (1H, *d*, *J* = 7.8 Hz), 3.97 (1H, *m*), 2.88 (1H, *dd*, *J* = 5.4 Hz), 2.52 (1H, *dd*, *J* = 8.3 Hz). ^{13}C-NMR(ppm, CD_3COCD_3) δ :80.1 (C-2), 68.8 (C-3), 30.5 (C-4), 101.1 (C-4a), 157.2 (C-5), 96.0 (C-6), 157.6 (C-7), 20.5 (C-8), 158.1 (C-8a), 132.6 (C'-1), 115.6 (C-2'.), 146.1 (C-3'.), 146.0 (C-4'), 96.6 (C-5'), 116.2 (C-6').

Compound 2

(1,7- di - (4-hydroxyphenyl)–5-hepten-3-one (platyphyllenone)) was positive to DSA, obtained as colorless oil (Yield: 5.5mg). TLC (CMW, 40:10:1, v/v): Rf 0.66. FD-MS *m/z* : 296 $[M]^+$ (100); EI-HR-MS *m/z* : 296.1374 $[M]^+$ (calcd. for $C_{19}H_{20}O_3$: 296.1413); EI-MS *m/z* (rel. int.): 296 (15.93), 176 (14.49), 107 (100), 75 (6.07); ^{1}H-NMR (ppm, $CDCl_3$): δ 6.98 (4H, *dd*, *J* = 8.0 Hz), 6.74 (4H, *dd*, *J*= 8.0 Hz), 6.84 (1H, *m*), 6.08 (1H, *brd*), 2.80 (4H, *m*), 2.65 (2H, *m*), 2.47 (2H, *q*, *J* = 7.1 Hz). ^{13}C-NMR(ppm, $CDCl_3$) δ : 34.4 (C-1), 33.6 (C-2), 146.5 (C-3), 130.8 (C-4), 199.8 (C-5), 42.0 (C-6), 29.7 (C-7), 132.9 (C-1'. or C-1"), 133.4 (C-1'. or C-1"), 129..5 (C-2'. 2". 6'. 6"), 115.4 (C'-3'. 3". 5'.5"), 154.0 (C'-4'. 4").

Compound 3

(4'-hydroxy-3'-methoxyphenol-ß-D-[6-*O*-(4"-hydroxy-3",5"-dimeth-oxylbenzoate)]-glucopyranoside) was positive to DSA. (Yield: 6.0mg). TLC (CMW, 40:10:1, v/v): Rf 0.43. FD-MS *m/z* (rel. int.): 482 $[M]^+$ (100). EI-HR-MS *m/z* : 482.1345 $[M]^+$ (calcd. for $C_{22}H_{26}O_{12}$: 482.1424); EI-MS *m/z* (rel. int.): 429 (6.12), 282 (9.20), 207 (6.35), 75 (5.10), 35 (100). ^{1}H-NMR (ppm, CD_3OCD_3): δ 7.27 (2H, *s*), 6.94 (1H, *d*, *J* = 2.0 Hz), 6.92 (1H, *d*, *J* = 2.0 Hz), 6.10 (1H, *dd*, *J* = 3.0 , 2.0Hz), 6.42 (1H, *s*), 3.80 (6H, *s*, OMe x 2), 3.71 (3H, *s*, OMe). ^{13}C-NMR(ppm, CD_3OCD_3) δ : 104.7(C-1), 75.3 (C-2), 78.2 (C-3), 72.1 (C-4), 75.8 (C-5), 65.4 (C-6), 155.2 (C'-1), 107.6 (C-2'), 152.5 (C-3'.), 141.4 (C-4'), 130.4(C-5'), 121.0(C-6'), 142.4(C-1"), 108.7(C-2".6"), 148.9 (C-3".5"), 102.3(C-4"), 167.0(C-α).

Compound 4

((1,7-di-(4-hydroxyphenyl)-heptane-3-one-5-ol-ß-D-glucopyranoside (platyphylloside)) was positive to DSA, obtained as colorless powder (Yield: 22.8mg). TLC (CMW,40:10:1, v/v): Rf 0.35. Mp 189.5-190° $[\alpha]^{25}_D$ −14.3° ±0.1° (c 2.30, MeOH), FD-MS *m/z* (rel. int.): 476 (5.05); $C_{25}H_{32}O_9$. $[M]^+$ 296 (100): $[M^+$-Glu]; EI-HR-MS *m/z*: 296.1406 [M-Glu] (calcd. for $C_{19}H_{20}O_3$: 296.1413); EI-MS *m/z* (rel. int.): 296 (8.11), 176 (14.91), 107 (100), 75 (11.08), 71 (1.83); ^{1}H-NMR (ppm, CD_3COCD_3): δ 7.03 (4H, *dd*, *J* = 8.0 Hz), 6.73 (4H, *dd*, *J*= 8.0 Hz), 4.18 (1H, *m*), 2.84 (1H, *d*), 2.82 (1H, *d*), 2.76 (4H, *m*), 2.61 (2H, *m*), 1.79 (2H, *m*). ^{13}C-NMR(ppm, CD_3COCD_3) δ : 29.9 (C-1), 46.5 (C-2), 210.1 (C-3), 48.7 (C-4), 76.3 (C-5), 38.7 (C-6), 31.5 (C-7), 133.4 (C-1'. 1"), 130.6 (C-2'. 2". 6'. 6"), 116.4 (C'-3'. 3". 5'.5"), 156.6 (C'-4'. or C-4"), 156.8 (C'-4'. or C-4"), 103.7 (C-1'"), 75.6 (C-2'"), 77.9 (C-3'"), 72.2 (C-4'"), 78.5 (C-5'"), 63.4 (C-6'").

Compound 5

(3,4,5-trimethoxyphenol-ß-D-glucopyranoside) was negative to DSA, obtained as white needles from F3 (Yield: 8.0 mg). TLC (CMW, 40:10:1, v/v): 0.37. mp 201-203. FD-MS *m/z* (rel. int.): 346 $[M]^+$ (100); EI-HR-MS *m/z* : 346.1229 $[M]^+$ (calcd. for $C_{15}H_{22}O_9$: 346.1264); EI-MS m/z (rel. int.): 346 (4.37), 211 (1.54), 184 (100), 169 (64.29), 141 (11.26); ^{1}H-NMR (ppm, CD_3OD): δ 6.48 (2H, *s*), 4.82 (1H, *d*, *J* = 7.6 Hz), 3.92 (1H, *dd*, *J* = 12.3, 5.3 Hz), 3.80 (6H, *s*, OMe X 2), 3.69 (3H, *s*, OMe), 3.66 (1H, *dd*, *J*= 12.3, 2.6 Hz), 3.32-3.47 (4H, overlapping). ^{13}C-NMR(ppm, CD_3OD) δ : 103.5 (C-1), 75.3 (C-2), 78.7 (C-3), 72.0

(C-4), 78.4 (C-5), 63.0 (C-6), 156.3 (C'-1), 96.5 (C-2'. 6'), 155.1 (C-3'.5'), 134.8 (C-4').

Compound 6

(4- hydroxyphenylbutane -2-ol-ß-D- glucopyranoside (betuloside)) was positive to DSA., obtained as colorless crystals, mp 188-189℃, (Yield:4.8mg). TLC (CMW, 40:10:1, v/v): Rf 0.33. $[\alpha]^{25}_{D}$ –45.3° ±0.1° (c 2.30, MeOH); FD-MS *m/z* (rel. int.): 328 $[M]^+$ (100); EI-HR-MS *m/z* : 328.1497 $[M]^+$ (calcd. for $C_{16}H_{24}O_7$: 328.1522); EI-MS *m/z* (rel. int.): 328 (4.53), 296 (1.61), 207 (6.90), 177 (15.35), 148 (32.32), 133 (14.14), 107 (100); ^{1}H-NMR (ppm, CD_3OD): δ 7.03 (2H, *d*, *J* = 8.0 Hz), 6.67 (2H, *d*, *J* = 8.0 Hz), 3.30 (1H, *m*), 2.60 (2H, *m*), 1.84 (1H, *m*), 1.68 (1H, *m*), 1.20 (3H, *d*, *J* = 6.4 Hz). ^{13}C-NMR(ppm, CD_3COD) δ : 20.7 (C-1). 72.6 (C-2). 41.4 (C-3). 32.6 (C-4). 135.5 (C-1'). 131.2 (C-2'. 6'.). 116.8 (C'-3'. 5'.). 157.0 (C'-4'.). 103.1 (C-1"). 75.9 (C-2"). 79.0 (C-3"). 75.9 (C-4"). 78.6 (C-5"). 63.7 (C-6").

Results and Discussion

Compound 1

(+)-3,3',4',5,7-pentahydroxyflavan ((+)-catechin)

Compound 1 was positive to DSA, showing that it was a phenolic compound. The molecular weight of compound 1 was 290 in the FD-MS. The spectrum of ^{13}C-NMR of compound 1 showed the presence of two aromatic rings, two methine carbons, and one methylene carbon. The ^{1}H-NMR spectrum revealed the aromatic proton signals at δ 6.85 (1H, *d*, *J*=2,0Hz), 5.98(1H, *d*, *J*=2,4Hz) and 6.73(1H, *dd*, *J*=2,4, 3.0Hz), indicating the presence of a ABX system. These three protons were assigned to C-2', C-3' and C-6' on this benzene ring. Furthermore, two singlets at δ 6.74 (1H) and 5.84 (1H) were assigned to C-6 and C-8 of another benzene ring. Two double doublet peaks at δ 2.88 (1H, *dd*, *J*=16.5, 5.4Hz) and 2.52 (1H, *dd*, *J*=16.2, 8.3 Hz) were methlene protons of C-4. Based the above analyses, compound 1 was presumed to be one of the flavan-3-ol derivatives. By comparison of NMR signals with those of known related compounds, compound 1 was determined as (+)-catechin (Shimomura *et al.* 1988; Fuchino *et al.* 1996; Pan 1995).

Compound 2

1,7-di-(4-hydroxyphenyl)- 5-hepten-3-one (platyphyllenone)

Compound 2 showed a molecular ion peak at m/z 296 in the FD-MS. The ^{1}H-NMR spectrum of compound 2 revealed two AA'BB' type spin systems at δ 6.98 (4H, *dd*, *J* = 8.0 Hz) and 6.74 (4H, *dd*, *J* = 8.0 Hz) assigned to eight aromatic protons of C2', 6' and C2", 6" and C3', 5' and C3", 5", which indicated the existence of two 1, 4-disubstituted benzene rings in the compound 2. The presence of a double bond was also suggested by the signals at δ 6.84 (1H, *m*) and 6.08 (1H, *brd*). In addition, the signals at δ 2.47 and 2.65 were assigned to be methylenes adjacent to a benzyl ring and a carbonyl group, respectively. The multiplets at δ 2.80 integrated to four protons were assigned to two deshielded methylenes adjacent to the double bond and another a benzyl ring. Thus, the structure of compound 2 was established as 1, 7-di-(4-hydroxyphenyl)-5-hepten-3-one. This compound was named as plataphyllenone and it derived from a ketol precursor, platyphyllonol by ß -elimination reaction. (Terazawa, M. *et al.* 1984; 1973).

Compound 3

4' -hydroxy- 3'–methoxyphenol–ß–D-[6-*O*-(4"- hydroxy -3",5"-dimethoxylbenzoate)]-gluco- pyranoside, a new compound

Compound 3 was positive to DSA, showing that it was a phenolic compound. It showed a molecular ion peak at m/z 482 in the FD-MS. The spectrum of ^{13}C-NMR of compound 3 showed the presence of two aromatic rings. The ^{1}H-NMR spectrum (Table 1) revealed the aromatic proton signals at δ 6.94 (1H, *d*, *J*=2,0Hz), 6.42(1H, *d*, *J*=2,0Hz) and 6.11(1H, *dd*, *J*=2,0, 3.0Hz), indicating the presence of a ABX system. These three protons were assigned to C-2', C-3' and C-6' on this benzene ring. Furthermore, a singlet at δ 7.27 (2H, s) due to two symmetric benzene prontons was assigned to the protons of C-2" and C-6". It can be deduced that C-2" and C-6" were adjacent to carbonyl group, because the chemical shift of these two protons were in downfield. A singlet at δ 3.80 (6H) indicated the presence of two symmetric methoxyl groups, suggesting the presence of syringyl nucleus. A singlet at δ 3.71 (3H) was due to another methoxyl group of the another benzene ring. The presence of a glucopyranosyl moiety in compound 3 was confirmed by ^{13}C-NMR spectrum (Table1), which showed six signals at δ 104.7(C-1), 75.3(C-2), 78.2(C-3), 72.1 (C-4), 75.8(C-5), and 65.4(C-6). The mode of the glucosidic linkage was determined to be ß-form based on the coupling constant of the anomeric proton signal at δ 4.66 (1H, *d*, *J* = 7.6 Hz) in the ^{1}H-NMR spectrum. Thus, compound 3 was supposed to be a 4-hydroxy-3,5-dimethoxy benzoic acid ester of 4-hydroxy-3-methoxyphenol -O-ß-D-glucopyranoside as 4'-hydroxy-3'-methoxy–phenol-ß-D- [6-*O*-(4"-hydroxy -3",5" -dimethoxylbenzoate)] -glucopyranoside. To our knowledge, the compound has not been reported so far.

Compound 4

1,7-di-(4-hydroxyphenyl)-heptane-3-one-5-ol-ß-D-glucopyranoside (platyphylloside)

The FD-MS of compound 4 showed a fragment ion at *m/z* 296, resulting from the loss of a glucosyl moiety. The molecular formula of compound 4 was deduced from the FD-MS spectrum of m/z 476 (M^+, $C_{25}H_{32}O_9$). Compound 4 was proved to be closely related to compound 2, the largest difference being the displacement of double bond by a glucopyranosyl moiety (^{13}C-NMR data). The mode of glucosidic linkage was determined to be ß -from based on the

large coupling constant of the anomeric proton signal at δ 4.82 (1H, *d*, *J* = 7.6 Hz). Based on the spectral aspects, compound 4 was concluded to be 1,7-di-(4-hydroxyphenyl)-heptane-3-one-5-ol-ß-D-glucopyranolside, which was isolated firstly by Terazawa *et al.* (1984) and named as platyphylloside. The absolute configuration of C-5 was identified as an *S* by a direct comparison of the [α]D value with published data for platyphylloside, which is known as a compound showing an inhibitory effect on ruminant digestibility *in vitro* (Sunnerheim, K. *et al.* 1988).

Compound 5

3,4,5-trimethoxyphenol- ß- D-glucopyranoside

Compound 5 showed a molecular ion peak at m/z 346 (M^+) in the FD-MS. By the data of ^{1}H- and ^{13}C-NMR spectra, the existence of three aromatic methoxyl groups, an aromatic ring and a glucopyranosyl was indicated. A singlet at δ 6.48 in the ^{1}H-NMR spectrum indicated the presence of two aromatic protons. The data of the ^{13}C-NMR spectrum of compound 5 suggested the existence of a 3, 4, 5-trimethoxyl benzene ring. A singal at δ 156.3 in ^{13}C-NMR spectrum was assigned to the aromatic carbon C-1' which connected to the glucosyl residue. The presence of a glucopyranosyl moiety in compound 5 was confirmed by ^{13}C-NMR spectrum, which showed six signals at δ 103.5 (C-1), 75.3 (C-2), 78.7 (C-3), 72.0 (C-4), 78.4 (C-5), and 63.0 (C-6). The mode of the glucoside linkage was determined to be ß-form based on the coupling constant of the anomeric proton signal at δ 4.82 (1H, *d*, *J* = 7.6 Hz) in the ^{1}H-NMR spectrum. Thus, the structure of compound 5 was determined to be 3, 4, 5-trimethoxyphenol-ß-D-glucopyranoside. (Hayashi *et al.* 1990; Shimomura *et al.* 1988).

Compound 6

4-hydroxyphenylbutane-2-ol-ß-D-glucopyranoside (betuloside)

Compound 6 was positive to DSA, showing that it was a phenolic compound. The molecular weight was observed at m/z 328 in the FD-MS. The ^{1}H-NMR showed a double doublet of AA'BB' type at δ 7.03 (2H, *d*, *J* = 8.0 Hz) and 6.67 (2H, *d*, *J* = 8.0 Hz) assignable to four aromatic protons of C2', 6' and C3', 5', indicating the existence of a 1, 4-disubstituted benzene ring in compound 5. One methyl at δ 1.20 (3H, *m*), two methylenes at δ 2.60 (2H, *m*) and [1.84 (1H, *m*), 1.68 (1H, *m*)] and a methine at δ 3.30 (1H, *m*) were observed. Furthermore, the presence of a glucopyranosyl moiety was suggested by ^{13}C-NMR spectrum, which showed six signals at δ 103.1 (C-1"), 75.9 (C-2"), 79.0 (C-3"), 75.9 (C-4"), 78.6 (C-5") and 63.7 (C-6"). The mode of the glucosidic linkage was determined to be ß-form based on the large coupling constant of the anomeric proton signal at δ 4.33 (1H, *d*, *J* = 7.9 Hz) in the ^{1}H-NMR spectrum. The HMBC spectrum revealed a connection between the glucosyl residue and the aglycone: the anomeric proton signal of glucosyl moiety at δ 4.33 correlated with the signal of C-2. This result showed that the glucosyl residue is linked to C-2. Thus, compound 6 is concluded to be 4-(4'-hydroxyphenyl) butanol-2-ß-D-glucopyranoside, which was known as betuloside. The absolute configuration of C-2 in compound 6 was identified as *R* by a direct comparison of the [α] D value with published data for *R*-rhododendrin (Fuchino *et al.* 1996).

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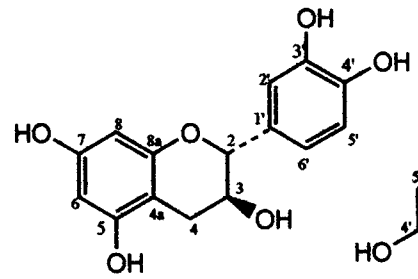
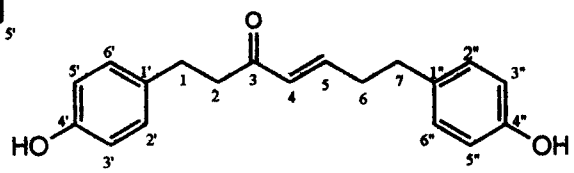
Table 1. NMR spectral data of compound 3
(In CD_3COCD_3, 270 MHz)

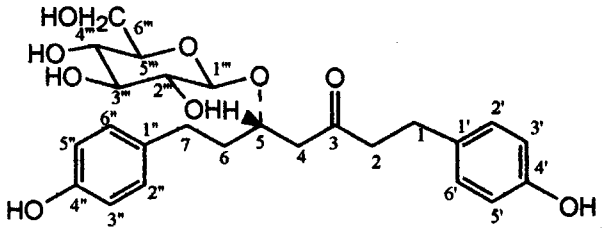
^{13}C-NMR		^{1}H-NMR			
Glucosyl moiety					
C-1	104.7	4.66	1H	*d*	*J*=7.5 Hz
C-2	75.3	3.45			
C-3	78.2	3.51	3H	*m*	
C-4	72.1	3.45			
C-5	75.8	3.72	1H	*m*	
C-6	65.4	4.36	1H	*dd*	*J*=12.4, 4.4 Hz
		4.77	1H	*dd*	*J*=12.4, 2.0 Hz
A-ring					
C-1'	141.4	—			
C-2'	121.1	6.94	1H	*d*	*J*=2.0 Hz
C-3'	152.5	—			
C-4'	155.2	—			
C-5'	102.3	6.42	1H	*d*	*J*=3.0 Hz
C-6'	107.6	6.11	1H	*dd*	*J*=3.0, 2.0 Hz
$C_{3'}$-OMe	56.8	3.71	3H	*s*	
B-ring					
C-1"	142.4	—			
C-2", 6"	108.7	7.27	2H	*s*	
C-3", 5"	148.9	—			
C-4"	130.4	—			
C-α	167.1	—			
$C_{3''}$-OMe	57.3	3.81	3H	*s*	
$C_{5''}$-OMe	57.3	3.81	3H	*s*	



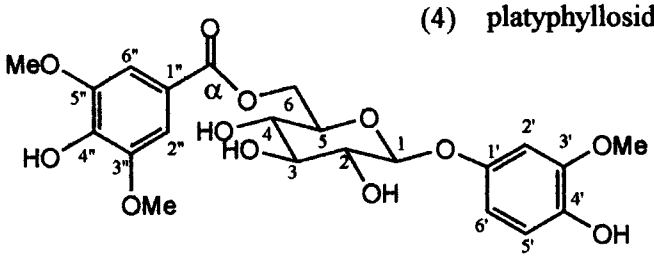
(1) (+)-catechin



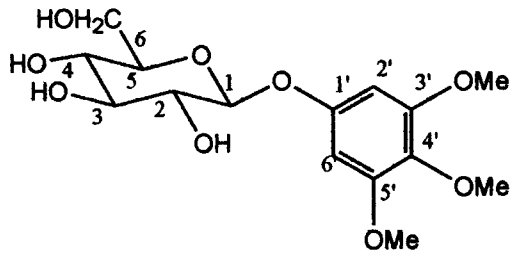
(2) plataphyllenone



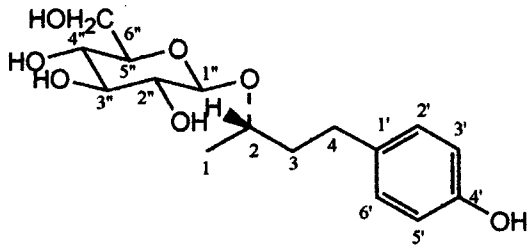
(4) platyphylloside



(3) 4'-hydroxy-3'-methoxyphenol-β-D-[6-O-(4-hydroxy-3,5-dimethoxyl-benzoate)]glucopyranoside



(5) 3,4,5-trimethoxy-phenyl-β-D-glucopyranoside



(6) betuloside

Fig. Compounds isolated from inner bark of shirakamba *Betula platyphylla* Sukatchev var. *japonica* Hara