# Indonesian Medicinal Plants. IX.[1] Chemical Structures of Gongganosides A, B, and C, Three New Quinovic Acid Glycosides from the Bark of *Bhesa paniculata* (Celastraceae)

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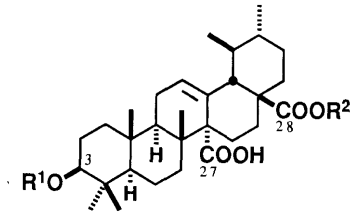
**Three new quinovic acid glycosides, named gongganosides A (1), B (2), and C (3), were isolated from the bark of *Bhesa paniculata* (Celastraceae), an Indonesian medicinal plant collected in Sumatra Island. The chemical structures have been elucidated on the basis of chemical and physicochemical evidence as quinovic acid 3-*O*-*β*-D-xylopyranosyl(1→3)-*α*-L-rhamnopyranoside for 1, 28-*O*-*β*-D-glucopyranosylquinovic acid 3-*O*-*α*-L-rhamnopyranoside for 2, and 28-*O*-*β*-D-glucopyranosyl-quinovic acid 3-*O*-*β*-D-xylopyranosyl(1→3)-*α*-L-rhamnopyranoside for 3.**

**Keywords** Indonesian medicinal plant; *Bhesa paniculata*; Celastraceae; quinovic acid glycoside; gongganoside

The bark of *Bhesa paniculata* ARN. (Celastraceae), which is called "gonggang" in Province Bengkulu, Sumatra Island, Indonesia, has been traditionally used for medicinal treatment of vomiting and diarrhea.[2] As a part of our chemical characterization studies of Indonesian medicinal plants,[1,3] we have been investigating the chemical constituents of the bark of *Bhesa paniculata* and have isolated three new quinovic acid glycosides, named gongganosides A, B, and C, from the ethyl acetate-soluble portion of the methanol extract. This paper deals with the structure elucidation of these triterpene glycosides.

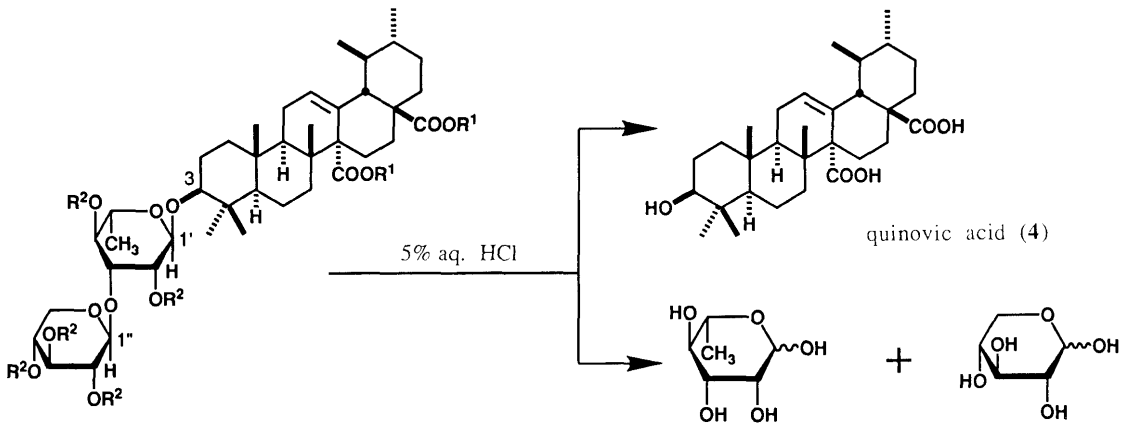
The methanol extract of the bark was partitioned into a mixture of ethyl acetate and water. The water-soluble portion was again partitioned into *n*-butanol and water to give an *n*-butanol-soluble portion (13%) and a water-soluble portion (15%).

Separation and purification of the ethyl acetate-soluble portion (4.6% yield from the bark), by silica gel and Sephadex LH-20 column chromatography and subsequent high-performance liquid chromatography (HPLC) with reverse-phase adsorbent, provided gongganosides A (**1**, 0.037% from the bark), B (**2**, 0.036%), and C (**3**, 0.047%) together with quinovic acid (**4**, 0.045%),[4] 3-oxoquinovic acid[5] (**5**, 0.0027%), quinovic acid 3-*O*-*β*-D-quinovopy-




| | $R^1$ | $R^2$ |
|---|---|---|
| gongganoside A (**1**) : | β-D-xyl(1→3)-α-L-rha | H |
| gongganoside B (**2**) : | α-L-rha | β-D-glc |
| gongganoside C (**3**) : | β-D-xyl(1→3)-α-L-rha | β-D-glc |
| quinovic acid (**4**) : | H | H |

Fig. 1




gongganoside A (**1**) : $R^1$=H, $R^2$=H
**1a** : $R^1$=$CH_3$, $R^2$=Ac

L-rhamnose

D-xylose

(1 : 1)

Chart 1

TABLE I. $^{13}$C-NMR Data for Gongganosides A (**1**), B (**2**), and C (**3**) (in $CD_3OD$)

| | | 1 | 2 | 3 |
|---|---|---|---|---|
| | C-1 | 39.8 | 39.8 | 39.8 |
| | C-2 | 26.6[a)] | 26.6[a)] | 26.6[a)] |
| | C-3 | 90.3 | 90.3 | 90.3 |
| | C-4 | 40.0 | 40.0 | 40.0 |
| | C-5 | 56.6 | 56.6 | 56.6 |
| | C-6 | 19.4 | 19.4 | 19.4 |
| | C-7 | 37.6[b)] | 37.0[b)] | 37.0[b)] |
| | C-8 | 40.6 | 40.8 | 40.8 |
| | C-9 | 48.0 | 48.0 | 48.0 |
| | C-10 | 37.9 | 37.9 | 37.9 |
| | C-11 | 23.8 | 23.9 | 23.9 |
| | C-12 | 130.4 | 130.9 | 130.9 |
| | C-13 | 133.9 | 133.2 | 133.2 |
| | C-14 | 57.3 | 57.2 | 57.3 |
| | C-15 | 25.7[a)] | 25.8[a)] | 25.8[a)] |
| | C-16 | 26.5[a)] | 26.4[a)] | 26.4[a)] |
| | C-17 | 49.5 | 49.8 | 49.8 |
| | C-18 | 55.5 | 55.3 | 55.3 |
| | C-19 | 40.4 | 40.2 | 40.2 |
| | C-20 | 38.3 | 38.2 | 38.2 |
| | C-21 | 31.2 | 31.1 | 31.1 |
| | C-22 | 38.0[b)] | 38.0[b)] | 38.0[b)] |
| | C-23 | 28.7 | 28.7 | 28.7 |
| | C-24 | 17.1[c)] | 17.0[c)] | 17.1[c)] |
| | C-25 | 16.9[c)] | 16.9[c)] | 16.9[c)] |
| | C-26 | 19.1[d)] | 19.2[d)] | 19.2[d)] |
| | C-27 | 179.0 | 179.1 | 179.1 |
| | C-28 | 181.6 | 177.9 | 177.9 |
| | C-29 | 18.2[d)] | 18.1[d)] | 18.1[d)] |
| | C-30 | 21.5 | 21.5 | 21.5 |
| Rha | C-1 | 104.0 | 104.4 | 104.0 |
| | C-2 | 72.2 | 72.5 | 72.2 |
| | C-3 | 82.2 | 72.5 | 82.2 |
| | C-4 | 73.0 | 74.1 | 73.0 |
| | C-5 | 69.8 | 69.9 | 69.8 |
| | C-6 | 17.9 | 17.8 | 17.9 |
| Xyl | C-1 | 106.6 | | 106.5 |
| | C-2 | 75.2 | | 75.2 |
| | C-3 | 77.6 | | 77.5 |
| | C-4 | 71.1 | | 71.2 |
| | C-5 | 66.9 | | 66.9 |
| Glc | C-1 | | 95.6 | 95.6 |
| | C-2 | | 73.9 | 73.9 |
| | C-3 | | 78.2 | 78.2 |
| | C-4 | | 71.1 | 71.1 |
| | C-5 | | 78.6 | 78.6 |
| | C-6 | | 62.5 | 62.5 |

*a—d*) Assignments may be interchanged in each column.

ranoside[6] (**6**, 0.065%), and 28-*O*-*β*-D-glucopyranosylquinovic acid 3-*O*-*β*-D-quinovopyranoside (**7**, 0.033%).[6]

**Gongganoside A (1)** Gongganoside A (**1**) gave a quasi-molecular ion peak $(M+Na)^+$ at *m/z* 787, which corresponded to $C_{41}H_{64}NaO_{13}$, in the positive fast atom bombardment-mass (FAB-MS) spectrum. The infrared (IR) spectrum of **1** showed significant absorption bands due to a hydroxyl (3430 $cm^{-1}$) group, a carbonyl (1686 $cm^{-1}$) group, and a carbon–carbon double bond (1636 $cm^{-1}$).

Acidic hydrolysis of gongganoside A (**1**) with 5% aqueous hydrogen chloride gave the aglycone (**4**), which was identical with quinovic acid,[3] and a mixture of rhamnose and xylose (1 : 1) whose absolute configurations

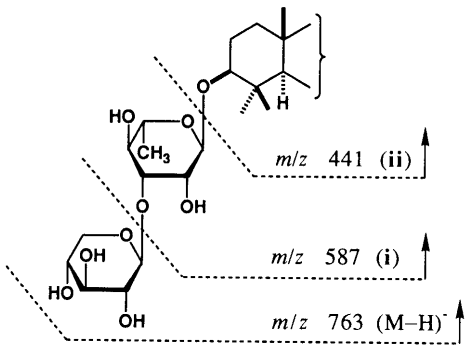



Fig. 2. Negative FAB-MS for Gongganoside A (**1**)

were determined to be L- and D-, respectively, by gas-liquid chromatographic (GLC) analysis.[7]

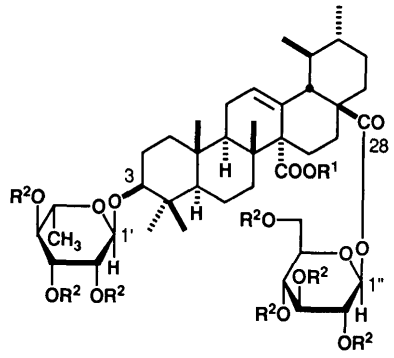
The proton and carbon-13 nuclear magnetic resonance ($^1$H- and $^{13}$C-NMR) spectra of **1** exhibited signals characteristic of a quinovic acid glycoside containing rhamnose and xylose moieties (Table I). Two anomeric proton signals were observed in the $^1$H-NMR spectrum of **1** at $\delta$ 4.70 (1H, d, $J$=1.2 Hz, 1′-H of L-rhamnopyranose) and $\delta$ 4.47 (1H, d, $J$= 7.1 Hz, 1″-H of D-xylopyranose), indicating a *β*-anomeric configuration. In the $^{13}$C-NMR spectrum of **1**, two anomeric carbon signals were observed at $\delta_C$ 104.0 ($J_{C-H}$=167.2 Hz, C-1′ of L-rhamnopyranose, the coupling constant indicates that the anomeric configuration is *α*[8]) and $\delta_C$ 106.6 (C-1″ of D-xylopyranose). Thus, it has been found that gongganoside A (**1**) consists of quinovic acid (**4**), *α*-L-rhamnose, and *β*-D-xylose.

In order to determine the location of the disaccharide sequence, gongganoside A (**1**) was treated with diazomethane followed by acetylation to give a dimethyl ester pentaacetate (**1a**). This result suggested that gongganoside A (**1**) is a monodesmoside, and that the saccharide moiety is not attached to the carboxyl functions in quinovic acid (**4**).

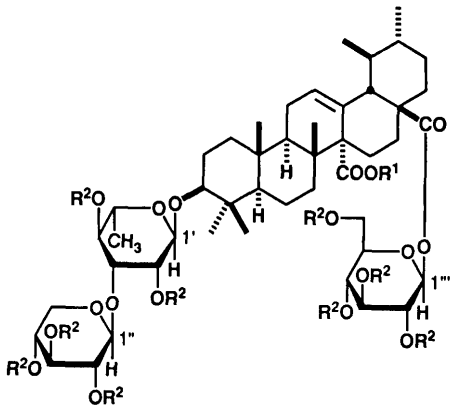
A heteronuclear multiple bond correlation (HMBC) experiment on **1** showed the presence of two characteristic cross-peaks between the anomeric proton ($\delta$ 4.70, 1′-H) of the L-rhamnosyl moiety and the hydroxymethine carbon ($\delta_C$ 90.3, 3-C) in the aglycone (**4**), and between the anomeric proton ($\delta$ 4.47, 1″-H) of the D-xylosyl moiety and the hydroxymethine carbon ($\delta_C$ 82.2, 3′-C) of the L-rhamnosyl moiety. Furthermore, gongganoside A (**1**) gave characteristic negative FAB ions at *m/z* 763 $(M-H)^-$, 719 $[(M-H)-CO_2]^-$, 587 (**i**), and 441 (**ii**) (Fig. 2).

Based on the foregoing evidence, the structure of gongganoside A (**1**) has been concluded to be quinovic acid 3-*O*-*β*-D-xylopyranosyl(1→3)-*α*-L-rhamnopyranoside.

**Gongganoside B (2)** Gongganoside B (**2**) gave a positive FAB ion at *m/z* 817 ($M+Na^+$, $C_{42}H_{66}NaO_{14}$). The IR spectrum of **2** showed absorption bands due to a hydroxyl group (3430 $cm^{-1}$), an ester group (1730 $cm^{-1}$), a carboxyl group (1684 $cm^{-1}$), and a carbon–carbon double bond (1638 $cm^{-1}$). On acidic hydrolysis with 5% aqueous hydrogen chloride, **2** gave quinovic acid (**4**), and a mixture of L-rhamnose and D-glucose in a ratio of 1 : 1



2 : $R^1$=H, $R^2$=H
2a : $R^1$=$CH_3$, $R^2$=Ac



3 : $R^1$=H, $R^2$=H
3a : $R^1$=$CH_3$, $R^2$=Ac

Fig. 3

as indicated by GLC analysis.[7]

The $^1$H- and $^{13}$C-NMR spectra of **2** exhibited signals characteristic of a quinovic acid glycoside containing rhamnosyl and glucosyl moieties (Table I). In the $^1$H-NMR spectrum of **2**, two anomeric proton signals were observed at $\delta$ 4.70 (1H, d, $J$=1.1 Hz, 1′-H of L-rhamnopyranose) and $\delta$ 5.37 (1H, d, $J$=8.0 Hz, 1″-H of D-glucopyranose) indicating $\beta$-anomeric configuration, while the $^{13}$C-NMR spectrum showed two anomeric carbon signals at $\delta_C$ 104.4 ($J_{C-H}$=166.4 Hz, C-1′ of L-rhamnopyranose, indicating $\alpha$-anomeric configuration[8]) and $\delta_C$ 95.6 (C-1″ of D-glucopyranose). Thus, the structure of **2** has been shown to comprise quinovic acid (**4**), $\alpha$-L-rhamnose, and $\beta$-D-glucose.

On methylation with diazomethane followed by acetylation, gongganoside B (**2**) gave a monomethyl ester heptaacetate (**2a**), indicating that gongganoside B (**2**) is a bisdesmoside-type glycoside. Furthermore, an HMBC experiment on **2** revealed two characteristic cross-peaks between the anomeric proton ($\delta$ 4.70, 1′-H) of the rhamnosyl moiety and the hydroxymethine carbon ($\delta_C$ 90.3, 3-C) in the aglycone (**4**), and between the anomeric proton ($\delta$ 5.37, 1″-H) of the glucosyl moiety and the carbonyl carbon ($\delta_C$ 177.9, 28-C) of **4**.

Consequently, the structure of gongganoside B (**2**) has been concluded to be 28-*O*-$\beta$-D-glucopyranosylquinovic acid 3-*O*-$\alpha$-L-rhamnopyranoside.

**Gongganoside C (3)** In the positive FAB-MS spectrum, gongganoside C (**3**) gave a quasi-molecular ion peak $(M+Na)^+$ at $m/z$ 949 which corresponded to $C_{47}H_{74}NaO_{18}$. The IR spectrum of **3** showed a similar absorption pattern to that of gongganoside A (**1**). The $^1$H- and $^{13}$C-NMR spectra of **3** showed signals characteristic of a quinovic acid glycoside containing rhamnose, xylose, and glucose moieties (Table I). Acidic hydrolysis of **3** with 5% aqueous hydrogen chloride gave quinovic acid (**4**) and a mixture of L-rhamnose, D-xylose, and D-glucose in a ratio of 1 : 1 : 1.[7]

The $^1$H-NMR spectrum of **3** showed signals ascribable to three anomeric protons at $\delta$ 4.47 (d, $J$= 7.0 Hz, 1″-H of D-xylopyranose, indicating $\beta$-anomeric configuration), $\delta$ 4.69 (d, $J$=1.1 Hz, 1′-H of L-rhamnopyranose), and $\delta$ 5.37 ($J$=8.0 Hz, 1‴-H of D-glucopyranose, indicating $\beta$-anomeric configuration). Furthermore, in the $^{13}$C-NMR spectrum of **3**, three anomeric carbon signals were observed at $\delta_C$ 104.0 ($J_{C-H}$=165.4 Hz, C-1′ of L-rhamnopyranose, indicating $\alpha$-anomeric configuration[8]), $\delta_C$ 106.5 (C-1″ of D-xylopyranose), and $\delta_C$ 95.6 (C-1‴ of D-glucopyranose).

Treatment of gongganoside C (**3**) with diazomethane and subsequent acetylation provided a monomethyl ester nonaacetate (**3a**), indicating that **3** is a bisdesmoside-type glycoside. Furthermore, an HMBC experiment on **3** exhibited three characteristic cross-peaks between the anomeric proton ($\delta$ 4.69, 1′-H) of rhamnose and the hydroxymethine carbon ($\delta_C$ 90.3, 3-C) in the aglycone (**4**), between the anomeric proton ($\delta$ 4.47, 1″-H) of xylose and the hydroxymethine carbon ($\delta_C$ 82.2, 3′-C) of rhamnose, and also between the anomeric proton ($\delta$ 5.37, 1‴-H) of glucose and the carboxyl carbon ($\delta_C$ 177.9, 28-C) of **4**.

Based on the foregoing evidence, the structure of gongganoside C (**3**) has been concluded to be 28-*O*-$\beta$-D-glucopyranosylquinovic acid 3-*O*-$\beta$-D-xylopyranosyl(1→3)-$\alpha$-L-rhamnopyranoside.

In parallel studies, we have chemically investigated the constituents of the *n*-butanol-soluble portion of the bark. The results will be reported elsewhere.

## Experimental

Melting points were determined on a Yanagimoto micromelting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DX302 digital polarimeter in a 0.5 dm tube. FAB-MS were taken on a JEOL JMS-DX303 spectrometer. $^1$H- and $^{13}$C-NMR spectra were measured with a Bruker AC300P spectrometer using tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in $\delta$ (ppm) and coupling constants ($J$ values) are given in hertz (Hz). The following abbreviations are used: s=singlet, d=doublet, t=triplet, m=multiplet, and br=broad. IR spectra were taken with a Hitachi EPI-G3 spectrometer. HPLC was carried out with a JASCO FLC-A10 and a Shimadzu LC-7A. GLC was carried out with a Shimadzu GC-7A gas chromatograph. For column chromatography, Kieselgel 60 (70—230 mesh, Merck) was used. Thin layer chromatography (TLC) was conducted on precoated Kieselgel 60 $F_{254}$ plates (0.2 mm, Merck).

**Plant Materials** *Bhesa paniculata* (Celastraceae) was collected in the Culup area of Sumatra Island, Province Bengkulu, Indonesia, in August 1990. It was identified at Herbarium Bogoriense, Research and Development Centre for Biology-LIPI, Indonesia. Voucher specimens have been deposited at Herbarium Bogoriense and Faculty of Pharmaceutical Sciences, Osaka University.

**Isolation of Gongganosides A (1), B (2), and C (3)** The air-dried bark (2.2 kg) of *Bhesa paniculata* ARN. (Celastraceae) was extracted three times with methanol (5 l each) at room temperature. The solvent was evaporated off under reduced pressure to yield the MeOH extract (700 g, 32% from the bark). The MeOH extract was partitioned into an ethyl acetate and water (1 : 1) mixture. The ethyl acetate phase was separated and evaporated under reduced pressure to give the EtOAc extract (101 g, 4.6%), while the water phase was treated with *n*-butanol. The solvent from both phases was evaporated off under reduced pressure to give the *n*-butanol extract (285 g, 13%) and the $H_2O$ extract (318 g, 15%). The EtOAc extract (25 g) was subjected to repeated silica gel column chromatography [eluting with $CHCl_3$ : MeOH = 10 : 1 → MeOH, $CHCl_3$ : MeOH = 50 : 1, $CHCl_3$ : MeOH : $H_2O$ = 7 : 3 : 1 (lower phase)], Sephadex LH-20 column chromatography (eluting with MeOH), and reversed-phase HPLC (Wakosil-II5$C_{18}$ HG, 0.25 m × 10 mm, $CH_3CN$ : $H_2O$ = 1 : 2) to afford gongganosides A (**1**, 204 mg, 0.037%), B (**2**, 198 mg, 0.036%), and C (**3**, 260 mg, 0.047%), quinovic acid (**4**, 248 mg, 0.045%),[4] 3-oxoquinovic acid (**5**, 15 mg, 0.0027%),[5] quinovic acid 3-*O*-*β*-D-quinovopyranoside (**6**, 358 mg, 0.065%),[6] and 28-*O*-*β*-D-glucopyranosylquinovic acid 3-*O*-*β*-D-quinovopyranoside (**7**, 182 mg, 0.033%).[6]

Gongganoside A (**1**): A white amorphous solid, $[\alpha]_D$ +18.3° (*c* = 1.04, in MeOH at 25°C). IR (KBr) $cm^{-1}$: 3430, 1686, 1636, 1453, 1055. $^1$H-NMR ($CD_3OD$) *δ*: 0.74 (3H, s, 24-$H_3$), 0.89 (3H, s, 26-$H_3$), 0.91 (totally 9H, br d, 23-$H_3$, 29-$H_3$, 30-$H_3$), 0.98 (3H, s, 25-$H_3$), 1.23 (3H, d, *J* = 6.2 Hz, 6′-$H_3$), 2.24 (1H, d, *J* = 10.6 Hz, 18-H), 3.06 (1H, dd, *J* = 4.7, 10.6 Hz, 3-H), 4.47 (1H, d, *J* = 7.1 Hz, 1″-H), 4.70 (1H, d, *J* = 1.2 Hz, 1′-H), 5.60 (1H, br s, 12-H). $^{13}$C-NMR: as given in Table I. Positive FAB-MS *m/z*: 787 $(M+Na)^+$. High-resolution positive FAB-MS *m/z*: Calcd for $C_{41}H_{64}NaO_{13}$: 787.4245, Found: 787.4248 $(M+Na)^+$. Negative FAB-MS *m/z*: 763 $(M-H)^-$, 719, 587, 441.

Gongganoside B (**2**): A white amorphous solid, $[\alpha]_D$ +31.6° (*c* = 1.13, in MeOH at 22°C). IR (KBr) $cm^{-1}$: 3430, 1730, 1684, 1638, 1458, 1055. $^1$H-NMR ($CD_3OD$) *δ*: 0.78 (3H, s, 24-$H_3$), 0.88 (3H, s, 26-$H_3$), 0.91 (totally 9H, br d, 23-$H_3$, 29-$H_3$, 30-$H_3$), 0.97 (3H, s, 25-$H_3$), 1.22 (3H, d, *J* = 6.2 Hz, 6′-$H_3$), 2.28 (1H, d, *J* = 10.0 Hz, 18-H), 3.05 (1H, dd, *J* = 4.5, 10.9 Hz, 3-H), 4.70 (1H, d, *J* = 1.1 Hz, 1′-H), 5.37 (1H, d, *J* = 8.0 Hz, 1″-H), 5.62 (1H, br s, 12-H). $^{13}$C-NMR: as given in Table I. Positive FAB-MS *m/z*: 817 $(M+Na)^+$. High-resolution positive FAB-MS *m/z*: Calcd for $C_{42}H_{66}NaO_{14}$: 817.4350, Found: 817.4327 $(M+Na)^+$. Negative FAB-MS *m/z*: 793 $(M-H)^-$, 631, 587, 441.

Gongganoside C (**3**): A white amorphous solid, $[\alpha]_D$ +11.8° (*c* = 1.19, in MeOH at 19°C). IR (KBr) $cm^{-1}$: 3430, 1730, 1692, 1638, 1457, 1075. $^1$H-NMR ($CD_3OD$) *δ*: 0.78 (3H, s, 24-$H_3$), 0.88 (3H, s, 26-$H_3$), 0.91 (totally 9H, br d, 23-$H_3$, 29-$H_3$, 30-$H_3$), 0.98 (3H, s, 25-$H_3$), 1.23 (3H, d, *J* = 6.1 Hz, 6′-$H_3$), 2.28 (1H, d, *J* = 9.8 Hz, 18-H), 3.05 (1H, dd, *J* = 4.7, 10.4 Hz, 3-H), 4.47 (1H, d, *J* = 7.0 Hz, 1″-H), 4.69 (1H, d, *J* = 1.1 Hz, 1′-H), 5.37 (1H, d, *J* = 8.0 Hz, 1‴-H), 5.62 (1H, br s, 12-H). $^{13}$C-NMR: as given in Table I. Positive FAB-MS *m/z*: 949 $(M+Na)^+$. High-resolution positive FAB-MS *m/z*: Calcd for $C_{47}H_{74}NaO_{18}$: 949.4773, Found: 949.4783 $(M+Na)^+$. Negative FAB-MS *m/z*: 925 $(M-H)^-$, 763, 719, 587, 441.

**Acidic Hydrolysis of Gongganoside A (1)** Gongganoside A (**1**, 15 mg) was treated with 5% aqueous HCl (2.0 ml) and the whole mixture was heated at 80°C for 2 h. After cooling, the reaction mixture was filtered to collect the precipitate (6 mg, 63%), which was found to be identical with quinovic acid (**4**)[4] by IR, $^1$H-NMR, $^{13}$C-NMR comparisons. The filtrate was neutralized with $AgCO_3$ powder and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a product, which was then treated with bis(trimethylsilyl)trifluoroacetamide (0.2 ml) and dry pyridine (0.1 ml) at room temperature for 10 min. The reaction mixture was subjected to GLC analysis to determine the sugar composition, and TMS-rhamnose and TMS-xylose were found in 1 : 1 ratio by comparison with authentic samples. GLC conditions: column, TC-17 (GL Sciences Inc.), i.d. 0.25 mm × 30 m; column temperature, 170—270 °C (8 °C/min); carrier gas, $N_2$; flow rate, 0.92 ml/min; injection temperature, 270 °C.

**Determination of Absolute Configurations of Monosaccharides** GLC analyses for determinations of absolute configurations of monosaccharides for gongganosides A (**1**), B (**2**) and C (**3**) were carried out by means of the procedure described in the literature.[7]

**Methylation of Gongganoside A (1) Followed by Acetylation Giving 1a** A solution of gongganoside A (**1**, 20 mg) in MeOH (3 ml) was treated with diazomethane solution in diethyl ether at 0 °C for 1 h. The mixture was evaporated under reduced pressure to give a product (20 mg). The product was then treated with acetic anhydride (1.0 ml) and dry pyridine (2.0 ml) and the whole was left standing at room temperature for 12 h. The reaction mixture was poured into ice-water and extracted with $CHCl_3$. Work-up of the $CHCl_3$ extract in a usual manner gave a product (21 mg), which was purified by column chromatography ($SiO_2$ 3 g, $CHCl_3$ : MeOH = 5 : 1) to afford **1a** (18 mg, 68%).

**1a**: A white amorphous solid, $[\alpha]_D$ +15.9° (*c* = 1.05, $CHCl_3$ at 24°C). IR ($CHCl_3$) $cm^{-1}$: 1749, 1720, 1606, 1378. $^1$H-NMR ($CDCl_3$) *δ*: 1.15 (3H, d, *J* = 6.3 Hz, 6′-$H_3$), 2.03 (3H, s, –$OCOCH_3$), 2.04 (6H, s, –$OCOCH_3$ × 2), 2.11 (3H, s, –$OCOCH_3$), 2.12 (3H, s, –$OCOCH_3$), 2.26 (1H, d, *J* = 11.4 Hz, 18-H), 3.08 (1H, br t, *J* = *ca.* 7.0 Hz, 3-H), 3.37 (1H, dd, *J* = 7.8, 12.0 Hz, 5″-$H_a$), 3.62 and 3.63 (3H each, both s, –$COOCH_3$ × 2), 3.87 (1H, dq, *J* = 9.9, 6.3 Hz, 5′-H), 4.03 (1H, dd, *J* = 3.3, 9.9 Hz, 3′-H), 4.10 (1H, dd, *J* = 4.7, 12.0 Hz, 5″-$H_b$), 4.62 (1H, d, *J* = 6.2 Hz, 1″-H), 4.76 (1H, d, *J* = 1.6 Hz, 1′-H), 4.83 (1H, dd, *J* = 6.2, 7.8 Hz, 2″-H), 4.89 (1H, ddd, *J* = 4.7, 7.8, 7.8 Hz, 4″-H), 5.03 (1H, dd, *J* = 9.9, 9.9 Hz, 4′-H), 5.08 (1H, dd, *J* = 7.8, 7.8 Hz, 3″-H), 5.14 (1H, dd, *J* = 1.6, 3.3 Hz, 2′-H), 5.64 (1H, br s, 12-H). $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 16.4 (25-C), 16.5 (24-C), 17.1 (29-C), 17.3 (6′-C), 18.2 (6-C), 18.3 (26-C), 20.5, 20.7 20.8, 21.0, 21.1 (totally 5C, –$COCH_3$ × 5), 21.0 (30-C), 22.8 (11-C), 24.7 (15-C), 25.1 (16-C), 25.3 (2-C), 28.2 (23-C), 29.9 (21-C), 36.1 (7-C) 36.7 (10-C), 36.9 (22-C), 37.0 (20-C), 38.8 (4-C, 19-C), 38.9 (1-C), 39.5 (8-C), 47.3 (9-C), 48.5 (17-C), 51.3, 51.5 (totally 2C, –$COOCH_3$ × 2), 53.8 (18-C), 55.5 (5-C), 56.2 (14-C), 61.6 (5″-C), 66.5 (5′-C), 68.7 (4″-C), 70.2 (2″-C), 70.8 (3″-C), 72.1 (2′-C), 72.7 (4′-C), 74.8 (3′-C), 89.1 (3-C), 99.4 (1′-C), 101.1 (1″-C), 129.3 (12-C), 132.1 (13-C), 169.3, 169.7, 169.8, 170.1, 170.4 (totally 5C, –$COCH_3$ × 5), 175.5 (27-C), 178.0 (28-C). Positive FAB-MS *m/z*: 1025 $(M+Na)^+$. High-resolution positive FAB-MS *m/z*: Calcd for $C_{53}H_{78}NaO_{18}$: 1025.5085. Found: 1025.5080 $(M+Na)^+$.

**Acidic Hydrolysis of Gongganoside B (2)** Gongganoside B (**2**, 12 mg) was treated with 5% aqueous HCl (2.0 ml) and the whole mixture was heated at 80 °C for 2 h. After cooling, the reaction mixture was filtered to collect the precipitate (5 mg, 67%), which was found to be identical with quinovic acid (**4**)[4] by IR, $^1$H-NMR, $^{13}$C-NMR comparisons. The filtrate was neutralized with $AgCO_3$ powder and the precipitate was removed by filtration. The filtrate was concentrated under reduced pressure to give a product, which was then treated with bis(trimethylsilyl)trifluoroacetamide (0.2 ml) and dry pyridine (0.1 ml) at room temperature for 10 min. The reaction mixture was subjected to GLC analysis to determine the sugar composition, and TMS-rhamnose and TMS-glucose were found in 1 : 1 ratio by comparison with authentic samples. GLC conditions: the same as those for gongganoside A (**1**).

**Methylation of Gongganoside B (2) Followed by Acetylation Giving 2a** A solution of gongganoside B (**2**, 18 mg) in MeOH (3 ml) was treated with diazomethane solution in diethyl ether at 0 °C for 1 h. The solvent from the whole mixture was evaporated under reduced pressure to give a product (17 mg). The product was treated with acetic anhydride (1.0 ml) and dry pyridine (2.0 ml) and the whole was left standing at room temperature for 12 h. The reaction mixture was poured into ice-water and extracted with $CHCl_3$. Work-up of the $CHCl_3$ extract in a usual manner gave a product (22 mg), which was purified by column chromatography ($SiO_2$ 3 g, $CHCl_3$ : MeOH = 5 : 1) to afford **2a** (19 mg, 76%).

**2a**: A white amorphous solid, $[\alpha]_D$ +40.8° (*c* = 0.24, $CHCl_3$ at 25 °C). IR (KBr) $cm^{-1}$: 1751, 1718, 1608, 1377. $^1$H-NMR ($CDCl_3$) *δ*: 1.19 (3H, d, *J* = 6.3 Hz, 6′-$H_3$), 1.99 (3H, s, –$OCOCH_3$), 2.02 (3H, s, –$OCOCH_3$), 2.03 (6H, s, –$OCOCH_3$ × 2), 2.05 (3H, s, –$OCOCH_3$), 2.07 (3H, s, –$OCOCH_3$), 2.15 (3H, s, –$OCOCH_3$), 2.21 (1H, d, *J* = 11.5 Hz, 18-H), 3.09 (1H, br t, *J* = *ca.* 7.9 Hz, 3-H), 3.62 (3H, s, –$COOCH_3$), 3.79 (1H, ddd, *J* = 2.1, 4.3, 9.7 Hz, 5″-H), 4.00 (1H, dq, *J* = 10.0, 6.3 Hz, 5′-H), 4.04 (1H, dd, *J* = 2.1, 12.4 Hz, 6″-$H_a$), 4.26 (1H, dd, *J* = 4.3, 12.4 Hz, 6″-$H_b$), 4.78 (1H, d, *J* = 1.5 Hz, 1′-H), 5.06 (1H, dd, *J* = 10.0, 10.0 Hz, 4′-H), 5.12 (1H, dd, *J* = 9.7, 9.7 Hz, 4″-H), 5.16 (1H, dd, *J* = 8.0, 9.7 Hz, 2″-H), 5.21 (1H, dd, *J* = 1.5, 3.5 Hz, 2′-H), 5.25 (1H, dd, *J* = 9.7, 9.7 Hz, 3″-H), 5.30 (1H, dd, *J* = 3.5, 10.0 Hz, 3′-H), 5.58 (1H, d, *J* = 8.0 Hz, 1″-H), 5.67 (1H, br s, 12-H). $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 16.4 (25-C), 16.5 (24-C), 17.0 (29-C), 17.3 (6′-C), 18.2 (6-C), 18.3 (26-C), 20.6, 20.7, 20.8, 20.9, 21.0 (totally 7C, –$OCOCH_3$ × 7), 21.0 (30-C), 22.7 (11-C), 24.6 (15-C), 25.1 (16-C), 25.3 (2-C), 28.2 (23-C), 29.7 (21-C), 35.4 (7-C) 36.6 (10-C), 37.0 (22-C), 37.1 (20-C), 38.8 (4-C, 19-C), 38.9 (1-C), 39.6 (8-C), 47.2 (9-C), 48.5 (17-C), 51.3 (–$COOCH_3$), 53.5 (18-C), 55.6 (5-C), 56.1 (14-C), 61.6 (6″-C), 66.5 (5′-C), 68.0 (4″-C), 69.2 (3′-C), 70.0 (2″-C), 70.2 (2′-C), 71.3 (4′-C), 72.5 (5″-C), 72.8 (3″-C), 89.5 (3-C), 91.5 (1″-C),

99.6 (1′-C), 130.0 (12-C), 131.2 (13-C), 169.0, 169.5, 170.0, 170.1, 170.3, 170.6 (totally 7C, $-O\underline{C}OCH_3 \times 7$), 175.4 (28-C), 175.5 (27-C). FAB-MS *m/z*: 1125 $(M+Na)^+$. High-resolution FAB-MS *m/z*: Calcd for $C_{57}H_{82}NaO_{21}$: 1125.5246. Found: 1125.5234 $(M+Na)^+$.

**Acidic Hydrolysis of Gongganoside C (3)** Gongganoside C (**3**, 15 mg) was treated with 5% aqueous HCl (2.0 ml) at 80 °C for 2 h. After cooling, the reaction mixture was filtered to collect the precipitate (6 mg, 76%), which was found to be identical with quinovic acid (**4**) by IR, $^1$H-NMR, and $^{13}$C-NMR comparisons. The filtrate was neutralized with $AgCO_3$ powder and the precipitate was removed by filtration. The solvent from the filtrate was evaporated off under reduced pressure to give a product, which was then treated with bis(trimethylsilyl)trifluoroacetamide (0.2 ml) and dry pyridine (0.1 ml) at room temperature for 10 min. The reaction mixture was subjected to GLC analysis to determine the sugar composition, and TMS-rhamnose, TMS-xylose, and TMS-glucose were found in 1 : 1 : 1 ratio by comparison with authentic samples. GLC conditions: the same as those for gongganosides A (**1**).

**Methylation of Gongganoside C (3) Followed by Acetylation Giving 3a** A solution of **3** (15 mg) in MeOH (3 ml) was treated with diazomethane solution in diethyl ether at 0 °C for 1 h. The solvent was evaporated under reduced pressure from the reaction mixture to give a product (15 mg). The product was treated with acetic anhydride (1.0 ml) and dry pyridine (2.0 ml) and the whole was left standing at room temperature for 12 h. The reaction mixture was poured into ice-water and then extracted with $CHCl_3$. Work-up of the $CHCl_3$ extract in a usual manner gave a product (19 mg), which was purified by column chromatography ($SiO_2$ 2 g, $CHCl_3$ : MeOH = 5 : 1) to afford **3a** (16 mg, 75%).

**3a**: A white amorphous solid, $[\alpha]_D$ +18.0° (*c* = 0.59, $CHCl_3$ at 26 °C). IR (KBr) $cm^{-1}$: 1752, 1717, 1605, 1379. $^1$H-NMR ($CDCl_3$) $\delta$: 1.15 (3H, d, *J* = 6.3 Hz, 6′-H), 2.02 (6H, s, $-OCOCH_3 \times 2$), 2.03 (6H, s, –OCOCH3 × 2), 2.04 (6H, s, $-OCOCH_3 \times 2$), 2.07 (3H, s $-OCOCH_3$), 2.11 (3H, s, $-OCOCH_3$), 2.12 (3H, s, $-OCOCH_3$), 2.20 (1H, d, *J* = 11.3 Hz, 18-H), 3.07 (1H, br t, *J* = *ca.* 6.6 Hz, 3-H), 3.37 (1H, dd, *J* = 7.8, 12.0 Hz, 5″-$H_a$), 3.62 (3H, s, $-COOCH_3$), 3.78 (1H, ddd, *J* = 2.2, 4.3, 9.8 Hz, 5‴-H), 3.87 (1H, dq, *J* = 9.8, 6.3 Hz, 5′-H), 4.03 (1H, dd, *J* = 3.3, 9.9 Hz, 3′-H), 4.04 (1H, dd, *J* = 2.2, 12.4 Hz, 6‴-$H_a$), 4.11 (1H, dd, *J* = 4.6, 12.0 Hz, 5″-$H_b$), 4.26 (1H, dd, *J* = 4.3, 12.4 Hz, 6″-$H_b$), 4.63 (1H, d, *J* = 6.2 Hz, 1″-H), 4.76 (1H, d, *J* = 1.6 Hz, 1′-H), 4.83 (1H, dd, *J* = 6.2, 8.1 Hz, 2″-H), 4.89 (1H, ddd, *J* = 4.6, 7.8, 7.8 Hz, 4″-H), 5.03 (1H, dd, *J* = 9.8, 9.9 Hz, 4′-H), 5.05—5.21 (4H, m, 2‴-H, 2′-H, 4‴-H, and 3″-H), 5.25 (1H, dd, *J* = 9.2, 9.2 Hz, 3‴-H), 5.58 (1H, d, *J* = 8.0 Hz, 1‴-H), 5.67 (1H, br s, 12-H). $^{13}$C-NMR ($CDCl_3$) $\delta_C$: 16.4 (25-C), 16.5 (24-C), 17.0 (29-C), 17.3 (6′-C), 18.2 (6-C), 18.3 (26-C), 20.5, 20.6, 20.7, 20.9, 21.0 (totally 9C, $-OCO\underline{C}H_3 \times 9$), 21.0 (30-C), 22.7 (11-C), 24.7 (15-C), 25.1 (16-C), 25.3 (2-C), 28.2 (23-C), 29.7 (21-C), 35.4 (7-C) 36.6 (10-C), 37.0 (22-C), 37.1 (20-C), 38.8 (4-C, 19-C), 38.9 (1-C), 39.6 (8-C), 47.2 (9-C), 48.5 (17-C), 51.3 ($-COO\underline{C}H_3$), 53.8 (18-C), 55.5 (5-C), 56.1 (14-C), 61.7 (5″-C, 6‴-C), 66.5 (5′-C), 68.0 (4‴-C), 68.8 (4″-C), 70.0 (2‴-C), 70.3 (2″-C), 70.8 (3″-C), 72.0 (2′-C), 72.7 (3‴-C, 5‴-C), 72.8 (4′-C), 74.8 (3′-C), 89.0 (3-C), 91.5 (1‴-C), 99.5 (1′-C), 101.1 (1″-C), 130.0 (12-C), 131.2 (13-C), 169.0, 169.3, 169.4, 169.8, 170.0, 170.1, 170.4, 170.6 (totally 9C, $-O\underline{C}OCH_3 \times 9$), 175.3 (28-C), 175.5 (27-C). FAB-MS *m/z*: 1341 $(M+Na)^+$. High-resolution FAB-MS *m/z*: Calcd for $C_{66}H_{94}NaO_{27}$: 1341.5880. Found: 1341.5902 $(M+Na)^+$.

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