Three New Phenylethanoid Glycosides from *Caryopteris incana* and Their Antioxidative Activity

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Three new phenylethanoid glycosides, incanoside C, incanoside D and incanoside E were isolated together with one known glycoside, β -D-fructofuranosyl- α -D-(6-O-[*E*]-sinapoyl) glucopyranoside from the whole plant of *Caryopteris incana* (THUNB.) MIQ. On the basis of chemical and spectral analyses, the structures of the new compounds were elucidated to be 1-O-(3,4-dihydroxyphenyl)ethyl-O- β -D-glucopyranosyl(1 $\rightarrow$ 2)- α -L-rhamnopyranosyl(1 $\rightarrow$ 3)-4-O-feruloyl- β -D-glucopyranoside (incanoside C), 1-O-(3-hydroxy-4-methoxyphenyl)ethyl-O- β -D-glucopyranosyl(1 $\rightarrow$ 2)- α -L-rhamnopyranosyl(1 $\rightarrow$ 3)-4-O-feruloyl- β -D-glucopyranoside (incanoside D) and 1-O-(3-methoxy-4-hydroxyphenyl)ethyl-O- β -D-glucopyranosyl(1 $\rightarrow$ 2)- α -L-rhamnopyranosyl(1 $\rightarrow$ 3)-4-O-feruloyl- β -D-glucopyranoside (incanoside E). The three new phenylethanoid glycosides exhibited radical scavenging activities against DPPH radical and inhibitory activities against the oxidation of linoleic acid.

Key words *Caryopteris incana* (THUNB.) MIQ.; Verbenaceae; phenylethanoid glycoside; incanoside; antioxidative activity

Recent developments in biomedical science have shown that free radicals are involved in many diseases. They attack the unsaturated fatty acids in the biomembrane resulting in membrane lipid peroxidation, which is strongly connected to aging, carcinogenesis and atherosclerosis.^{1–3} Free radicals also attack DNA and cause mutation leading to cancer.⁴ In addition, lipid peroxidation is an important deterioration reaction in the processing and storage of foods. Therefore, it is important to look for new effective radical scavengers.

In a continuation of our antioxidant discovery program, we isolated potent radical-scavenging phlinoside A (**1**) and four other phenylpropanoid glycosides from *C. incana* (THUNB.) MIQ.⁵ Further fractionation of radical scavengers has led to the isolation of four other active glycosides. These were identified as three new phenylethanoid glycosides, incanoside C (**2**), incanoside D (**3**) and incanoside E (**4**), and

one known compound, β -D-fructofuranosyl- α -D-(6-O-[*E*]-sinapoyl)glucopyranoside (**5**). Herein we report their isolation, structural elucidation and antioxidative activities.

Compound **5** was identified as β -D-fructofuranosyl- α -D-(6-O-[*E*]-sinapoyl)glucopyranoside on the basis of comparison of its spectral data with those of β -D-fructofuranosyl- α -D-(6-O-[*E*]-feruloyl)glucopyranoside.⁶

Incanoside C (**2**) was isolated as an amorphous powder. Its molecular formula, C₃₆H₄₈O₂₀, was determined from its high-resolution FAB mass spectra (m/z 801.2892 [M+H]⁺, Calcd for 801.2820). Its spectral data, including UV, IR, FAB-MS, and NMR, indicated that it was related to phlinoside A (**1**). The ¹H- and ¹³C-NMR spectra of **2** showed that the signals were in good agreement with those of **1**, except for differences in the acyl ester moiety, *i.e.* the existence of an additional methoxyl group [δ_H 3.88 (3H, s); δ_C 56.7 (OMe)]. Key

Fig. 1. Structures of Phenylethanoid Glycosides from *Caryopteris incana*

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Table 1. ^1H - and ^{13}C -NMR Spectral Data of Compounds **2**–**4** (400 MHz and 100 MHz, Respectively, CD_3OD)

C	2		3		4	
	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}
Aglycone						
1		131.6		132.9		131.6
2	6.73 (br s)	117.2	6.73 (d, 1.9)	112.9	6.85 (d, 1.9)	113.8
3		144.7		147.6		145.9
4		146.1		147.7		148.8
5	6.70 (d, 8.3)	116.5	6.82 (d, 8.3)	117.3	6.69 (br s)	116.1
6	6.57 (d, 8.3)	121.5	6.69 (dd, 8.3, 1.9)	121.2	6.69 (br s)	122.4
7	2.78 m	36.7	2.80 m	36.5	2.78 m	36.8
8	3.71 m, 4.04 m	72.4	3.72 m, 4.06 m	72.1	3.73 m, 4.08 m	72.2
OMe			3.81 (s)	56.4	3.84 (s)	56.4
Inner glucose						
1'	4.37 (d, 7.8)	104.3	4.37 (d, 7.8)	104.2	4.37 (d, 7.8)	104.2
2'	3.39 (dd, 9.3, 7.8)	76.2	3.39 (dd, 9.3, 7.8)	76.1	3.39 (dd, 9.3, 7.8)	76.1
3'	3.78 (t, 9.3)	82.9	3.77 (t, 9.3)	82.8	3.77 (t, 9.3)	82.8
4'	4.92 (t, 9.3)	70.5	4.91 (t, 9.3)	70.4	4.91 (t, 9.3)	70.4
5'	3.54 m	76.0	3.54 m	76.0	3.54 m	76.0
6'	3.52 ^a , 3.66 ^a	62.4	3.52 ^a , 3.65 ^a	62.3	3.53 ^a , 3.66 ^a	62.4
Rhamnose						
1''	5.58 brs	102.4	5.58 brs	102.2	5.58 brs	102.2
2''	3.98 (dd, 3.4, 1.5)	83.0	3.97 (dd, 3.4, 1.5)	83.0	3.97 (dd, 3.4, 1.5)	83.0
3''	3.67 (dd, 9.6, 3.4)	71.9	3.66 (dd, 9.6, 3.4)	71.8	3.66 (dd, 9.6, 3.4)	71.8
4''	3.30 ^a	74.2	3.29 ^a	74.1	3.29 ^a	74.1
5''	3.56 m	70.5	3.56 m	70.4	3.56 m	70.4
6''	1.08 (d, 6.4)	18.5	1.07 (d, 6.4)	18.4	1.08 (d, 6.4)	18.4
Outer glucose						
1'''	4.41 (d, 7.3)	107	4.39 (d, 7.3)	106.9	4.41 (d, 7.3)	106.9
2'''	3.28 ^a	75.5	3.28 ^a	75.4	3.28 ^a	75.4
3'''	3.34 ^a	78.0	3.34 ^a	77.9	3.34 ^a	77.9
4'''	3.30 ^a	71.5	3.30 ^a	71.4	3.30 ^a	71.4
5'''	3.30 ^a	78.2	3.30 ^a	78.1	3.30 ^a	78.1
6'''	3.90 (d, 11.7, 1.5) 3.64 ^a	63.0	3.90 (d, 11.7, 1.5) 3.63 ^a	62.8	3.90 (d, 11.7, 1.5) 3.64 ^a	62.8
Ester moiety						
1''''		127.8		127.6		127.6
2''''	7.19 (d, 2.0)	112.0	7.19 (d, 2.0)	111.8	7.19 (d, 2.0)	111.8
3''''		149.2		149.4		149.4
4''''		150.9		150.8		150.8
5''''	6.81 (d, 8.3)	116.7	6.81 (d, 8.3)	116.5	6.81 (d, 8.3)	116.5
6''''	7.08 (d, 8.3, 2.0)	124.5	7.08 (d, 8.3, 2.0)	124.3	7.08 (d, 8.3, 2.0)	124.3
7''''	7.66 (d, 16.0)	148.0	7.66 (d, 16.0)	147.9	7.66 (d, 16.0)	147.9
8''''	6.38 (d, 16.0)	115.2	6.38 (d, 16.0)	115.0	6.38 (d, 16.0)	115
CO		168.4		168.2		168.2
OMe	3.88 (s)	56.7	3.88 (s)	56.5	3.88 (s)	56.5

a) Overlapped with other signals.

correlation via long-range coupling (COLOC) correlation (Fig. 2) observed between this methoxyl group and C-3''' (δ 146.8) of the ester group, indicated that the additional methoxyl was attached to C-3''' of the ester group. Acid hydrolysis of compound **2** afforded two glucoses, one rhamnose (identified by GC) and ferulic acid (identified by HPLC). The absolute configurations of the two glucoses and rhamnose were identified as D and L, respectively, by the Oshima method.⁷⁾ Thus, the structure of **2** was established as 1-*O*-(3,4-dihydroxyphenyl)ethyl-*O*- β -D-glucopyranosyl(1 $\rightarrow$ 2)- α -L-rhamnopyranosyl(1 $\rightarrow$ 3)-4-*O*-feruloyl- β -D-glucopyranoside. In good agreement with this, mild hydrolysis of **2** furnished leucosceptoside A (**6**) identified by co-TLC with the authentic sample.⁸⁾

The ^1H - and ^{13}C -NMR spectra of compound **3** were similar to those of **2** but differed from the signals arising from their aglycone moieties due to the presence of one additional

methoxyl group in **3**. The nuclear overhauser effect (NOE) spectrum showed that the irradiation of this methoxyl group (δ 3.81) caused enhancement of the H-5 signal (δ 6.82) of the phenylethoxy group, indicating that this additional methoxyl group is attached to C-4. Its heteronuclear multiple bond correlation (HMBC) spectrum also supports this fact (Fig. 2). The FAB-MS spectra of **2** and **3** exhibited molecular ion peaks at m/z 801 and 815 $[\text{M}+\text{H}]^+$, respectively, confirming these structural differences. The absolute configurations of the two glucoses and rhamnose were also identified as D and L, respectively, by the Oshima method.⁷⁾ Thus, the structure of incanoside D (**3**) was determined to be 1-*O*-(3-hydroxy-4-methoxyphenyl)ethyl-*O*- β -D-glucopyranosyl(1 $\rightarrow$ 2)- α -L-rhamnopyranosyl(1 $\rightarrow$ 3)-4-*O*-feruloyl- β -D-glucopyranoside.

The FAB-MS spectrum of compound **4** showed the same molecular ion and main fragments (m/z 815 $[\text{M}+\text{H}]^+$, 653

Fig. 2. COLOC or HMBC Correlation ($^{13}\text{C} \rightarrow ^1\text{H}$) of Incanoside C (2) and D (3) (COLOC for 2 and HMBC for 3)

$[\text{M}-\text{glc}+\text{H}]^+$, 507 $[\text{M}-\text{glc}-\text{rha}+\text{H}]^+$, 339 $[\text{M}-\text{glc}-\text{rha}-\text{aglycone}+\text{H}]^+$, 177 $[\text{feruloyl}]^+$ as those of 3. The UV, IR, ^1H - and ^{13}C -NMR spectra for 3 and 4 were also just about the same except for the signals given from phenylethoxy groups with the methoxyl group at a different position. In the NOE spectrum, the methoxy signal in phenylethoxy group at δ 3.84 exhibited a NOE with H-2 signal at δ 6.85, indicating that the aglycone of 4 is (3-methoxy-4-hydroxy phenyl)-ethoxy group. Thus, the structure of compound 4 was 1-*O*-(3-methoxy-4-hydroxyphenyl)ethyl-*O*- β -D-glucopyranosyl-(1 $\rightarrow$ 2)- α -L-rhamnopyranosyl(1 $\rightarrow$ 3)-4-*O*-feruloyl- β -D-glucopyranoside.

1,1-Diphenyl-2-picrylhydrazyl (DPPH) Radical Scavenging and Antioxidative Activity Phenylethanoid glycosides are water soluble natural products widely distributed in the plant kingdom, most of which are isolated from traditional medicinal plants. Significant biological activities, such as enzyme inhibition, and immunomodulatory, antiviral and cytotoxic effects have been reported.^{9,10} Recently some phenylethanoid glycosides have been reported to be good antioxidants and free radical scavengers in some *vitro* antioxidative assay models, and the number of phenolic hydroxyl groups in the structures of the phenylethanoids is related to their scavenging activities.^{11,12}

Figure 3 shows the DPPH radical scavenging activity of

Fig. 3. DPPH Radical Scavenging Activity of Compounds 2–5, *dl*- α -Tocopherol and Ascorbic Acid

Each value is the average of duplicate determinations. Incanoside C (2) —■—, incanoside D (3) —◆—, incanoside E (4) —□—, compound 5 —○—, *dl*- α -tocopherol —●—, ascorbic acid —△—.

compounds 2–5. Compounds 2–4 have potent DPPH radical scavenging activities, more than *dl*- α -tocopherol and ascorbic acid, which are known as natural antioxidants. Thus, compounds 2–4 may also be good radical scavengers.

It is generally thought that the inhibition of lipid peroxidation by antioxidants may be due to their free radical scavenging activities. Superoxide indirectly initiates lipid peroxidation because superoxide anion acts as a precursor of singlet oxygen and hydroxyl radical.¹³ Hydroxyl radical eliminates hydrogen atoms from the membrane lipid which results in lipid peroxidation. The inhibition of the above phenylethanoid glycosides against the oxidation of linoleic acid was therefore tested using the β -carotene bleaching method.¹⁴ The inhibitory percentages of phlinoside A (1), incanoside C (2), incanoside D (3) and *dl*- α -tocopherol were 39%, 33%, 22%, and 73%. Thus, the inhibitory activity of these compounds may also be related to the number of their phenolic hydroxyl groups.

Experimental

General The experimental procedures and plant material were the same as reported in ref. 5.

Isolation Fraction 6 (1.8 g) reported in ref. 5 had DPPH radical scavenging activity and was further purified by a second polyamide column (60 g, 2.5 $\times$ 30 cm), eluted with H_2O -MeOH [1:0 (800 ml); 7:3 (800 ml); 1:1 (500 ml)] and followed by Sephadex LH-20 column chromatography (MeOH- H_2O 1:1) to give compound 5 (20 mg) and a mixture containing 3 and 4. The mixture was further purified by a semi-preparative HPLC on a C₁₈ (Develosil-HG-5, 10 $\times$ 200 mm, MeOH- H_2O 4:6, 1.5 ml/min) to give pure 3 (15 mg) and 4 (6 mg). Fraction 9 (2.2 g) mostly containing 2 had potent DPPH radical scavenging activity and was purified by polyamide column (60 g, 2.5 $\times$ 30 cm) chromatography eluted with increasing amounts of MeOH in H_2O , and further purified by Sephadex LH-20 column chromatography (MeOH) to give compound 2 (250 mg).

Incanoside C (2) Off-white amorphous powder. ^1H - and ^{13}C -NMR spectral data are shown in Table 1. IR: ν_{max} (KBr) cm^{-1} : 3390 (br, OH), 1691 (O=C=O), 1625, 1596, 1513, 1368, 1278, 1158. UV: λ_{max} (MeOH) nm (ϵ): 219 (24660), 289 (15000), 329 (20510). FAB-MS: m/z 801 $[\text{M}+\text{H}]^+$, 639 $[\text{M}-\text{glc}+\text{H}]^+$, 493 $[\text{M}-\text{glc}-\text{rha}+\text{H}]^+$, 339 $[\text{M}-\text{glc}-\text{rha}-\text{aglycone}+\text{H}]^+$. High-resolution FAB-MS m/z 801.2892 (Calcd for $\text{C}_{36}\text{H}_{49}\text{O}_{20}$: 801.2820).

Incanoside D (3) Off-white amorphous powder. ^1H - and ^{13}C -NMR

spectral data are shown in Table 1. IR: $\nu_{\max}$ (KBr) cm^{-1} : 3389 (br, OH), 1691 (O=C=O), 1620, 1695, 1515, 1370, 1278, 1155. UV: $\lambda_{\max}$ (MeOH) nm (ϵ): 219 (15000), 288 (8280), 328 (11470). FAB-MS: m/z 815 $[\text{M}+\text{H}]^+$, 653 $[\text{M}-\text{glc}+\text{H}]^+$, 507 $[\text{M}-\text{glc}-\text{rha}+\text{H}]^+$, 339 $[\text{M}-\text{glc}-\text{rha}-\text{aglycone}+\text{H}]^+$, 177 $[\text{feruloyl}]^+$. High-resolution FAB-MS m/z 815.3003 (Calcd for $\text{C}_{37}\text{H}_{51}\text{O}_{20}$: 815.2977).

Incanoside E (4) Off-white amorphous powder. ^1H - and ^{13}C -NMR spectral data are shown in Table 1. IR: $\nu_{\max}$ (KBr) cm^{-1} : 3388 (br, OH), 1691 (O=C=O), 1620, 1690, 1514, 1370, 1275, 1155. UV: $\lambda_{\max}$ (MeOH) nm (ϵ): 218 (15200), 289 (8300), 327 (11450). FAB-MS: m/z 815 $[\text{M}+\text{H}]^+$, 653 $[\text{M}-\text{glc}+\text{H}]^+$, 507 $[\text{M}-\text{glc}-\text{rha}+\text{H}]^+$, 339 $[\text{M}-\text{glc}-\text{rha}-\text{aglycone}+\text{H}]^+$, 177 $[\text{feruloyl}]^+$. High-resolution FAB-MS m/z 815.3002 (Calcd for $\text{C}_{37}\text{H}_{51}\text{O}_{20}$: 815.2977).

β -D-Fructofuranosyl- α -D-(6-O-[E]-sinapoyl)glucopyranoside (5) Off-white amorphous powder, ^1H -NMR (400 MHz, CD_3OD) δ : 3.20–4.20 (m), 3.87 (6H, s, OCH_3), 4.27 (1H, dd, $J=11.9, 5.3$ Hz, H-6 of glucose), 4.50 (1H, dd, $J=11.9, 1.9$ Hz, H-6 of glucose), 5.42 (1H, d, $J=3.4$ Hz, H-1 of glucose); sinapoyl 6.47 (1H, d, $J=16.0$ Hz, H-8), 6.93 (2H, s, H-2, H-6), 7.63 (1H, d, $J=16.0$ Hz, H-7). ^{13}C -NMR (100 MHz, CD_3OD) δ : glucose 93.2 (C-1), 73.2 (C-2), 74.6 (C-3), 71.8 (C-4), 72.0 (C-5), 65.1 (C-6); fructose 105.2 (C-2), 79.2 (C-3), 76.0 (C-3), 83.8 (C-4), 64.2 (C-5 or C-6), 64.3 (C-1 or C-6); sinapoyl 126.6 (C-1), 106.9 (C-2 and C-6), 149.4 (C-3, C-5), 139.6 (C-4), 147.2 (C-7), 115.7 (C-8), 169.1 (C-9).

Mild Acid Hydrolysis¹⁵⁾ Mild acid hydrolysis of compound **2** (0.5% in MeOH) was carried out on four TLC plates by adding 5 μl of a solution of **2** and 5 μl of 3 N HCl to the start as a spot. Each plate was heated to 100 °C for 5, 10, 15 and 30 min and then developed with $\text{CHCl}_3:\text{CH}_3\text{OH}:\text{H}_2\text{O}$ (7:3:0.5). The products of hydrolysis were identified after spraying with H_2SO_4 (5%) reagent and comparing with authentic samples of Leucosceptoside A.

Acid Hydrolysis A solution of compounds **2** and **3** (ca. 4 mg each) in 4% H_2SO_4 (5 ml) was heated at 90 °C for 3 h. After cooling and filtering, the residue was dissolved in 30 ml H_2O and then extracted with EtOAc (3 $\times$ 30 ml). The EtOAc layer was concentrated to dryness, the residue was analyzed by HPLC and the retention time was compared with those of authentic materials. Conditions: Column: ODS-HG-5, 150 mm $\times$ 4.6 mm. Flow rate: 1.0 ml/min. Eluent: linear gradient of MeOH (0–100%) in 5% MeOH containing 1% AcOH. t_{R} : ferulic acid 18.6 min. The aqueous layer was neutralized with BaCO_3 and filtered. The filtrate was passed through an Amberlite IR-45 (OH^-) column, followed by an Amberlite IR-120 (H^+) column. The final eluate was concentrated and the residue was dissolved in distilled water containing inositol as an internal standard. The mixture was evaporated to dryness. The residue was trimethylsilylated and detected by GC. The GC conditions were as follows: column: 3% Silicone OV-1/Gaschrom Q (60–80 mesh), 1.5 m $\times$ 2 mm; column temperature: 80–300 °C at a rate of 4 °C/min; carrier gas N_2 ; t_{R} (min): 18.58, 20.40 (trimethylsilyl(TMSi) derivatives of rhamnose); 26.15 and 29.01 (TMSi derivatives of glucose).

Determination of the Configuration of Sugars in Compounds **2 and **3**** A solution of compound **2** or **3** (8 mg each) in 4% H_2SO_4 (5 ml) was hydrolyzed using the same method as above. The sugar residue was dissolved in 1 ml H_2O , L-(–)- α -methylbenzylamine (8 mg) and $\text{Na}(\text{BH}_3\text{CN})$ (5 mg) in EtOH (1 ml) was added. The mixture was allowed to stand overnight, followed by the addition of AcOH (0.2 ml) and then was evaporated to dryness. The reaction mixture was acetylated with 1:1 Ac_2O –pyridine (1 ml) and was heated in a sealed tube for 1 h at 100 °C. Water (1 ml) was added and the mixture was evaporated to dryness so that it gave an oily residue. The residue was dissolved in 1 ml water, and extracted with chloroform. HPLC of the extract showed that glucose and rhamnose in **2** and **3** were D and L configurations, respectively, according to the method of Oshima *et al.*⁷⁾

Scavenging Effect against DPPH Radical Using TLC¹⁶⁾ A 6×10^{-5} M DPPH solution was sprayed on a developed TLC plate. The active compounds against DPPH radical showed light yellow spots on a plate of purple

DPPH background.

Scavenging Effect against DPPH Radical Using the Colorimetry Method¹⁷⁾ A MeOH solution (0.2 ml) of test compounds at various concentrations was added to a 2.8 ml MeOH solution containing DPPH (1.5×10^{-4} M). The reaction mixture was shaken vigorously and then kept at room temperature for 30 min. The absorbance of the remaining DPPH was measured in 1 cm cubettes using a Shimadzu UV-1200 spectrophotometer at 520 nm, and the radical-scavenging activity of each compound was expressed by the ratio of decrease in the absorbance of DPPH (%), relative to the absorbance (100%) of DPPH solution in the absence of sample.

Measurement of Antioxidative Activity by β -Carotene Bleaching Method¹⁵⁾ A β -carotene solution was prepared at a concentration of 3.7 mM in acetone. The concentration of linoleic acid solution was 4.3 mM in a pH 7 McIlvaine buffer containing Tween 80 at a concentration of 0.8 mg/ml. Lipoxigenase (Oriental Co., from soybean, 126500 units/mg) was used after diluting with H_2O to a concentration of 0.2 mg/ml. A 50 μl aliquot of lipoxigenase solution was added to a mixture containing 2.4 ml of the McIlvaine buffer (pH=7), 0.5 ml of a linoleic acid solution, 0.2 ml of the β -carotene solution and 50 μl of a 3 mM phenylethanoid solution. After 1 min, the bleaching rate of β -carotene was measured at 460 nm. The inhibitory ratio (I.R.) of each compound toward carotene bleaching is expressed as follows: I.R. (%) = $100\times[(a-b)/a]$, where a is the decrease in absorbance at 460 nm due to β -carotene decomposition in control, b is the decrease in absorbance at 460 nm of the β -carotene solution with added samples.

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