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SHORT COMMUNICATION

Isolation and identification of flavonoids from *Coreopsis lanceolata* L. petals

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The methanol extract of *Coreopsis lanceolata* L. petals was acid-hydrolysed, and 7,3′,4′-trihydroxy-8-methoxyflavanone (**1**) and 6,3′,4′-trihydroxy-7-methoxyaurone (leptosidin) (**2**) were successfully isolated. The structure of compound **1** is designated to flavanone based on X-ray crystallographic analysis and NMR spectroscopic analysis. Compound **1** showed high-antioxidant effects based on diphenylpicrylhydrazyl radical scavenging assay (94.3% scavenging rate) and superoxide dismutase-like activity assay (23.9% inhibition rate).

Keywords: *Coreopsis lanceolata* L; 7,3′,4′-trihydroxy-8-methoxyflavanone; leptosidin

1. Introduction

Coreopsis lanceolata L. is a denizen native of North America and makes a yellow flower bloom from May to June in Japan. Now, it has been appointed to a specified foreign organism in February 2006 because of its strength of propagative power, in Japan. Therefore, *C. lanceolata* L. was gathered and burned off. So, we became interested in the utilisation of *C. lanceolata* L. and their ingredients. We have already reported the isolation and physiological activities of 3,4,2′,4′-tetrahydroxy-3′-methoxychalcone-4′-glucoside from *C. lanceolata* L. petals (Tanimoto et al. 2009). In this paper, we wish to report the isolation and physiological activities of the unknown flavonoids of *C. lanceolata* L. petals.

2. Results and discussion

The dried petals of *C. lanceolata* L. were extracted with methanol by soxhlet apparatus. The methanol extract was hydrolysed with 6M hydrochloric acid and column-chromatographed on silica gel with chloroform–methanol (9:1) as elution to give three fractions. The physiological activities of the three fractions were assessed on the basis of diphenylpicrylhydrazyl (DPPH) free radical scavenging assay (Tominaga et al. 2005) and superoxide dismutase (SOD)-like activity assay (Tada et al. 1996). The results are shown in Table 1. The second fraction showed highest antioxidant effect (96.3% scavenging rate) among the three fractions based on DPPH radical scavenging assay. In case of SOD-like activity assay also, the second fraction exhibited highest antioxidant effect (94.1% inhibition rate). Next, attempt to characterise antioxidant compounds in the second fraction was made. The second fraction was re-fractionated with preparative thin layer chromatography (chloroform–methanol, 9:1) to give yellowish orange solid **1** ($R_f = 0.41$) and orange solid **2** ($R_f = 0.28$). . Recrystallisation of solid **1** from methanol was successful and gave citrine needle crystals, while recrystallisation of solid **2** could not be

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Table 1. Antioxidant activities of fractions 1–3.

Fraction	DPPH radical scavenging assay[a] Scavenging rate (%)[b]	SOD-like activity assay[c] Inhibition rate (%)
1	85.5	48.5
2	96.3	94.1
3	94.3	83.9
α-Tocopherol[d]	93.5	–
Ascorbic acid[e]	–	10.8

[a] Sample concentration: 1 mg/ml.
[b] Final concentration: 0.4 mg/ml.
[c] Sample concentration: 1 mg/ml.
[d] Concentration: 1 mM.
[e] Concentration: 0.1 mg/ml.

done. Structures of **1** and **2** were assigned on the basis of their ^{1}H NMR, ^{13}C NMR, H-C COSY NMR and mass spectral data. ^{1}H NMR spectrum of **1** shows a signal for methine proton (dd, $J = 2.9$ and 12.5 Hz) at δ 5.40, two methylene protons (dd, $J = 2.9$ and 16.9 Hz) at δ 2.65 and (dd, $J = 12.6$ and 16.9 Hz) at δ 3.04, respectively. These coupling constants of 2.9 Hz and 12.5 Hz were assigned vicinal coupling constants between two methylene protons and methine proton. The coupling constant between B-ring aromatic protons at δ 6.78 (d, $J = 1.5$ Hz) and δ 6.94 (d, $J = 1.5$ Hz) was assigned para-coupling. Therefore, B-ring was decided as the 3,4-dihydroxyphenyl group, and coupling constant between A-ring aromatic protons at δ 6.59 (d, $J = 8.8$ Hz) and δ 7.42 (d, $J = 8.8$ Hz) was assigned vicinal coupling constant. Additional X-ray analysis of **1** was assigned 7,3′,4′-trihydroxy-8-methoxyflavanone (**1**) (Figures 1 and 2). On the other hand, the ^{1}H NMR spectrum of **2** shows signals for three B-ring aromatic protons at δ 6.84 (d, $J = 8.3$ Hz), 7.24 (dd, $J = 2.0$ and 8.3 Hz) and 7.42 (d, $J = 2.0$ Hz), respectively. Therefore, B-ring of **2** was also assigned 3,4-dihydroxyphenyl group. The two A-ring aromatic protons were observed at δ 6.76 (d, $J = 8.3$ Hz) and 7.32 (d, $J = 8.3$ Hz), respectively. Therefore, A-ring of **2** was similar to that of **1**. Two A-ring aromatic carbons were observed at δ 157.73 and 157.83. Moreover, the olefinic proton was observed at δ 6.63 (s). These results indicated that the structure of **2** was not flavone or isoflavone. The ^{1}H NMR and ^{13}C NMR spectra of **2** were compared with that of 6,7,3′,4′-tetrahydroxyaurone (Sashida et al. 1991) and the synthesised 6,3′,4′-trihydroxy-7-methoxyaurone (for the isolation of leptosin and leptosidin, see: Geissman & Heaton 1943; Seikel & Geissman 1950; Geissman & Mojé 1951; Shimokoriyama & Hattori 1953), which was prepared from 7-methoxy-6-hydroxy-3(*2H*)-benzofuranone and 3,4-di(methoxymethoxy)benzaldehyde using aluminium oxide (Bolek & Gutschow 2005). The ^{13}C NMR spectrum of **2** shows a signal for olefinic carbon at δ 112.30. According to ^{13}C NMR study of aurones (Pelter et al. 1979), a signal for olefinic carbon of *Z*-isomer has been observed at about 110 ppm, whereas that of *E*-isomer shows at about 120 ppm. Therefore, the structure of **2** was assigned as (*Z*)-6,3′,4′-trihydroxy-7-methoxyaurone.

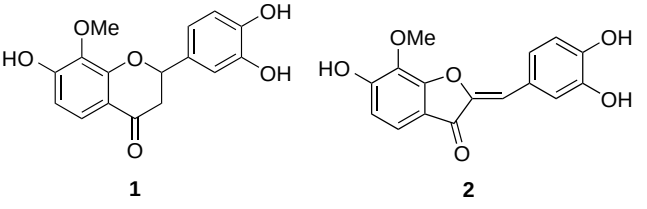

Figure 1. Structures of the isolated compounds of **1** and **2** from *C. lanceolata* L.

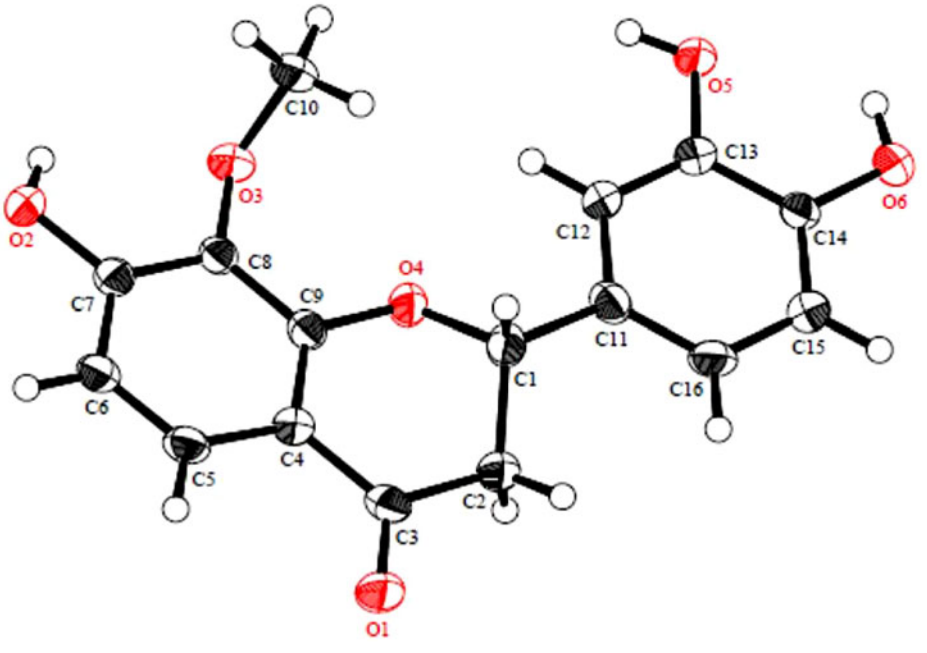

Figure 2. Ortep diagram of compound **1**.

Table 2. Antioxidant activities of compound **1**.

Compound	DPPH radical scavenging assay[a]		SOD-like activity assay[d] Inhibition rate (%)
	Scavenging rate (%)[b]	SC50[c]	
1	94.3	6.3	23.9
α-Tocopherol	94.7	6.8	–
Ascorbic acid	–		10.8

[a] Sample concentration: 0.1 mM.
[b] Final concentration: 0.04 mM.
[c] 50% scavenging concentration (μM).
[d] Sample concentration: 0.1 mg/ml.

DPPH radical scavenging rate and active oxygen inhibition rate of **1** were 94.3% and 23.9%, respectively (Table 2). High DPPH radical scavenging activity of fraction 2 seemed to be strongly contributed by compound **1**.

3. Conclusions

Thus, 7,3′,4′-trihydroxy-8-methoxyflavanone and (*Z*)-6,3′,4′-trihydroxy-7-methoxyaurone were newly isolated from *C. lanceolata* L. petals. The structures of **1** and **2** were successfully clarified on the basis of NMR spectroscopy. Compound **1** showed antioxidant effect (94.3% scavenging rate) equal to or higher than that of α-tocopherol based on DPPH radical scavenging assay. In case of SOD-like activity assay also, compound **1** exhibited higher antioxidant effect (23.9% inhibition rate) than ascorbic acid.

4. Supplementary material

Experimental details relating to this paper are available online. Crystallographic data for the structure of **1** as reported in this paper are deposited with the Cambridge Crystallographic Data Centre, under reference number CCDC 935091. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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