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Two New Acylated Flavanone Glycosides from the Leaves and Branches of Phyllanthus emblica

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Two new acylated flavanone glycosides, (S)-eriodictyol 7-O-(6′-O-trans-p-coumaroyl)-β-D-glucopyranoside (1) and (S)-eriodictyol 7-O-(6′-O-galloyl)-β-D-glucopyranoside (2) were isolated from the leaves and branches of Phyllanthus emblica together with a new phenolic glycoside, 2-(2-methylbutyryl)phloroglucinol 1-O-(6′-O-β-D-apiofuranosyl)-β-D-glucopyranoside (3), as well as 22 known compounds. Their structures were determined by spectral and chemical methods.

Key words Phyllanthus emblica; Euphorbiaceae; acylated flavanone glycoside

Phyllanthus emblica L. (Euphorbiaceae) is a shrub or tree native to subtropical and tropical areas of China, India, Indonesia and the Malay Peninsula. The fruit has been widely used for antinflammatory and antipyretic treatment. The root, leaves and bark are also used for the treatment of indigestion, diarrhea or dysentery, eczema and wart. As a continue...

Results and Discussion

As described in the previous paper, the EtOH extract of the fresh leaves and branches of P. emblica was suspended in water and then extracted with Et2O. The Et2O layer was partitioned between hexane and MeOH, and the MeOH layer was further chromatographed successively over Sephadex LH-20, silica gel, MCI-gel CHP 20P and Chromatorex ODS to afford 1 and 2, as well as 17 known compounds. The known ones were identified as naringenin, eriodictyol, kaempferol, dihydorkempferol, quercetin, naringenin 7-O-glucoside (prunin), naringenin 7-O-(6′-O-galloyl)-glucoside, naringenin 7-O-(6′-O-trans-p-coumaroyl)glucoside, kaempferol 3-O-rhamnoside, quercetin 3-O-rhamnoside, myricetin 3-O-rhamnoside, 2-(2-methylbutyryl)phloroglucinol 1-O-β-D-glucopyranoside (multifidol glucoside), (−)-epigallocatechin 3-O-gallate, 1,2,3,6-tetra-O-, 1,2,4,6-tetra-O-, and 1,2,3,4,5-penta-O-galloyl-β-D-glucose, and decarboxyellagic acid by comparison of the physical and spectral data with literature values.

The water layer was separated first by Sephadex LH-20 column chromatography, and the obtained fraction 1 was subjected to MCI-gel CHP 20P, Chromatorex ODS, and silica gel to afford 3, together with 8 known constituents identified as eriodictyol 7-O-glucoside, kaempferol 3-O-rhamnoside, quercetin 3-O-rhamnoside, myricetin 3-O-rhamnoside, rutin, 3-O-methylellagic acid 4′-O-α-L-rhamnopyranoside and tuberonic acid glucoside. This is the first time that tuberonic acid glucoside was obtained from P. emblica, which has a nycinastic movement.

Compound 1, a yellow amorphous powder, had a molecular formula C_{36}H_{34}O_{14} on the basis of its 13C-NMR spectral data (Table 1), negative-ion FAB-MS [m/z 595, (M− H)] and elemental analysis. The 1H- and 13C-NMR spectra of 1 were closely related to those of eriodictyol 7-O-glucoside except for the appearance of additional signals [δ 7.52, 6.35 (each d, J = 16.0 Hz) and δ 7.49, 6.79 (each 2H, d, J = 8.5 Hz)] arising from a trans-p-coumaroyl group. Acidic hydrolysis of 1 in aqueous MeOH yielded eriodictyol, D-glucose and coumaric acid methyl ester, confirming the components of the molecule 1.

The position of the p-coumaroyl group was determined to be the glucose C-6′ position on the basis of the downfield shift of the glucose C-6′ (δ 63.3) and H-6′ (δ 4.42 (dd, δ J = 2.0, 12.0 Hz) and 4.14 (dd, δ J = 6.5, 12.0 Hz)) by comparison with those of eriodictyol 7-O-glucoside [δ 60.8; δ 4.03, 3.85]. The linkage of the glucopyranosyl moiety at the 7-hydroxyl group of eriodictyol was confirmed by the HMBC correlation between the glucose C-1 and C-7 (δ 156.1). The absolute stereochemistry at C-2 was assigned to be S by observation of a positive Cotton effect at 337 nm and a negative one at 294 nm in the cir...
cicular dichroism (CD) spectrum.\textsuperscript{23,24} Therefore, the structure of 1 was established as (\textit{S})-eridictyol 7-O-(6\textsuperscript{a}-O-trans-p-coumaroyl)-\textit{p}-glucopyranoside.

Compound 2 was obtained as a yellow amorphous powder and gave dark blue coloration with the ferric chloride reagent. Comparison of the \textsuperscript{1}H- and \textsuperscript{13}C-NMR spectral data (Table 1) with those of 1 showed that their structures were very similar except for the presence of a galloyl group in 2 instead of the coumaroyl group in 1. The presence of the galloyl group in 2 could be easily recognized from the characteristic two-proton singlet at \( \delta 6.91 \) and seven \( sp^2 \) carbon signals \( [\delta 145.6 \text{(2C), 138.6, 119.4, 108.8 (2C), 165.9} ] \) in the \textsuperscript{1}H- and \textsuperscript{13}C-NMR spectra. Acidic hydrolysis of 2 yielded eridictyol, glucose and gallic acid, confirming that 2 was a galloyl ester of eridictyol glucoside. The location of the ester group in 2 was characterized as 2-(2-methylbutyryl)phloroglucinol (multifidol), \textsuperscript{12} D-glucose (\textit{p}-D-glucopyranoside). The absolute configuration of C-2 was assigned as \( \textit{S} \) according to the positive Cotton effect at 280 nm in the CD spectrum.\textsuperscript{12}

Up to now, we have studied the chemical constituents of the roots, fruit juice, and leaves and branches of \textit{P. emblica},\textsuperscript{1–5} and obtained a number of polyphenols and sesquiandpenoids which might be the potent bioactive principles of the plant. Studies of the antioxidant and antiproliferative activities of these components are now in progress.

\textbf{Experimental}

The instruments used for obtaining physical data and experimental conditions for chromatography were the same as we described previously.\textsuperscript{2–5}

\textbf{Plant Material} The leaves and branches of \textit{Phyllanthus emblica} were collected at Xishuangbanna, Yunnan, the People’s Republic of China. A voucher specimen is deposited in the Herbarium of Kunming Institute of Botany, Chinese Academy of Sciences.

\textbf{Extraction and Isolation} As described in the previous paper,\textsuperscript{21} the EtOH extract of the fresh leaves and branches (15 kg) of \textit{P. emblica} was suspended in water and then partitioned with Et\textsubscript{2}O. After being concentrated to dryness, the Et\textsubscript{2}O layer (198.0 g) was further partitioned between hexane and MeOH. The MeOH layer (100.34 g) was chromatographed over Sephadex LH-20 (80—100% MeOH, and then 50% acetonitrile) to give four fractions.

\begin{table}
\centering
\caption{\textsuperscript{13}C-NMR Data of Compounds 1—5} \label{tab:nmr_data}
\begin{tabular}{lcccccc}
\hline
Compound & \textsuperscript{13}C-NMR Data & & & & & \\
& & \textsuperscript{1}H & \textsuperscript{3}H & \textsuperscript{4}H & \textsuperscript{5}H & \\
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& & \textsuperscript{1}H & \textsuperscript{3}H & \textsuperscript{4}H & \textsuperscript{5}H & \\
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with 1 M H2SO4 (3 ml) at 80 °C for 3 h. The reaction mixture was extracted with Et2O and the Et2O layer was applied to Sephadex LH-20 and silica gel layer by comparison with the authentic samples.

Chromatorex ODS (40—100% MeOH) and Si gel (CHCl3–MeOH–H2O, 1—5). Fraction 1 was subjected to MCI-gel CHP 20P (0—100% MeOH), and afforded seven fractions (fraction 1—7). A solution of carboxyellagic acid (105 mg), naringenin 7-O-glucopyranoside (75 mg), and 1,2,3,4,6-penta-O-rhamnoside (20 mg), (221 mg), dehydratocaffeic acid (20 mg) in MeOH (1 ml) was treated.

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References and Notes