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The Polyphenolic Constituents of *Engelhardtia serrata* Stem Bark

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Abstract

From the stem bark of *Engelhardtia serrata*, gallic acid (**1**), phlorizine (**2**), (−)-gallocatechin (**3**), ellagic acid (**4**), and 3, 3′-di-*O*-methyl ellagic acid-4-*O*-β-D-xylopyranoside (**5**) were isolated. Their structures were determined by detailed analysis of spectroscopic data and direct comparison with published data. This is the first report of compounds **1**–**5** isolated from *E. serrata*.

Keywords: Polyphenolic constituents, *Engelhardtia serrata*, Juglandaceae.

Introduction

The stem bark of *Engelhardtia* sp. (Juglandaceae) has been applied as an important source of tannins for a long time. Several flavonoids have been isolated from the leaves of *E. chrysolepos* (Kasai et al., 1988). A recent pharmacological study revealed that the flavonoids isolated from leaves of *Engelhardtia* sp. presented various pharmacological properties, such as anti-oxidative, anti-allergic, anti-inflammatory and anti-cancer activity (Mizutani, 1995). The stem bark of *Engelhardtia serrata*, whose leave is used as a popular sweet-tea in the Guangdong province of China, is usually used as a folk medicine for the treatment of rheumatism, diarrhea. Little work has been done on the chemical components of this plant. We report in this paper the isolation and identification of gallic acid, phlorizine, (−)-gallocatechin, ellagic acid, 3, 3′-di-*O*-methyl ellagic acid-4-*O*-β-D-xylopyranoside.

Materials and methods

General experimental procedure

Melting points: Yanaco MP-S3 micro-melting point apparatus, uncorr. IR: Bruker IFS-55 (KBr). Optical rotations: Perkin-Elmer 241 polarimeter. ^{1}H and ^{13}C-NMR: JEOL JNM-GX400 (^{1}H 300 MHz, ^{13}C 75 MHz) spectrometer. MS: Shimadzu QP5050 GC-MS. ODS-ss-1020T (Senshu Scientific Co., Ltd.). Sephadex LH-20 (25–100 μm, Pharmacia). C. C. silica gel H (10–40 μm, Qingdao Haiyang Chemical Factory). TLC: silica gel G (10–40 μm, Qingdao Haiyang Chemical Factory).

Plant material

Stem bark of *E. sterra* was collected in Yunnan province of China, Qishi Sun in October 1998. A voucher specimen (99036) is deposited at the Division of Pharmacognosy, Shenyang Pharmaceutical University.

Extraction and isolation

The air-dried stem bark (3 kg) of *E. sterra* was extracted with C_2H_5OH/H_2O (6 : 4, 2 × 10 L) under refluxing. The extracts were concentrated under reduced pressure to dryness; the residue (315 g) was suspended in 3000 ml water and partitioned with chloroform and ethyl acetate successively. The ethyl acetate extract (8 g) containing the polyphenolic components was subjected to gel filtration with Sephadex LH-20

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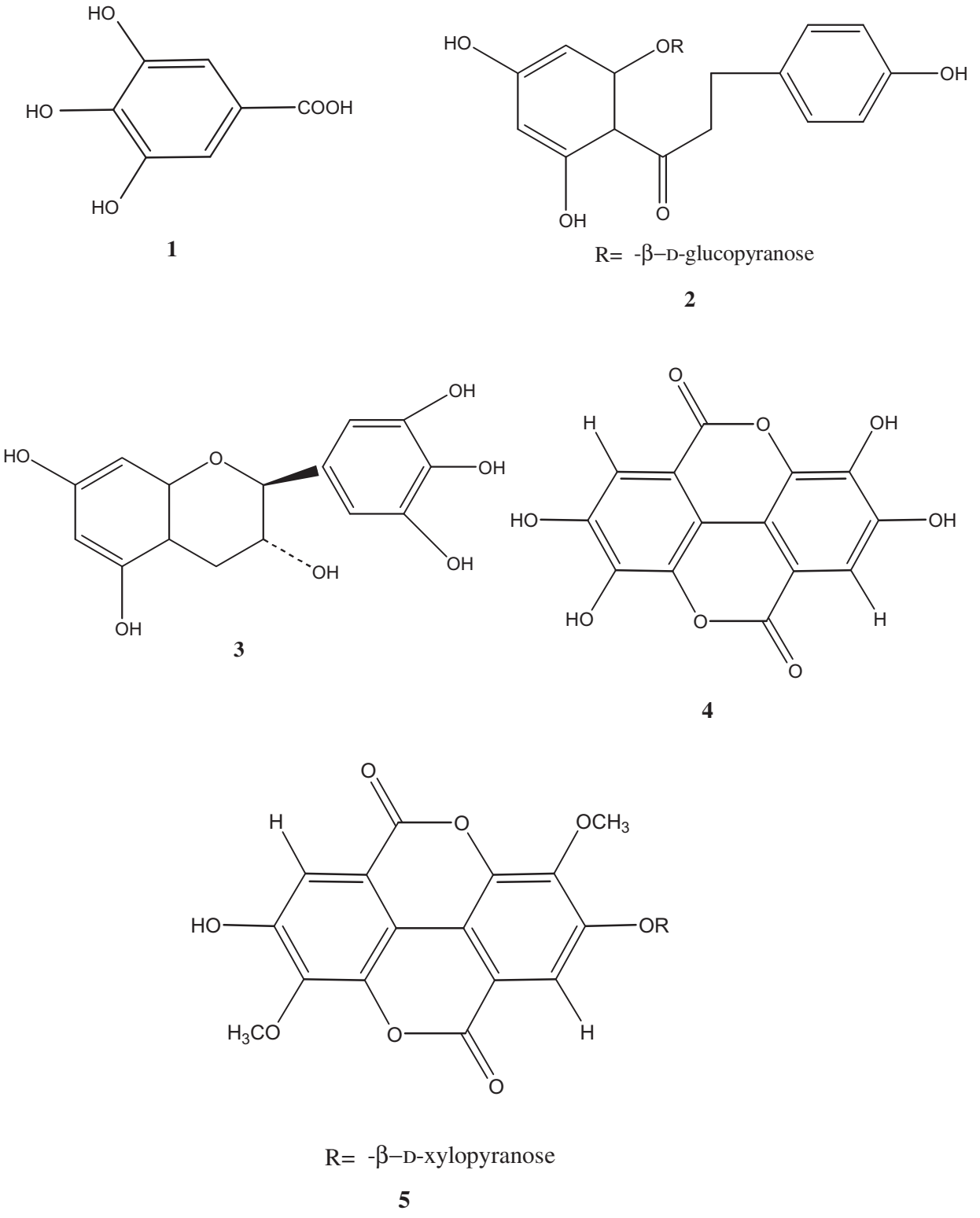

Figure 1. Structure of isolated compounds.

using a mixture of CH_3OH in H_2O (60–100%) to afford 12 fractions according to TLC analysis. Compound **1** (20 mg) was purified from fraction 3 by recrystallization from methanol. Fraction 5 (CH_3OH 60%, 0.5 g) was applied to CC on ODS with CH_3OH/H_2O (3 : 7) to yield compound **2** (8 mg). Compound **3** (100 mg) was isolated from fraction 6 (CH_3OH 70%, 0.6 g) by CC on ODS with CH_3OH/H_2O (2 : 8). Fraction 9 (CH_3OH 70%, 1.0 g) was chromatographed

on silica gel H eluted with CH_3Cl/CH_3OH from 9 : 1 to 6 : 4 to yield compound **4** (9 mg, CH_3Cl/CH_3OH 8 : 2) and compound **5** (12 mg, CH_3Cl/CH_3OH 7 : 3).

Acid hydrolysis

Each compound (2 mg) was heated with HCl 10% (2 ml) in a sealed tube at 100 °C for 4 h. The aglycone was extracted with ethyl acetate; the aqueous layer was concentrated to dryness. The sugar moiety was identified by co-TLC with an authentic sample using solvent system $EtOAc/CH_3OH/H_2O/CH_3COOH$ (65 : 15 : 15 : 25). The plates were sprayed with naphtoresorcinol phosphoric reagent by heating at 100 °C.

Results and discussion

Compounds **1–5** were identified as gallic acid, phlorizine, (−)-gallocatechin, ellagic acid and 3, 3′-di-*O*-methyl ellagic acid-4-*O*-β-D-xylopyranoside by means of spectroscopic analysis and comparison with reported data. This is the first report of compounds **1–5** from the stem bark of *Engelhardtia serrata*.

Compounds **1–5** belong to polyphenolic constituents. They should be regarded as the characteristic components in the stem bark of *E. serrata*. Compounds **1**, **3** and **4** are well-known polyphenolic constituents. Their structures were determined by careful elucidation of NMR data and comparison with literature data (Kanojia et al., 1995; Zhang et al., 1980). Compound **2** is a dihydrochalcone glycoside. Dihydrochalcones in nature are few and of sporadic occurrence, our report served as a new example. Its structure was definitely assigned by careful analysis of its 1-D and 2-D NMR data that were superimposable with literature data (Teusen et al., 1977). The sugar moiety was also confirmed to be β-D glucose by acid hydrolysis and comparison with published data (Gorin & Mazurek, 1975). Compound **5** is hydrolysable tannin possessing an ellagic acid skeleton. When comparing its spectrum with that of 3, 3′, 4-tri-*O*-methyl ellagic acid, great similarity was observed except for the sugar part (Liu et al., 1992). The presence of β-D-xylopyranose was confirmed by acid hydrolysis and comparison with literature data (Gorin & Mazurek, 1975). The entire structure was definitely constructed by detailed analysis of its 2-D NMR data.

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