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FLAVONOL GLYCOSIDES FROM THE FRUITS OF *RHAMUS LEPTOPHYLLA*

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Key Word Index—*Rhamnus leptophylla*; Rhamnaceae; Chinese folk medicine; flavonol glycosides; multiflorin A; alaternin; kaempferol-3-*O*-β-rhamninoside.

Abstract—From the fruits of *Rhamnus leptophylla*, three flavonol glycosides were isolated in high yields and identified as multiflorin A, kaempferol-3-*O*-β-rhamninoside and alaternin, respectively. The isolation of multiflorin A is significant, since this plant is used as a purgative in China.

INTRODUCTION

Rhamnus leptophylla Schneid. (Rhamnaceae), a tall shrub, is widely grown from central to southern China and is commonly found on mountain slopes, in valleys and by the roadside. Leaves, roots and fruits of this plant have been used as a purgative, digestive and diuretic in China. We now report the isolation and identification of flavonol glycosides from the fuits of this plant (Chinese name: jiang li mu zi).

RESULTS AND DISCUSSION

The methanolic extract of the dried fruits was chromatographed, as described in the Expermmental, affording three flavonol glycosides (**1**–**3**) in yields of 1.7, 10.0 and 1.3%, respectively. Compounds **1** and **3** were obtained as yellow powders, and identified as multiflorin A and alaternin (=catharticin), respectively, by comparison of spectral and physical data with those in the literature [1, 2].

Compound **2**, a yellow powder, was identified as kaempferol-3-*O*-rhamninoside, i.e. kaempferol-3-*O*-α-rhamnopyranosyl-(1→3)-α-rhamnopyranosyl-(1→6)-β-galactopyranoside, which has already been isolated from *Rhamnus alaternus* and *R. catharticus* [2]. The identification was based on the comparison of ^{13}C NMR spectrum with that of the reported data as well as on the methylation analysis [3, 4] and MS of the peracetate.

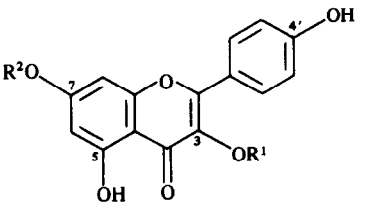
Multiflorin A (**1**) was previously isolated from purgative drugs based on the fruits of *Rosa multiflora* Thunb. and the flowers of *Prunus percica Batsch.* and the potent purgative activity of **1** was reported [5–7]. Accordingly, the use of the fruits 'jiang li mu zi' as a purgative in China, can be rationalized by the presence of compound **1**.

EXPERIMENTAL

Plant material. Fruit of *Rhamnus leptophylla* Schneid. were collected in the forest (700–1200 m above sea-level) of Mt. Emei, Sichuan, China in 1985.

Extraction and isolation. Dried fruits (100 g) were defatted by extraction with hot n-C_6H_{12} and the residues were extracted with hot MeOH. After removal of solvents by evapn, the MeOH extract (26 g) was chromatographed on silica gel ($CHCl_3$–MeOH–H_2O 30:10:1 homogeneous) to give five fractions, Frs 1–5. Fr. 2 was separated by CC on silica gel ($CHCl_3$–MeOH 5:1), LiChroprep RP-8 (Merck) (55% aq. MeOH) and then by HPLC on TSK-gel ODS-120T (TOSOH, Tokyo, Japan) (55% aq. MeOH) to yield **1** (1.7%). CC of Fr. 4 on LiChroprep RP-8 (55% aq. MeOH) gave **2**. CC of Fr. 5 on silica gel ($CHCl_3$–MeOH–H_2O 30:10:1 and 10:5:1 each homogeneous) also gave **2**. Total yield of **2** was 10.0%. Fr. 3 was purified by CC on silica gel ($CHCl_3$–MeOH–H_2O 30:10:1) and then CC on Sephadex LH-20 (MeOH) to yield **3** (1.3%).

Multiflorin A (**1**). A yellow powder, Mg–HCl test: positive, UV λ_{max}^{MeOH} nm 264, 342 ($\log\varepsilon$ 4.8, 3.0, respectively). $[\alpha]_D^{25}$ −131.5° (MeOH, *c* 1.17).



	R¹	R²
1	α-Rha(1→4)β-Glc(1→6)-Ac,	H
2	β-Gal(1→6)α-Rha(1→3)α-Rha,	H
3	β-Gal(1→6)α-Rha(1→3)α-Rha,	Me

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Kaempferol-3-O-β-*rhamninoside* (**2**). A yellow powder, UV λ_{max}^{MeOH} nm 266 350 (log ε 4.3, 4.2, respectively), $[\alpha]_D^{22}$ −42.7° (MeOH, *c* 0.99), Mg–HCl test: positive, MS (peracetate): *m/z* 791 [(Gal-Rha-Rha)Ac_8]$^+$, 503 [(Rha-Rha)Ac_5]$^+$ and 273 [(Rha)-Ac_3]$^+$. Methylation analysis of the sugar moiety was carried out according to the method of refs [3, 4].

Rhamnocitrin-3-O-β-*rhamninoside* (**3**). A yellow powder, Mg–HCl test: positive, $[\alpha]_D^{13}$ −45.1° (MeOH, *c* 0.71).

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A BENZOFURAN FROM *AGERATUM HOUSTONIANUM*

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Key Word Index—*Ageratum houstonianum*; Asteraceae; benzofuran; structure elucidation.

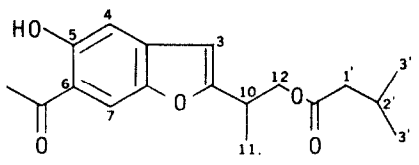
Abstract—A new benzofuran was isolated from roots of *Ageratum houstonianum* that was characterized by the presence of the acetyl substituent at C-6 and not at C-5 as usually encountered. The structure elucidation is described.

INTRODUCTION

Ageratum houstonianum Mill. (tribe Eupatorieae) has attracted considerable attention due to the presence of the chromene derivatives precocene I and II that act as antijuvenile hormones against a plethora of susceptible insects [1]. Whereas the leaves and flowering heads of *A. houstonianum* are the favoured organs of precocene accumulation, the roots are distinguished by the accumulation of benzofuran derivatives [2]. Recently [2] we have reported on the structure elucidation of several benzofurans from roots of *A. houstonianum* that were distinguished by the presence of the acetyl substituent at C-6 of the aromatic ring and not at C-5 as previously reported [4] and usually encountered with benzofurans from species of the Asteraceae [5]. In continuation of our studies on *A. houstonianum*, we have now isolated a further unusual benzofuran derivative from roots and wish to report on the structure elucidation.

RESULTS AND DISCUSSION

The new benzofuran (**1**) exhibited a ^{1}H NMR spectrum typical for a acetylbenzofuran as indicated by the signal of



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