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Separation and Identification of Thellungianol from Thellung Pimpinella (*Pimpinella thellungiana*)

Xue Kongfang, Ma Pei (Beijing Institute of Pharmaceutical Industry, Beijing 100020)
Wang Jingzun, Wang Lei (Beijing Institute of Microchemistry)

Abstract A new cyclohexanol derivative was isolated from the n-butanol extract of the whole plant of *Pimpinella thellungiana* Walff.. Its structure was elucidated on the basis of spectroscopic analysis (UV, IR, MS, ^{1}H, ^{13}C NMR, DEPT and ^{1}H-^{1}H 2 D-COSY) as 1-butyl-3, 4, 5-trihydroxy-cyclohexanol (Ⅱ). Another known organic acid, shikimic acid (Ⅰ) was isolated for the first time from this fraction.

Key Words *Pimpinella thellungiana* cyclohexanol 1-butyl-3, 4, 5-trihydroxy-cyclohexanol shikimic acid

羊红膻根化学成分的研究
Ⅲ. 羊红膻素 F 的分离和鉴定

陕西省中医药研究院中药研究所(西安 710003) 乔博灵* 王长岱 李富贤 米彩峰 石惠丽 高山岛纯子**

摘 要 从草药羊红膻根中又分得 2 个化合物,经光谱解析(UV, IR, ^{1}H、^{13}CNMR, DEPT 及 ^{1}H-^{1}HCOSY, ^{1}H-^{13}CCOSY),确定这 2 个化合物的结构为:4-羟基-丙烯苯-(2-甲基丁酸)酯(Ⅰ),2-羟基-5-甲氧基-丙烯苯-(2-甲基丁酸)酯(Ⅱ)。Ⅰ为新化合物,定名为羊红膻素 F。Ⅱ为首次从本植物中分得。

关键词 羊红膻根 4-羟基-丙烯苯-(2-甲基丁酸)酯

羊红膻为伞形科茴芹属植物缺刻叶茴芹 *Pimpinella thellungiana* Wolff.。我们从羊红膻根中已分得多个成分,并已相继报道[1,2]。此次报道又分离并鉴定的 2 个化合物,经 UV、IR、^{1}HNMR、^{13}CNMR 等光谱测定,确定化合物Ⅰ为 4-羟基-丙烯苯-(2-甲基丁酸)酯,定名为羊红膻素 F,此为一新化合物;化合物Ⅱ为 2-羟基-5-甲氧基-丙烯苯-(2-甲基丁酸)酯,此成分系首次从本植物中分得。其化学结构式见图 1。

化合物Ⅰ为无色液体。质谱分子离子峰为 218,DEPT 谱显示它有 3 个甲基,1 个亚甲基,7 个次甲基,结合元素分析确定其分子式为 $C_{14}H_{18}O_2$。比较Ⅰ与Ⅱ的核磁氢谱,可以发现,Ⅰ的核磁氢谱上无甲氧基信号,另苯环氢的信号不同于Ⅱ,其它信号均与Ⅱ完全相同,Ⅰ和Ⅱ的核磁碳谱也显示相同的情况。Ⅰ的 ^{1}H-NMR 谱 δ7.0(2 H, dd, J = 8.7, 1.8 Hz), δ7.3(2 H, dd, J = 8.7, 1.8 Hz)说明苯环上的取代为对位取代,因而我们推定化合物

* Address: Qiao boling, Institute of Chinese Materia Medica, Shanxi Academy of Traditional Chinese Medicine, Xinan
** 日本三菱化成综合研究所

Ⅰ有与Ⅱ相似的结构，只缺甲氧基，而且苯环取代为对位。而化合物Ⅱ的光谱，显示了它为已知结构成分，即2-羟基-5-甲氧基-丙烯苯-(2-甲基丁酸)酯，与文献[3]一致。综上，推定化合物Ⅰ的结构应为4-羟基-丙烯苯-(2-甲基丁酸)酯。此成分已通过合成得到证实。

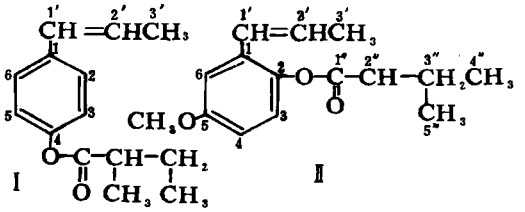

图1　化合物Ⅰ和Ⅱ的化学结构式

1　仪器与试剂

紫外用Shimadzu UV-260型紫外光谱测定。红外用JASCOA-102型红外光谱仪测定。核磁用Bruker AC-250 250MHz FT-NMR核磁共振仪测定。质谱用日本岛津GCMS-QP1000色质联用仪测定。所用试剂均为日本产品。实验材料由陕西省黄龙县药材公司订购。

2　提取与分离

将羊红膻根粉碎成粗粉，以石油醚冷浸3次，7 d1次。回收石油醚，石油醚提取物进行水蒸汽蒸馏，制得挥发油部位。挥发油部位上硅胶柱，以正己烷-乙酸乙酯不同比例洗脱，19∶1流份再上硅胶柱，以正己烷-二氯甲烷-甲醇不同比例洗脱，二氯甲烷流份经ODS柱，1∶9(H_2O-MeOH)流份可得化合物Ⅰ；1∶8(H_2O-MeOH)流份经制备薄层板展开，可得化合物Ⅱ。

3　结构鉴定

化合物Ⅰ：无色液体。分子式$C_{14}H_{18}O_2$。^{1}H-NMR($CDCl_3$，TMS内标)δppm：7.30(2 H，dd，J＝8.7，1.8 Hz，$C_{3,5}$-H)，7.00(2 H，dd，J＝8.7，1.8 Hz，$C_{2,6}$-H)，6.18(1 H，m，$C_{2'}$-H)，6.29(1 H，d，J＝9.5 Hz，$C_{1'}$-H)，2.62(1 H，m，$C_{2''}$-H)，1.67(2 H，m，$C_{3''}$-H)，1.03(3 H，t，$C_{4''}$-H)，1.31(3 H，d，$C_{5''}$-H)，1.86(3 H，d，J＝6.4 Hz，$C_{3'}$-H)。^{13}C-NMR($CDCl_3$，TMS内标)δppm：130.06(C_1)，125.06($C_{2,6}$)，135.50($C_{3,5}$)，149.53(C_4)，126.55($C_{1'}$)，121.41($C_{2'}$)，18.32($C_{3'}$)，175.04($C_{1''}$)，41.04($C_{2''}$)，26.72($C_{3''}$)，11.50($C_{4''}$)，16.46($C_{5''}$)。其归属由^{1}H-^{1}H COSY，^{1}H-^{13}C COSY得到确定。

化合物Ⅱ：无色液状。分子式$C_{15}H_{20}O_3$。UVλ_{max}^{MeOH}nm：245(sh)。^{1}H-NMR($CDCl_3$，TMS内标)δppm：6.90(1 H，d，J＝8.8 Hz，C_3-H)，6.78(1 H，dd，J＝8.8，2.9 Hz，C_4-H)，6.99(1 H，d，J＝2.9 Hz，C_6-H)，6.29(1 H，d，J＝9.5 Hz，$C_{1'}$-H)，6.18(1 H，m，$C_{2'}$-H)，1.86(3 H，d，J＝6.4 Hz，$C_{3'}$-H)，2.62(1 H，m，$C_{2''}$-H)，1.67(2 H，m，$C_{3''}$-H)，1.03(3 H，t，$C_{4''}$-H)，1.31(3 H，d，$C_{5''}$-H)，3.76(3 H，s，-OMe)。^{13}C-NMR($CDCl_3$，TMS内标)δppm：131.16(C_1)，141.26(C_2)，122.99(C_3)，113.07(C_4)，157.17(C_5)，110.84(C_6)，128.19($C_{1'}$)，124.40($C_{2'}$)，18.61($C_{3'}$)，175.14($C_{1''}$)，41.06($C_{2''}$)，26.63($C_{3''}$)，11.51($C_{4''}$)，16.61($C_{5''}$)，55.33(-OMe)。其归属由^{1}H-^{1}H COSY，^{1}H-^{13}C COSY得到确定，且以上数据与文献[3,4]报道一致。

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Studies on the Chemical Constituents of the Root of Thellung Pimpinella (*Pimpinella thellungiana*) (Ⅱ): Separation and Identification of Thellungianin F

Qiao Boling，Wang Changdai，Li Fuxian，*et al* (Institute of Chinese Materia Medica，Shanxi Academy of Traditional Chinese Medicine，Xian 710003)

Abstract　Two compounds were isolated from the root of *Pimpinella thellungiana* Wolff.. On the ba-

sis of spectral analysis (UV, IR, ^{1}HNMR, ^{13}CNMR, DEPT, ^{1}H-^{1}H COSY, ^{1}H-^{13}C COSY), they were identified as 4-propenyl-phenyl-2-methyl butanoate(Ⅰ) and 4-methoxy-1-propenyl-phenyl-2-methyl butanoate(Ⅱ). Ⅰ is a new compound named thellungianin F. Ⅱ was obtained from this plant for the first time.

Key Words *Pimpinella thellungiana* thellungianin F

A New Indole Derivative Isolated from the Root of Tuber Fleeceflower(*Polygonum multiflorum*)

Yang Xiuwei* Gu Zheming** Ma Chaomei** Masao Hattori*** Tsuneo Namba***

National Research Laboratory of Natural and Biomimetic Drugs, Beijing Medical University(100083)

Abstract From the root of *Polygonum multiflorum* Thunb., a new indole derivative, named Indole-3(L-α-amino-α-hydroxy propionic acid)methyl ester(Ⅺ), was isolated together with the ten known compounds, chrysophanol(Ⅰ), physcione(Ⅱ), emodin(Ⅲ), citreorosein(Ⅳ), chrysophanol 8-O-β-D-glucopyranoside(Ⅴ), physcione 8-O-β-D-glucopyranoside(Ⅵ), emodin 8-O-β-D-glucopyranoside(Ⅶ), torachrysone 8-O-β-D-glucopyranoside(Ⅷ), 2, 3, 5, 4′-tetrahydroxystilbene2-O-β-D-glucopyranoside(Ⅸ), and methylgallate(Ⅹ). Their structures were determined by spectroscopic means. These anthraquinone compounds and aloe-emodin(Ⅻ), rhein(ⅩⅢ), aloe-emodin 8-O-β-D-glucopyranoside(ⅩⅣ), chrysophanol 8-O-β-D-(6′-O-malonyl)glucopyranoside(ⅩⅤ), sennoside A (ⅩⅥ) and sennoside B(ⅩⅦ) had no inhibitory effect against recombinant HIV-1 protease at concentration of 100 μmol/L in vitro.

Key Words Root of *Polygonum multiflorum* Indole derivative Indole-3(L-α-amino-α-hydroxy propionic acid)methyl ester Recombinant HIV-1 protease

1 Introduction

The root of *Polygonum multiflorum* Thunb. (*Polygonaceae*), He shou wu, is a tonic drug, invigorate the liver and kidney, tonifying the kidney, and for treatment of yin-deficiency of liver and kidney, vertigo, insomnia, lassitude of the loins and legs in Chinese medicine[1]. Our pharmacological results showed that five-day successive *po* administration of an EtOH extract of root of *P. multiflorum* can inhibit significantly the activity of monoamine oxidase B(MAO-B), though the extract showed no activity for MAO-A in male senescence-accelerated mice[2].

As a part of our chemical investigations on the active constituents from natural sources, we report chemical investigation of the root of *P. multiflorum* which led to the isolation of eleven compounds from the EtOAc and n-BuOH soluble fractions of the ethanolic extract, and inhibitory effects of some anthraquinone compounds against recombinant(REC) HIV-1 protease in *vitro*.

2 Results and Discussion

An ethanolic extract of the root of *P. multiflorum* was fractionated into EtOAc- and n-BuOH-soluble fractions. Repeated column chromatography of these fractions led to the isolation of eleven compounds. One new indole derivitive was isolated and identified as Indole-3(L-α-amino-α-hydroxy propionic acid) methyl ester (Ⅺ). Ten known

* 北京医科大学天然药物及仿生药物国家重点实验室(北京, 100083)
* * Chengdu College of Traditional Chinese Medicine, Chengdu 610075, China
* * * Research Institute for Wakan-Yaku, Toyama Medical and Pharmaceutical University, 2630 Sugitani, Toyama 930-01, Japan