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Chemical Constituents of *Plumbago zeylanica L.*

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Abstract. To investigate the chemical constituents from the Plumbago zeylanica L. the chemical constituents were isolated by various column chromatographic methods and their structures were elucidated as plumbazeylanone(1), plumbagic acid(2), β-sitosterol(3), lupeol(4), lup-20(29)-en-3, 21-dione(5), norcanelilline(6), 3-O-glucopyranosyl plumbagicacid methylester(7), uridine(8), daucosterol(9).Compound 4-6 and 8 were first time were isolated from this plant for the first time.

Introduction

Plumbago zeylanica L.,a plant in the *Plumbaginaceae* family, is mainly distributed in regions of East Asia.this plant have been traditionally used for the treatment of rheumatic pain, menostasis, carbuncle, pruitus, apoplexy hemiplegia and bumping in China [1].Its early phytochemical work on this palnt has resulted in the isolation of some compounds,including various types of flavonoids, coumarines and triterpenoids coumarins[2], naphthoquinones[3] triterpenoids and steroids[4]. In order to isolate the activity compounds, the Whole plant of *Plumbago zeylanica L* were chosen for more detailed investigation of its chemical constituents. In this paper, nine compounds were isolated from *Plumbago zeylanica L* .On the basis of the spectral and chemical properties,they were identified as plumbazeylanone(1),plumbagic acid(2),β-sitosterol (3),lupeol(4),lup-20(29)-en-3,21-dione(5),norcanelilline(6),3-O-glucopyranosyl- -plumbagicacid methylester(7),uridine(8),daucosterol(9). Compound 4,5,6 and 8 were first time were isolated from this plant for the first time.

Experimental

Apparatus and reagents:NMR spectra were recorded on Bruker AVANCE DRX500 (500 MHz for^{1}H and 125 MHz for^{13}C) spectrometer with TMS as internal standard. ESI-MS was performed on an Agilent 1100 Series LC/MSD Trap mass spectrometer. Melting points were determined on an X-4 micromelting apparatus and were uncorrected. Silica gel(200-300mesh,Qingdao),ODS (50 μm,YMC) and Sephadex LH-20 (Pharmacia) were used for column chromatography.

Plant material: The dried whole plant of *P. zeylanica* were collected in August 2009 YunNan province, China . The identification of the plant was performed by Pro.Tian Jun-Xue. A voucher specimen (No. HH1543) of this collection has been deposited at Department of Chemistry, HongHe University, YunNan China .

Extraction and Isolation: The air-dried whole plants (5kg) of *P. zeylanica* were extracted three times with 80 % EtOH , each time three hours. The EtOH extract was concentrated under vacuum to yield the crude extract (110 g). The crude extract was suspended in water and then successively extracted with petroleum ether (3×2L), EtOAc(3×2L), and n-BuOH (3×2L), respectively. The EtOAc solution was concentrated and given a residue (31 g), which was separated by a silica gel column chromatography using gradient mixtures of CHCl3-MeOH (100:0-0:100) as eluents to yield eleven fractions. Then the eleven fractions were further purified by silica gel (mesh 200-300) and Sephadex LH-20 column chromatography to yield compounds 1 (21 mg), 2(27 mg), 3 (33 mg), 4 (19 mg), 5 (14 mg), 6 (11 mg), 7 (15mg), 8 (20 mg), 9 (75 mg) ,respectively.

Identification

Compound 1: Red needles.ESI/MS m/z 189$[M+H]^+$.^{1}H-NMR (500MHz,$CDCl_3$)δ:2.21(3H,s,2-CH_3),6.77(1H,s,H-3),7.26(1H,m,H-6), 7.62(2H,m,H-7,8),11.94(1H,s,OH). Compound 1 was characterized as plumbazey--lanone by comparison of its physical and spectral data with the literature [5].

Compound 2:yellow oily matter. ESI-MS m/z 225$[M+H]^+$,^{1}H-NMR (500MHz, $CDCl_3$)δ: 1.28 (3H, m, 3-CH_3), 2.53(1H, m, α-H2), 3.02(1H, m, β-H2), 3.87(1H, m,H-3), 6.79(1H, m,H-5'),7.09 (1H, d, J=6.8Hz, H-4'),7.28 (1H, d, J = 8.2Hz, H-6'), 12.46 (1H, s,COOH).^{13}C-NMR($CDCl_3$)δ:178.3(C-1),37.4(C-2),37.2 (C-3),209.5(C-4),117.4(C-1'),149.6(C-2'),146.5(C-3'),121.6(C-4'),121.2(C-5')120.7(C-6'),19.1(3-CH_3).compound 2 was characterized as plumbagic acid by compareison of its physical and spectral data with the literature [6].

Compound3： White needle crystals, mp 135-137°C. Compound3 showed the same color and equal R_f value to the standard of β-sitosterol using TLC and eluted with different developing solvent systems, 3 was identified as β-sitosterol.

Compound4： White amorphous powder, ^{1}H-NMR(500 MHz, $CDCl_3$)δ: 0.79 (3H, s, H-24), 0.81 (3H, s,H-25), 0.82 (3H, s, H-23), 0.98 (3H,s, H-26), 1.01 (3H, s, H-27),1.02 (3H, s, H-28), 1.70 (3H, s, H-30), 2.38(1H, m, H-2), 3.22 (1H, dd, J = 11.2, 6.0 Hz, H-2), 4.59 (1H, d, J = 2.1 Hz, H-30), 4.72 (1H,d, J = 2.1 Hz, H-30).^{13}C NMR (125 MHz, $CDCl_3$) δ:38.9 (C-1), 27.7 (C-2), 79.2 (C-3), 39.1 (C-4), 55.5(C-5), 18.7 (C-6), 34.5 (C-7), 40.3 (C-8), 50.5 (C-9),37.2 (C-10), 21.2 (C-11), 25.3 (C-12), 38.0 (C-13), 42.6(C-14), 27.1 (C-15), 35.7 (C-16), 43.5 (C-17), 48.8(C-18), 48.6 (C-19), 151.7 (C-20), 30.4 (C-21), 40.7(C-22), 28.6 (C-23), 15.7 (C-24), 16.0 (C-25), 16.1(C-26), 14.9 (C-27), 18.3 (C-28), 109.7 (C-29), 19.8(C-30). Compound 4 was characterized as lupeol by comparison of its physical and spectral data with the literature[7].

Compound5: Colorless crystals. ^{1}H-NMR (500 MHz ,$CDCl_3$) δ:0.90 (3H,s, H-24), 0.94 (3H, s, H-23), 1.02 (3H, s, H-25), 1.05 (3H, s, H-26), 1.08 (3H, s, H-27),1.10 (3H, s, H-28), 4.79 (1H,s,H-30),4.97(1H,s,H-30′),3.81(1H,d,J=13.7Hz,H-19), 1.69(3H,s,H-29).^{13}C-NMR(125MHz ,CDCl3)δ:39.7(C-1),34.9(C-2),217.4(C-3),47.1(C-4), 55.4 (C-5), 18.5 (C-6), 33.4 (C-7) , 41.3 (C-8), 49.4 (C-9), 37.2 (C-10), 19.3(C-11), 26.7(C-12), 37.2 (C-13), 42.5 (C-14), 26.9 (C-15), 34.3 (C-16), 37.9 (C-17), 47.3 (C-18), 59.5 (C-19), 143.6 (C-20), 218.1 (C-21), 55.1 (C-22), 21.3(C-23), 25.5 (C-24), 15.5(C-25), 15.8 (C-26), 14.5 (C-27) , 21.4 (C-28), 20.6(C-29), 115.3 (C-30) . Compound 5 was characterized as lup-20(29)-en-3,21-dione by comparison of its physical and spectral data with the literature[8].

Compound 6： White needles crystals, ESI-MS m/z 286 $[M+H]^+$.^{1}H NMR (500 MHz, CD_3OD) δ:2.73 (1H, m, H-9), 3.05, 3.21 (2H,m, H-3), 3.27, 3.44 (2H,m, H-11), 3.87 (3H, s, -OCH3), 4.59 (1H, dd, J = 6.2, 9.6Hz, H-7), 6.65 (1H, s, H-13), 6.74 (1H, d, J = 6.2 Hz, H-15),6.77 (1H, dd, J = 6.2, 6.8 Hz, H-16), 6.83 (1H, d, J =6.8Hz,H-17), 7.10(1H,s,H-5),7.16(1H,s,H-8).^{13}C-NMR(125MHz,CD3OD) δ:58.5(C-1), 42.5(C-2), 31.2(C-3), 127.9(C-4), 112.7 (C-5), 141.5 (C-6), 118.3 (C-7), 158.9 (C-8), 116.6 (C-9), 132.7(C-10),121.8(C-11),57.7(C-12).Compound 6 was characterized as norcanelilline by comparison of its physical and spectral data with the literature[9].

Compound7: White amorphous powder ,ESI-MS m/z 401 $[M+H]^+$. ^{1}H NMR (500 MHz, CD_3OD) δ:1.27 (3H, d, J =7.2 Hz, Me-3), 2.51(1H, dd, J =16.8, 6.1 Hz, Ha-2), 2.95 (1H, dd, J=16.8, 8.5 Hz, Hb-2), 3.71 (3H, s, -OMe), 3.98 (1H, m, H-3),4.87 (2H, d, J=6.5Hz, H-1''), 6.90 (1H, m, H-5'), 7.33 (1H, d, J=8.2Hz, H-4'), 7.67 (1H, d, J=8.2Hz,H-6').^{13}C-NMR (125 MHz ,CD_3OD) δ:19.1 (3-CH_3), 38.8(C-2), 9.3 (C-3), 53.2 (–OCH3), 62.9 (C-1''), 71.7 (C-4''), 75.2(C-2''), 77.9 (C-3''), 78.5 (C-5''), 103.7 (C-1''), 119.6(C-5'), 121.5(C-1'), 123.9 (C-4'), 125.7 (C-6'), 147.6(C-3'), 154.3 (C-2'), 173.7 (C-1), 209.8 (C-4). Compound 7 was characterized as 3-O-glucopyranosylplumbagic acid methylester by comparison of its physical and spectral data with the literature[2].

Compound 8: White amorphous powder. ^{1}H-NMR (500 MHz, C_6D_5 N) δ:8.73(1H, d, J= 8.0 Hz，H-6)，5.67(1H, d, J=8.0 Hz, H-5), 6.85 (1H, H-1). ^{13}C-NMR (125 MHz , C_6D_5N) δ: 61.5(C-5), 72.0 ,(C-2), 75.8(C-3), 86.9(C-4), 90.9(C-1), 102.7(C-5), 142.2(C-6), 153.1(C-2), 163.9(C-4). Compound 8 was characterized as uridine by comparison of its physical and spectral data with the literature[10].

Compound 9： White amorphous powder, mp 294-296°C. Compound 9 showed the same color and equal R_f value to the standard of daucosterol using TLC and eluted with different developing solvent systems. 9 was identified as daucosterol.

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