Investigation on the whole plant of *Ceratostigma willmottianum* for bioactive compounds has led to the identification of 15 compounds. Two of them were characterized as new compounds, plumbolactones A (5-(2,3-dihydroxyphenyl)dihydro-4-methyl-2(3H)-furanone, 1) and B (3-(1,2-dihydroxypropyl)-5-hydroxy-1(3H)-isobenzofuranone, 2), while the other 13 were known compounds, plumbagic acid (3), isoshinanolone, epiisoshinanolone, plumbagin (4), N-trans-caffeoyltyramine, N-trans-feruloyltyramine, myricetin, quercetin, tricetin 3',5'-dimethyl ether, vanillic acid, syringic acid, caffeic acid, and 6,7-dihydroxycoumarin. The structures of the new compounds were assigned by 2D-NMR techniques.

*Ceratostigma willmottianum* Stapf (Plumbaginaceae) is a perennial herb distributed in Yunnan province of China. It is used as a folk medicine to treat rheumatism, traumatic injury, and parotitis. The chemical constituents of this plant have not been investigated before. This paper describes the isolation and structure elucidation of two new compounds plumbolactones A (5-(2,3-dihydroxyphenyl)dihydro-4-methyl-2(3H)-furanone, 1) and B (3-(1,2-dihydroxypropyl)-5-hydroxy-1(3H)-isobenzofuranone, 2), as well as 13 known compounds, plumbagic acid (3), isoshinanolone, epiisoshinanolone, plumbagin (4), N-trans-caffeoyltyramine, N-trans-feruloyltyramine, myricetin, quercetin, tricetin 3',5'-dimethyl ether, vanillic acid, syringic acid, caffeic acid, and 6,7-dihydroxycoumarin.

**Results and Discussion**

Plumbolactone A (1), C_{11}H_{12}O_{4} (HRMS, found 208.0706, requires 208.0732), was crystallized from n-hexane–acetone as small colorless prisms, $\alpha^2_{D} = -21.39^\circ$ (c 0.03, in CH$_3$OH). The mass spectrum of plumbolactone A (1) contained an apparent molecular ion at m/z 208, corresponding to a molecular formula C$_{11}$H$_{12}$O$_{4}$. The $^{13}$C NMR spectrum exhibited 11 resonance signals, providing further support for the assigned molecular formula. Observation of the $^{13}$C NMR resonances for six aromatic and one carbonyl carbon (177.18 ppm) accounted for a total of 5 degrees of unsaturation. The remaining 1 degree of unsaturation was assumed for the presence of one additional ring system. The IR spectrum indicated the presence of hydroxyl (3360 and 3260 cm$^{-1}$) and carbonyl carbon (1710 cm$^{-1}$) groups. The $^1$H NMR spectrum of compounds 1 was performed in C$_5$D$_5$N to give an excellent result. The aromatic region of the $^1$H NMR spectrum displayed a classic pattern for a 1,2,3-trisubstituted aromatic ring [6.87 (1H, t, $J = 7.9$ Hz), 7.03 (1H, dd, J = 7.9, 1.5 Hz), 7.16 (1H, dd, J = 7.9, 1.5 Hz)]. A four-carbon subunit was identified as $-\text{CHCH(CH}_3\text{)CH}_2\text{COO}$ as the side chain of plumbagic acid (3) from this plant, and that the nonequivalent methylene signals appears at $\delta$ 2.87 and 2.36 ppm led to a suggestion that the carbonyl carbon was possibly connected to the methylene to form a five-carbon subunit $-\text{CHCH(CH}_3\text{)CH}_2\text{COO}$ as the side chain of plumbagic acid (3). This conclusion was confirmed by the correlation between the methane proton signals and the aromatic ring in the COLOC experiment. The COLOC experiment also showed the correlation between H-5 and C-2, indicating the presence of a five-membered lactone ring. The final connection between the aromatic ring and the five-membered lactone ring was determined on the basis of the correlations of H-5 with C-7 and C-8, leading to a planar structure assignment as shown for compound 1. The relative configuration...
ration of 1 was assigned on the basis of the NOESY spectrum. The aromatic ring and the methyl group were assigned a cis-configuration based on the strong correlations of C-4-CH₃ protons with the aromatic protons H-11 and H-12. The H-3α and H-3β were also assigned by NOESY to the signals at δ 2.36 and 2.87 ppm, respectively, judging from the fact that the H-3/ has stronger correlation with C-4-CH₃ than H-3α does. The IR absorption band of a five-membered lactone ring normally appears at 1780–1760 cm⁻¹. Compound 1 displayed an absorption band at 1710 cm⁻¹, indicating that the ester group was possibly hydrogen bonded with the hydroxyl groups on the aromatic ring, since the hydrogen bonding to a carbonyl group will cause a shift to lower frequency by 40–60 cm⁻¹. The structure of plumbolactone A was thus assigned as 1, but its absolute stereochemistry was not determined.

Plumbolactone B (2) was obtained as an amorphous powder. The mass spectrum of compound 2 contained a weak molecular ion at 224, and the 13C NMR spectrum displayed 11 carbon signals, corresponding to a molecular formula of C₁₁H₁₂O₅. The IR spectrum indicated the presence of hydroxyl groups (3400 cm⁻¹, broad band) and an ester group (1757 cm⁻¹). Observation of 13C NMR signals for six aromatic and one carbonyl carbon (175.85 ppm) accounted for a total of 5 degrees of unsaturation. The other 1 degree of unsaturation was assumed to result from the presence of one additional ring system. The aromatic region of the 1H NMR spectrum displayed a typical pattern for a 1,2,4-trisubstituted aromatic ring (8.37 (1H, d, J = 1.3 Hz, H-7), 8.08 (1H, dd, J = 8.1, 1.3 Hz, H-5), and 7.34 (1H, d, J = 8.1 Hz, H-4)). The quaternary carbon signal at δ 16.94 was attributable to C-5 or C-6 bearing a hydroxyl group according to the 1,2,4-trisubstituted aromatic ring system. The most downfield proton signal at δ 8.37 (1H, d, J = 1.3 Hz) resulting from the deshielding effect of a carbonyl group was assigned to H-7, indicating that the hydroxyl group is attached to the C-6 position. The proton signals at δ 8.08 (1H, dd, J = 8.1, 1.3 Hz) and 7.34 (1H, d, J = 8.1 Hz) were attributable to H-5 and H-4, respectively. The proton signals at δ 4.40 (1H, t, J = 8.6 Hz) and 4.50 (1H, m) were assigned to the H-10 and H-11 geminal with a hydroxyl group, respectively. The plane structure of plumbolactone B was thus established as 2. The relative stereochemistry at C-3 position was not readily established by the available data.

The other 13 known compounds were identified as plumbagin (4), N-trans-cafeoyltyramine, N-trans-feruloyltyramine, myricetin, quercetin, tricetin 3′, 5′-dimethyl ether, vanillic acid, syringic acid, caffeic acid, and 6,7-dihydroxycoumarin by physical constants and spectral data.

**Experimental Section**

**General Experimental Procedures.** Melting points were determined on a Kofler apparatus and were uncorrected. IR spectral data were measured on a FT-5DX instrument with KBr disks. EIMS were obtained on a AutoSpec mass spectrometer. 1H NMR and 13C NMR were recorded on a Bruker AM-400 instrument with TMS as an internal standard and CD₃OD as solvent.

**Plant Material.** C. willmottianum Stapf was collected at Tonghai county of Yunnan province, China. It was authenticated by Prof. Zhongwen Lin at the Kunming Institute of Botany, Academia Sinica, where a voucher specimen was deposited.

**Extraction and Partition.** The air-dried powdered whole herb of C. willmottianum (5 kg) was extracted three times with 95% EtOH at room temperature. The extract was evaporated to dryness under reduced pressure, and the residue (285 g) was then dissolved in water (2500 mL). The aqueous solution was partitioned with petroleum ether, ethyl acetate and 1-butanol to afford three fractions P (31 g), E (93 g), and N (65 g), respectively. The aqueous solution was evaporated to dryness under reduced pressure to obtain fraction W (98 g).

**Isolation and Purification.** Fraction E (90 g) was chromatographed on a column of silica gel (900 g), eluting with petroleum ether–acetone (8:1, 6:1, 5:1, 4:1, 3:1, 2:1, 1:1, 1:2, and acetone) to give fractions 1–35. Fractions 3–6 were combined and afforded plumbagin (1.2 g). Fraction 7 was chromatographed on a silica gel column eluting with petroleum ether–acetone (6:1) to obtain a mixture of isolshinanolone and epiosishinanolone (1.8, 3.0 g). It was then rechromatographed on a silica gel column, eluting with cyclohexane–2-propanol (20:1) to yield isolshinanolone (100 mg) and epiosishinanolone (1.5 g). Fractions 9–11 were combined and chromatographed on a silica gel column to give plumbagic acid (3.2 g). Fractions 12–15 were combined and chromatographed on MCI-gel CHP 20P eluting with methanol–water (7:3) to give vanillic acid (74 mg) and a crude sample of plumbolactone A, which was then crystallized from hexane–acetone to yield 1.7 g of white prisms. Fractions 16–21 were combined and chromatographed on MCI-gel CHP 20P, eluting with methanol–water (7:3) to give syringic acid (70 mg), caffeic acid (154 mg), and a mixture of amides which was further chromatographed on silica gel eluting with petroleum ether–ethyl acetate (4:1) to afford N-trans-cafeoyltyramine (40 mg) and N-trans-feruloyltyramine (23 mg). The fraction 23 was chromatographed on a silica gel, eluting with petroleum ether–acetone (4:1) to give 6, 7-dihydroxycoumarin (28 mg). Fractions 24–27 were combined and chromatographed on MCI-gel CHP 20P, eluting with methanol–water (7:3) to give plumbolactone B (29 mg). Fraction 22 was chromatographed on a silica gel, eluting with chloroform–methanol (6:1) to yield tricetin 3′,5′-dimethyl ether (150 mg). Fractions 30–33 were combined and chromatographed on a MCI-gel CHP 20P eluting with methanol–water (7:3) to give quercetin (7.8 g) and myricetin (6.5 g).
Plumbolactone A (1): C_{11}H_{12}O_{4} (HRMS, found 208.0706, requires 208.0732); [α]_D^{20} = -21.39° (c 0.03, in MeOH); IR ν max (KBr, cm⁻¹) 3360, 3260, and 1710; ¹H NMR (C₅D₅N, 400 MHz) δ (ppm) 2.36 (1H, dd, J = 16.6, 8.1 Hz, H-3α), 2.87 (1H, dd, J = 16.6, 8.1 Hz, H-3β), 2.76 (1H, m, H-4), 5.80 (1H, dd, J = 7.0Hz, H-5), 1.15 (3H, d, J = 7Hz, H-6), 7.03 (1H, dd, J = 7.9, 1.5 Hz, H-12), 6.87 (1H, t, J = 7.9 Hz, H-11), and 7.16 (1H, dd, J = 7.9, 1.5 Hz, H-10); ¹³C NMR (C₅D₅N, 99.96 MHz) δ (ppm) 177.08 (C-2), 38.38 (C-3), 37.32 (C-4), 84.43 (C-5), 17.77 (C-6), 127.05 (C-7), 145.58 (C-8), 147.10 (C-9), 119.80 (C-10), 117.83 (C-11), and 116.25 (C-12); EIMS m/z 208 [M]+ (86), 190 [M-H₂O]+ (95), 161 (82), 147 (100), and 137 (84).

Plumbolactone B (2): IR ν max (KBr, cm⁻¹) 3200–3500, 1770; ¹H NMR (C₅D₅N, 400 MHz) δ (ppm) 8.37 (1H, d, J = 1.3 Hz, H-7), 8.08 (1H, dd, J = 8.1, 1.3 Hz, H-5), 7.34 (1H, d, J = 8.1 Hz, H-4), 4.95 (1H, d, J = 8.6 Hz, H-3), 4.40 (1H, t, J = 8.6 Hz, H-10), 4.50 (1H, m, H-11), and 1.46 (3H, d, J = 6.1Hz, H-12); ¹³C NMR (C₅D₅N, 99.96 MHz) δ (ppm) 175.85 (C-1), 75.73 (C-3), 116.17 (C-4), 123.40 (C-5), 169.43 (C-6), 118.31 (C-7), 152.08 (C-8), 147.01 (C-9), 80.53 (C-10), 77.91 (C-11), and 18.40 (C-12); EIMS m/z 204 [M]+ (86), 190 [M – H₂O]+ (95), 161 (82), 147 (100), and 137 (84).

Plumbabic acid (3): IR ν max (KBr, cm⁻¹) 3250, 1735, 1700, and 1632; ¹H NMR (C₅D₅N, 400 MHz) δ (ppm) 2.98 (1H, dd, J = 17.6, 8.8 Hz, H-2a), 2.48 (1H, dd, J = 17.6, 5.2 Hz, H-2b), 3.98 (1H, m, H-3), 1.22 (3H, d, J = 7.2 Hz, H-5), 7.32 (1H, d, J = 8.0Hz, H-11), 6.81 (1H, t, J = 8.0Hz, H-10) and 7.10 (1H, d, J = 8.0Hz, H-9); ¹³C NMR (C₅D₅N, 99.96 MHz) δ (ppm) 177.38 (C-1), 36.74 (C-2), 84.43 (C-3), 77.91 (C-4), 117.86 (C-5), 145.78 (C-7), 150.27 (C-8), 120.48 (C-9), 120.48 (C-10), and 119.11 (C-11); EIMS m/z 224 [M]+ (67), 206 [M – H₂O]+ (59), 190 (34), 178 (69), 163 (53), 147 (31), 137 (100), and 109 (57).

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References and Notes