

Table I ^{13}C NMR data of 1-3 in CD_3OD
(400 M Hz, δ in ppm with reference to the signal of CD_3OD)

	1	2	3
P-coumaroyl moiety			
1,1'	129.5	130.1	130.1
	126.1	126.1	126.1
2,2',6,6'	130.7	130.8	130.9
	130.1	130.1	130.2
3,3',5,5'	117.6	117.6	117.7
	117.0	117.0	117.0
4,4'	161.7	161.7	161.8
	160.0	159.3	159.0
7,7'	145.5	145.5	146.0
	143.8	143.5	143.5
8,8'	118.9	119.4	119.5
	115.1	115.0	114.7
9,9'	169.4	169.4	169.3
	167.4	167.3	167.0
Glucose moiety			
1''	102.1	99.6	99.5
2''	74.9	74.8	74.6
3''	78.4	76.0	73.3
4''	71.6	71.6	72.2
5''	75.7	75.9	73.3
6''	64.5	64.1	63.0
OAc		170.1	170.3
			170.0
		21.0	20.9
			20.9

EXPERIMENT

General All melting points were measured on a XRC-1 micro melting point apparatus produced by Sichuan University and uncorrected. Optical rotations were taken on a JASCO-20C digital polarimeter. IR spectra were recorded with a Perkin-Elmer 577 spectrometer. UV spectra were obtained on a UV 210A spectrometer. MS spectra were measured on a VG Autospec spectrometer. NMR spectra were run on a Bruker AM-400 spectrometer. The chemical shifts (δ) were expressed in ppm with reference to the solvent signals. Coupling constants (J) were given in Hz.

Plant material The aerial parts of *Bidens bipinnata* Linn. were collected in Kunming, Yunnan, China, in July 20, 1994. A voucher specimen is kept in the Herbarium of Kunming Institute of Botany.

Extraction and isolation The dried ground aerial parts of *Bidens bipinnata* Linn. (3.5kg) were extracted with ethanol (4×20 L) at room temperature during four weeks to give crude extract (392 g), which was then partitioned with petroleum ether, ethyl acetate and n-butanol successively. The AcOEt part (110 g) was subjected to silica gel column (1.0 kg, 220-300 mesh) eluting with petroleum ether by increasing amount of ethyl acetate to afford six fractions.

After repeating silica gel and reversed phase silica gel as well as Sephadax LH-20 (eluent: MeOH-H₂O) column chromatography, eight compounds: 1(20 mg), 2(100 mg), 3(40 mg), 4(80 mg), 5(700

mg), 6(800 mg), 7(50 mg) and 8 (35 mg) were obtained.

4-O-(6'' -O-p-Coumaroyl-β-D-glucopyranosyl)-p-coumaric acid (1), — C₂₄H₂₄O₁₀. White powders; EIMS (70 eV) m / z(%): 309 [M-coumaric acid]⁺(4), 164[coumaric acid]⁺(36), 147(56), 119(14), 107(19) and 79(100); ¹³C and ¹H NMR data see Table 1 and 2 respectively.

4-O-(2'' -O-Acetyl-6'' -O-p-coumaroyl-β-D-glucopyranosyl)-p-coumaric acid (2)—C₂₆H₂₆O₁₁, white powders; IR_{ν_{max}^{KBr}cm⁻¹: 3480, 1702,1623, 1595, 1500, 1370, 1248, 1170, 1086, 1045 and 825; UVλ_{max}^{MeOH}nm(log ε):218.5, 223.0, 285.0, 293.0 and 304.0; EIMS (70 eV)m / z(%): 351[M-coumaric acid]⁺(16), 164[coumaric acid]⁺(57), 147(100), 119(22), 107(14), 91(25) and 79(15);FABMS (positive ion mode) m / z(%): 515[M+H]⁺(2); ¹³C and ¹H NMR data see Table 1 and 2 respectively.}

Table 2 ¹H NMR data of 1-3 in CD₃OD
(400 M Hz, δ in ppm with reference to the signal of CD₃OD)

	1	2	3
P-Coumaroyl moiety			
2,2'	7.60(d,8.7)	7.61(D,8.5)	7.59(d,8.5)
6,6'	7.56(d,8.6)	7.57(d,8.5)	7.58(d,8.5)
3,3'	7.34(d,8.7)	7.32(d,8.5)	7.29(d,8.5)
5,5'	7.21(d,8.6)	7.21(d,8.5)	7.20(d,8.5)
7	7.98(d,15.9)	7.94(d,15.9)	7.96(d,16.0)
7'	7.92(d,15.9)	7.91(d,15.9)	7.95(d,16.0)
8	6.75(d,15.9)	6.78(d,15.8)	6.75(d,16.0)
8'	6.63(d,15.9)	6.63(d,15.8)	6.64(d,16.0)
Glucose moiety			
1''	5.66(d,7.2)	5.69(d,8.1)	5.68(m,overlap)
2''	4.24(dd,7.2,9.3)	5.87(dd,8.1,9.0)	5.86(dd,7.7,9.4)
3''	4.35(m,overlap)	4.40(dd,9.0,9.0)	4.48(dd,9.4,9.4)
4''	4.35(m,overlap)	4.23(dd,9.0,9.3)	5.68(m,overlap)
5''	4.35(m,overlap)	4.34(m)	4.40(m)
6'' a	5.17(dd,3.2,11.8)	5.13(dd,3.4,11.8)	4.74(dd,2.4,12.0)
6'' b	4.92(dd,6.6,11.8)	4.89(dd,6.2,11.8)	4.67(dd,5.9,12.0)
OAc		2.08(s)	2.08(s)
			2.05(s)

4-O-(2'' ,4'' -O-Diacetyl-6'' -O-p-coumaroyl-β-glucopyranosyl)-p-coumaric acid (3)—C₂₈G₂₈O₁₂, white powders, mp: 192~194℃, [α]_D²⁵-60.1° (C₂D₂N, c 0.362); IR_{ν_{max}^{KBr}cm⁻¹:3440, 1735, 1722, 1700, 1642, 1618, 1520, 1390, 1250, 1190, 1078, 994 and 848; UVλ_{max}^{MeOH}nm (log ε): 216.5(4.38), 284.0(4.53), 289.0(4.52, sh) and 305.0(4.46, sh); EIMS(70 eV)m / z(%): 393[M-coumaric acid]⁺(8), 164[coumaric acid]⁺(44), 147(100), 119(19), 107(9), 91(21) and 65 (16); FABMS(negative ion mode):555[M-H]⁻(100); HR FABMS (negative ion mode) m / z: 556.1632 (calc. 556.1581); ¹³C and ¹H NMR data see Table 1 and 2 respectively.}

(Z)-6-O-(4'' ,6'' -Diacetyl-β-D-glucopyranosyl)-6,7,3',4'-tetrahydroxyaurone (4)—C₂₅H₂₄O₁₃, orange crystals (MeOH-H₂O), mp: 195~197℃; IR_{ν_{max}^{KBr}cm⁻¹: 3220-3360(br.), 1725, 1685, 1835, 1590, 1504, 1360,1270, 1168, 1085 and 1035; UVλ_{max}^{MeOH}nm(log ε): 238.5(4.06, sh), 272.0(4.01), 328.0(4.11), 417.0(4.38); +NaOMe:264.0,285.0(sh), 348.5, 493.0; +AlCl₃:250.0(sh), 292, 5, 321.0, 456.5; +AlCl₃+HCl: 242.0(sh), 277.5, 323.5, 415.0;+NaOAc:263.5, 358.0, 482.5; +NaOAc+H₃BO₃: 284.5, 327.5, 443.0;EIMS (70 eV)}

m/z(%): L286[aglycone]⁺(100), 258[agl-CO]⁺(4), 229[acetylglucosyl-H₂O]⁺(14), 169(16), 153(43), 152(62), 127(26), 115(21), FABMS (positive ion mode) m/z(%): 533[M+H]⁺(7) and 287[agl+H]⁺(16).

3β-Gluco-β-sitosterol (5)—C₃₅H₆₀O₆, white powders; EIMS (70 eV) m/z(%): 414, 396, 382, 329, 255, 213, 145 and 81; ¹H NMR (pyridine-d₅) δ: 3.96(1H, m, H-3), 5.34(1H, br.s, H-6), 0.65-1.02(18H, m, 6 × CH₃), 5.05(1H, d, J=7.6, Hz, H-1'), 4.05(1H, dd, J=7.6, 9.0 Hz, H-2'), 4.29(1H, m, H-3'), 4.29(1H, m, H-4'), 3.96(1H, m, H-5'), 4.41(1H, dd, J=5.2, 11.8 Hz H-6' b) and 4.58(1H, d, J=11.8 Hz H-6' a).

3β-Gluco-stigmasterol (6)—C₃₅H₅₈O₆, white powders; EIMS (70 eV) m/z(%): 412, 397, 369, 312, 300, 269, 253, 133, 109, 95, 81, 69 and 55; ¹H NMR (pyridine-d₅) δ: 3.96(1H, m, H-3), 5.34(1H, br.s, H-6), 5.20(1H, dd, J=8.6, 15.0 Hz, H-22), 5.05(1H, m, H-23), 0.66-1.02(18H, m, 6 × CH₃), 5.05(1H, m, H-1'), 4.05(1H, dd, J=7.6, 8.8 Hz H-2'), 4.28(1H, m, H-3'), 4.28(1H, m, H-4'), 3.96(1H, m, H-5'), 4.41(1H, dd, J=5.2, 11.7 Hz H-6' b) and 4.56(1H, d, J=11.7 Hz H-6' a).

Butanedioic acid (7)—C₄H₆O₄, colorless crystals (from MeOH), mp: 167~170°C; IR_{max}^{KBr}cm⁻¹: 3300-2500(br.), 1690(br.), 1405, 1300, 1193, 910, 795 and 630; EIMS (70eV) m/z(%): 119[M+H]⁺(17), 100(61), 74(78) and 55(100); ¹³C NMR (pyridine-d₅) δ: 175.3(C-1) and 30.4(C-2); ¹H NMR δ: 12.59(1H, br.s, OH) and 3.00 (each 2H, s, 2 × CH₂).

3β-D-Glucopyranosyloxy-1-hydroxy-6(E)-tetradecene-8,10,12-triynone (8)—C₂₀H₂₆O₇, brown powders; IR_{max}^{KBr}cm⁻¹: 3340, 2895, 2200, 1605, 1413, 1360, 1158, 1070 and 1010; UV_{max}^{MeOH}nm: 231.0, 233.5(sh), 240.0, 257.5, 272.0, 288.5, 308.0 and 329.0; EIMS (70 eV) m/z(%): 216[aglycone]⁺(65), 198(46), 165(49), 153(70), 141(55), 127(100), 115(70), 101(54), 85(57), 77(47), 73(95) and 60(78); FABMS (positive ion mode) m/z: 379[M+H]⁺; ¹³C NMR (pyridine-d₅) δ: 58.4(C-1), 39.5(C-2), 78.8(C-3), 349(C-4), 29.5(C-5), 152.0(C-6), 108.2(C-7), 60.1(C-8)*, 65.4(C-9)*, 67.4(C-10)*, 73.8(C-11)*, 76.0(C-12)*, 79.4(C-13)*, 4.1(C-14), 104.6(C-1'), 75.4(C-2'), 78.2(C-3'), 72.5(C-4'), 76.6(C-5') and 63.5(C-6'); ¹H NMR (pyridine-d₅) δ: 1.93(2H, m, H₂-2), 1.68(2H, m, H₂-4), 2.38 and 2.52(each 1H, m, H-5), 6.41(1H, dt, J=7.0, 16.0 Hz, H-6), 5.62(1H, d, J=16.0 Hz H-7), 4.86(1H, d, J=7.8 Hz, H-1') and 4.60(1H, dd, J=2.2, 11.4 Hz H-6' a).

Acknowledgments The authors are grateful to the staff of analytical group of Laboratory of Phytochemistry for their help in the measurements of spectral data.

参 考 文 献

- 邓 勇, 王鹏瑞, 刘清明等, 1993. 云南中药资源名录. 北京: 科学出版社, 559
 吴征镒, 尹文清, 包士英等, 1984. 云南种子植物名录. 昆明: 云南人民出版社, 1337
 Rucker G, Kehrbaum S, Sakulas H, et al., 1994a. Acetylated Aurone Glucosides from *Microglossa pyrifolia*. *Planta Med.* 60: 288~289
 Rucker G, Kehrbaum S, Sakulas H et al., 1994b. Acetylenic Glucosides from *Microglossa pyrifolia*. *Planta Med.* 58: 266~269
 Sashida Y, Ogawa K, Kitada M, et al., 1991. New Aurone Glucosides and New Phenylpropanoid Glucosides from *Bidens pilosa*. *Chem Pharm Bull.* 39: 709~711