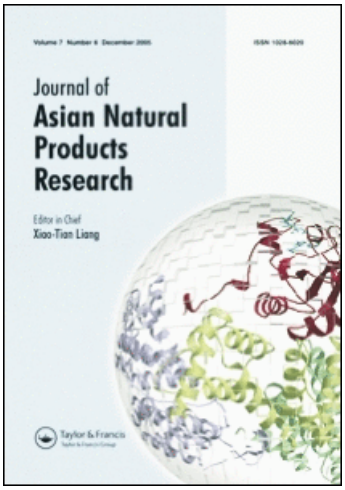

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Constituents from the roots of Heracleum rapula Franch

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CONSTITUENTS FROM THE ROOTS OF *HERACLEUM RAPULA* FRANCH

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A new coumarin glucoside, 8-hydroxy-5-*O*-β-D-glucosylpsoralen, along with 17 known coumarins and one steroid, was isolated from the roots of *Heracleum rapula* Franch. Four coumarin glucosides, including the new one, were obtained from the water-soluble fraction. The other coumarins isolated from the ethyl acetate-fraction included 10 furanocoumarins, a simple coumarin and three types of bicoumarins. Their structures were elucidated by means of spectroscopic analysis.

Keywords: *Heracleum rapula*; Coumarin glucosides; Furanocoumarin; Bicoumarin

INTRODUCTION

Heracleum rapula Fr. (*Umbelliferae*), is a kind of medicinal plant widely distributed in Yunnan province of China. As a frequently used drug for rheumatic disease in traditional Chinese medicine, it can "dispel wind, remove dampness, expel cold, relieve pain, dredge all the channels and vessels, promote blood circulation and relax muscles and tendons". It has been proved by pharmacological experiments that the petroleum ether extract had antipyretic, analgesic and diaphoretic activities [1]. A number of closely related furanocoumarins have been isolated from the petroleum ether extract of the roots of the plant [2–4]. According to the procedure of Chinese folk medicine, the water extract should possess antibiotic and antiasthmatic effects, which have been supported by the results of pharmacological experiments [1]. Therefore, it is worthwhile to carry out further investigation on related constituents in the water fraction of the plant.

In this paper, our careful examinations on both the water-soluble fraction and the ethyl acetate fraction of the roots of this plant led to the isolation of one new coumarin glucoside, 8-hydroxy-5-*O*-β-D-glucosylpsoralen (**1**), and three known coumarin glucosides, 1′-*O*-β-D-glucopyranosyl-(2′*S*)-marmesin (**2**), 1′-*O*-β-D-glucopyranosyl-(2′*S*,3′*R*)-3′-hydroxymarmesin (**3**) [5–7] and 3″-*O*-β-D-glucopyranosyl-(2″*R*)-heraclenol (**4**) [8], along with 14

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coumarins, which included three types of bicoumarins, moellendorffiline (**5**) [11], rivulobirin B (**6**) and rivulobirin A (**7**) [12], 10 furanocoumarins, 8-geranyloxypsoralen (**8**) [2], heraclenin (**9**) [3], imperatorin (**10**) [4], *R*-heraclenol (**11**) [2], *O*-isopropylideneheraclenol (**12**) [13], bergapten (**13**) [3], isopimpinellin (**14**) [7], sphondin (**15**) [4], isobergapten (**16**) [5] and pimpinellin (**17**) [7], and a simple coumarin, angelical (**18**) [14]. A steroid, pregnenolone (**19**) [15] was also isolated. Among all the above-mentioned coumarins, the three known coumarin glucosides were rich in the water-soluble fraction. Compounds **2**, **3**, **5**–**7** and **18** were isolated from this plant for the first time. All the structures were elucidated by spectroscopic methods. The assignments of the NMR data of compounds **1**, **4**, **5**–**7** were established by 2D NMR experiments.

RESULTS AND DISCUSSION

Compound **1**, light brown amorphous powder, showed a molecular ion peak at *m/z* 379 and a base peak at *m/z* 217 in negative FABMS spectrum. Its strong yellowish green fluorescence under UV light (265 nm) and the signals of the aromatic region in its ^{1}H and ^{13}C NMR spectra were typical of furocoumarins [9]. The shapes and the absorption of UV curve [λ_{max} 313.5, 282, 269.5, 244.5, 221 nm] indicated a 5,8-dioxygenated psoralen skeleton [10], which was supported by the base peak at *m/z* 217 for $C_{11}H_5O_5$ in negative FABMS spectrum. On comparing the ^{1}H NMR and ^{13}C NMR spectra, compound **1** presented quite similar to compound **14** except for the signals of sugar moiety. In the ^{1}H NMR spectrum, a noticeable doublet signal at δ 5.48 (1H, d, $J = 7.6$ Hz) was attributed to the anomeric proton of the glucopyranosyl moiety. By consideration of the coupling constants, the sugar moiety should be β-linkage. Complex signals appearing at δ 3.9–4.8 corresponded to protons of the glucose. In the lowfield region, the characteristic signals at δ 6.30 (1H, d, $J = 9.7$ Hz), 8.84 (1H, d, $J = 9.7$ Hz), 7.88 (1H, s) and 7.81 (1H, s) were assigned to H-3, H-4, H-2′ and H-3′, which were confirmed by ^{1}H–^{1}H COSY spectrum.

The ^{13}C NMR spectrum of compound **1** showed twelve carbon signals at δ 100–160 due to the eleven carbons of the linear furanocoumarin nucleus and the anomeric carbon of the glucose, and five carbon signals at δ 60–80 owing to the saccharide moiety.

The anomeric proton signal at δ 5.48 showed ^{1}H–^{13}C long-range correlations with the carbon signal at δ 139.4 (C-5), which gave further connection with δ 7.81 (H-3′) in HMBC spectrum (see Fig. 1). These data unambiguously suggested that the glucose was attached to C-5 of the linear furanocoumarin nucleus. The full assignments were established by means of 2D NMR (including HMQC, ^{1}H–^{1}H COSY, HMBC experiments).

Therefore, the structure of compound **1** was deduced as 8-hydroxy-5-*O*-β-D-glucosylpsoralen (Fig. 1).

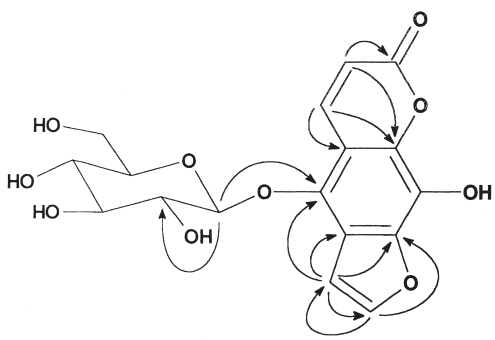


FIGURE 1 The key correlations of compound **1** in HMBC spectrum.

The new coumarin glucoside, in which the glucose was directly linked to the coumarin nucleus with no further in between, was quite different from the other three ones, which was found to be rare in naturally occurring coumarins. Very interestingly, 3″-*O*-β-D-glucopyranosyl-(2″*R*)-heraclenol (**4**) and its aglycone, heraclenol (**11**), were found to be rich in aqueous and EtOAc parts, respectively. However, a considerable amounts of 1′-*O*-β-D-glucopyranosyl-(2′*S*)-marmesin (**2**) and 1′-*O*-β-D-glucopyranosyl-(2′*S*,3′*R*)-3′-hydroxymarmesin (**3**) have been isolated from the aqueous fraction, neither of their corresponding aglycones were obtained from the EtOAc fraction, even in trace amounts. This might be one of the important reasons that resulted in the different bioactivities of its two parts (EtOAc and H_2O) [1].

EXPERIMENTAL SECTION

General Experimental Procedures

Optical rotations were measured on a HORIBA SEPA-300 high sensitive spectropolarimeter or Perkin–Elmer model 241 polarimeter. IR spectra were recorded on a Bio-Rad FTS-135 spectrometer with KBr pellets. UV spectral data were obtained on a Shimadzu double-beam UV 210A spectrometer. MS and HR-MS were taken on a VG Auto Spec-3000 or on a Finnigan MAT 90 instrument. 1D and 2D NMR experiments were performed either on a Bruker AM-400 or DRX-500 spectrometer. Unless otherwise specified, chemical shifts (δ) were expressed in ppm with reference to the solvent signals. Column chromatogrphy was performed either on Si gel (200–300 mesh, Qingdao Marine Chemical Inc., China), Si gel H (60 μ, Qingdao Marine Chemical Inc., China), Lichroprep RP_{18} gel (40–63 μm, Merck, Darmstadt, Germany), Diaion HP-20, MCI gel CHP-20P (70–150 μ, Mitsubishi Chemical Corporation, Tokyo, Japan). Fractions were monitored by TLC and spots were visualized by heating Si gel plates sprayed with 10% H_2SO_4 in EtOH.

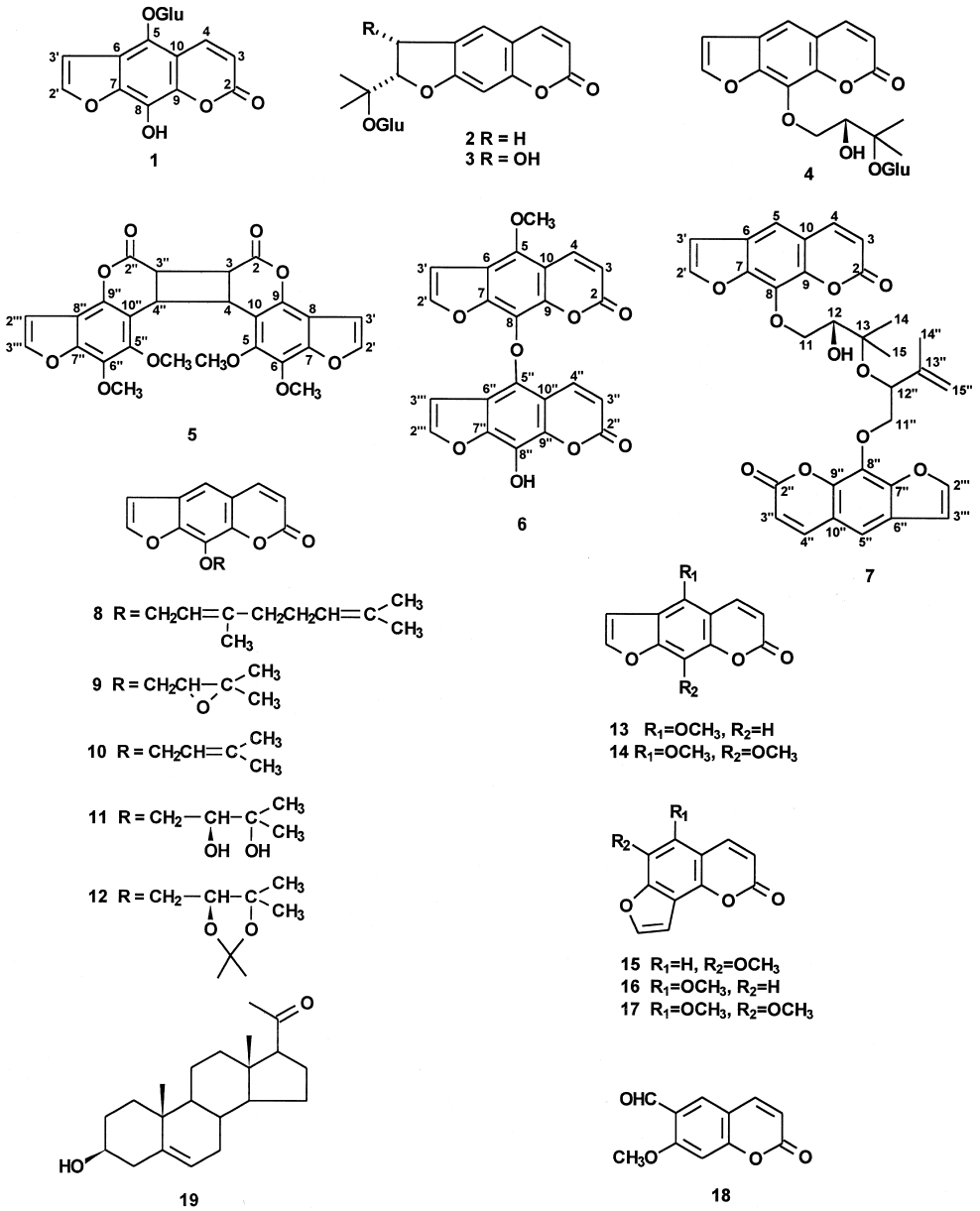
Plant Material

The roots of *H. rapula* (*Umbelliferae*) were collected in Dali Prefecture of Yunnan Province. The plant material was identified by Prof. Zhong-Wen Lin, and a voucher specimen (KIB 99-7-10-014 Lin) is deposited in the Herbarium of the Department of Taxonomy, Kunming Institute of Botany, Academia Sinica.

Extraction and Isolation

The fresh roots of *H. rapula* (12.1 kg) were extracted with acetone (3 × 30 l). After evaporation of the acetone *in vacuo*, the concentrated extract was suspended in water and partitioned with ethyl acetate to afford 140.0 g of ethyl acetate-soluble residue and water-soluble fraction. The latter was subjected to column chromatography over Diaion HP-20 eluting with H_2O, aqueous MeOH (30 → 50%) and MeOH, and was divided into four portions.

The MeOH portion (10 g) was subjected to column chromatography over silica gel (200–300 mesh, 800 g) developing with $CHCl_3$/Me_2CO (6:4, 5:5) and Me_2CO to divide into three parts. The Me_2CO part was collected and combined by monitoring with TLC to give six fractions. Fraction 5 was repeatedly chromatographed over silica gel (200–300 mesh, 100 g) eluting with $CHCl_3$/MeOH (9:1). The latter fraction was further purified by column chromatography over MCI-gel CHP-20P (50 g) developing with aqueous MeOH (20 → 30 → 40%) to afford compound **1** (10 mg).



Fraction 6 and 7 of the eluate from Me_2CO part was subjected to middle-pressure column chromatography over silica gel (60 μ, 400 g) eluting with $CHCl_3$/MeOH (9:1) to yield compounds **3** (230 mg) and **4** (200 mg).

In the same way, 205 mg of compound **2** was obtained after the $CHCl_3$/Me_2CO (5:5) part was rechromatographed by middle-pressure column chromatography over silica gel (60 μ, 200 g) developing with $CHCl_3$/MeOH (9:1).

140.0 g of ethyl acetate-soluble residue was chromatographed over silica gel eluting with chloroform, chloroform/acetone (9:1, 4:1) and acetone to give fractions I–IV. The fractions were collected and combined by monitoring with TLC. Fraction I was repeatedly subjected to middle-pressure column chromatographed on silica gel column using petroleum-

TABLE I The ^{13}C NMR data of compound **1** (δ in ppm, pyridine-d_5, 125 MHz)

Carbon	δ, ppm *(DEPT)*	*Carbon*	δ, ppm *(DEPT)*
2	161.0 (s)	2′	146.1 (d)
3	113.1 (d)	3′	106.6 (d)
4	141.3 (d)	Glucose moiety	
5	139.4 (s)	1″	107.1 (d)
6	119.1 (s)	2″	75.6 (d)
7	147.6 (s)	3″	79.0 (d)
8	129.2 (s)	4″	71.5 (d)
9	140.3 (s)	5″	78.6 (d)
10	110.4 (s)	6″	62.7 (t)

ether/EtOAc (4:1, 3:1, 2:1) as eluent to yield compounds **8** (60 mg), **9** (55 mg), **10** (46 mg), **13** (12 mg), **15** (10 mg) and **16** (12 mg), respectively. Fraction II was treated with the same means developing with petroleum-ether/EtOAc in stepwise gradient mode to afford compounds **5** (8 mg), **7** (12 mg), **11** (3 g), **12** (30 mg), **14** (13 mg), **17** (16 mg), **18** (14 mg) and **19** (10 mg). Fraction III was rechromatographed by middle-pressure column chromatography over silica gel (60 μ, 50 g) with $CHCl_3$/MeOH (19:1) as eluent to afford compound **6** (12 mg).

8-Hydroxy-5-O-β-D-glucosylpsoralen (1)

$C_{17}H_{16}O_{10}$, light-brown amorphous powder; $[\alpha]_D^{24.8} = -20.0$ to -30.0 (c 0.04, C_5H_5N); UV (H_2O) λ_{max} log ε: 313.5 (4.2), 282 (4.2), 269.5 (4.4), 244.5 (4.3), 221 (4.6), 199 (4.4) nm; IR (KBr) ν_{max} 3409, 3227, 3140, 3116, 2921, 1700, 1597, 1474, 1367, 1347, 1316, 1260, 1206, 1153, 1136, 1083, 1064, 1042, 1002, 824, 785, 758, 721, 648, 609, 566, 504, 428, 418 cm^{-1}; ^1H NMR (C_5H_5N, 500 MHz) δ 6.30 (1H, d, $J = 9.7$ Hz, H-3), 8.84 (1H, d, $J = 9.7$ Hz, H-4), 7.88 (1H, brs, H-2′), 7.81 (1H, brs, H-3′), 5.48 (1H, d, $J = 7.6$ Hz, H-1″), 4.38 (1H, overlap, H-2″), 4.05 (1H, brs, H-3″), 4.37 (1H, overlap, H-4″), 4.36 (1H, overlap, H-5″), 4.56 (1H, d, $J = 11.0$ Hz, H-6″a), 4.39 (1H, overlap, H-6″b); ^{13}C NMR (C_5H_5N, 125 MHz), see Table I; EIMS m/z 218 $[M - glu]^+$ (100), 202 (8), 190 (20), 174 (5), 162 (21), 145 (11), 134 (23), 127 (6), 105 (12), 95 (12), 85 (25), 73 (35), 57 (30); negative FABMS m/z 379 $[M - H]^-$ (84), 217 (100), negative HRFABMS m/z 379.0636 (calcd for $C_{17}H_{16}O_{10}$, 379.0665).

TABLE II The ^1H NMR data of compounds **2** and **3** (400 MHz, J in Hz, δ in ppm, pyridine-d_5)

Proton	***2***	***3***
3	6.28 (1H, d, $J = 9.5$ Hz)	6.25 (1H, d, $J = 9.5$ Hz)
4	7.60 (1H, d, $J = 9.5$ Hz)	7.62 (1H, d, $J = 9.5$ Hz)
5	7.05 (1H, s)	7.55 (1H, s)
8	6.77 (1H, s)	6.82 (1H, s)
2′	4.95 (1H, t, $J = 8.7$ Hz)	4.71 (1H, d, $J = 6.8$ Hz)
3′	3.15 (1H, dd, $J = 8.7$, 16.1 Hz)	5.60 (1H, brs)
	3.54 (1H, dd, $J = 8.7$, 16.1 Hz)	
1′-CH_3	1.55 (3H, s), 1.53 (3H, s)	1.90 (6H, s)
Glu-1	5.15 (1H, d, $J = 7.7$ Hz)	5.32 (1H, d, $J = 7.8$ Hz)
Glu-2	3.96 (1H, t, $J = 8.0$ Hz)	3.91 (1H, overlap)
Glu-3	4.26 (1H, overlap)	4.25 (1H, overlap)
Glu-4	3.90 (1H, m)	4.21 (1H, overlap)
Glu-5	4.24 (1H, overlap)	3.88 (1H, overlap)
Glu-6	4.29 (2H, brs)	4.28 (2H, overlap)

TABLE III The ^{13}C NMR data of compounds **2** and **3** (100 MHz, δ in ppm, pyridine-d_5)

Carbon	***2***	***3***	*Carbon*	***2***	***3***
2	161.2 (s)	160.9 (s)	3′	29.9 (t)	71.6 (d)
3	112.2 (d)	112.5 (d)	1′	78.0 (s)	78.7 (s)
4	144.1 (d)	144.3 (d)	1′-CH_3	23.7 (q)	26.2 (q)
5	124.0 (d)	125.9 (d)		22.4 (q)	23.2 (q)
6	125.8 (s)	129.3 (s)	Glu-1	99.0 (d)	98.9 (d)
7	164.0 (s)	163.2 (s)	Glu-2	75.2 (d)	75.0 (d)
8	97.6 (d)	98.3 (d)	Glu-3	78.8 (d)	78.7 (d)
9	156.2 (s)	157.1 (s)	Glu-4	71.8 (d)	71.6 (d)
10	112.9 (s)	113.5 (s)	Glu-5	78.1 (d)	78.3 (d)
2′	91.0 (d)	92.7 (d)	Glu-6	62.8 (t)	62.5 (t)

1′-O-β-D-Glucopyranosyl-(2′S)-marmesin (2)

$C_{20}H_{24}O_9$, pale-yellow amorphous powder; ^1H NMR (C_5D_5N, 400 MHz), see Table II; ^{13}C NMR (C_5D_5N, 100 MHz), see Table III; EIMS *m/z* 408 $[M]^+$ (29), 275 (3), 257 (1), 246 (10), 229 (72), 213 (38), 188 (99), 187 (100), 175 (11), 159 (10), 145 (7), 131 (16), 115 (6), 102 (5), 85 (10), 74 (13), 69 (12), 59 (12).

1′-O-β-D-Glucopyranosyl-(2′S,3′R)-3′-hydroxymarmesin (3)

$C_{20}H_{24}O_{10}$, pale-yellow amorphous powder; ^1H NMR (C_5D_5N, 400 MHz), see Table II; ^{13}C NMR (C_5D_5N, 100 MHz), see Table III; EIMS *m/z* 424 $[M]^+$ (13), 406 (1), 262 (3), 242 (38), 227 (31), 213 (22), 204 (17), 187 (100), 175 (7), 158 (18), 145 (12), 131 (8), 115 (12), 102 (10), 85 (12), 73 (31), 60 (32), 55 (33).

3″-O-β-D-Glucopyranosyl-(2″R)-heraclenol (4)

$C_{22}H_{26}O_{11}$, light-brown amorphous powder; $[\alpha]_D^{24.8}$ − 7.05 (*c* 0.75, C_5H_5N); UV (H_2O) λ_{max} log ε: 303.5 (4.5), 260.5 (4.5), 247 (4.7), 217.5 (4.8), 198 (4.7) nm; IR (KBr) ν_{max} 3579, 3560, 3451, 3402, 2981, 2911, 1695, 1623, 1586, 1466, 1440, 1400, 1338, 1222, 1188, 1163, 1126, 1096, 1067, 1018, 895, 875, 837, 752, 621, 501, 425 cm^{-1}; ^1H NMR (C_5D_5N, 400 MHz) δ 6.40 (1H, d, J = 9.5 Hz, H-3), 7.79 (1H, d, J = 9.5 Hz, H-4), 7.36 (1H, s, H-5), 7.82 (1H, d, J = 2.0 Hz, H-2′), 6.85 (1H, d, J = 2.0 Hz, H-3′), 5.10 (1H, dd, J = 2.3, 9.9 Hz, H-1″a), 5.00 (1H, dd, J = 7.7, 9.9 Hz, H-1″b), 4.68 (1H, m, H-2″), 1.66 (3H, s, 3″-CH_3), 1.68 (3H, s, 3″-CH_3), 5.22 (1H, d, J = 7.8 Hz, Glu-1), 4.00 (1H, t, J = 8.0 Hz, Glu-2), 4.35 (1H, m, Glu-3), 3.95 (1H, brs, Glu-4), 4.24 (1H, overlap, Glu-5), 4.50 (1H, d, J = 11.6 Hz, Glu-6a), 4.24 (1H, overlap, Glu-6b); ^{13}C NMR (C_5D_5N, 100 MHz) δ 160.5 (s, C-2), 114.9 (d, C-3), 144.9 (d, C-4), 113.7 (d, C-5), 126.6 (s, C-6), 148.2 (s, C-7), 132.8 (s, C-8), 143.7 (s, C-9), 117.1 (s, C-10), 147.4 (d, C-2′), 107.3 (d, C-3′), 76.2 (t, C-1″), 76.1 (d, C-2″), 79.4 (s, C-3″), 24.2 (q, 3″-CH_3), 22.7 (q, 3″-CH_3), 98.3 (d, Glu-1), 75.5 (d, Glu-2), 78.8 (d, Glu-3), 71.9 (d, Glu-4), 78.3 (d, Glu-5), 63.0 (t, Glu-6); EIMS *m/z* 466 $[M]^+$ (5), 315 (23), 287 (32), 269 (23), 245 (15), 215 (22), 202 (100), 185 (6), 174 (27), 157 (10), 129 (11), 116 (5), 101 (7), 89 (36), 73 (33), 60 (25); negative FABMS *m/z* 466 $[M]^-$ (100), 201 (96), negative HRFABMS *m/z* 466.1448 (calcd for $C_{22}H_{26}O_{11}$, 466.1475).

Moellendorffiline (5)

$C_{26}H_{20}O_{10}$, pale-yellow crystal; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.44 (2H, d, J = 2.2 Hz, H-2′, 2‴), 6.73 (2H, d, J = 2.2 Hz, H-3′, 3‴), 4.38 (2H, m, H-4, 4″), 4.02 (2H, m, H-3,

3″), 3.82 (6H, s, 5-OCH_3, 5″-OCH_3), 3.66 (6H, s, 6-OCH_3, 6″-OCH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.5 (2C, s, C-2, 2″), 148.3 (2C, s, C-7, 7″), 147.6 (2C, s, C-9, 9″), 144.5 (2C, d, C-2′, 2‴), 139.6 (2C, s, C-5, 5″), 134.6 (2C, s, C-6, 6″), 113.9 (2C, s, C-8, 8″), 106.5 (2C, s, C-10, 10″), 104.0 (2C, d, C-3′, 3‴), 60.7 (q, 5-OCH_3, 5″-OCH_3, 6-OCH_3, 6″-OCH_3), 39.9 (2C, d, C-3, 3″), 38.3 (2C, d, C-4, 4″); EIMS *m/z* 492 $[M]^+$ (0.5), 246 (100), 231 (80), 147 (20).

Rivulobirin B (6)

$C_{23}H_{12}O_9$, light-brown amorphous powder; ^{1}H NMR (C_5D_5N, 400 MHz) δ 8.70 (1H, d, $J = 9.8$ Hz, H-4″), 8.22 (1H, d, $J = 9.9$ Hz, H-4), 7.91 (1H, d, $J = 2.2$ Hz, H-2′), 7.76 (1H, d, $J = 2.2$ Hz, H-2‴), 7.37 (1H, d, $J = 2.2$ Hz, H-3′), 6.64 (1H, d, $J = 9.8$ Hz, H-3″), 6.50 (1H, d, $J = 9.9$ Hz, H-3), 6.11 (1H, d, $J = 2.2$ Hz, H-3‴), 4.29 (3H, s, $-OCH_3$); ^{13}C NMR (C_5D_5N, 100 MHz) δ 161.3 (s, C-2″), 160.3 (s, C-2), 150.5 (s, C-7), 148.0 (s, C-5), 146.9 (3C, C-2′, C-2‴, C-7″), 144.7 (s, C-9), 140.7 (s, C-9″), 140.4 (d, C-4″), 140.1 (d, C-4), 138.8 (s, C-5″), 129.0 (s, C-8″), 124.6 (s, C-8), 115.7 (s, C-6″), 115.0 (s, C-6), 114.0 (d, C-3″), 113.5 (d, C-3), 108.6 (s, C-10″), 107.8 (s, C-10), 106.5 (d, C-3′), 104.0 (d, C-3‴), 61.1 (q, $-OCH_3$); EIMS *m/z* 432 $[M]^+$ (100), 404 (6), 389 (8), 373 (2), 361 (4), 345 (2), 333 (4), 319 (1), 305 (4), 289 (1), 277 (2), 267 (2), 243 (7), 232 (28), 217 (29), 202 (8), 189 (16), 173 (10), 160 (11), 161 (11), 145 (10), 133 (6), 118 (9), 105 (8), 95 (13), 89 (18), 75 (18), 63 (18).

Rivulobirin A (7)

$C_{32}H_{28}O_{10}$, pale-yellow crystalline powder; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.70 and 7.69 (each 1H, d, $J = 9.6$ Hz, H-4 or H-4″, respectively), 7.67 and 7.62 (each 1H, d, $J = 1.9$ Hz, H-2′ or H-2‴, respectively), 7.28 (2H, s H-5 and H-5″), 6.75 (2H, d, $J = 1.9$ Hz, H-3′ and H-3‴), 6.31 and 6.29 (each 1H, d, $J = 9.5$ Hz, H-3 or H-3″, respectively), 5.16 (1H, s, H-15″a), 4.98 (1H, s, H-15″b), 4.72 (1H, dd, $J = 10.3$, 3.0 Hz, H-11a), 4.44 (1H, dd, $J = 10.2$, 8.0 Hz, H-11b), 4.00 (1H, dd, $J = 7.8$, 3.1 Hz, H-12), 4.37 (2H, d, $J = 6.3$ Hz, H-11″), 4.60 (1H, t, $J = 6.1$ Hz, H-12″), 1.81 (3H, s, H-14″), 1.37 (3H, s, 13-CH_3), 1.31 (3H, s, 13-CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.2 (2C, s, C-2 and C-2″), 148.1 (s, C-7 or C-7″), 147.7 (s, C-7 or C-7″), 146.7 (d, C-2′ or C-2‴), 146.6 (d, C-2′ or C-2‴), 144.7 (s, C-13″), 144.1 (2C, d, C-4 and C-4″), 143.3 (s, C -9 or C-9″), 143.1 (s, C-9 or C-9″), 132.0 (2C, s, C-8 and C-8″), 125.9 (2C, s, C-6 and C-6″), 116.4 (2C, s, C-10 and C-10″), 114.7 (2C, d, C-3 and C-3″), 113.5 (t, C-15″), 113.0 (2C, d, C-5 and C-5″), 106.6 (2C, d, C-3′ and C-3‴), 78.1 (s, C-13), 76.6 (d, C-12), 76.0 (t, C-11″), 75.2 (t, C-11), 75.1 (d, C-12″), 21.7 and 22.8 (each q, $13-2\times CH_3$), 18.7 (q, C-14″); EIMS *m/z* 572 $[M]^+$ (88), 543 (15), 522 (13), 491 (17), 409 (20), 393 (14), 361 (14), 339 (32), 325 (32), 312 (22), 255 (27), 235 (23), 201 (100), 181 (20), 134 (14), 108 (16), 73 (16).

8-Geranyloxypsoralen (8)

$C_{21}H_{22}O_4$, pale-yellow crystal; EIMS *m/z* 202 $[M - C_{10}H_{17}]^+$ (100), 185 (1), 174 (46), 157 (3), 145 (22), 136 (56), 129 (4), 121 (17), 107 (4), 93 (38), 89 (48), 81 (35), 69 (72), 63 (38), 53 (24), 41 (69).

Heraclenin (9)

$C_{16}H_{14}O_5$, pale-yellow crystal; EIMS *m/z* 286 $[M]^+$ (62), 243 (3), 229 (3), 215 (19), 202 (96), 185 (8), 174 (58), 157 (12), 145 (35), 129 (20), 118 (11), 101 (80), 89 (65), 85 (100), 75 (17), 63 (53), 59 (58), 41 (60).

Imperatorin (10)

$C_{16}H_{14}O_4$, pale-yellow crystal; EIMS *m/z* 202 $[M - C_5H_9]^+$ (100), 186 (1), 174 (50), 157 (2), 145 (20), 136 (2), 129 (5), 118 (11), 59 (44), 75 (8), 69 (39), 63 (35), 53 (21), 41 (59), 39 (30).

R-Heraclenol (11)

$C_{16}H_{16}O_6$, pale-yellow crystal; EIMS *m/z* 304 $[M]^+$ (54), 289 (21), 245 (15), 229 (4), 215 (29), 202 (100), 186 (11), 174 (69), 157 (11), 145 (32), 129 (19), 118 (15), 102 (9), 89 (56), 75 (15), 63 (48), 59 (73).

O-Isopropylideneheraclenol (12)

$C_{19}H_{20}O_6$, pale-yellow crystal; EIMS *m/z* 344 $[M]^+$ (11), 304 (7), 286 (41), 269 (9), 245 (8), 227 (2), 215 (28), 202 (100), 187 (8), 174 (36), 157 (8), 145 (10), 129 (10), 118 (4), 101 (3), 89 (23), 71 (10), 59 (23).

Bergapten (13)

$C_{12}H_8O_4$, pale-yellow crystal; EIMS *m/z* 216 $[M]^+$ (100), 201 (52), 188 (30), 173 (79), 159 (5), 157 (5), 145 (52), 131 (8), 116 (6), 109 (7), 101(7), 89 (40), 74 (20), 69 (10), 63 (31).

Isopimpinellin (14)

$C_{13}H_{10}O_5$, pale-yellow crystal; EIMS *m*/z 246 $[M]^+$ (98), 231 (100), 216 (15), 203 (20), 188 (24), 175 (21), 160 (24), 147 (11), 89 (10), 87 (12), 76 (13), 62 (7).

Sphondin (15)

$C_{12}H_8O_4$, pale-yellow crystal; EIMS *m/z* 216 $[M]^+$ (100), 201 (50), 188 (30), 173 (52), 159 (2), 157 (2), 145 (38), 129 (5), 116 (5), 108 (9), 101 (7), 95 (15), 89 (24), 79 (16), 74 (15), 63 (19).

Isobergapten (16)

$C_{12}H_8O_4$, pale-yellow crystal; EIMS *m/z* (%) 216 $[M]^+$ (100), 201 (22), 188 (38), 173 (87), 158 (7), 145 (32), 131 (4), 116 (4), 98 (5), 89 (25), 79 (4), 74 (8), 63 (20).

Pimpinellin (17)

$C_{13}H_{10}O_5$, pale-yellow crystal; EIMS *m/z* 246 $[M]^+$ (100), 231 (92), 217 (7), 203 (45), 188 (45), 175 (54), 160 (60), 147 (67), 132 (28), 119 (28), 104 (42), 91 (32), 76 (41), 66 (47).

Angelical (18)

$C_{11}H_8O_4$, colorless crystal; EIMS *m/z* 204 $[M]^+$ (100), 187 (31), 175 (30), 159 (28), 145 (18), 133 (19), 116 (16), 105 (18), 95 (9), 89 (22), 77 (25), 69 (21), 63 (28), 57 (24).

Pregnenolone (19)

$C_{21}H_{32}O_2$, colorless needle; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 5.35 (1H, brs, H-6), 3.50 (1H, m, H-3), 2.19 (3H, s, H-21), 1.01 (3H, s, C-18), 0.64 (3H, s, H-19); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 209.3 (s, C-20), 140.9 (s, C-5), 121.4 (d, C-6), 71.7 (d, C-3), 63.8 (d, C-17), 57.0 (d, C-14), 50.1 (d, C-9), 44.0 (s, C-13), 42.3 (t, C-2), 38.9 (t, C-4), 37.3 (t, C-1), 36.6 (s C-10), 32.0 (d, C-8), 31.8 (t, C-7), 31.7 (t, C-12), 31.4 (q, C-21), 24.5 (t, C-16), 23.0 (t, C-15), 21.1 (t, C-11), 19.4 (q, C-19), 13.2 (q, C-18); EIMS *m/z* 316 $[M]^+$ (100), 298 (50), 283 (40), 273 (8), 265 (11), 255 (15), 241 (11), 231 (36), 213 (22), 205 (25), 199 (11), 187 (22), 173 (14), 159 (28), 145 (38), 133 (27), 119 (31), 105 (56), 91 (67), 79 (53), 67 (35), 55 (40).

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