云 南 植 物 研 究 2003，25（4）：503 ~ 506
Acta Botanica Yunnanica

白叶香茶菜中的紫罗兰酮衍生物

赵爱华[1,2]，彭丽艳[1]，王宗玉[1]，孙汉董[1*]
（1 中国科学院昆明植物研究所植物化学与西部植物资源持续利用国家重点实验室，云南 昆明 650204；
2 昆明医学院药学系，云南 昆明 650031）

摘要：从白叶香茶菜 *Isodon leucophyllus*（Dunn）Kudo 地上部分的丙酮提取物中，分离得到 1 个新的紫罗兰酮类化合物和 6 个黄酮类化合物，经 IR，UV，MS，NMR 波谱数据分析，其结构分别确定为：13 – 羧基布卢姆醇 C（1），5，7，3′，4′ – 四甲氧基黄酮（2），线蓟素（3），5 – 羟基 – 6，7，3′，4′ – 四甲氧基黄酮（4），3′ – 羟基 – 5，7，8，4′ – 四甲氧基黄酮（5），异甜橙素（6）和异槲皮素（7）。其中，化合物 2 – 7 均为首次从该植物中得到。

关键词：白叶香茶菜；唇形科；13 – 羧基布卢姆醇 C；黄酮类化合物
中图分类号：Q 946 **文献标识码：**A **文章编号：**0253 – 2700(2003)04 – 0503 – 04

An Ionone Derivative from *Isodon leucophyllus*

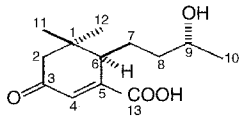
ZHAO Ai-Hua[1,2]，PENG Li-Yan[1]，WANG Zong-Yu[1]，SUN Han-Dong[1*]
（1 *State Key Laboratory of Phytochemistry and Plant Resources in West China*，*Kunming Institute of Botany*，*Chinese Academy of Sciences*，Kunming 650204，China；
2 *Department of Pharmacology*，*Kunming Medical College*，Kunming 650031，China）

Abstract： A new ionone derivative and six known flavonoids were isolated from the aerial parts of *Isodon leucophyllus*（Dunn）Kudo. Their structures were respectively elucidated as 13-carboxy-blumenol C **(1)**，5，7，3′，4′-tetramethoxyflavone **(2)**，cirsiliol **(3)**，5-hydroxy-6，7，3′，4′-tetramethoxyflavone **(4)**，3′-hydroxy-5，7，8，4′-tetramethoxyflavone **(5)**，isosinensetin **(6)** and isoquercetrin **(7)**，based on their spectra analysis. All of the six flavonoids were reported firstly from this plant.

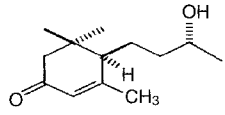
Key words： *Isodon leucophyllus*；Labiatae；13-carboxy-blumenol C；Flavonoids

Abundant diterpenoids in *Isodon* species have attracted the attentions of many phytochemists. However，literatures about the non-diterpenoids in genus *Isodon* have been seldom reported. *Isodon leucophyllus*（Dunn）Kudo has been also proved to be rich in diterpenoids（Chen *et al*，1999；Liao *et al*，1997，1998）. In continuation of our research work on this plant collected in Zhongdian County，a new ionone derivative **(1)** and six known flavonoids **(2 – 7)** were obtained besides a large amount of diterpenoids. This paper presents the isolation and structure elucidation of the new compound.

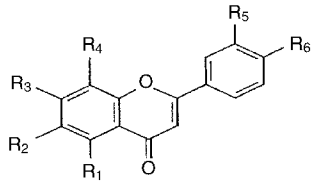
* To whom correspondence should be addressed. Tel：86 – 871 – 5223251 Fax：86 – 871 – 5216343
E – mail：hdsun@mail.kib.ac.cb
收稿日期：2003 – 03 – 14，2003 – 04 – 03 **接受发表**
作者简介：赵爱华（1965 – ）女，博士研究生，主要从事植物化学研究。



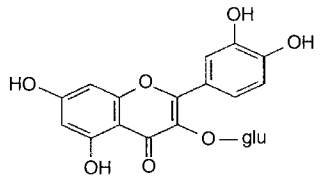
1



1a



2：R_2=R_4=H, R_1=R_3=R_5=R_6=OCH_3
4：R_4=H, R_1=OH, R_2=R_3=R_5=R_6=OCH_3
6：R_2=H, R_1=R_3=R_4=R_5=R_6=OCH_3



7

3：R_4=H, R_1=R_5=R_6=OH, R_2=R_3=OCH_3
5：R_2=H, R_5=OH, R_1=R_3=R_4=R_6=OCH_3

Results and Discussion

Compound **1** has the molecular formula $C_{13}H_{20}O_4$ by negative-ion high resolution FAB－MS (obsd 239.1283, calcd 239.1283). In the NMR spectra of **1**, the characteristic signals of two tertiary methyls [δ_C 27.8 (q), 28.3 (q); δ_H 1.03 (3H, s), 1.01 (3H, s)], one secondary methyl [δ_C 24.2 (q), δ_H 1.30 (3H, d, J = 6.0 Hz)] and one quaternary carbon [δ_C 36.5 (s)] were showed in high field, together with thirteen carbons in its molecular formular, indicating an ionone-like skeleton of **1**. An α, β-unsaturated moiety deduced by the following spectral data: UV absorption at λ_{max}^{KBr} 240 nm, IR band at ν_{max}^{KBr} 1774 cm^{-1} and ^{13}C NMR signals at δ_C 200.3 (s), 130.0 (d), 155.9 (s) and ^1H NMR signal at 7.10 (1H, s). From the HMBC spectrum of **1**, two AB spin system protons [δ_H 2.28, 2.68 (each 1H, d, J = 17.2 Hz)] due to H_2－2 showed cross peaks with the keto carbonyl carbon and the two tertiary methyl carbons which suggested the α, β-unsaturated moiety at C－5, C－4 and C－3. Comparing the ^{13}C NMR data of **1** with those of blumenol C (**1a**) (Toshio *et al*, 1988), the only difference is that a carboxylic carbonyl carbon signal at δ_C 170.4 (s) was replaced by a methyl signal at δ_C 24.5 (q) in blumenol C, which suggested that Me-13 of **1a** was oxidated into a carboxylic group in **1**. HMBC correlation from H－6 [δ_H 2.97 (1H, t, J = 6.3 Hz)] to the carboxylic carbon confirmed the above deduction. H－6 was determined as α-orientation on the basis of ROESY correlation between H－7 [δ_H 2.31 (1H, m)] and H_3－11 [δ_H 1.01 (3H, s)]. The relative stereochemistry of C－9 was generally considered to be same as that of blumenol C, judging from very similar ^{13}C NMR data at C－8, C－9 and C－10, and positive rotation values in both compounds. Thus, **1** was elucidated as 13-carboxy blumenol C.

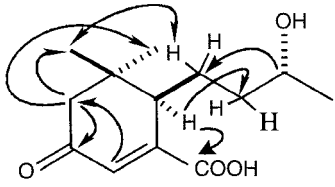


Fig. 1 The key HMBC (H→C) and ROESY (H↔H) correlations of **1**.

Compounds **2－7** were determined as 5, 7, 3′, 4′-tetramethoxyflavone **2** (Chien *et al*., 1984), cirsiliol (5, 3′, 4′-trihydroxy-6, 7-dimethoxyflavone) **3** (Shin *et al*, 1973), 5-hydroxy-6, 7, 3′, 4′-tetramethoxyflavone **4** (Karl *et al*, 1989), 3′-hydroxy-5, 7, 8, 4′-tetramethoxyflavone **5** (Zhong *et al*, 1984), isosinensetin (5, 7, 8, 3′, 4′-pentamethoxyflavone) **6** (George *et al*, 1984) and isoquercetrin (3-O-β-D-glucopyranosyl-5, 7, 3′, 4′-tetrahydroxyflavone) **7** (Wahono *et al*, 1991) respectively by comparing their spectral data with those reported in literatures.

Experimental

General Optical rotation was recorded on a SEPA－300 polarimetre. UV spectrum was obtained on a UV 210－A spectrometer. IR spectrum was measured on a Bio-Rad FTS－135 spectrometer with KBr pellets. 1D and 2D NMR spec-

tra were taken on a Bruker AM－400 and DRX－500 instrument with TMS as internal standard, respectively.

Plant Material The aerial parts of *I. leucophyllus* were collected in Zhongdian County, northwest of Yunnan Province in October 2001, and were identified by Professor Li Xi-Wen. The voucher specimen (KIB 01－10－183) is deposited in Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and isolation The dried and powdered aerial plants (2.1 kg) were extracted with 70% aq. acetone at room temperature for 4×24 h. The extract was concentrated in vacuo and filtered to remove pigment, then the filtrate was partitioned between EtOAc and H_2O. The EtOAc extract (57 g) was subjected to column chromatograph over silica gel and eluted with $CHCl_3/Me_2CO$ (from 1∶0 to 0∶1) to give seven fractions. Then compounds **2** (30 mg), **3** (45 mg), **4** (70 mg), **5** (120 mg) and **6** (24 mg) were purified from the $CHCl_3/Me_2CO$ (9∶1) fraction, **1** (14 mg) and **7** (840 mg) were obtained from the $CHCl_3/Me_2CO$ (6∶4) fraction after repeatly column chromatograph.

Table 1　^1H and ^{13}C NMR spectral data for **1** and **1a**[*]

position	**1**		**1a**	
	δ_C	δ_H	δ_C	δ_H
1	36.5 s		36.2 s	
2	47.5 t	2.28 (d, 17.2), 2.68 (d, 17.2)	47.2 t	2.03 (d, 17), 2.37 (d, 17)
3	200.3 s		199.2 s	
4	130.0 d	7.10 (s)	125.1 d	5.82 (s)
5	155.9 s		165.3 s	
6	45.2 d	2.97 (t, 6.3)	51.1 d	
7	28.3 t	1.67 (m), 2.31 (m)	26.3 t	
8	38.9 t	1.88 (m), 1.96 (m)	38.7 t	
9	67.3 d	4.00 (m)	68.2 d	3.75 (m)
10	24.2 q	1.30 (d, 6.0)	23.6 q	1.20 (d, 6.0)
11	27.8 q	1.01 (s)	27.0 q	1.02 (s)
12	28.3 q	1.03 (s)	28.8 q	1.07 (s)
13	170.4 s		24.5 q	2.00 (s)

[*] measured in $CDCl_3$ (Toshio *et al*, 1988)

Compound 1, colorless gum, $C_{13}H_{20}O_4$, $[\alpha]_D^{25}$ = + 57.76 (*c* 0.29, MeOH); UV λ_{max}^{KBr} (lg ε): 218 (3.98), 240 (3.83) nm; IR ν_{max}^{KBr}: 3439, 1774, 1645 cm^{-1}; FAB MS (negative) *m/z* (%): 239 $[M-H]^+$ (100); EI MS (70 eV) *m/z* (%): 222 $[M-H_2O]^+$ (54), 207 (14), 195 (21), 179 (24), 168 (35), 153 (22), 138 (33), 123 (45), 109 (40), 93 (79), 79 (24); ^1H NMR and ^{13}C NMR data (in C_5D_5N) see Table 1.

Compound 2, yellow crystals, $C_{19}H_{18}O_6$, ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.2 (s, C－2), 108.3 (d, C－3), 176.5 (s, C－4), 152.5 (s, C－5), 96.7 (d, C－6), 164.3 (s, C－7), 93.7 (d, C－8), 152.5 (s, C－9), 108.3 (s, C－10), 124.5 (s, C－1′), 109.8 (d, C－2′), 160.1 (s, C－3′), 160.6 (s, C－4′), 112.1 (d, C－5′), 119.9 (d, C－6′), 56.1, 56.0, 55.8 and 55.7 (each q, OCH_3); ^1H NMR (400 MHz, DMSO-d_6) δ: 7.65 (1H, dd, *J* = 8.4, 2.2 Hz, H－6′), 7.57 (1H, d, *J* = 2.2 Hz, H－2′), 7.06 (1H, br d, *J* = 8.4 Hz, H－5′), 6.85 (1H, d. *J* = 2.3 Hz, H－8), 6.70 (1H, s, H－3), 6.55 (1H, d, *J* = 2.3 Hz, H－6), 3.84, 3.82, 3.79 and 3.78 (each 3H, s, OCH_3); EIMS *m/z* (%): 342 $[M]^+$ (100), 325 (20), 313 (42), 296 (45), 281 (6), 269 (8), 241 (7), 226 (7), 162 (15).

Compound 3, yellow crystals, $C_{17}H_{14}O_7$, ^{13}C NMR (100 MHz, DMSO-d_6) δ: 165.1 (s, C－2), 103.5 (d, C－3), 182.9 (s, C－4), 152.9 (s, C－5), 132.7 (s, C－6), 159.4 (s, C－7), 92.2 (d, C－8), 153.4 (s, C－9), 105.9 (s, C－10), 122.4 (s, C－1′), 114.3 (d, C－2′), 146.6 (s, C－3′), 150.7 (s, C－4′), 116.9 (d, C－5′), 119.9 (d, C－6′), 60.9 and 57.2 (each q, OCH_3); ^1H NMR (400 MHz, DMSO-d_6) δ: 7.39 (1H, s, H－2′), 7.38 (1H, d, *J* = 8.0 Hz, H－6′), 6.89 (1H, d, *J* = 8.0 Hz, H－5′), 6.74 (1H, s, H－8). 6.63 (1H, s, H－3), 3.87 and 3.71 (each 3H, s, OCH_3); EIMS *m/z* (%): 328 $[M-2H]^+$ (100), 313 (77),

299 (18), 285 (16), 268 (6), 180 (15), 152 (31), 133 (12), 68 (20).

Compound 4, yellow crystals, $C_{19}H_{18}O_7$, ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.0 (s, C-2), 104.4 (d, C-3), 182.5 (s, C-4), 153.2 (s, C-5), 132.7 (s, C-6), 158.7 (s, C-7), 90.6 (d, C-8), 153.2 (s, C-9), 106.1 (s, C-10), 123.8 (s, C-1′), 111.2 (d, C-2′), 149.3 (s, C-3′), 152.3 (s, C-4′), 108.8 (d, C-5′), 120.1 (d, C-6′), 60.8, 56.3, 56.1 and 56.0 (each q, OCH_3); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.50 (1H, dd, J = 8.4, 1.6 Hz, H-6′), 7.31 (1H, d, J = 1.6 Hz, H-2′), 6.96 (1H, d, J = 8.4 Hz, H-5′), 6.58 (1H, s, H-8). 6.53 (1H, s, H-3), 3.97, 3.96, 3.95 and 3.91 (each 3H, s, OCH_3); EIMS m/z (%): 356 $[M-2H]^+$ (100), 341 (85), 327 (20), 313 (17), 297 (6), 280 (4), 255 (5), 180 (7), 162 (15), 152 (37).

Compound 5, yellow crystals, $C_{19}H_{18}O_7$, ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.6 (s, C-1), 106.9 (d, C-3), 176.8 (s, C-4), 152.5 (s, C-5), 98.1 (d, C-6), 158.4 (s, C-7), 140.7 (s, C-8), 154.9 (s, C-9), 112.8 (s, C-10), 124.1 (s, C-1′), 112.8 (d, C-2′), 147.6 (s, C-3′), 151.6 (s, C-4′), 113.6 (d, C-5′), 119.1 (d, C-6′), 62.8, 62.0, 57.4 and 56.7 (each q, OCH_3); ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.30 (1H, br d, J = 8.5 Hz, H-6′), 7.21 (1H, s, H-2′), 6.96 (1H, s, H-6), 6.88 (1H, br d, J = 8.5 Hz, H-5′), 6.39 (1H, s, H-3), 3.75, 3.67, 3.60 and 3.57 (each 3H, s, OCH_3); EIMS m/z (%): 356 $[M-2H]^+$ (34), 341 (100), 326 (11), 311 (13), 294 (11), 267 (4), 180 (2).

Compound 6, yellow crystals, $C_{20}H_{20}O_7$, ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.68 (1H, br d, J = 8.4 Hz, H-6′), 7.61 (1H, br s, H-2′), 7.13 (1H, s, H-3), 7.08 (1H, br d, J = 8.4 Hz, H-5′), 7.01 (1H, s, H-6), 4.17, 3.93, 3.83, 3.81 and 3.80 (each 3H, s, OCH_3); EIMS m/z (%): 372 $[M]^+$ (52), 357 (100), 341 (28), 313 (9), 282 (4), 195 (7), 179 (8), 167 (28).

Compound 7, yellow crystals, $C_{21}H_{20}O_{12}$, ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.57 (1H, d, J = 8.8 Hz, H-6′), 7.56 (1H, s, H-2′), 6.83 (1H, d, J = 8.8 Hz, H-5′), 6.39 (1H, d, J = 2.0 Hz, H-8), 6.19 (1H, d, J = 2.0 Hz, H-6), 5.44 (1H, d, J = 7.3 Hz, H-1″); FABMS (negative) m/z (%): 463 $[M-H]^+$ (100), 301 (47); EI MS (%) m/z: 302 (100), 286 (8), 273 (15), 245 (9), 229 (9), 153 (13), 137 (20).

References:

Chien CC, Yuh PC, Hong YH, *et al*, 1984. New flavones from *Bauhinia championii* Benth [J]. *Chem Pharm Bull*, **32** (1): 166—169

Chen SN, Lin ZW, Qin GW, *et al*, 1999. Diterpenoids from *Isodon leucophyllus* [J]. *Plant Med*, **65**: 472—474

George PR, Sally SB, 1984. Mass spectral analysis of some naturally occurring polymethoxyflavones [J]. *J Agric Food Chem*, **32** (3): 551—555

Karl EM, Inge MHO, Ingrid SK. 1989. Flavonoids from *Orthosiphon spicatus* [J]. *Plant Med*, **55**: 569—570

Liao X, Peng SL, Ding LS, 1997. Chemical constituents of *Rabdosia leucophylla* [J]. *Acta Bot Sin* (植物学报), **39** (11): 1073—1077

Liao X, Ding LS, Peng SL, 1998. *Ent*-kaurene diterpenoids from *Rabdosia leucophylla* [J]. *Phytochemistry*, **47** (2): 247—250

Shin M, Toshinobu K, Akira M, 1973. Synthetic studies of the flavone derivatives. I. Synthese of cirsiliol and cirsilineol [J]. *Chem Pharm Bull*, **21** (2): 2757—2759

Toshio M, Akira U, Nobuo T, *et al*, 1988. Studies on the glycosides of *Epimedium grandiflorum* Morr. var. *thunbergianum* (MIQ.) Nakai. Ⅲ [J]. *Chem Pharm Bull*, **36** (7): 2475—2484

Wahono S, Peter P, Victor W, *et al*, 1991. Qualitative and quantitative analysis of the phenolic constituents from *Orthosiphon aristatus* [J]. *Plant Med*, **57**: 176—180

Zhong JY, Wu ZS, 1984. Chemical constituents of *Clerodendrathus spicatus* [J]. *Acta Bot Yunnan* (云南植物研究), **6** (3): 344—345