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矮杨梅鲜叶的酚性化学成分

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摘要: 从云南产矮杨梅 (*Myrica nana* Cheval.) 鲜叶中分离了 10 个酚类化合物, 通过波谱数据鉴定为: 杨梅素、杨梅素 3-O- α -L-阿拉吡喃糖甙、杨梅素 3-O- β -D-半乳糖甙、杨梅甙 (即杨梅素 3-O- α -L-鼠李糖甙)、山奈酚 3-O- β -D-葡萄糖甙、(-) 表没食子儿茶素 3-O-没食子酸酯、(-) 表儿茶素 3-O-没食子酸酯、原飞燕草素 B-2、原飞燕草素 B-2 3'-O-没食子酸酯和没食子酸。

关键词: 杨梅科; 矮杨梅; 酚性化合物 鲜叶 酚类化合物, 生理活性

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Phenolic Constituents of the Fresh Leaves of *Myrica nana*

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Abstract: Ten phenolic compounds were isolated from the fresh leaves of *Myrica nana* Cheval. They were identified as myricetin, myricetin 3-O- α -L-arabino-pyranoside, myricetin 3-O- β -D-galactopyranoside, myricitrin (myricetin 3-O- α -L-rhamnopyranoside), kaempferol 3-O- β -D-glucopyranoside, (-) epigallocatechin 3-O-gallate, (-) epicatechin 3-O-gallate, prodelphinidin B-2, prodelphinidin B-2 3'-O-gallate and gallic acid, respectively, by means of spectral methods.

Key words: Myricaceae, *Myrica nana*, phenols

我国产杨梅属 (*Myrica* L.) 植物约 5 种, 主要分布于西南至东部地区。其中杨梅 (*M. rubra* (Lour.) Sieb. et Zucc.) 为常见果树, 民间用其根、树皮、叶和果入药。矮杨梅 (*M. nana* Cheval.) 又称云南杨梅, 广布于云贵高原, 是当地传统的野生果品, 并有生津止渴、利消化的作用, 民间亦用于治疗痢疾、腹泻、胃痛和风湿疼痛等症。杨梅属植物富含鞣质, 已报道从杨梅根皮、茎皮和叶中分离到一系列酚类化合物 (Nonaka 等, 1983, Yoshikawa 等, 1998)。近年来, 随着对植物酚类成分生理活性的认识不断提高, 从药用植物和经济植物中开发具生理活性的酚类成分作为天然药物和保健品的原料已日益引起重视。作为具生理活性的植物天然酚类化合物系统研究的一部分, 本文报道云南产矮杨梅鲜叶的酚类成分。

矮杨梅 80% 丙酮浸提物经葡聚糖凝胶和大孔吸附树脂柱层析反复分离, 得到 10 个化

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合物, 经光谱分析与文献比较, 分别鉴定为已知的: 杨梅素 (myricetin) (1) (Zou, 1995)、杨梅素 3-O- α -L-阿拉吡喃糖甙 (myricetin 3-O- α -L-arabinopyranoside) (2) (Kadota 等, 1990)、杨梅素 3-O- β -D-半乳糖甙 (myricetin 3-O- β -D-galactopyranoside) (3)、杨梅甙 (myricitrin) [即杨梅素 3-O- α -L-鼠李糖甙 (myricetin 3-O- α -L-rhamnopyranoside)] (4)、山奈酚 3-O- β -D-葡萄糖甙 (kaempferol 3-O- β -D-glucopyranoside) (5) (Markham 等, 1978)、(-) 表没食子儿茶素 3-O-没食子酸酯 (6)、(-) 表儿茶素 3-O-没食子酸酯 (7) (Zhang 等, 1995)、原飞燕草素 B-2 (prodelphinidin B-2) (8) 原飞燕草素 B-2 3'-O-没食子酸酯 (prodelphinidin B-2 3'-O-gallate) (9) (Nonaka 等, 1983) 和没食子酸 (10) (Zhang 等, 1995)。

以上结果表明, 矮杨梅叶中的酚类成分主要由黄酮类化合物及原花色素类化合物组成, 这两类化合物均有显著的生理活性。鉴于矮杨梅广布于云贵高原, 常成片野生于山间, 资源丰富, 有进一步研究与开发的价值。

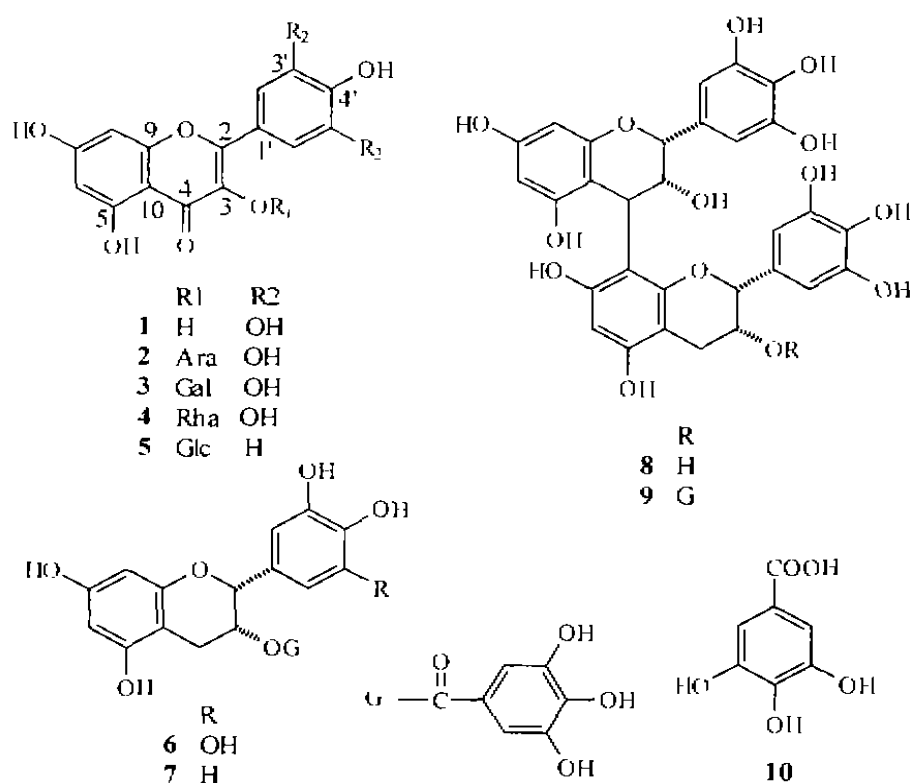


Fig. 1 The structures of compounds of 1-10

实验部分

IR 使用 Bio-Rad FTS-135 仪以 KBr 压片法测试; 旋光谱使用 SEPA-300 仪以甲醇为溶剂测定; ^{13}C 和 ^1H NMR 使用 Bruker-400 仪, 以 TMS 为内标在 $\text{DMSO}-d_6$ 、 $\text{Acetone}-d_6 + \text{D}_2\text{O}$ 或 CD_3OD 中测定; 负 FA-MS 质谱在 VG Autospec 300 质谱仪上测定。用 Sephadex LH-20 和 MCI gel CHP 20P 进行柱层析分离。

矮杨梅样品采集于中国科学院昆明植物研究所植物园,由龚洵副研究员鉴定,标本存于本所标本馆。

矮杨梅鲜叶 1.0kg 用 80% 丙酮浸提 3 次,浸提液减压回收丙酮后过滤,滤液用石油醚萃取,水层以大孔吸附树脂柱层析处理,水冲洗后用 MeOH 洗脱,回收甲醇,得褐黑色浸膏。将 MeOH 洗脱物溶于 250mL 水中,用 Sephadex HL-20 柱层析分离,含水甲醇梯度洗脱,得 3 个洗脱部位 (Fr.1-3)。Fr.1 用 MCI gel CHP 20P 柱层析分离,含水甲醇多次梯度洗脱,得化合物 **2** (50mg), **3** (60mg), **4** (50mg) 和 **10** (40mg)。Fr.2 用 MCI gel CHP 20P 柱层析分离,含水甲醇梯度洗脱,并经 Sephadex HL-20 柱层析纯化,含水甲醇或含水乙醇洗脱,得化合物 **1** (20mg), **5** (21mg), **6** (90mg) 和 **7** (35mg)。Fr.3 经 MCI gel CHP 20P 柱层析分离,含水甲醇洗脱,再用 Sephadex HL-20 柱层析纯化,含水甲醇和含水乙醇洗脱,得化合物 **8** (60mg) 和 **9** (70mg)。

杨梅素 (myricetin) (**1**) Negative FAB-MS, m/z (%): 317 $[M(C_{15}H_{10}O_8) - H]^-$ (100). $UV\lambda_{max}nm$ (MeOH): 208.5, 253.5, 286, 374. $IR\nu_{max}cm^{-1}$: 3369, 1658, 1609, 1513, 1317, 1242, 1203, 1163, 1025, 936, 832, 765. ^{13}C and 1H NMR see Table 1 and 2.

Table 1 ^{13}C data of compound 1~7 (values: δ_c)

Carbon	1*	2*	3*	4*	5*	6*	7*
2	146.85	156.60	156.51	157.69	158.52	78.08	78.59
3	135.88	134.05	133.95	134.43	135.50	69.28	69.95
4	175.77	177.66	177.64	177.94	179.53	26.61	26.60
5	160.74	161.36	161.44	161.45	163.05	157.44	157.78
6	98.17	98.85	98.96	98.86	99.96	96.57	96.61
7	163.87	164.33	164.50	164.33	166.03	157.75	157.78
8	93.21	93.63	93.69	93.74	94.81	95.89	95.92
9	156.10	156.44	156.45	156.59	159.00	157.09	157.23
10	102.99	104.07	104.11	104.21	105.50	99.11	99.44
1'	120.82	119.96	120.18	119.78	123.00	130.78	131.44
2'	107.20	108.63	108.76	108.09	132.27	106.83	115.11
3'	145.72	145.67	145.62	145.90	116.10	145.88	145.90
4'	135.88	136.96	136.96	136.62	161.55	133.03	145.90
5'	145.72	145.67	145.62	145.90	116.10	145.88	119.39
6'	107.20	136.96	136.96	108.09	132.27	106.83	116.02
substituent		Ara	Gal	Rha	Glc	Galloyl	Galloyl
1		101.86	102.26	102.06	104.30	121.96	121.48
2		71.97	71.45	70.53	75.75	110.06	110.26
3		70.85	73.48	70.77	78.09	146.25	146.26
4		66.47	68.26	71.41	71.45	138.78	139.79
5		64.77	76.14	70.17	78.38	146.25	146.26
6			60.31	17.70	62.72	110.06	110.26
7 (COO)						166.08	167.60

* The values were measured in DMSO- d_6 .

** The values were measured in Acetone- d_6 + D_2O .

杨梅素 3-O- α -L-阿拉吡喃糖甙 (myricetin 3-O- α -L-arabinopyranoside) (**2**) Negative FAB-MS, m/z (%): 447 $[M(C_{20}H_{18}O_{12}) - H]^-$ (100), 317 $[M(C_{15}H_9O_7)]^-$

(40). $UV\lambda_{max}nm$ (MeOH): 209.5, 252, 301.5, 261, $IR\nu_{max}cm^{-1}$: 3423, 1657, 1604, 1564, 1497, 1457, 1383, 1341, 1309, 1202, 1163, 1064, 1025, 940, 859. ^{13}C and 1H NMR see Table 1 and 2.

杨梅素 3-O- β -D-半乳糖甙 (myricetin 3-O- β -D-galactopyranoside) (3) Negative FAB-MS, m/z (%): 479 $[M(C_{21}H_{20}O_{13})-H]^-$ (100), 317 $[M(C_{15}H_9O_7)]^-$ (30). $UV\lambda_{max}nm$ (MeOH): 210, 262.5, 309.5, 367.5, $IR\nu_{max}cm^{-1}$: 3397, 1657, 1607, 1502, 1456, 1341, 1035, 1200, 1166, 1086, 1026, 635, 834, 766. ^{13}C and 1H NMR see Table 1 and 2.

Table 2 1H NMR data of compounds 1~7 (δ_H)

proton	1*	2*	3*	4*	5*	6**	7**
2						4.96, s	5.02, s
3						5.52, m	5.16, m
4						2.98, dd, $J=4.4, 16.2Hz$	3.0, dd, $J=5.0$, 16.4Hz
						2.83, dd, $J=2.4, 16.2Hz$	2.84, dd, $J=2.4, 16.4Hz$
6	6.36, d, $J=2.0Hz$	6.38, d, $J=1.6Hz$	6.36, d, $J=2.0Hz$	6.36, d, $J=2.0Hz$	6.38, d, $J=2.0Hz$	6.05, d, $J=2.4Hz$	5.95, s
8	6.17, d, $J=2.0Hz$	6.19, d, $J=1.6Hz$	6.18, d, $J=2.0Hz$	6.19, d, $J=2.0Hz$	6.19, d, $J=2.0Hz$	6.02, d, $J=2.4Hz$	5.95, s
2'	7.24, s	7.15, s	7.20, s	6.87, s	8.04, d, $J=8.4Hz$	6.62, s	6.93, d, $J=2.0Hz$
3'					6.87, d, $J=8.4Hz$		
5'					6.87, d, $J=8.4Hz$		6.70, d, $J=8.0Hz$
6'	7.24, s	7.15, s	7.20	6.87, s	8.04, d, $J=8.4Hz$	6.62, s	6.80, dd, $J=2.0, 8.0Hz$
Sugar		Ara	Gal	Rha	Glc		
1		4.68, s	5.33, d, $J=7.5Hz$	5.18, s	5.23, d, $J=7.0Hz$		
Galloyl						7.02, s	6.95, s

* The values were measured in DMSO- d_6 .** The values were measured in Acetone- $d_6 + D_2O$.

杨梅甙 (myricetrin) [即杨梅素 3-O- α -鼠李糖甙 (myricetin 3-O- α -L-rhamnopyranoside)] (4) Negative FAB-MS, m/z (%): 463 $[M(C_{21}H_{20}O_{12})-H]^-$ (100), 317 $[M(C_{15}H_9O_7)]^-$ (35). $UV\lambda_{max}nm$ (MeOH): 210, 261, 357, $IR\nu_{max}cm^{-1}$: 3391, 1657, 1609, 1503, 1452, 1353, 1302, 1201, 1164, 1090, 1057, 1022, 958, 915, 835, 812. ^{13}C and 1H NMR see Table 1 and 2.

山奈酚 3-O- β -D-葡萄糖甙 (kaempferol 3-O- β -D-glucopyranoside) (5) Negative FAB-MS, m/z (%): $[M(C_{21}H_{20}O_{11})-H]^-$ (100), 301 $[M(C_{15}H_9O_6)]^-$ (40). $UV\lambda_{max}nm$ (MeOH): 206.5, 266.5, 338, $IR\nu_{max}cm^{-1}$: 3370, 1658, 1607, 1565, 1495, 1361, 1303, 1283, 1210, 1179, 1120, 1066, 990, 892, 839, 811. ^{13}C and 1H NMR see Table 1 and 2.

(-) 表没食子儿茶素 3-O-没食子酸酯 [(-) epigallocatechin 3-O-gallate] (6). White amorphous powder. Negative FAB-MS, m/z (%): 457 $[M(C_{22}H_{18}O_{11})-H]^-$ (100). $[\alpha]_D^{25} = -143.9^\circ$ ($C=0.00323$, MeOH). $UV\lambda_{max}nm$ (MeOH): 210, 274.5, $IR\nu_{max}cm^{-1}$: 3371, 1693, 1612, 1536, 1519, 1452, 1338, 1315, 1237, 1144, 1096, 1033, 968, 821, 766, 735. ^{13}C

and ^1H NMR see Table 1 and 2.

(-) 表儿茶素 3-O-没食子酸酯 [(-) epicatechin 3-O-gallate] (7). White amorphous powder. Negative FAB-MS, m/z (%): 441 $[\text{M}(\text{C}_{22}\text{H}_{18}\text{O}_{10}) - \text{H}]^-$ (100). $[\alpha]_{\text{D}}^{24.3} - 164.9^\circ$ ($C = 0.0079$, MeOH). $\text{UV}\lambda_{\text{max}} \text{nm}$ (MeOH): 208.5, 274.5, $\text{IR}\nu_{\text{max}} \text{cm}^{-1}$: 3339, 1696, 1628, 1612, 1539, 1520, 1453, 1372, 1341, 1237, 1144, 1034, 1017, 821, 766, 735. ^{13}C and ^1H NMR see Table 1 and 2.

原飞燕草素 B-2 (prodelphinidin B-2) (8). White amorphous powder. Negative FAB-MS, m/z (%): 609 $[\text{M}(\text{C}_{30}\text{H}_{26}\text{O}_{14}) - \text{H}]^-$ (100). $[\alpha]_{\text{D}}^{24.4} + 50.8^\circ$ ($C = 0.00438$, MeOH). $\text{UV}\lambda_{\text{max}} \text{nm}$ (MeOH): 209.5, 269, $\text{IR}\nu_{\text{max}} \text{cm}^{-1}$: 3369, 1613, 1538, 1449, 1349, 1198, 1147, 1099, 1035, 832, 801, 736. ^{13}C NMR (Acetone- d_6 + D_2O): ring-A and ring-C: 877.00 (C-2), 79.57 (C-2'), 73.41 (C-3), 66.68 (C-3'), 37.04 (C-4), 29.71 (C-4'), 154.40, 156.25 (2C), 157.68, 158.10 (2C) (C-5, C-5', C-7, C-7', C-9, C-9'), 96.16, 96.57, 97.48 (C-6, C-6', C-8), 107.00 (C-8'), 100.69 (C-10), 101.45 (C-10'); ring-B: 133.43 (C-1, C-1'), 107.00 (C-2, C-6, C-2', C-6'), 146.35 (C-3, C-5, C-3', C-5'), 131.39 (C-4, C-4'). ^1H NMR (Acetone- d_6 + D_2O): ring-A and ring-C: 6.41 (2H, s, H-2, H-6), 6.66 (2H, s, H-2', H-6'), 6.10 (1H, s, H-6), 6.00 (1H, s, H-8), 5.90 (1H, s, H-6'), 4.97 (1H, s, H-2'), 4.82 (1H, s, H-2), 4.64 (1H, s, H-4), 4.31 (1H, s, H-3'), 3.89 (1H, s, H-3), 2.91 and 2.84 (2H, m, H-4').

原飞燕草素 B-2 3'-O-没食子酸酯 (prodelphinidin B-2 3'-O-gallate) (9). White amorphous powder. Negative FAB-MS, m/z (%): 761 $[\text{M}(\text{C}_{37}\text{H}_{30}\text{O}_{18}) - \text{H}]^-$ (100). $[\alpha]_{\text{D}}^{24.5} - 61.7^\circ$ ($C = 0.00316$, MeOH). $\text{UV}\lambda_{\text{max}} \text{nm}$ (MeOH): 210, 273, $\text{IR}\nu_{\text{max}} \text{cm}^{-1}$: 3378, 1694, 1612, 1538, 1452, 1338, 1232, 1144, 1096, 1034, 820, 802, 733. ^{13}C NMR (Acetone- d_6 + D_2O): ring-A and ring-C: 877.11 (C-2), 78.07 (C-2'), 73.06 (C-3), 68.99 (C-3'), 36.56 (C-4), 28.69 (C-4'), 154.40, 155.59, 156.09, 157.69, 158.10, 158.39 (C-5, C-5', C-7, C-7', C-9, C-9'), 96.01, 96.56, 97.38 (C-6, C-6', C-8), 107.79 (C-8'), 99.74 (C-10), 101.45 (C-10'); ring-B: 132.87, 133.03 (C-1, C-1'), 106.85, 106.87 (C-2, C-6, C-2', C-6'), 146.17, 146.21 (C-3, C-5, C-3', C-5'), 130.67, 131.74 (C-4, C-4'); Galloyl: 122.09 (C-1), 110.42 (C-2, C-6), 145.72 (C-3, C-5), 138.80 (C-4), 166.21 (C=O); ^1H NMR (Acetone- d_6 + D_2O): ring-A and ring-C: 6.49 (2H, s, H-2, H-6), 6.66 (2H, s, H-2', H-6'), 6.04 (1H, s, H-6), 6.01 (1H, s, H-8), 5.95 (1H, s, H-6'), 5.58 (1H, bs, H-3'), 5.14 (2H, bs, H-2, H-2'), 4.85 (1H, s, H-4), 4.01 (1H, s, H-3), 3.08 (1H, dd, $J = 4.4, 16.0\text{Hz}$, H-4'), 2.96 (1H, d, $J = 16.0\text{Hz}$, H-4'); ring-B: 6.46 (2H, s, H-2, H-6), 6.66 (2H, s, H-2', H-6'); Galloyl: 7.08 (2H, s, H-2, H-6).

没食子酸 (gallic acid) (10) Negative FAB-MS, m/z (%): 169 $[\text{M}(\text{C}_7\text{H}_6\text{O}_5) - \text{H}]^-$ (100). $\text{UV}\lambda_{\text{max}} \text{nm}$ (MeOH): 215.5, 267, $\text{IR}\nu_{\text{max}} \text{cm}^{-1}$: 3378, 1702, 1619, 1541, 1450, 1340,

1248, 1027, 868, 790, 766, 732. ^{13}C (CD_3OD): 121.99 (C-1), 110.34 (C-2, C-6), 146.26 (C-3, C-5), 139.50 (C-4), 170.49 (C=O); ^1H NMR (CD_3OD): 7.06 (2H, s, H-2, H-6).

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