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无花果亚属植物异戊烯基类黄酮及其生物活性研究进展

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摘要：无花果亚属隶属于桑科，既是重要的水果资源，也是优良的中药资源，广泛种植于热带、亚热带地区，因含有丰富的生物活性成分和保健功效，经济价值突出。无花果亚属植物中异戊烯基类黄酮含量丰富，结构多样，已报道有 37 种异黄酮、2 种黄烷酮、7 种黄酮和 1 种查尔酮。无花果异戊烯基类黄酮具有突出的抗氧化活性，能够缓解更年期症状，保护骨骼、预防炎症、预防癌症等。从化学结构和生物活性两方面对无花果亚属植物的异戊烯基黄酮类化合物的研究概况进行总结，以期为该属植物的开发和利用提供参考。

关键词：异戊烯基类黄酮；生物活性；桑科；无花果亚属；综述

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Prenylated Flavonoids in *Ficus* subgenus: Chemistry and Bioactivities

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Abstract: Subgenus *Ficus* belongs to Moraceae, which is an important resource of fruit and herbal medicine. *Ficus* subgenus is widely planted in tropical and subtropical areas. It has outstanding economic value because of abundant bioactive compounds and multiple health benefits. Prenylated flavonoids are the characteristic bioactive compounds of *Ficus* subgenus, including 37 isoflavones, 2 flavanones, 7 flavones, and 1 chalcone. Numerous biological activities have been reported for these prenylated flavonoids, such as menopause relief, bone protection, anti-inflammation, anti-oxidation, cancer prevention and anti-bacteria activities. The updated information regarding the prenylated flavonoids in *Ficus* subgenus was summarized, and also their chemical structures and biological activities. The information is helpful for the development and utilization of this subgenus.

Key words: Prenylated flavonoid; Biological activity; Moraceae; *Ficus* subgenus; Review

无花果亚属(*Ficus* subgenus)是榕属(*Ficus* genus)中最大的开花植物属，包含 700 余种植物[1]。原产于西南亚和地中海地区，现已在热带、亚热带及温带地区广泛种植[2]。无花果亚属植物具有重要的食用和药用价值[3–4]，其果实在很多国家可食用，根和叶则被应用于传统医药。在越南，地果(*F. tikoua*)广泛用于治疗水肿、痢疾、脓疱等病症[5]，因其提取物具有显著的抗菌活性[6]，常被用来提取精油。

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在印度，对叶榕(*F. hispida*)常用于治疗皮肤、呼吸系统和泌尿系统等的疾病[7]。作为无花果亚属中最具商业价值的水果，无花果(*F. carica*)既是口感甜美的水果食品，同时也具有祛痰、疏肝、消炎、抗癌功效并用于治疗肝脾疾病等[8–9]。查阅近年来国内外对无花果亚属植物化学成分和生物活性的报道，该亚属植物富含类黄酮[10]、三萜、香豆素等活性成分[11–12]。其中，一些香豆素类成分，如马豆素、补骨脂素、香柠檬烯等可减少氧化应激，防止胰岛 β 细胞损伤，表现出降血糖活性[13]。部分萜类成分，如鲍尔烯醇、羽扇豆醇、齐墩果酸等具有抗氧化、抗炎、保肝等功效[11]。此外，异戊烯基黄酮类物质是该类植物的特征性物质，已成为近年来学者们关注的热点，具有重要的药用价值。本文对无花果亚属中异戊烯基黄酮类化合物进行综述。

1 结构类型

无花果亚属植物中，已报道 47 个异戊烯基黄酮类化合物。异戊烯基主要存在形式有 13 种(图 1)，其中二甲基烯丙基是主要的结构类型。取代位点发生在类黄酮 A 环或 B 环，以 A-异戊烯基化为主，最常见的取代位点为 A-6 位和 A-8 位；部分取代发生在 B 环上，主要取代位点为 B-2′和 B-4′处。除异戊烯基取代外，黄酮母核上通常还连有羟基和甲氧基。无花果亚属植物异戊烯基黄酮的类黄酮骨架类型主要以异黄酮为主，还包含少量的黄烷酮、黄酮、查尔酮(图 2, 3)。

2 异戊烯基黄酮类成分和生物活性

黄酮类化合物是重要天然活性物质，安全性好，具有抗肿瘤、抗病毒、抗炎、抗菌等活性。已有化学及生物活性研究结果表明，大多数情况下，异戊烯基基团的引入会增加类黄酮的亲脂性，改善对生物膜的亲和性，显著提高生物活性[14–15]。表 1 列出了已报道的无花果亚属植物异戊烯基类黄酮的生物活性。

2.1 雌激素受体调节活性

异戊烯基异黄酮是无花果异戊烯基类黄酮的主要结构形式，在结构上与雌激素相似[16]，可以与雌激素 α、β 受体结合，并具有选择性。通过发挥雌激素受体调节活性，异戊烯基异黄酮可缓解更年

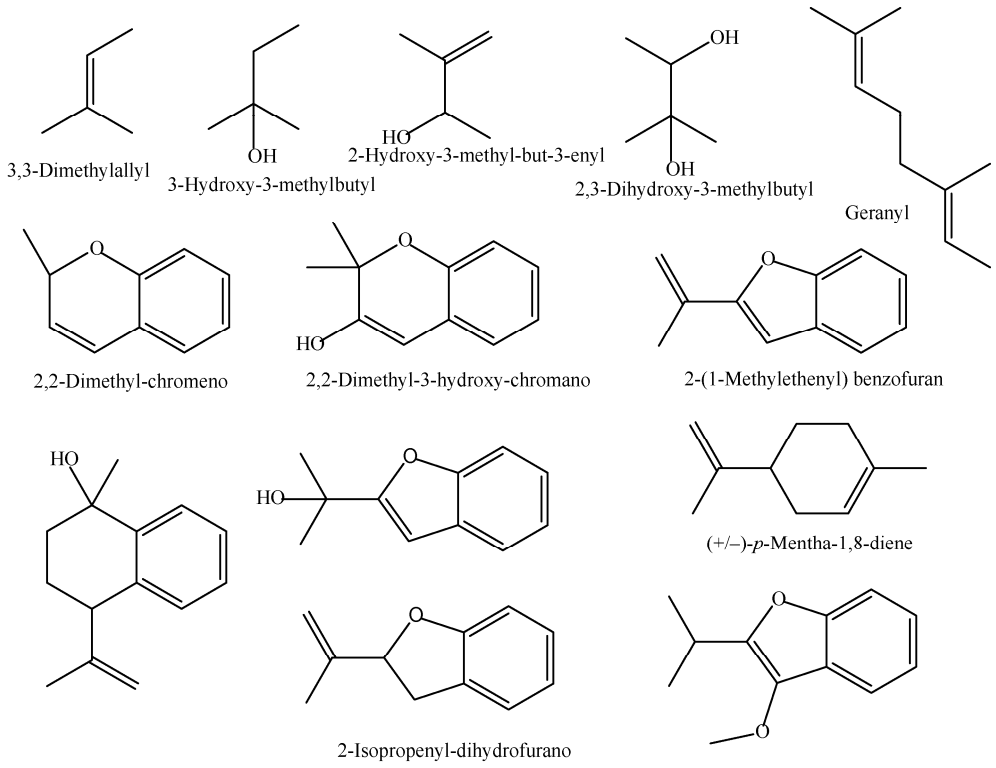

图 1 异戊烯基结构

Fig. 1 Structures of prenylation

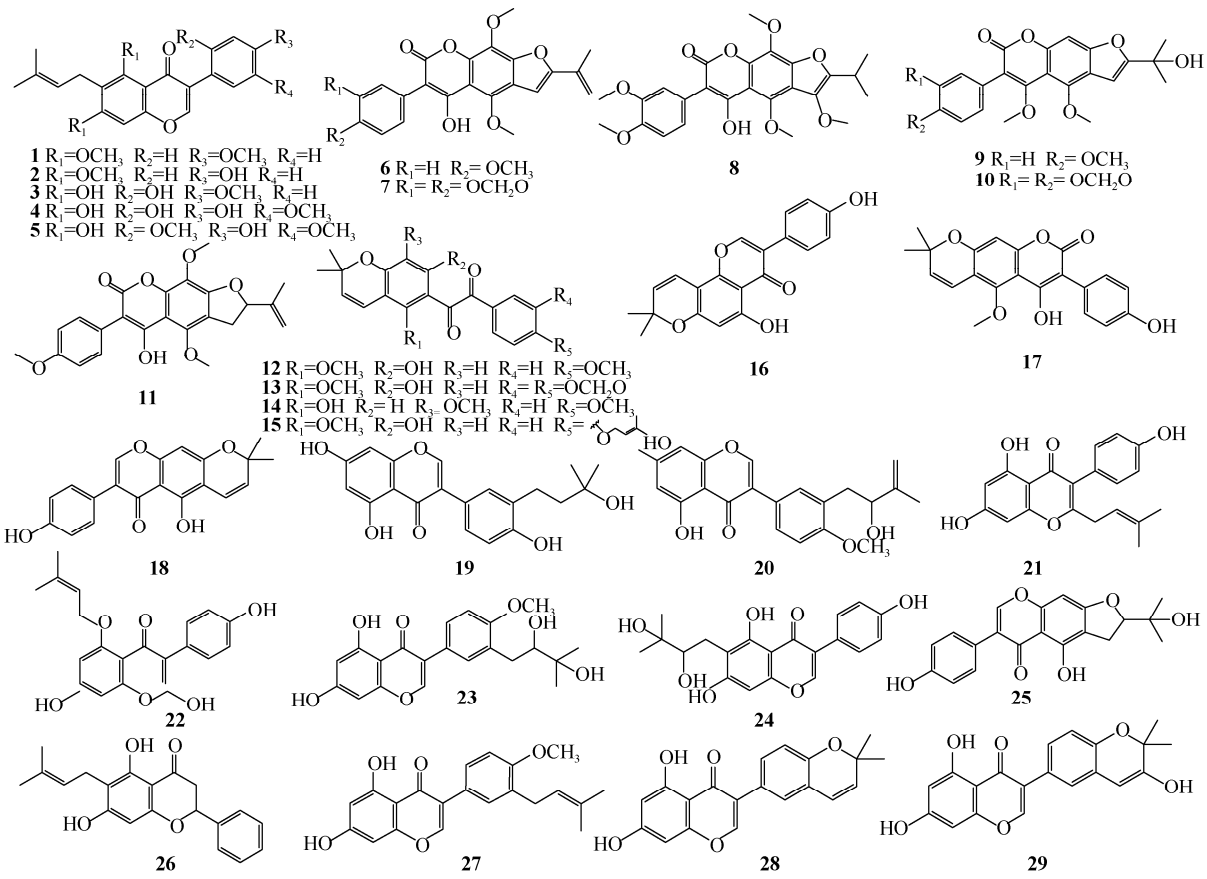

图 2 无花果亚属植物异戊烯基类黄酮成分结构(**1**～**29**)

Fig. 2 Structures of prenylated flavonoids in *Ficus* subgenus (**1**–**29**)

期症状，保护骨骼，预防乳腺癌[17]等疾病。在已经报道的 47 种异戊烯基类黄酮中，37 种为异戊烯基异黄酮。因此，无花果亚属植物是丰富的异戊烯基异黄酮资源，可用于功能食品或药物开发。

2.2 抗氧化

氧化损伤是引发癌症、心血管疾病、动脉粥样硬化等多种慢性病的重要因素[18]，常常伴随炎症的产生。通过抑制或延迟氧化反应来预防和治疗疾病十分重要[19]。作为膳食抗氧化剂，食源性黄酮类成分在减缓氧化损伤中具有重要作用。已有研究表明[5,7,11,20–21]，无花果中大部分异戊烯基类黄酮成分(化合物 **17**、**18**、**21**、**22**、**29**、**35**、**37**、**42**、**45**、**46**、**47**)表现出优良的清除 DPPH 自由基活性。抗氧化活性强弱和异戊烯基类黄酮的母核结构、官能团排列、酚羟基数目直接相关。B 环羟基与 2,3-烯基的存在是影响抗氧化活性的重要因素[22]。此外, Popoola 等[23]的研究表明，化合物 **26** 还可以抑制酪氨酸酶活性，减少体内自由基的积累，进而预防皮肤衰老。

2.3 预防炎症

炎症，通常是机体对抗外界感染而产生的防御性免疫反应[24]。炎症失衡可引发哮喘、糖尿病等多种急、慢性并发症[15]。在无花果异戊烯基类黄酮中，17 种成分通过调节促炎分子合成和炎症相关细胞因子分泌而表现出抗炎活性。其中，化合物 **1**~**15** 通过抑制 NO 的产生而缓解炎症反应[25]。化合物 **47** 对抑制单核细胞 / 巨噬细胞活化具有重要作用[26]。在这些具有抗炎活性的化合物中，**9**~**11**、**13** 表现出强抗炎活性(IC_{50} 值 <2 μmol/L)[25]。这几个物质的类黄酮骨架结构与异戊烯基结构特征是影响其抗炎活性的关键因素。

2.4 预防癌症

抗炎治疗是治疗早期肿瘤进展和恶性转化的一种有效的治疗方法。无花果异戊烯基类黄酮在发抗炎活性的同时，也具有抗癌细胞增殖作用[27]。

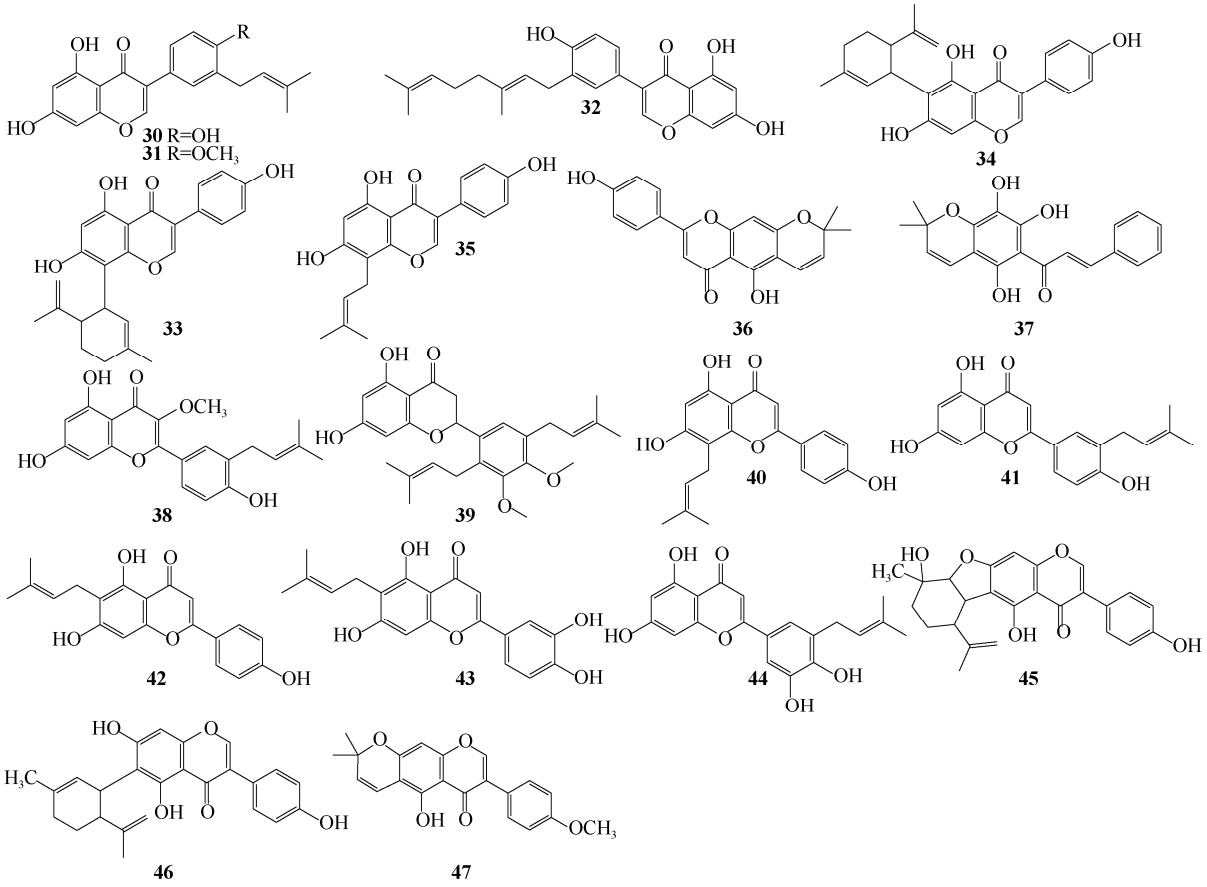

图 3 无花果亚属植物异戊烯基类黄酮成分结构(**30**～**47**)

Fig. 3 Structures of prenylated flavonoids in *Ficus* subgenus (**30**–**47**)

此外，异戊烯基类黄酮通过调节不同分子靶点发挥癌症预防作用。主要机制包括诱导细胞凋亡、抑制血管生成、调控遗传因子、转录因子等[28]。如化合物 **16** 可通过诱导细胞中 ROS 和 ERK 抑制癌细胞增殖[29]；化合物 **44** 可抑制 A549 和 NCI-292 细胞的增殖[30]。化合物 **18** 通过诱导肺细胞、食管鳞状细胞、肾细胞凋亡抗癌[21]；化合物 **20** 对 TPA 诱导的 Raji 细胞中 EBV-EA 活化的抑制作用明显[31]; 化合物 **35** 可抑制前列腺癌细胞系(DU-145)和静脉内皮细胞系(HUVEC)实现抗肿瘤和抗血管生成作用[32]；化合物 **42** 通过 MAPK 和 AKT 信号传导途径诱导 HeLa 细胞凋亡预防癌症[33]。

2.5 抗菌活性

不同于常规药物，植物类黄酮在发挥抗菌活性的同时具有较好的安全性，可以选择性地靶向细菌细胞，抑制毒性因子和微生物威胁的同时，不会引发抗生素耐药性等问题[53]，已成为目前最受欢迎的生物抗菌剂之一。无花果异戊烯基类黄酮物质中，化合物 **18** 和 **30** 对金黄色葡萄球菌，大肠杆菌、李斯特菌具有抑制作用[30–31]。化合物 **17** 可抑制结核分岐杆菌[38]，表现出抗结核作用，可用于开发肺部感染的抗菌药物。Lopes 等[28,33]的研究表明，化合物 **2** 和 **4** 具有明显抗真菌活性，可能是由于羟基化程度的增加导致对微生物的抑制能力提升。此外，化合物 **21** 和 **22** 也表现出抗菌活性[11]，其抗菌机理还需进一步研究。

2.6 其他活性

Sakat 等[7]报道，化合物 **31**～**34** 和 **38** 可通过抑制 α-葡萄糖苷酶活性预防糖尿病。与目前在 T2D 的治疗中使用的 α-葡萄糖苷酶抑制剂(如阿卡波糖)相比，不产生胃肠道副作用，有希望成为新型和更安全的治疗药物。Jung-Hae 等[43]报道，化合物 **28** 可通过抑制血小板来预防血栓。Matsuda 等[42]的研究表明，化合物 **24** 可抑制 D-半乳糖胺诱导的小鼠原代肝细胞的细胞毒性，具有保肝作用。Williams 等[35]的研究表明，化合物 **3**、**25** 和 **33** 可通过抑制 BACE1 活性预防阿尔兹海默症。

表 1 无花果亚属植物异戊烯基类黄酮

Table 1 Prenylated flavonoids in *Ficus* subgenus

编号 No.	成分 Component	部位 Part	类别 Type	主要活性 Main activity	取代位点 Replace site	植物 Species	文献 Reference
1	Ficucaricone D	果实 Fruit	异黄酮 Isoflavone	①②	A	无花果 *F. carica*	[25]
2	4′-羟基-5,7-二甲氧基-6-(3-甲基-2-丁烯基)-异黄酮 4′-Hydroxy-5,7-dimethoxy-6-(3-methyl-2-butenyl)-isoflavone	果实 Fruit	异黄酮 Isoflavone	①②③	A	无花果 *F. carica*	[25,34]
3	甘草宁 Gancaonin N	果实 Fruit	异黄酮 Isoflavone	①②④	A	无花果 *F. carica*	[25,35]
4	Isopiscerythrone	果实 Fruit	异黄酮 Isoflavone	①②⑤	A	无花果 *F. carica*	[25]
5	Viridiflorin	果实 Fruit	异黄酮 Isoflavone	①②	A	无花果 *F. carica*	[25]
6	Asthonningine B	果实 Fruit	异黄酮 Isoflavone	①②	A	无花果 *F. carica*	[25]
7	Thonningine A	果实 Fruit	异黄酮 Isoflavone	①②	A	无花果 *F. carica*	[25]
8	3″,4″-Dihydrothonningine C	果实 Fruit	异黄酮 Isoflavone	①②	A	无花果 *F. carica*	[25]
9	无花果酮 A Ficucaricone A	果实 Fruit	异黄酮 Isoflavone	①②	A	无花果 *F. carica*	[25]
10	无花果酮 B Ficucaricone B	果实 Fruit	异黄酮 Isoflavone	①②	A	无花果 *F. carica*	[25]
11	Indicanine A	果实 Fruit	异黄酮 Isoflavone	②	A	无花果 *F. carica*	[25,36]
12	1-[6-羟基-2-甲氧基-2″,2″-二甲基-吡喃酮-(5″,6″:3,4)]-2-(4′-甲氧基苯基)-1,2-联苯酰 1-[6-Hydroxy-2-methoxy-2″,2″-dimethyl-pyrano-(5″,6″:3,4)]-2-(4′-methoxyphenyl)-1,2-ethanedione	果实 Fruit	异黄酮 Isoflavone	①②	A	无花果 *F. carica*	[25]
13	1-[6-羟基-2-甲氧基-2″,2″-二甲基-吡喃酮-(5″,6″:3,4)]-2-(3′,4′-甲氧基苯基)-1,2-联苯酰 1-[6-Hydroxy-2-methoxy-2″,2″-dimethylpyrano-(5″,6″:3,4)]-2-(3′,4′-methylenedioxyphenyl)-1,2-ethanedione	果实 Fruit	异黄酮 Isoflavone	①②	A	无花果 *F. carica*	[25,37]
14	二烯雌酮 Dielsianone	果实 Fruit	异黄酮 Isoflavone	②	A	无花果 *F. carica*	[25]
15	Ficucaricone C	果实 Fruit	异黄酮 Isoflavone	①②	A	无花果 *F. carica*	[25]
16	Derrone	果实 Fruit	异黄酮 Isoflavone	⑦	A	莲叶榕 *F. nymphaeifolia*	[25,29]
17	Indicanine B	果实 Fruit	异黄酮 Isoflavone	②⑫	A	无花果 *F. carica*	[20,25,31,38]
18	猫尾草异黄酮 Alpinum isoflavone	果实 Fruit	异黄酮 Isoflavone	⑥⑦⑫	A	小叶铺地榕, 对叶榕 *F. tikoua*, *F. hispida*	[7,21,39]
19	Isowigtheone hydrate	果实 Fruit	异黄酮 Isoflavone	⑦	B	对叶榕 *F. hispida*	[7,40]
20	5,7-Dihydroxy-4′-methoxy-3′-(3-methyl-2-hydroxybuten-3-yl) isoflavone	果实 Fruit	异黄酮 Isoflavone	⑦	B	对叶榕 *F. hispida*	[7,40]
21	异丙基羟基染料木素 Prenylhydroxygenistein	叶子 Leaf	异黄酮 Isoflavone	⑥⑦⑫	C	无花果 *F. carica*	[11]
22	异戊二烯基染料木素 Prenylgenistein	叶子 Leaf	异黄酮 Isoflavone	⑥⑦⑫	A	无花果 *F. carica*	[11]
23	5,7-二羟基-4-甲氧基-3′-(2,3-二羟基-3-甲基丁基)异黄酮 5,7-Dihydroxy-4-methoxy-3′-(2,3-dihydroxy-3-methylbutyl) isoflavone	树皮 Bark	异黄酮 Isoflavone	⑥⑦⑫	B	莲叶榕 *F. nymphaeifolia*	[41]
24	Erycibenin A	树皮 Bark	异黄酮 Isoflavone	⑧	A	莲叶榕 *F. nymphaeifolia*	[41,42]
25	Erythrinin C	树皮 Bark	异黄酮 Isoflavone	④	A	莲叶榕 *F. nymphaeifolia*	[35,41]
26	异甘草素 Isoglabranin	树皮 Bark	二氢异黄酮类 Dihydroisoflavones	⑫	A	台湾榕 *F. formosana*	[23,41]
27	3′-(3-Methylbut-2-enyl) biochanin A	树皮 Bark	异黄酮 Isoflavone	⑦	B	莲叶榕 *F. nymphaeifolia*	[41]
28	Isoderrone	树枝 Branch	异黄酮 Isoflavone	⑨⑩	B	对叶榕 *F. hispida*	[7,43]
29	Ficuisoflavone	树枝 Branch	异黄酮 Isoflavone	⑫	B	对叶榕 *F. hispida*	[7,44]
30	Isowighteone	树枝 Branch	异黄酮 Isoflavone	⑥	B	对叶榕 *F. hispida*	[7,45]
31	3′-(3-Methylbut-2-en-1-yl) biochanin A	树枝 Branch	异黄酮 Isoflavone	⑨	B	对叶榕 *hispida*	[7,46]
32	Myrsininone A	树枝 Branch	异黄酮 Isoflavone	⑥⑨	B	对叶榕 *F. hispida*	[7,47]
33	补骨脂香豆素 A Ficusin A	树枝 Branch	异黄酮 Isoflavone	⑨	A	对叶榕 *F. hispida*	[7,35]
34	4′,5,7-Trihydroxy-6-[(1R*,6R*)-3-methyl-6-(1-methylethenyl)cyclohex-2-en-1-yl]isoflavone	树枝 Branch	异黄酮 Isoflavone	⑨	A	对叶榕 *F. hispida*	[7,46]
35	黄羽扇豆魏特酮 Lupiwighteone	树枝 Branch	异黄酮 Isoflavone	⑥⑦⑫	A	对叶榕 *F. hispida*	[7,32]
36	Carpachromene	树枝 Branch	黄酮类 Flavones	⑫	A	对叶榕 *F. hispida*	[7,48]
37	Mallotus A	树枝 Branch	查尔酮 Chalcones	⑫	A	对叶榕 *F. hispida*	[7,49]

续表(Continued)

编号 No.	成分 Component	部位 Part	类别 Type	主要活性 Main activity	取代位点 Replace site	植物 Species	文献 Reference
38	5,7,4′-Trihydroxy-3-methoxy-3′-(3-methylbut-2-en-1-yl) flavone	树枝 Branch	黄酮类 Flavones	⑨	B	对叶榕 *F. hispida*	[7,46]
39	无花果酮 A Ficusflavonid A	根 Root	二氢黄酮类 Dihydroisoflavones		B	粗叶榕 *F. hirta*	[50]
40	甘草黄酮 C 4′,5,7-Trihydroxy-8-prenylflavone	根 Root	黄酮类 Flavones		A	粗叶榕 *F. hirta*	[50]
41	3′-Isoprenylgenistein	根 Root	黄酮类 Flavones	⑪	B	粗叶榕 *F. hirta*	[50,51]
42	异戊烯基芹菜素 6-Prenylapigenin	根 Root	黄酮类 Flavones	⑦⑫	A	粗叶榕 *F. hirta*	[33,50,52]
43	6-C-Prenyl luteolin	根 Root	黄酮类 Flavones		A	粗叶榕 *F. hirta*	[50]
44	朝藿素 D Epimedokoreanin D	根 Root	黄酮类 Flavones	⑦	B	粗叶榕 *F. hirta*	[30,50]
45	Ficusin C	根 Root	异黄酮 Isoflavone	⑫	A	地果 *F. tikoua*	[5]
46	6-[(1R*,6R*)-3-Methyl-6-(1-methylethenyl)-2-cyclohexen-1-yl]-5,7,4′-trihydroxyisoflavone	根 Root	异黄酮 Isoflavone	④⑫	A	地果 *F. tikoua*	[5,35]
47	4′-*O*-Methylalpinumisoflavone	根 Root	异黄酮 Isoflavone	①⑫	A	地果 *F. tikoua*	[5,26]

①: 抗炎; ②: 抗细胞增殖; ③: 抗皮肤炎症; ④: 预防阿尔兹海默症; ⑤: 抗真菌; ⑥: 抗菌; ⑦: 预防癌症; ⑧: 保肝作用; ⑨: 预防糖尿病; ⑩: 预防血栓; ⑪: 促进骨细胞增殖; ⑫: 抗氧化。

①: Anti-inflammatory; ②: Cell proliferation-inhibitory; ③: Anti-dermatitis; ④: Alzheimer's disease prevention; ⑤: Antifungal activity; ⑥: Antibacterial; ⑦: Cancer prevention; ⑧: Hepatoprotective activity; ⑨: Anti-diabetic; ⑩: Thromboprophylaxis; ⑪: Proliferation-promote of osteoblast; ⑫: Antioxidant.

3 展望

因为富含结构多样、活性突出的异戊烯基类黄酮物质，无花果亚属植物已成为功能食品、天然药物领域的重要原料来源。在未来研究中，仍需加强对无花果亚属植物的化学成分发掘，深入阐明其生物活性作用机理以及构效关系。相关研究结果对于该亚属植物的综合开发与利用具有重要意义。

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