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泽漆化学成分及药理作用研究进展

杨 莉, 陈海霞, 高文远*

(天津大学药物科学与技术学院, 天津 300072)

摘 要:泽漆 *Euphorbia helioscopia* 在我国分布广泛, 具有多种药理活性, 临床用于治疗腹水、水肿、肺结核、颈淋巴结核、痰多咳嗽、癰疮, 民间还用于治疗宫颈瘤、食道癌等。泽漆主要含二萜酯类、黄酮、三萜、甾醇、多酚类、氨基酸及天然油脂类化合物。现归纳近年来泽漆化学成分、药理作用和临床应用等方面的研究成果, 为全面开发利用药用植物泽漆提供参考。

关键词:泽漆; 生物活性; 二萜酯类化合物

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* 通讯作者 高文远 Tel: (022)87401895 E-mail: pharmsgao@tju.edu.cn

Advances in studies on chemical constituents in *Euphorbia helioscopia* and their biological activities

YANG Li, CHEN Hai-xia, GAO Wen-yuan

(School of Pharmaceutical Science and Technology, Tianjin University, Tianjin 300072, China)

Key words: *Euphorbia helioscopia* L.; biological activities; diterpene esters

泽漆是大戟属(*Euphorbia* L.)植物泽漆 *Euphorbia helioscopia* L. 的干燥全草,别名猫儿眼睛草、五凤灵芝等,分布于除新疆、西藏以外的全国各地。长期以来泽漆一直作为民间草药,味苦,性微寒,有毒,归肺、小肠、大肠经。据《本草纲目》记载,泽漆有利水消肿、消痰退热、散结杀虫等功效。临床用于治疗腹水、水肿、肺结核、颈淋巴结核、痰多咳嗽、癰疮,民间还用于治疗宫颈癌、食道癌等,并具有一定疗效,因此泽漆是一味很有研究开发价值的药材。纵观泽漆的文献未见关于化学成分及其药理活性的综述报道,现归纳近年来泽漆化学成分、药理作用和临床应用等方面的研究成果,为全面开发利用药用植物泽漆提供参考。

1 化学成分

泽漆主要含二萜酯类、黄酮类化合物,是其主要的生物活性物质,另外还含有三萜、甾醇、多酚类、氨基酸、天然油脂类化合物等多种成分。

1.1 二萜酯类化合物:二萜酯类化合物是泽漆的主要有效成分,主要分布于泽漆的乳汁中,根部也有分布。二萜酯类化合物对皮肤有刺激性,有辅助抗癌的作用。泽漆中二萜酯类

化合物的结构见图1和表1。从泽漆中分离得到的二萜酯类化合物共有52个,其中千金二萜(Lathyrane)型酯有3个化合物^[1],假白榄酮(Jatrophone)型酯有37个化合物^[1~4],松香烷(Abietane)型二萜酯有4个化合物^[2,4],巨大戟烷(Ingane)型酯有6个化合物^[5],4个巴豆萜烷(Tigliane)型二萜酯^[6]。

1.2 三萜类和倍半萜类化合物:泽漆中发现的三萜化合物有19aH-羽扇豆醇(19aH-lupeol)^[7,8]和羽扇豆醇乙酸酯^[8]。倍半萜类挥发油橄榄醇和 β -桉油醇^[9],最近报道^[4]从大戟属中分离得到了3种倍半萜:hemisteapsin、4,5-二羟基-布卢门醇A、淫羊藿苷B2苷元。

1.3 多酚类化合物:从泽漆中分离得到的多酚类化合物主要包括可水解鞣质和单元体多酚,可水解鞣质有泽漆鞣质A、泽漆鞣质B、泽漆新鞣质A、泽漆新鞣质B、泽漆半新鞣质^[10],其中泽漆鞣质A(结构见图2)具有抗过敏和平喘的作用。单元体多酚主要有原儿茶酸、没食子酸、短叶苏木酚(brevifolin)、1,2,3-三氧-没食子酰-葡萄糖苷(1,2,3-tri-O-galloyl- β -D-glucose)、鞣云实精(corilagin)等化合物^[11]。

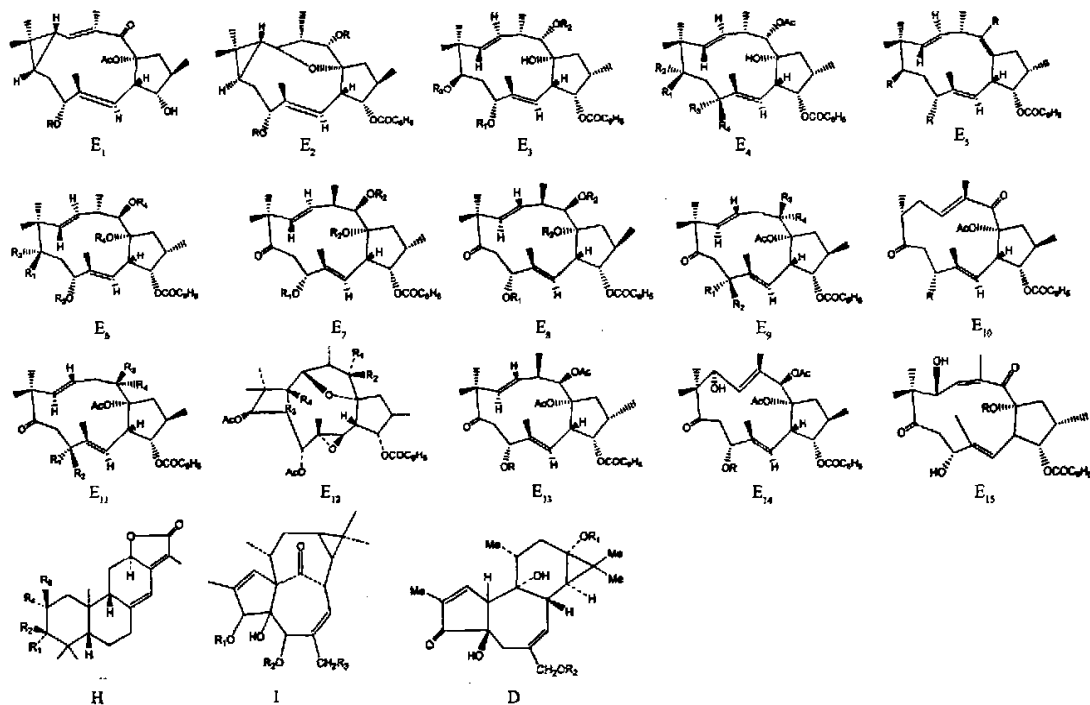


图1 泽漆中二萜酯类化合物结构母核

Fig. 1 Skeleton of diterpene esters from *E. helioscopia*

表 1 泽漆中二萜酯类化合物

Table 1 Diterpene esters from *E. helioscopia*

化合物	母核	取代基	化合物	母核	取代基
千金二萜烷型酯			泽漆双环萜 A	E ₁₂	R ₁ =OAc, R ₃ =OH, R ₂ =R ₄ =H
泽漆三环萜 A	E ₁	R=(2E,4Z)-2,4-octadienoyl	泽漆双环萜 B	E ₁₂	R ₁ =R ₃ =OH, R ₂ =R ₄ =H
泽漆三环萜 B	E ₁	R=4,5-epoxy-trans-2-octenoyl	泽漆双环萜 C	E ₁₂	R ₁ =OAc, R ₃ =OCOC ₆ H ₅ , R ₂ =R ₄ =H
泽漆环萜	E ₂	R=COC ₆ H ₅	泽漆双环萜 D	E ₁₂	R ₁ R ₂ =R ₃ R ₄ =O
假白桦酮型酯			泽漆双环萜 E	E ₁₂	R ₁ R ₂ =O, R ₃ =OH, R ₄ =H
大戟苷	E ₃	R ₁ =R ₂ =R ₃ =Ac	泽漆新萜 A	E ₈	R ₁ =Nic*, R ₂ =R ₃ =Ac
大戟苷 A	E ₃	R ₁ =H, R ₂ =R ₃ =Ac	泽漆新萜 B	E ₁₃	R=Nic
大戟苷 B	E ₃	R ₁ =R ₂ =Ac, R ₃ =H	泽漆新萜 C	E ₁₄	R=Ac
大戟苷 C	E ₄	R ₁ =OAc, R ₂ =H, R ₃ =R ₄ =O	泽漆新萜 D	E ₁₅	R=Ac
大戟苷 D	E ₆	R ₁ =OAc, R ₂ =H, R ₃ =R ₄ =Ac	松香烷型二萜酯		
大戟苷 E	E ₅	R=OAc	泽漆内酯 A	H	R ₁ =OH, R ₂ =H, R ₃ =R ₄ =H
大戟苷 F	E ₄	R ₁ =R ₂ =O, R ₃ =OH, R ₄ =H	泽漆内酯 B	H	R ₁ =H, R ₂ =OH, R ₃ =R ₄ =H
大戟苷 G	E ₄	R ₁ =R ₂ =O, R ₃ =OAc, R ₄ =H	2α-羟基-泽漆内酯 B	H	R ₁ =OH, R ₂ =H, R ₃ =R ₄ =O
大戟苷 H	E ₆	R ₁ =R ₂ =O, R ₃ =R ₄ =Ac	泽漆内酯 C	H	R ₁ =R ₂ =O, R ₃ =R ₄ =H
大戟苷 I	E ₆	R ₁ =R ₂ =O, R ₃ =H, R ₄ =Ac	巨大戟烷型二萜酯		
大戟苷 J	E ₇	R ₁ =R ₂ =Ac	3-O-当归甾巨大戟二萜	I	R ₁ =COC(CH ₃) ₂ CHCH ₃ , R ₂ =H, R ₃ =OH
大戟苷 K	E ₇	R ₁ =H, R ₂ =Ac	3-O-(2,4,6-三烯酯)巨大戟二萜	I	R ₁ =CO(CH=CH) ₃ (CH ₂) ₂ CH ₃ , R ₂ =H, R ₃ =OH
泽漆苷 A	E ₈	R ₁ =H, R ₂ =R ₃ =Ac	3-O-(2,4-二烯酯)巨大戟二萜	I	R ₁ =CO(CH=CH) ₂ (CH ₂) ₂ CH ₃ , R ₂ =H, R ₃ =OH
泽漆苷 B	E ₈	R ₁ =R ₂ =R ₃ =Ac	3-O-当归甾-20-脱氧巨大戟二萜	I	R ₁ =COC(CH ₃) ₂ CHCH ₃ , R ₂ =R ₃ =H
泽漆苷 C	E ₈	R ₁ =COC ₆ H ₅ , R ₂ =R ₃ =Ac	5-O-当归甾-20-脱氧巨大戟二萜	I	R ₁ =R ₃ =H, R ₂ =COC(CH ₃) ₂ CHCH ₃
泽漆苷 D	E ₉	R ₁ =R ₂ =O, R ₃ =OAc, R ₄ =H	巴豆萜烷型二萜酯		
泽漆苷 E	E ₉	R ₁ =OH, R ₂ =H, R ₃ =R ₄ =O	12-脱氧佛波醇-13-乙酸	D	R ₁ =COCH ₂ Ph, R ₂ =Ac
泽漆苷 F	E ₉	R ₁ =OAc, R ₂ =H, R ₃ =R ₄ =O	苯酯-20-乙酸酯		
泽漆苷 G	E ₈	R ₁ =R ₃ =H, R ₂ =Ac	12-脱氧佛波醇-13-癸二烯酯-20-乙酸酯	D	R ₁ =CO(CH ₂) ₁₀ Me, R ₂ =Ac
泽漆苷 H	E ₈	R ₁ =R ₂ =Ac, R ₃ =H	12-脱氧佛波醇-13-(2-甲基-顺-2-丁烯酸酯)-20-乙酸酯	D	R ₁ =COCMe=CHMe, R ₂ =Ac
泽漆苷 I	E ₈	R ₁ =R ₂ =H, R ₃ =Ac	12-脱氧佛波醇-13-(2-甲基-顺-2-丁烯酸酯)	D	R ₁ =COCMe=CHMe, R ₂ =H
泽漆苷 J	E ₈	R ₁ =R ₃ =Ac, R ₂ =H			
泽漆苷 K	E ₈	R ₁ =Ac, R ₂ =R ₃ =H			
泽漆苷 L	E ₁₀	R=OH			
表泽漆苷 A	E ₁₁	R ₁ =OH, R ₃ =OAc, R ₂ =R ₄ =H			
表泽漆苷 B	E ₁₁	R ₁ =OAc, R ₃ =OAc, R ₂ =R ₄ =H			
表泽漆苷 D	E ₁₁	R ₁ =R ₂ =O, R ₃ =OAc, R ₄ =H			
表泽漆苷 F	E ₁₁	R ₁ =OAc, R ₂ =H, R ₃ =R ₄ =O			

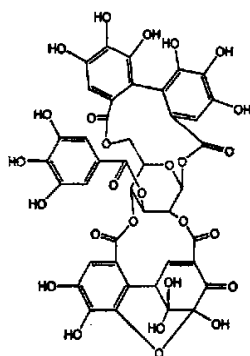
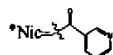


图 2 泽漆萜素 A^[12] 的结构

Fig. 2 Chemical structure of helioscopinin A

1.4 黄酮类化合物:泽漆中分离得到的黄酮类化合物主要包括槲皮素^[13]、山奈酚和以槲皮素为苷元的黄酮苷,如槲皮素-3-β-葡萄糖苷、槲皮素-3-β-半乳糖苷(金丝桃苷),槲皮素-3-β-半乳糖苷-2"-没食子酸盐^[14],槲皮素-5,3-二-D-半乳糖苷^[15]、槲皮素-3-双半乳糖苷(泽漆新苷, heliosin)^[14]等,据文

献报道^[4],泽漆中还含有甘草查耳酮 A、甘草查耳酮 B、光甘草酮、2',4,4'-三羟基查耳酮、4',5,7-三羟基二氢黄酮、刺甘草素(echinatin)等。

1.5 氨基酸:泽漆中分离得到两种氨基酸,即间二羟基苯甘氨酸和 3,5-二羟基苯甘氨酸^[16]。

1.6 油脂类化合物:泽漆中的油脂类化合物有月桂酸、肉豆蔻酸、棕榈酸、硬脂酸、油酸、亚油酸、花生酸、山萘酸等,还有二十八烷醇、二十七烷醇等^[17]。

2 药理作用

泽漆一直作为民间草药,味苦,性微寒,有毒。有利尿消肿、化痰散结、杀虫止痒的功效,临床用于治疗腹水、水肿、肺结核、颈淋巴结、痰多喘咳、癰疮。民间还用于治疗宫颈癌、食道癌等,有一定疗效。

2.1 抗肿瘤作用:在泽漆根体外抗肿瘤实验研究中,泽漆根水提取液(EWE)对人肝癌 7721 细胞、人宫颈癌 HeLa 细胞、人胃癌 MKN-45 细胞均有明显的抑制作用,提示泽漆有可能通过细胞毒作用发挥抗肿瘤作用,而且其直接细胞毒作用与时间、剂量呈正相关^[18]。

在EWE体内抗肿瘤作用研究中,以H₂₂、S₁₈₀荷瘤小鼠为模型,观察其抗肿瘤作用。结果EWE 10 g/kg有明显的体内抗移植瘤和延长荷瘤小鼠存活活期的作用,并且EWE还能降低荷瘤小鼠脾指数,使之趋向正常值。这提示EWE不仅能抑制体内肿瘤生长,还能提高机体的免疫能力^[19]。

通过对复方泽漆散对移植性C57BL/6J小鼠Lewis肺癌及S₁₈₀荷瘤鼠的抑制肿瘤实验表明,该方中剂量组对肿瘤细胞有明显的抑制作用,其抑瘤率大于30%,通过光谱、电镜观察细胞的病理学形态及超微结构证实,该方有促进肿瘤细胞凋亡和坏死、抑制肿瘤细胞有丝分裂的作用,并可影响线粒体的形态和功能^[20]。

2.2 抑制蘑菇酪氨酸酶活性:酪氨酸酶又称多酚氧化酶,其活性中心含有金属铜离子,广泛存在于动植物体和人体内,是生物体合成黑色素等色素的关键酶,抑制其活力即可抑制黑色素的生成。研究发现白化病等色素障碍性疾病、恶性黑色素瘤和老年性痴呆的发生与治疗,均与酪氨酸酶直接相关。在体外实验研究中发现,从泽漆中提取的可水解凝质酸对蘑菇酪氨酸酶有抑制作用^[21]。

2.3 平喘止咳作用:泽漆是一味疗效确切的化痰止咳药物,主要是通过化痰,使痰量减少,而达到止咳、平喘的目的。从泽漆中提取的多酚类化合物helioscopinin A,可通过抑制白三烯D₄诱导的反应而发挥抗变态反应和平喘的作用^[12]。另据报道,heliosin具有止咳作用^[13]。

2.4 抑菌作用:采用抑菌圈法分别测定泽漆醋酸乙酯粗提物对小麦赤霉病菌、小麦根腐病菌、番茄早疫病菌、苹果炭疽病菌、西瓜枯萎病菌、苹果腐烂病菌、葡萄白腐病菌、烟草赤星病菌等8种常见的植物病原菌的抑菌作用,结果表明:当在培养基中加入粗提物质量浓度为0.01 g/mL时,对小麦赤霉病菌、番茄早疫病菌、苹果炭疽病菌、苹果腐烂病菌、葡萄白腐病菌的相对抑制率达70%以上;当质量浓度为0.005 g/mL时,对小麦赤霉病菌、番茄早疫病菌、苹果炭疽病菌的相对抑制率达60%以上^[22]。

2.5 毒性及不良反应:泽漆的乳汁液对皮肤、黏膜有很强的刺激性。接触皮肤可致发红,甚至发炎、溃烂。如误服泽漆鲜草或乳白汁液后,口腔、食管、胃黏膜均可发炎、糜烂,有灼痛、恶心、呕吐、腹痛、腹泻水样便,严重者致脱水,甚至出现酸中毒。但小鼠灌胃泽漆125 g/kg亦未致死。临床用其煎液内服,即使剂量大至150 g/d,也未见明显毒性反应,可能有毒成分不溶于水。个别报道仅有口干、胃部不适、上腹疼痛等轻度反应,但仅占服药者的6.89%。研究发现,泽漆中的主要有毒物质为二萜酯类化合物,如大戟型二萜酯不仅对皮肤有刺激作用,还有或多或少的肿瘤促进作用^[23]。

3 临床应用

3.1 治疗鼻咽癌:李银良等^[24]用白毛苍耳汤和华蟾泽漆散治疗鼻咽癌,自1994—2005年,对观察的各期鼻咽癌患者286例,治愈率达41.96%,临床治愈率32.8%,好转23.43%,无效1.74%,总有效率为98.26%。

3.2 对肾脏的作用

3.2.1 丝虫性乳糜尿:泽漆可治疗乳糜尿,水煎30 min,分3次服,连服10 d,小便转清,乳糜试验转阴^[25]。

3.2.2 急性肾小球炎:泽漆复方可治疗急性肾小球炎,根据宣肺降逆可利水消肿,处方:桂枝、甘草各6 g,生姜、泽泻、泽漆、茯苓皮、石决明各30 g,半夏、紫菀、白前各12 g,黄芩、茯苓、白术、大腹皮、钩藤各15 g,服药后,浮肿明显消退,咽痛消失^[25]。

3.3 治疗支气管炎:据临床观察,用止漆散和泽漆汤加减治疗支气管炎,对急性支气管炎显效率达58.30%~67.92%,对慢性支气管炎45%。两方分别重在治疗咳嗽和痰多,可根据病症发展的不同阶段及个体差异,交叉使用两方^[26]。

3.4 治疗流行性腮腺炎:复方泽漆膏(泽漆1 000 g,鲜地丁50 g,金银花30 g,冰片0.5 g)可治疗流行性腮腺炎。将上述药品洗净去尘切碎,置入锅内,加水2 000 mL,煮沸30 min后滤过,弃去药渣,收取过滤液1 200 mL,再用文火煮至膏状,随后加入冰片,充分调和均匀,即得。临床观察,单侧流行性腮腺炎145例中,痊愈93例,显效48例,有效4例;双侧发病58例,痊愈34例,显效18例,有效6例^[27]。

4 结语

泽漆是一味产地广泛的大戟科植物,历代本草古籍都有记载,早在汉代已用于临床。在化学结构、结构鉴定和生物活性方面的研究已经取得了较为系统和深入的研究。但许多活性的研究均为简单粗提物,功效成分尚未明确,缺乏可控的质量标准。现代药理研究发现了泽漆的一些新的生物活性及其作用机制,因此,还有待进一步利用现代药学的研究手段,对其有效成分进行合理的开发利用,将其直接开发成新药,或以有效成分为先导化合物,设计合成更有效的新药,扩展这一药用植物的应用范围。

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曼地亚红豆杉研究进展

冯巍, 谈锋*, 谢峻

(西南大学生命科学学院, 三峡库区生态环境教育部重点实验室, 重庆市三峡库区植物生态与资源重点实验室, 重庆 400715)

摘要:曼地亚红豆杉 *Taxus media* 是东北红豆杉 *T. cuspidata* 和欧洲红豆杉 *T. baccata* 的天然杂交种。其枝叶中的紫杉醇量较高, 是利用红豆杉树皮提取抗癌药物紫杉醇的最佳替代原料。综述了曼地亚红豆杉的生物学特性及品系、生理生态、繁殖技术、细胞培养、紫杉醇生物合成相关酶基因的克隆及表达和分离纯化工艺等方面的研究进展。

关键词:曼地亚红豆杉; 紫杉醇; 生物合成

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Advances in studies on *Taxus media*

FENG Wei, TAN Feng, XIE Jun

(Key Laboratory of Eco-environments in Three Gorges Reservoir Region, Ministry of Education, Key Laboratory of Plant Ecology and Resources in Three Gorges Reservoir Region, School of Life Science, Southwest University, Chongqing 400715, China)

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作者简介: 冯巍(1983—), 女, 生化与分子生物学硕士研究生。

Tel: (023)68367091 Fax: (023)68252365 E-mail: feng2@swu.edu.cn

*通讯作者 谈锋 Tel: (023)68252698 Fax: (023)68252365 E-mail: tanfeng@swu.edu.cn