天然姜黄素类化合物的化学结构研究概况Δ

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摘　要　目的：综述天然姜黄素类化合物的化学结构研究概况，为该类化合物的进一步研究提供参考。方法：以“Curcumin”“Curcuminoids”“Darylheptanoids”“Structure identification”“姜黄素”“姜黄素类化合物”“二芳基庚烷类化合物”“结构鉴定”等为关键词，组合检索1985－2014年Medline、SciFinder Scholar、中国期刊全文数据库中关于天然姜黄素类化合物的相关报道，并归纳其结构及来源。结果与结论：共检索到相关文献57篇，其中有效文献34篇。天然姜黄素主要来源于姜科、桦木科、豆科、槭树科、马尾树科、胡桃科、蒟蒻薯科等植物。天然姜黄素类化合物的成分按化学结构特征可分为单氧代型、双氧代型、三氧代型、吡喃取代型、呋喃取代型、大环醚型、二聚体型等7个类型；其作为对人体无毒的天然药物，具有潜在的临床应用价值，值得进一步研究。

关键词　天然姜黄素类化合物；二芳基庚烷类化合物；姜科；姜黄素；化学结构

姜黄素类化合物主要是从姜科等药用植物中分离到的一类二芳基庚烷类化合物，在桦木科、豆科、槭树科、马尾树科、胡桃科、蒟蒻薯科等植物中也有发现。其以庚烷为母体，在第1、7位有芳基取代。以姜黄素、单去甲氧基姜黄素和双去甲氧基姜黄素最为常见。姜黄素类化合物具有良好的抗氧化、抗炎、抗肿瘤、降血糖、抗人类免疫缺陷病毒（HIV）等药理作用，并可用于治疗心血管疾病及阿尔茨海默病等[1]。笔者以“Curcumin”“Curcuminoids”“Darylheptanoids”“Structure identification”“姜黄素”“姜黄素类化合物”“二芳基庚烷类化合物”“结构鉴定”等为关键词，组合检索1985－2014年Medline、SciFinder Scholar、中国期刊全文数据库中关于天然姜黄素类化合物的相关报道，归纳其结构及来源。结果，共检索到相关文献57篇，其中有效文献34篇。现就天然姜黄素类化合物的化学结构研究概况综述如下，以期为该类化合物的进一步研究提供参考。

1　天然姜黄素类化合物的类型

按庚烷母体结构中的庚烷连接链上含氧取代基的种类和数目，以及是否成环，可将姜黄素类化合物分为单氧代型、双氧代型、三氧代型、吡喃取代型、呋喃取代型、大环醚型、二聚体型等7个类型，现分别进行介绍。

1.1　单氧代型姜黄素类化合物

该类化合物主要是庚烷或戊烷链上有1个羰基或1个醇基取代，且多有双键存在，共12个，分别是：7-（4-Hydroxy-3-methoxyphenyl-1-（4-hydroxyphenyl）-4-heptene-3-one（1）[2]、1，7-Bis（4-hydroxylphenyl）-4，6-heptadien-3-one（2）[3]、7-（4-Hydroxy-3-methoxyphenyl）-1-（4-hydroxyphenyl）-4，6-heptadien-3-one（Tsaokoarylone）（3）[4]、1，7-Bis（4-hydroxy-3-methoxyphenyl）-1，4，6-heptatrien-3-one（4）[5]、1-（3，5-Dihydroxy-4-methoxyphenyl）-7-phenyl-3-heptanone（5）、1-（2，4-Dihydroxy-3-methoxyphenyl）-7-（4-methoxyphenyl）-3-heptanone（6）[6]、1，7-Bis（3-hydroxy-4-*O*-*β*-*D*-glucopyranosylphenyl）heptan-3-one（Plantagineoside A）（7）[7]、5-Acetoxy-1，7-diphenyl-1，3-heptadiene（8）[8]、5-Hydroxy-1-phenyl-7-（4-hydroxyphenyl）-1-heptene（9）、5-Hydroxy-1-phenyl-7-（3，4-dihydroxyphenyl）-1-heptene（10）[9]、5-Hydroxy-1，7-diphenyl-1，3-heptadiene（11）[8]、（3*S*）-1，7-Bis（3-hydroxy-4-*O*-*β*-*D*-glucopyranosylphenyl）heptan-3-ol（plantagineoside B）（12）[7]。其具体结构见图1。

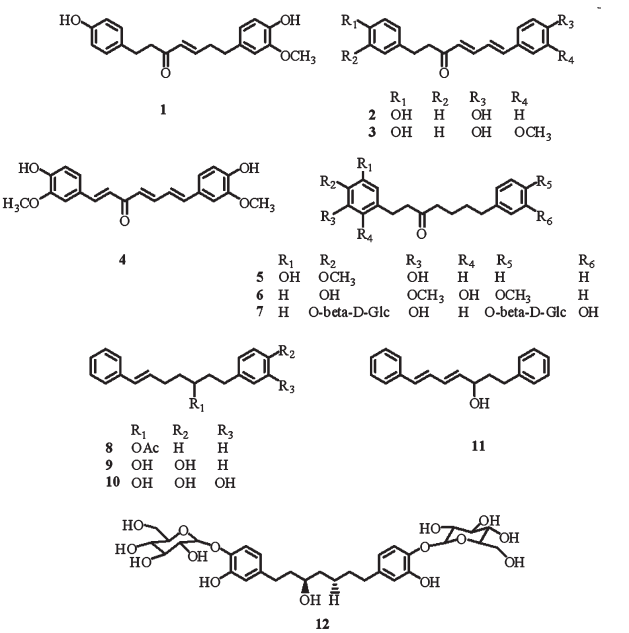

图1　单氧代型姜黄素类化合物

1.2　双氧代型姜黄素类化合物

该类化合物的庚烷链上主要有以下几种取代模式：*β*-二酮基、酮-烯醇、1个羰基和1个醇基、2个醇基、1个醇基和1个糖基取代，共66个，分别是：Curcumin（13）、Demethoxycurcumin（14）、Bisdemethoxycurcumin（15）[1]、1-（4-Hydroxyphenyl）-7-（3，4-dihydroxyphenyl）-1，6-heptadiene-3，5-dione（16）[10]、5-Hydroxy-1-（4-hydroxy-3-methoxyphenyl）-7-（4-hydroxyphenyl）-4，6-heptadiene-3-one（Letestuianin A）（17）[11]、5-Hydroxy-1-（3-me-

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thoxy-4-hydroxyphenyl)-7-phenyl-4, 6-heptadien-3-one (18)[12]、1, 7-Bis (4-hydroxyphenyl) -3, 5-heptandione (Letestuianin C) (19)[11]、Terpecurcumin B(20)、Terpecurcumin C(21)、Terpecurcumin D(22)、Terpecurcumin E(23)、Terpecurcumin F(24)、Terpecurcumin G (25)、Terpecurcumin H (26)、Terpecurcumin I (27)、Terpecurcumin A(28)、Bisabolocurcumin ether(29)、Demethoxybisabolo curcumin ether(30)、Didemethoxybisabolocurcumin ether (31)[13]、(5*S*) -5-methoxy-1, 7-bis (4-hydroxyphenyl)-1-hepten-3-one(32)[3]、(4*E*, 6*R*)-6-hydroxy-7-(4-hydroxy-3-methoxyphenyl)-1-phenyl-4-heptene-3-one(Alpinoid B)(33)、(4*E*,6*R*)-6-hydroxy-1,7-diphenyl-4-heptene-3-one(Alpinoid C)(34)[14]、(2*S*)-2-hydroxy-1,7-diphenyl-4*E*-heptene-3-one(Alpinoid E)(35)[15]、(5*S*)-5-hydroxy-7-(3,4-dihydroxyphenyl)-1-phenyl-3-heptanone (36)[16]、(5*S*) -5-hydroxy-7- (4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl)-3-heptanone(37)[17]、(5*S*)-5-hydroxy-1- (4-hydroxyphenyl) -7-phenyl-3-heptanone (38)、(5*S*) -5-hydroxy-1- (4-hydroxyphenyl) -7- (3, 4-dihydroxyphenyl) -3-heptanone (39)、(5*S*) -5-hydroxy-1- (4-hydroxy-3-methoxyphenyl)-7-(4-hydroxyphenyl)-3-heptanone(40)、(5*S*)-5-hydroxy-1,7-bis(4-hydroxyphenyl)-3-heptanone(41)[18]、(5*R*)-5-hydroxy-7- (3-methoxy-4, 5-dihydroxyphenyl) -1-phenyl-3-heptanone(42)、(5*R*)-5-hydroxy-1-(3, 4-dihydroxyphenyl)-7-(4-hydroxy-3-methoxyphenyl)-3-heptanone(43)[16]、5-Hydroxy-1-(3, 4-dihydroxy-5-methoxyphenyl)-7-(4-hydroxy-3-methoxyphenyl)-3-heptanone(44)、5-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(3,4-dihydroxy-5-methoxyphenyl)-3-heptanone(45)、5-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(3, 4-dihydroxyphenyl) -3-heptanone (46)[19]、5-Methoxy-7- (4-hydroxy-3-methoxyphenyl)-1-(4-hydroxyphenyl)-3-heptanone(47)[17]、5-Ethoxyl-7- (4-hydroxy-3-methoxy-phenyl) -1-phenyl-3-heptanone (48)[20]、(5*S*)-5-acetoxy-1, 7-bis(4-hydroxy-3-methoxyphenyl)-3-heptanone(5-acetoxy hexahydrocurcumin)(49)[19]、(3*S*, 5*S*)-3-hydroxy-5-methoxy-1-(4-hydroxyphenyl)-7-phenyl-6-heptene (50)、(3*S*, 5*R*)-3-hydroxy-5-methoxy-1-(4-hydroxyphenyl)-7-phenyl-6-heptene (51)、(3*S*, 5*S*)-3-hydroxy-5-ethoxy-1-(4-hydroxyphenyl)-7-phenyl-6-heptene (52)、(3*S*, 5*R*)-3-hydroxy-5-ethoxy-1-(4-hydroxyphenyl)-7-phenyl-6-heptene (53)[3]、(3*R*, 5*S*) -3-acetoxy-5-hydroxy-1, 7-bis (4-hydroxy-3-methoxyphenyl)-heptane (54)、(3*R*, 5*S*) -3, 5-dihydroxy-1-(4-hydroxy-3, 5-dimethoxyphenyl) -7- (4-hydroxy-3-methoxyphenyl) heptane (55)[19]、Rel-(3*R*, 5*S*) -3, 5-dihydroxy-1-(3, 4-dihydroxy phenyl)-7-(4-hydroxyphenyl)heptane(56)、Rel-(3*R*,5*S*)-3,5-dihydroxy-1- (4-hydroxy-3-methoxyphenyl) -7- (4-hydroxyphenyl) heptane (57)、Rel-(3*R*, 5*S*) -3, 5-dihydroxy-1-(3-methoxy-4, 5-dihydroxyphenyl)-7-(4-hydroxyphenyl)heptane(58)[18]、(3*R*, 5*R*)-1, 7-diphenylheptane-3, 5-diol(Yashabushidiol B)(59)[21]、(3*R*,5*R*)-1-(4-hydroxyphenyl)-7-phenylheptane-3,5-diol(60)[22]、(3*R*, 5*R*) -3, 5-dihydroxy-1-(3, 4-dihydroxyphenyl) -7-(4-hydroxyphenyl)heptane(61)、(3*R*,5*R*)-3,5-dihydroxy-1,7-bis(3,4-dihydroxy phenyl) heptane (62)[23]、(3*R*, 5*R*)-3-acetoxy-5-hydroxy-1, 7-bis(4-hydroxyphenyl)heptane(63)、(3*R*,5*R*)-3-acetoxy-5-hydroxy-1, 7-bis (3, 4-dihydroxyphenyl) heptane (64)、(3*R*, 5*R*) -3, 5-diacetoxy-1-(3, 4-dihydroxyphenyl) -7-(4-hydroxyphenyl)heptane(65)、(3*R*,5*R*)-3-acetoxy-5-hydroxy-1-(3,4-dihydroxyphenyl) -7-(4-hydroxyphenyl) heptane (66)、(3*R*,5*R*)-3, 5-dihydroxy-1-(4-hydroxy-3-methoxy phenyl)-7-(3, 4-dihydroxyphenyl) heptane (67)[18]、(3*S*, 5*S*)-3, 5-diacetoxy-1, 7-bis(4-hydroxy-3-methoxyphenyl)heptane(68)[19]、Octahydrocurcumin(69)[22]、(3*S*, 5*S*)-3-acetoxy-5-hydroxy-1-(3, 4-dihydroxyphenyl)-7-(4-hydroxyphenyl)heptane(70)[18]、Meso-1, 7-diphenylheptane-3, 5-diol(Yashabushidiol A)(71)[21]、(3*R*, 5*R*)-3, 5-dihydroxy-1-(3, 4-dihydroxyphenyl)-7-(4-hydroxyphenyl)-heptane-3-*O*-*β*-*D*-glucopyranoside(72)、(3*R*, 5*R*)-3, 5-dihydroxy-1-(4-hydroxy-3-methoxyphenyl) -7- (4-hydroxyphenyl) -heptane-3-*O*-*β*-*D*-glucopyranoside(73)、(3*R*, 5*R*)-3, 5-dihydroxy-1, 7-bis(3, 4-dihydroxyphenyl)-heptane-3-*O*-*β*-*D*-glucopyranoside(74)、(3*R*,5*R*)-3,5-dihydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(3, 4-dihydroxyphenyl) -heptane-3-*O*-*β*-*D*-glucopyranoside (75)、(3*R*, 5*R*) -3, 5-dihydroxy-1, 7-bis (4-hydroxy-3-methoxyphenyl)-heptane-3-*O*-*β*-*D*-glucopyranoside(76)、(3*R*,5*R*)-3,5-dihydroxy-1,7-bis(4-hydroxyphenyl)-heptane-3-*O*-*β*-*D*-glucopyranoside(77)、(3*R*,5*R*)-3,5-dihydroxy-1-(3,4-dihydroxyphenyl)-7-(4-hydroxy phenyl) -heptane-5-*O*-*β*-*D*-glucopyranoside (78)[23]。其具体结构见图2。

1.3 三氧代型姜黄素类化合物

该类化合物的庚烷链上主要有以下几种取代模式:*β*-二酮基和1个醇基、酮-烯醇和1个醇基、2个非*β*-二酮基和1个醇基、1个酮基和2个醇基,以及3个醇基取代,共8个,分别是:1-Hydroxy-1,7-bis(4-hydroxy-3-methoxyphenyl)-6- heptene-3, 5-dione(79)[22]、1, 5-Dihydroxy-1, 7-bis(4-hydroxy phenyl)-4, 6-heptadiene-3-one (80)、1, 5-Dihydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(4-hydroxyphenyl)-4, 6-heptadiene-3-on(81)、1, 5-Dihydroxy-1-(4-hydroxyphenyl)-7-(4-hydroxy-3-methoxy phenyl)-4, 6-heptadiene-3-one(82)、3-Hydroxy-1, 7-bis(4-hydroxy phenyl)-6-heptene-1,5-dione(83)[10]、(1*R*,5*S*)-1,7-diphenylheptane-3-one-1,5-diol(Yashabushiketodiol A)(84)、1,7-Diphenylheptan-3-one-1,5-diol(Yashabushiketodiol B)(85)、(1*R*, 3*R*, 5*S*) -1, 7-diphenylheptane-1, 3, 5-triol (Yashabushitriol) (86)[21]。其具体结构见图3。

1.4 吡喃取代型姜黄素类化合物

该类化合物的结构特征为庚烷链上的2个羟基分子内缩合成醚后而成的1个吡喃环,共10个,分别是:(1*R*,3*R*,5*S*)-1,7-bis(4-hydroxyphenyl)-1,5-epoxy-3-hydroxy-hept-6-ene(87)、(1*R*,3*R*,5*R*)-1,7-bis(4-hydroxyphenyl)-1,5-epoxy-3-hydroxy-heptane(88)、(1*S*, 3*S*, 5*S*)-1,7-bis(4-hydroxyphenyl)-1,5-epoxy-3-hydroxyheptane(89)、(1*R*, 3*S*, 5*R*)-1,7-bis(4-hydroxyphenyl)-1,5-epoxy-3-hydroxy-heptane(90)、(1*S*, 3*R*, 5*S*)-1,7-bis(4-hydroxyphenyl)-1,5-epoxy-3-hydroxyheptane(91)[24-25]、(3*S*, 5*S*, 6*S*, 7*R*)-5, 6-dihydroxy-1, 7-bis (4-hydroxyphenyl)-4-de-*O*-methylcentrolobine (92)、(3*S*, 5*R*, 6*S*, 7*R*)-5, 6-dihydroxy-1, 7-bis (4-hydroxy phenyl) -4-de-*O*-methylcentrolobine (93)、(3*S*, 5*S*, 6*R*, 7*R*)-5, 6-dihydroxy-1, 7-bis(4-hydroxyphenyl) -4-de-*O*-methylcentrolobine (94)[26]、(3*S*, 7*R*) -5, 6-dehydro-1, 7-bis (4-hydroxyphenyl) -4-de-*O*-methylcentrolobine (95)[26]、Cyclocurcumin(96)[27]。其具体结构见图4。

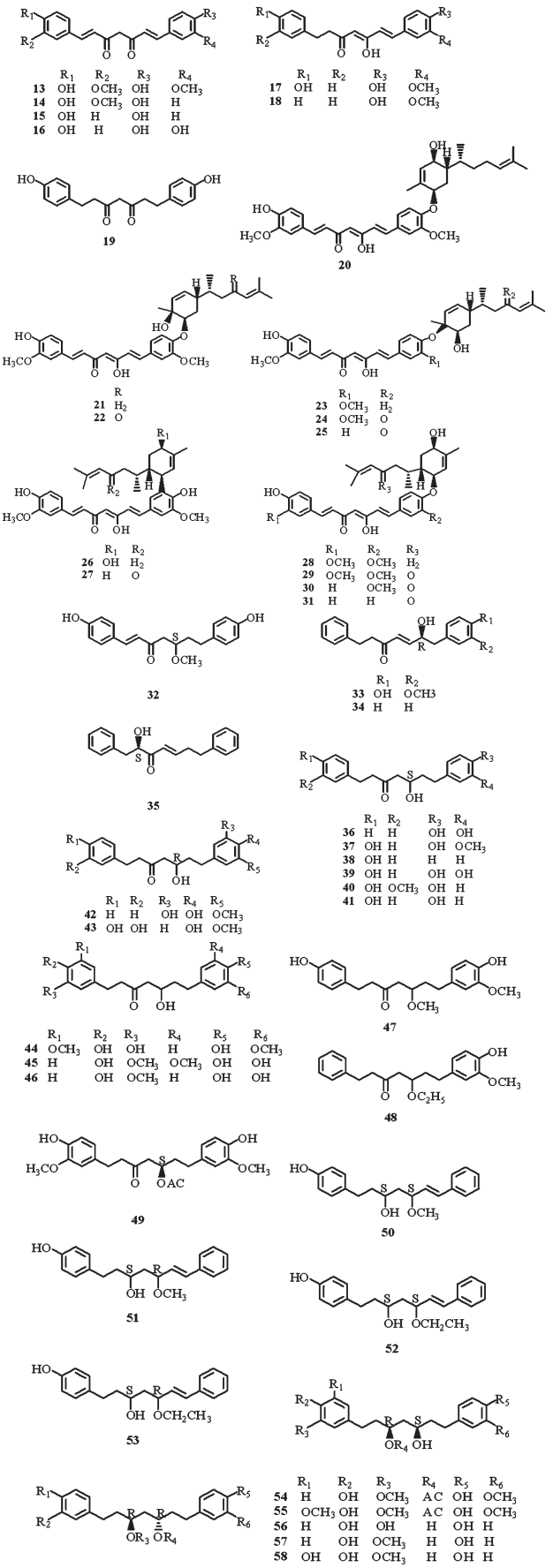
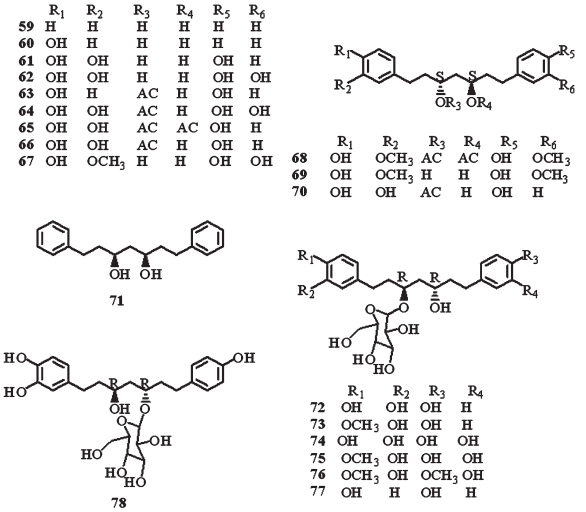


图2　双氧代型姜黄素类化合物



续图2

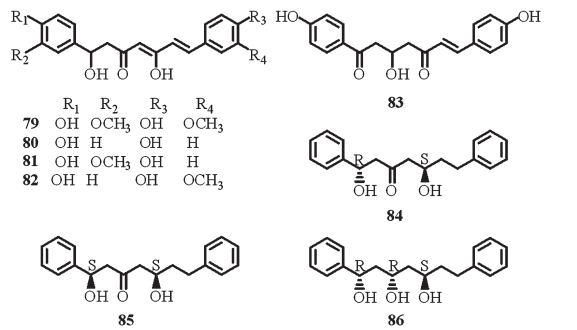


图3　三氧代型姜黄素类化合物

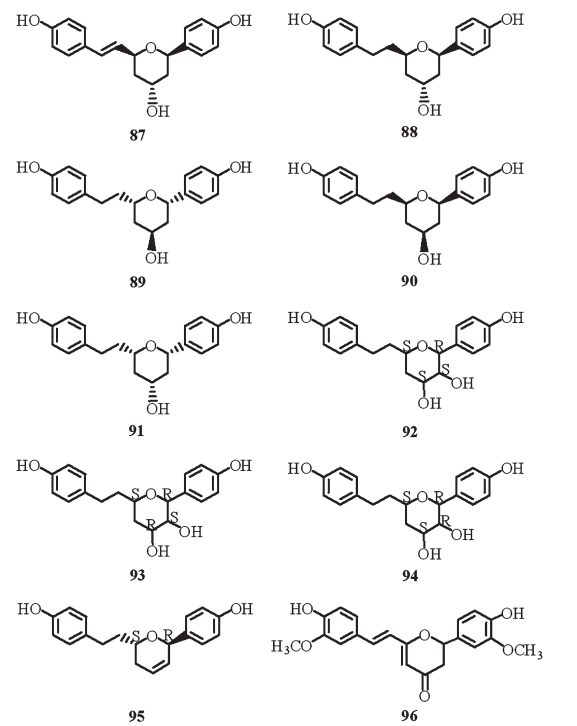


图4　吡喃取代型姜黄素类化合物

1.5　呋喃取代型姜黄素类化合物

该类化合物的结构特征为庚烷链上的酮-烯醇分子内缩合而成的吡喃环，共2个，分别是：3，6-Furan-7-(4-hydroxy-3-me-

thoxyphenyl)-1-phenylheptane(Alpinoid D)(97)、3,6-Furan-1,7-diphenylheptane(98)[15]。其具体结构见图5。

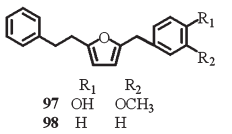


图5 呋喃取代型姜黄素类化合物

1.6 大环醚型姜黄素类化合物

该类化合物的结构特征为第1、7位的2个芳环上的酚羟基缩合成醚而使整个分子呈现1个大环醚结构,也有芳环上碳碳键相连形成大环,共17个,分别是:Acerogenins I(99)、Acerogenins F(100)、Acerogenins J(101)[28]、(10*R*)-17-methoxy-2-oxatricyclo[13.2.2.13,7]eicosa-3,5,7(20),15,17,18-hexaene-4,10-diol(102)[17]、Rhoiptelol(103)[29]、Acerogenins L(104)[28]、(+)-galeon(105)[30]、Acerogenins H(106)[28]、(9*R*)-4,9-dihydroxy-17-methoxy-2-oxatricyclo[13.2.2.13,7]eicosa-3,5,7(20),15,17,18-hexaen-10-one(107)[17]、Garugamblin-3(108)[31]、Aceroside Ⅲ(109)、(8*R*,9*R*)-17-methoxy-2-oxatricyclo[13.2.2.13,7]icosa-1(17),3(20),4,6,15,18-hexaene-4,9,10-triol-9-*O*-*β*-*D*-glucopyranoside(jugcathayenoside)(110)[30]、Acerogenin K(111)、Acerogenin E(112)[28]、3,17-dihydroxytricyclo[12.3.1.12,6]nonadeca-1(18),2,4,6(19),14,16-hexaen-9,11-dione(113)、3,11,17-trihydroxytricyclo[12.3.1.12,6]nonadeca-1(18),2,4,6(19),14,16-hexaen-9-one(alnusonol)(114)、3,17-dihydroxytricyclo[12.3.1.12,6]-nonadeca-1(18),2,4,6(19),10,14,16-heptaen-9-one(alnusone)(115)[32]。其具体结构见图6。

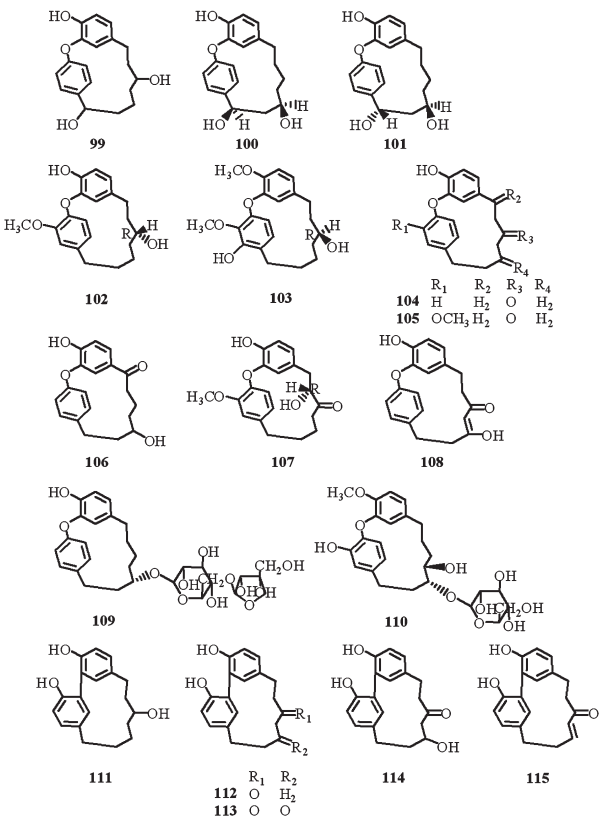


图6 大环醚型姜黄素类化合物

1.7 二聚体型姜黄素类化合物

该姜黄素类化合物主要以二聚体形式存在,如(5*R*,5'*R*)-7,7'-(6,6'-dihydroxy-5,5'-dimethoxy[1,1'-biphenyl]-3,3'-diyl) bis[5-methoxy-1-phenylheptan-3-one](Alpinoid A)(116)[14]、2-Benzyl-3-hydroxy-3,5-diphenethyl-6-(3-phenylpropanoy)-cyclohexanone(Alpinin A)(117)[33]。其具体结构见图7。

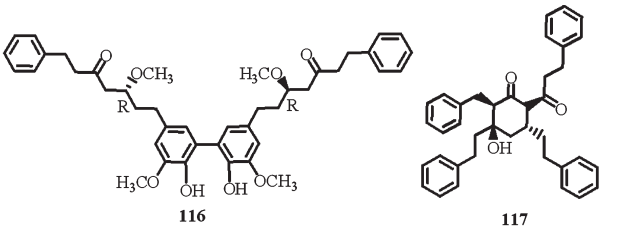


图7 二聚体型姜黄素类化合物

2 各种类型的姜黄素类化合物的主要来源

姜黄素类化合物主要分布在姜科植物中,如姜黄属姜黄、莪术、广西莪术,姜属植物姜,山姜属高良姜、益智、草豆蔻、云南草蔻,豆蔻属草果等。此外,桦木科桤木属旅顺桤木,巴西豆科 *Centrolobium robustum* Mart.和 *Centrolobium tomentosum* Benth.,槭树科槭属毛果槭,马尾树科马尾树属马尾树,胡桃科化香树属化香树,胡桃科胡桃属胡桃楸、野核桃,蒟蒻薯科蒟蒻薯属箭根薯、*T. plantaginea*,薯蓣科薯蓣属 *Dioscorea villosa* 等植物中亦有报道该类化合物的存在。

双氧代型中的苷类主要分布在蒟蒻薯科蒟蒻薯属箭根薯等;三氧代型主要分布在姜科姜黄属姜黄、桦木科桤木属旅顺桤木等;吡喃取代型主要分布在巴西豆科 *C. robustum* Mart.和 *C. tomentosum* Benth.、姜科山姜属云南草蔻等;呋喃取代型主要分布在姜科山姜属高良姜等;大环醚型主要分布在槭树科槭属毛果槭、马尾树科马尾树属马尾树、胡桃科胡桃属胡桃楸等;二聚体型主要分布在姜科山姜属高良姜等。

3 结语

天然姜黄素来源广泛,主要来源于姜科,在桦木科、巴西豆科、槭树科、马尾树科、胡桃科、蒟蒻薯科等中也有大量发现,丰富了天然姜黄素类化合物结构的多样性。姜黄素类化合物具有广泛的药理活性,在人体内发挥着药效作用。因此,天然姜黄素类化合物作为对人体无毒的天然药物,具有潜在的临床应用价值,值得进一步研究[34]。

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