

五味子科植物的木脂素成分*

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Lignans from Plants of Schisandraceae

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Abstract: Plants of Schisandraceae family are rich sources of lignans, which have been found to possess some beneficial pharmacological effects including antihepatitis, antitumor and anti-HIV activities. In order to search for more bioactive natural products and avoid confusion arisen from the same structures under different names by authors in the literature, the paper has reviewed 150 new lignans from plants of Schisandraceae in the literature published mainly after 1990, including dibenzocyclooctadiene, spirobenzofuranoid dibenzocyclooctadiene, 4-aryltetralin, 2, 3-dimethyl-1, 4-diarylbutane and 2, 5-diaryl tetrahydrofuran lignans.

Key words: Schisandraceae; Lignans; Structure type

五味子科植物分为五味子属(*Schisandra*)和南五味子属(*Kadsura*) 2 个属, 其中五味子(*S. chinensis*)为著名中药, 其应用已有 2000 多年的历史, 一直为我国药典所收载, 该科其它许多种也在民间广泛应用^[1]。20 世纪 70 年代初, 我国临床研究发现五味子能明显降低肝炎患者血清谷丙转氨酶水平, 引起广泛研究的热潮, 并由此开发出治疗肝炎药物联苯双酯^[2]。迄今, 国内外已对二十余种五味子科植物进行了研究, 分离鉴定出大约 200 个成分, 其中 150 多个为木脂素。五味子科木脂素结构类型多, 立体化学复杂, 而且生物活性广泛。除了众所周知的保肝降酶作用外, 近年来发现五味子科木脂素成分对中枢神经系统

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有抑制作用, 还具有抗爱滋病毒、抗癌和 PAF 拮抗等多种活性^[3~6]。因此, 国内外对该领域的研究十分活跃, 前人积累了较多的化学和药理研究资料。文献中木脂素的命名往往根据研究者和植物种类而定, 常常出现异名同物情况, 造成不少混乱。曾有文献总结了 20 世纪 90 年代以前从五味子科植物中分得木脂素 60 余个^[1,7], 为便于今后对五味子科植物的深入研究, 继续从中寻找生理活性成分, 笔者主要根据 20 世纪 90 年代以后的文献报道, 对其中分离的 150 种新木脂素按结构类型进行了整理。

1 联苯环辛二烯木脂素

联苯环辛二烯木脂素普遍存在于五味子科植物, 是主要的生理活性成分。目前在 17 种五味子科植物中已发现 104 个这类化合物(见图 1; 表 1: 1~ 104)。这类木脂素的母核是联苯环辛二烯, 联苯环上的 C-4 和 C-11 位有 2 个芳香质子, 其它位置即 C-1~ 3 和 C-12~ 14 均为含氧取代基, 包括甲氧基, 亚甲二氧基, 羟基和酯基。亚甲二氧基位于 C-12(13) 和 (或) C-2(3) 位; 羟基多在 C-1, C-12, C-14 位, 少数在 C-3 位。联苯环上一般只有一个酚羟基, 少数有 2 个酚羟基或者一个酚羟基和一个酯基, 而酯基只出现在 C-14 或 C-1 位。gomisin D (34) 和 E (35) 是 2 个仅有的带有 C-14 位醚键, 并与 C-6 形成大环内酯的木脂素, 结构新颖。在环辛二烯的八元环结构中, 若有取代基, 一般是羟基(在 C-6, C-7 位多为

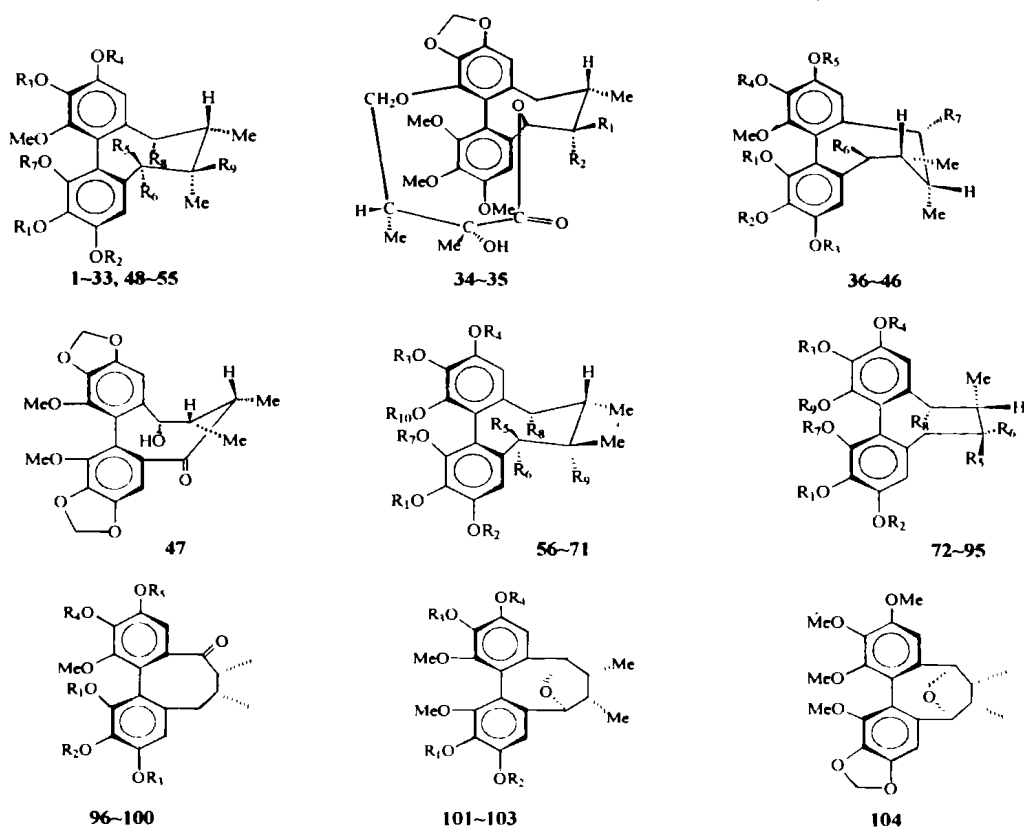


图 1 五味子科植物中新联苯环辛二烯木脂素的结构

Fig. 1 Structures of new dibenzocyclooctadiene lignans from plants of Schisandraceae

表 1 五味子科植物中的新联苯环辛二烯木脂素

Table 1 New dibenzocyclooctadiene lignans from plants of Schisandraceae

No.	化合物 Compounds	结构 Structures	植物来源 Plant sources	参考文献 References
1	gom isin N	R ₁ = R ₂ = R ₇ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = R ₆ = R ₈ = R ₉ = H	<i>S. chinensis</i>	[1, 7]
2	(-)-rubschisandrin	R ₁ + R ₂ = CH ₂ , R ₃ = R ₄ = R ₇ = Me, R ₅ = R ₆ = R ₈ = R ₉ = H	<i>S. rubriflora</i>	[1, 7]
3	wuweizisu C (schisandrin C)	R ₁ + R ₂ = R ₃ + R ₄ = CH ₂ , R ₅ = R ₆ = R ₈ = R ₉ = H, R ₇ = Me	<i>S. chinensis</i> , <i>S. rubriflora</i>	[1, 7]
4	(-)-gom isin K ₁	R ₁ = R ₂ = R ₃ = R ₇ = Me, R ₄ ~ R ₆ , R ₈ = R ₉ = H	<i>S. chinensis</i>	[1, 7]
5	gom isin J	R ₁ = R ₃ = R ₇ = Me, R ₂ , R ₄ ~ R ₆ , R ₈ = R ₉ = H	<i>S. chinensis</i> , <i>K. coccinea</i>	[1]
6	(-)-gom isin L ₂	R ₁ + R ₂ = CH ₂ , R ₃ = R ₇ = Me, R ₄ ~ R ₆ , R ₈ = R ₉ = H	<i>S. chinensis</i>	[1]
7	(-)-gom isin L ₁	R ₁ + R ₂ = CH ₂ , R ₃ = R ₄ = R ₇ = Me, R ₅ = R ₆ = R ₈ = R ₉ = H	<i>S. chinensis</i>	[1]
8	gom isin U	R ₁ ~ R ₃ , R ₇ = Me, R ₄ = R ₆ = R ₈ = R ₉ = H, R ₅ = OH	<i>S. spheanthera</i>	[8]
9	benzoyl gom isin U	R ₁ ~ R ₃ , R ₇ = Me, R ₄ = R ₆ = R ₈ = R ₉ = H, R ₅ = OBen	<i>S. spheanthera</i>	[9]
10	gom isin S	R ₁ ~ R ₃ , R ₇ = Me, R ₄ = R ₅ = R ₈ = R ₉ = H, R ₆ = OH	<i>S. chinese</i>	[8]
11	epigom isin O	R ₁ = R ₂ = R ₇ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = R ₈ = R ₉ = H, R ₆ = OH	<i>S. chinese</i> , <i>S. spheanthera</i>	[1]
12	tigloyl gom isin O	R ₁ = R ₂ = R ₇ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = OTig, R ₆ = R ₈ = R ₉ = H	<i>S. spheanthera</i>	[9]
13	kadsurin	R ₁ = R ₂ = R ₇ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = R ₆ = R ₉ = H, R ₈ = OAc	<i>K. japonica</i> , <i>K. interior</i> , <i>K. heteroclita</i>	[10]
14	heteroclitin A	R ₁ = R ₂ = R ₇ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = R ₆ = R ₉ = H, R ₈ = O-2-Methylbutyryl	<i>K. heteroclita</i>	[11]
15	heteroclitin B	R ₁ = R ₂ = R ₇ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = R ₆ = R ₉ = H, R ₈ = OAng	<i>K. heteroclita</i>	[11]
16	heteroclitin C	R ₁ = R ₂ = R ₇ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = R ₆ = R ₉ = H, R ₈ = OTig	<i>K. heteroclita</i>	[11]
17	binankadsurin A	R ₁ = R ₂ = Me, R ₃ + R ₄ = CH ₂ , R ₅ ~ R ₇ = R ₉ = H, R ₈ = OH	<i>K. sp</i>	[12]
18	acetyl binankadsurin A	R ₁ = R ₂ = Me, R ₃ + R ₄ = CH ₂ , R ₅ ~ R ₇ = R ₉ = H, R ₈ = OAc	<i>K. japonica</i> , <i>K. coccinea</i> , <i>K. sp</i>	[7]
19	angeloyl binankadsurin A	R ₁ = R ₂ = Me, R ₃ + R ₄ = CH ₂ , R ₅ ~ R ₇ = R ₉ = H, R ₈ = OAng	<i>K. japonica</i> , <i>K. sp</i> <i>K. longipedunculata</i>	[7, 12]
20	caproyl binankadsurin A	R ₁ = R ₂ = Me, R ₃ + R ₄ = CH ₂ , R ₅ ~ R ₇ = R ₉ = H, R ₈ = OCap	<i>K. japonica</i>	[7]
21	benzoyl binankadsurin A	R ₁ = R ₂ = Me, R ₃ + R ₄ = CH ₂ , R ₅ ~ R ₇ = R ₉ = H, R ₈ = OBen	<i>K. longipedunculata</i>	[13]
22	isovaleroyl binankadsurin A	R ₁ = R ₂ = Me, R ₃ + R ₄ = CH ₂ , R ₅ ~ R ₇ = R ₉ = H, R ₈ = Oiso-Valeroyl	<i>K. longipedunculata</i>	[13]
23	isobutyryl binankadsurin A	R ₁ = R ₂ = Me, R ₃ + R ₄ = CH ₂ , R ₅ ~ R ₇ = R ₉ = H, R ₈ = Oiso-Butyryl	<i>K. longipedunculata</i>	[13]
24	Butyryl binankadsurin A	R ₁ = R ₂ = Me, R ₃ + R ₄ = CH ₂ , R ₅ ~ R ₇ = R ₉ = H, R ₈ = OButyryl	<i>K. sp</i>	[13]
25	deangeloyl schisantherin F	R ₁ ~ R ₃ = Me, R ₄ ~ R ₇ = R ₉ = H, R ₈ = OH	<i>K. longipedunculata</i> <i>K. japonica</i>	[14]
26	schisantherin F	R ₁ ~ R ₃ = Me, R ₄ ~ R ₆ = R ₉ = H, R ₇ = Ang, R ₈ = OH	<i>K. sp</i>	[7]
27	angeloyl binankadsurin B	R ₁ ~ R ₄ = Me, R ₅ ~ R ₇ = R ₉ = H, R ₈ = Ang	<i>K. japonica</i>	[15]
28	acetyl binankadsurin B	R ₁ ~ R ₄ = Me, R ₅ ~ R ₇ = R ₉ = H, R ₈ = OAc	<i>K. japonica</i>	[15]

续表 1

No.	化合物 Compounds	结构 Structures	植物来源 Plant sources	参考文献 References
29	schisantherin P	R ₁ + R ₂ = R ₃ + R ₄ = CH ₂ , R ₅ = R ₉ = H, R ₆ = R ₈ = OH, R ₇ = Me	<i>K. coccinea</i> , <i>K. angustifolia</i>	[16]
30	benzoyl gomisin P	R ₁ = R ₂ = R ₇ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = R ₈ = H, R ₆ = OBen, R ₉ = OH	<i>S. spheanthera</i>	[17]
31	tigloyl gomisin P	R ₁ = R ₂ = R ₇ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = R ₈ = H, R ₆ = OTig, R ₉ = OH	<i>S. spheanthera</i> , <i>K. heteroclita</i> , <i>K. longipedunculata</i> , <i>S. chinese</i>	[1, 7]
32	angeloyl gomisin P	R ₁ = R ₂ = R ₇ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = R ₈ = H, R ₆ = OAng, R ₉ = OH	<i>S. spheanthera</i> , <i>S. chinese</i> <i>K. heteroclita</i>	[1, 7]
33	schisanhenrin	R ₁ = R ₂ = R ₇ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = OAng, R ₆ = R ₈ = H, R ₉ = OH	<i>S. henryi</i>	[1]
34	gomisin D	R ₁ = Me, R ₂ = OH	<i>S. chinese</i> , <i>K. coccinea</i>	[1]
35	gomisin E	R ₁ = OH, R ₂ = Me	<i>S. chinese</i> , <i>K. coccinea</i>	[1, 7]
36	gomisin O	R ₁ ~ R ₃ = Me, R ₄ + R ₅ = CH ₂ , R ₆ = OH, R ₇ = H	<i>S. chinese</i> , <i>S. rubriflora</i>	[1, 7]
37	6-O-benzoyl gomisin O	R ₁ ~ R ₃ = Me, R ₄ + R ₅ = CH ₂ , R ₆ = OBen, R ₇ = H	<i>S. chinese</i>	[18]
38	rubischisantherin	R ₁ ~ R ₃ = Me, R ₄ + R ₅ = CH ₂ , R ₆ = OAc, R ₇ = H	<i>S. rubriflora</i>	[1, 7]
39	angeloyl gomisin O	R ₁ ~ R ₃ = Me, R ₄ + R ₅ = CH ₂ , R ₆ = OAng, R ₇ = H	<i>S. chinese</i>	[1, 7]
40	angeloyl isogomisin O	R ₁ = R ₄ = R ₅ = Me, R ₂ + R ₃ = CH ₂ , R ₆ = OAng, R ₇ = H	<i>S. chinese</i>	[1, 7]
41	benzoyl isogomisin O	R ₁ = R ₄ = R ₅ = Me, R ₂ + R ₃ = CH ₂ , R ₆ = OBen, R ₇ = H	<i>S. chinese</i> , <i>K. coccinea</i>	[1, 7]
42	gomisin R	R ₁ = Me, R ₂ + R ₃ = R ₄ + R ₅ = CH ₂ , R ₆ = OH, R ₇ = H	<i>S. chinese</i>	[1, 7]
43	angeloyl gomisin R	R ₁ = Me, R ₂ + R ₃ = R ₄ + R ₅ = CH ₂ , R ₆ = OAng, R ₇ = H	<i>K. longipedunculata</i> , <i>K. interior</i>	[1, 7]
44	interiotherin A	R ₁ = Me, R ₂ + R ₃ = R ₄ + R ₅ = CH ₂ , R ₆ = OBen, R ₇ = H	<i>K. interior</i>	[19]
45	schisan-lignanol D	R ₁ = Me, R ₂ + R ₃ = R ₄ + R ₅ = CH ₂ , R ₆ = H, R ₇ = OH	<i>S. viridis</i>	[20]
46	schisantherin K	R ₁ = OTig, R ₂ ~ R ₅ = Me, R ₆ = OAc, R ₇ = H	<i>S. viridis</i>	[21]
47	schisantherin Q	R ₁ = OTig, R ₂ ~ R ₅ = Me, R ₆ = OAc, R ₇ = OH	<i>K. coccinea</i>	[16]
48	schisantherin L	R ₁ + R ₂ = R ₃ + R ₄ = CH ₂ , R ₅ = OAng, R ₆ = R ₉ = H, R ₇ = Me, R ₈ = OH	<i>K. coccinea</i>	[22]
49	acetyl schisantherin L	R ₁ + R ₂ = R ₃ + R ₄ = CH ₂ , R ₅ = OAng, R ₆ = R ₉ = H, R ₇ = Me, R ₈ = OAc	<i>K. coccinea</i>	[22]
50	schisantherin M	R ₁ + R ₂ = R ₃ + R ₄ = CH ₂ , R ₅ = OAng, R ₆ = R ₉ = H, R ₇ = Me, R ₈ = OTig	<i>K. coccinea</i>	[22]
51	schisantherin N	R ₁ + R ₂ = R ₃ + R ₄ = CH ₂ , R ₅ = R ₈ = OAng, R ₆ = R ₉ = H, R ₇ = Me	<i>K. coccinea</i>	[22]
52	angustifolin A	R ₁ + R ₂ = R ₃ + R ₄ = CH ₂ , R ₅ = R ₈ = OBen, R ₆ = R ₉ = H, R ₇ = Me	<i>K. angustifolia</i>	[23]
53	angustifolin B	R ₁ + R ₂ = R ₃ + R ₄ = CH ₂ , R ₅ = OBen, R ₆ = R ₉ = H, R ₇ = Me, R ₈ = OAc	<i>K. angustifolia</i>	[23]
54	angustifolin C	R ₁ + R ₂ = R ₃ + R ₄ = CH ₂ , R ₅ = OBen, R ₆ = R ₉ = H, R ₇ = Me, R ₈ = OH	<i>K. angustifolia</i>	[23]
55	angustifolin D	R ₁ ~ R ₄ = R ₇ = Me, R ₆ = R ₉ = H, R ₅ = R ₈ = OAc	<i>K. angustifolia</i>	[5]
56	benzoyl gomisin Q	R ₁ ~ R ₄ , R ₇ = R ₁₀ = Me, R ₅ = OBen, R ₆ = R ₈ = H, R ₉ = OH	<i>S. spheanthera</i>	[17]
57	angeloyl gomisin Q	R ₁ ~ R ₄ , R ₇ = R ₁₀ = Me, R ₅ = OAng, R ₆ = R ₈ = H, R ₉ = OH	<i>S. chinese</i>	[1, 7]

续表 1

No.	化合物 Compounds	结构 Structures	植物来源 Plant sources	参考文献 References
58	gom isin F	$R_1+ R_2=CH_2, R_3= R_4= R_7= R_{10}=Me, R_5=OAng, R_6= R_8=H, R_9=OH$	<i>S. chinese</i>	[1, 7]
59	gom isin G	$R_1+ R_2=CH_2, R_3= R_4= R_7= R_{10}=Me, R_5=OBen, R_6= R_8=H, R_9=OH$	<i>S. chinese</i>	[1, 7]
60	kadsum arin A	$R_1+ R_2=CH_2, R_3= R_4= R_{10}=Me, R_5= R_7= R_9=H, R_6=OAc$	<i>K. matsudai, S. arisanensis</i>	[24]
61	schisantherin A (wuw eizi ester A) (gom isin C)	$R_1= R_2= R_7= R_{10}=Me, R_3+ R_4=CH_2, R_5=OBen, R_6= R_8=H, R_9=OH$	<i>S. chinese S. spheanthera</i>	[1, 7]
62	schisantherin B (wuw eizi ester B) (gom isin B)	$R_1= R_2= R_7= R_{10}=Me, R_3+ R_4=CH_2, R_5=OAng, R_6= R_8=H, R_9=OH$	<i>S. chinese, S. spheanthera S. henryi, K. longipedunculata, K. heteroclita</i>	[1, 7]
63	schisantherin C	$R_1= R_2= R_7= R_{10}=Me, R_3+ R_4=CH_2, R_5=OTig, R_6= R_8=H, R_9=OH$	<i>S. spheanthera</i>	[1, 7]
64	schisantherin D	$R_1+ R_2= R_3+ R_4=CH_2, R_5=OBen, R_6= R_8=H, R_7= R_{10}=Me, R_9=OH$	<i>S. spheanthera, S. chinese K. interior</i>	[1, 7]
65	interiotherin B	$R_1+ R_2= R_3+ R_4=CH_2, R_5=OAng, R_6= R_8=H, R_7= R_{10}=Me, R_9=OH$	<i>K. interior</i>	[19]
66	schisantherin E	$R_1\sim R_3= R_7= R_{10}=Me, R_4= R_6= R_8=H, R_5=OBen, R_9=OH$	<i>S. spheanthera</i>	[1, 7]
67	schisantherin I	$R_1\sim R_3= R_7= R_{10}=Me, R_4= R_6=H, R_5=OBen, R_8=OCap, R_9=OH$	<i>K. sp</i>	[7]
68	schisantherin J	$R_1= R_2= R_7= R_{10}=Me, R_3+ R_4=CH_2, R_5=OBen, R_6=H, R_8=Oiso-Valeroyl, R_9=OH$	<i>K. Longipedunculata</i>	[14]
69	kadsurarin	$R_1= R_2= R_7= R_{10}=Me, R_3+ R_4=CH_2, R_5=OAng, R_6=H, R_8=OAc, R_9=OH$	<i>K. japonica, K. sp</i>	[10]
70	schisantherin G	$R_1= R_2= R_7=Me, R_3+ R_4=CH_2, R_5=OAng, R_6= R_{10}=H, R_8=OAc, R_9=OH$	<i>K. sp</i>	[7]
71	schisantherin H	$R_1= R_2=Me, R_3+ R_4=CH_2, R_5= OAng, R_6= R_7= R_{10}=H, R_9=OH$	<i>K. sp</i>	[7]
72	deoxyschizandrin (wuw eizisu A) (schisandrin A)	$R_1\sim R_4= R_6= R_7= R_9=Me, R_5= R_8=H$	<i>S. spheanthera, S. chinese, S. rubriflora, K. coccinea, S. propinqua var sinensis</i>	[1]
73	(+)gom isin K ₂	$R_1\sim R_3= R_6= R_7= R_9=Me, R_4= R_5= R_8=H$	<i>S. chinese</i>	[1, 7]
74	schisanhenol ((+) gom isin K ₃)	$R_1\sim R_4= R_6= R_7=Me, R_5= R_8= R_9=H$	<i>S. chinese, S. henryi, S. sp, S. rubriflora, S. spheanthera, S. propinqua var intermedia, K. longipedunculata</i>	[1, 7]
75	schisanhenol acetate	$R_1\sim R_4= R_6= R_7=Me, R_5= R_8=H, R_9=Ac$	<i>S. rubriflora</i>	[1, 7]
76	schizandrin	$R_1= R_2= R_6= R_7= R_9=Me, R_3+ R_4=CH_2, R_5= R_8=H$	<i>S. chinese</i>	[1]
77	isokadsuranin	$R_1= R_2= R_6= R_7= R_9=Me, R_3+ R_4=CH_2, R_5= R_8=H$	<i>K. coccinea</i>	[1, 7]
78	kadsuranin	$R_1+ R_2=CH_2, R_3= R_4= R_6= R_7= R_9=Me, R_5= R_8=H$	<i>K. longipedunculata</i>	[1, 7]
79	wuw eizisu B (schisandrin B)	$R_1+ R_2=CH_2, R_3= R_4= R_6= R_7= R_9=Me, R_5= R_8=H$	<i>S. chinese</i>	[1]
80	(±)gom isin M ₁	$R_1+ R_2=CH_2, R_3= R_4= R_6= R_7=Me, R_5= R_8= R_9=H$	<i>S. chinese</i>	[1]
81	R(+)gom isin M ₁	$R_1+ R_2=CH_2, R_3= R_4= R_6= R_7=Me, R_5= R_8= R_9=H$	<i>K. longipedunculata</i>	[1, 3]

续表 1

No.	化合物 Compounds	结构 Structures	植物来源 Plant sources	参考文献 References
82	R ⁻ (+)-angeloyl gomisin M ₁	R ₁ + R ₂ = CH ₂ , R ₃ = R ₄ = R ₆ = R ₇ = Me, R ₅ = R ₈ = H, R ₉ = Ang	<i>K. longipedunculata</i>	[1, 7]
83	kadsutherin	R ₁ = R ₂ = R ₆ = R ₇ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = R ₈ = H, R ₉ = Ang	<i>K. coccinea</i>	[1, 7]
84	schisanhenol B	R ₁ = R ₂ = R ₆ = R ₉ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = R ₇ = R ₈ = H	<i>S. rubriflora</i>	[1, 7]
85	(+)-gomisin M ₂	R ₁ + R ₂ = CH ₂ , R ₃ = R ₄ = R ₆ = R ₉ = Me, R ₅ = R ₇ = R ₈ = H	<i>S. chinese</i> , <i>K. coccinea</i> , <i>K. longipedunculata</i>	[1, 7]
86	R ⁻ wuweizisu C	R ₁ + R ₂ = R ₃ + R ₄ = CH ₂ , R ₆ = R ₇ = R ₉ = Me, R ₅ = R ₈ = H	<i>K. longipedunculata</i> , <i>K. coccinea</i>	[1, 7]
87	schisantherin O	R ₁ = R ₂ = R ₆ = R ₉ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = R ₇ = H, R ₈ = OAc	<i>K. coccinea</i>	[22]
88	schisandrin (schisandrol A) (wuw eizialcohol A)	R ₁ ~ R ₄ = R ₆ = R ₇ = R ₉ = Me, R ₅ = OH, R ₈ = H	<i>S. chinese</i> , <i>K. longipedunculata</i> , <i>K. heteroclita</i>	[1]
89	gomisin A (wuw eizi alcohol B) (schisandrol B)	R ₁ = R ₂ = R ₆ = R ₇ = R ₉ = Me, R ₃ + R ₄ = CH ₂ , R ₅ = OH, R ₈ = H	<i>S. chinese</i> , <i>K. heteroclita</i>	[1]
90	gomisin H	R ₁ ~ R ₄ = R ₆ = R ₇ = Me, R ₅ = OH, R ₈ = R ₉ = H	<i>S. chinese</i> , <i>K. longipedunculata</i>	[1, 7]
91	angeloyl gomisin H	R ₁ ~ R ₄ = R ₆ = R ₇ = Me, R ₅ = OH, R ₈ = H, R ₉ = Ang	<i>S. chinese</i> , <i>K. heteroclita</i> , <i>K. longipedunculata</i>	[1, 7]
92	tigloyl gomisin H	R ₁ ~ R ₄ = R ₆ = R ₇ = Me, R ₅ = OH, R ₈ = H, R ₉ = Tig	<i>S. chinese</i>	[1, 7]
93	benzoyl gomisin H	R ₁ ~ R ₄ = R ₆ = R ₇ = Me, R ₅ = OH, R ₈ = H, R ₉ = Ben	<i>S. chinese</i>	1, 7
94	gomisin T	R ₁ ~ R ₃ = R ₆ = R ₇ = R ₉ = Me, R ₄ = R ₈ = H, R ₅ = OH	<i>S. chinese</i>	[8]
95	isochisandrin	R ₁ ~ R ₅ = R ₇ = R ₉ = Me, R ₆ = OH, R ₈ = H	<i>S. chinese</i> , <i>S. spheanthera</i>	[25]
96	schisanlignone A	R ₁ ~ R ₅ = Me	<i>K. sp</i>	[12]
97	schisanlignone B	R ₁ ~ R ₄ = Me, R ₅ = OH	<i>K. sp</i>	[12]
98	schisanlignone C	R ₁ = R ₄ = R ₅ = Me, R ₂ + R ₃ = CH ₂	<i>S. viridis</i>	[20]
99	schisanlignone D	R ₁ = Me, R ₂ + R ₃ = R ₄ + R ₅ = CH ₂	<i>S. viridis</i>	[20]
100	schisanlignone E	R ₁ = Ben, R ₂ = R ₃ = Me, R ₄ + R ₅ = CH ₂	<i>S. viridis</i>	[21]
101	kadsulignan L	R ₁ = R ₂ = Me, R ₃ + R ₄ = CH ₂	<i>K. coccinea</i> , <i>K. angustifolia</i>	[26]
102	kadsulignan M	R ₁ = Me, R ₂ = H, R ₃ + R ₄ = CH ₂	<i>K. coccinea</i>	[26]
103	kadsulignan N	R ₁ ~ R ₄ = Me	<i>K. coccinea</i> , <i>K. angustifolia</i>	[26]
104	neokadsuranin		<i>K. coccinea</i>	[26]

β 取代; C-9 位为 α 取代)、酯基(在 C-6 位, β 取代, C-9 位, α -取代)和酮基(在 C-6, C-9 位), 酯基多为当归酸酯(angeloate)、乙酸酯、苯甲酸酯、顺芷酸酯(tigloate)等。此外, 在南五味子属植物中发现几个 6 α , 9 α 氧桥连接的四氢呋喃环型木脂素(101~ 104)。C-7, C-8 位无氧取代时, 2 个甲基均为顺式, α 取向, 当 C-7 有羟基取代时, 2 个甲基有时为反式, 有时为顺式, Me-8 均为 α 取向。

由于联苯旋转受阻引起分子的立体异构, 联苯环辛二烯木脂素可分为联苯 S 和 R 构型 2 个系列, 加上分子中可存在其它手性中心, 本类化合物的立体异构较多。八元环构象多数为扭曲的船椅式(TBC), 部分为扭曲的船式(TB)。

本类化合物异名同物现象较多, 如我国学者分离得到的五味子酚(schisanhenol, 74)

与日本学者得到的(+) gom isin K₃ 结构完全相同; 其它如wuw eizisu C (3) 与 schisandrin C, schisantherin A (61) 与 gom isin C 和wuw eizi ester A, schisantherin B (62) 与 gom isin B 和wuw eizi ester B, deoxyschizandrin (72) 与wuw eizisu A 和 schisandrin A, wuw eizisu B (79) 与 schisandrin B, schisandrin (88) 与五味子醇甲(wuw eizi alcohol A, schisandrol A), gom isin A (89) 与五味子醇乙(wuw eizi alcohol B, schisandrol B) 完全相同。

2 螺苯骈呋喃联苯环辛二烯木脂素

到目前为止在 7 种植物中发现此类结构的木脂素 25 个(见图 2; 表 2: 105~ 129), 其结构的变化是在联苯环辛二烯木脂素的基础上, 以 C-16 为中心, 与其它含氧取代基形成一个新的呋喃环, 同时含 C-16 的一个芳环烯酮化。多数螺环为 C-16 与 C-14 的含氧取代基形成, 芳环上的烯酮化主要有 $\alpha, \beta, \alpha', \beta'$ 二烯酮和 $\alpha, \beta, \gamma, \delta$ 二烯酮 2 种形式。只有 heteroclitin F (128) 中 C-2 和 C-3 之间键断裂。kadsulignan A (126)、B (127)、C (129) 和 heteroclitin F 的结构十分新颖。

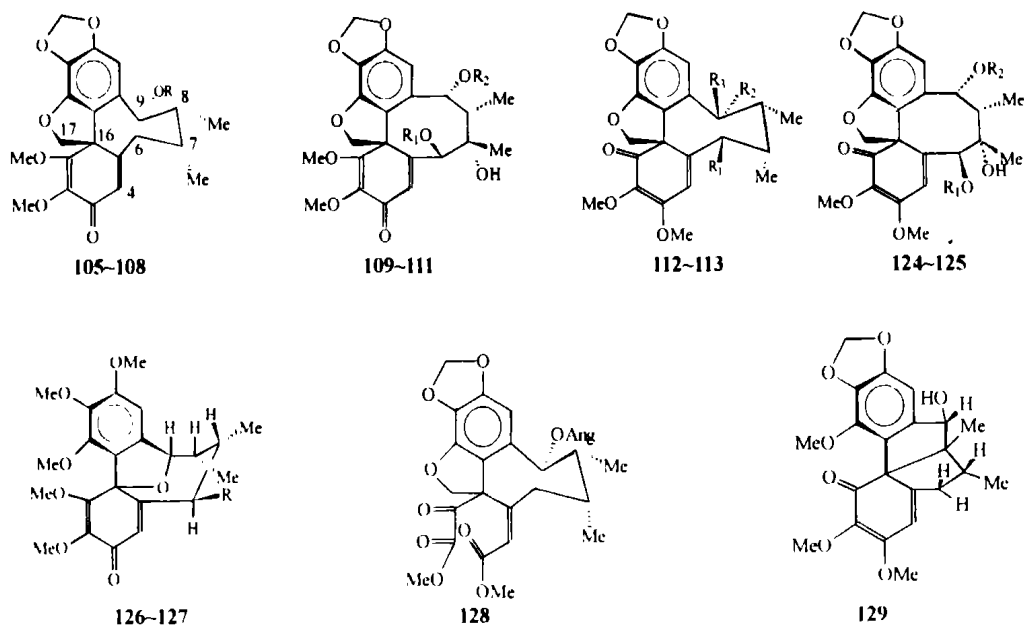


图 2 五味子科植物中新螺苯骈呋喃联苯环辛二烯木脂素的结构

Fig. 2 Structures of new spirobenzofuranoid dibenzocyclooctadiene lignans from plants of Schisandraceae

表 2 五味子科植物中的新螺苯骈呋喃联苯环辛二烯木脂素

Table 2 New spirobenzofuranoid dibenzocyclooctadiene lignans from plants of Schisandraceae

No.	化合物 Compounds	结构 Structures	植物来源 Plant sources	参考文献 References
105	interiorin	R = Ang	<i>K. interior</i> , <i>K. heteroclita</i>	[1]
106	interiorin B	R = Tig	<i>K. interior</i>	[27]
107	interiorin C	R = Ac	<i>K. interior</i>	[27]
108	interiorin D	R = Ben	<i>K. interior</i>	[27]
109	kadsulignan E	R ₁ = Ac, R ₂ = Ben	<i>K. longipedunculata</i>	[28]
110	kadsulignan F	R ₁ = Ang, R ₂ = Ac	<i>K. longipedunculata</i>	[28]

续表 2

No.	化合物 Compounds	结构 Structures	植物来源 Plant sources	参考文献 References
111	kadsulignan G	R ₁ = Ang, R ₂ = Ang	<i>K. longipedunculata</i>	[28]
112	Kadsulignan H	R ₁ = H, R ₂ = Obutyryl, R ₃ = H	<i>K. sp</i>	[29]
113	kadsulignan I (propoxyl oxokadsurane)	R ₁ = H, R ₂ = OPropoxyl, R ₃ = H	<i>K. sp, K. coccinea</i>	[29]
114	kadsulignan J (isovaleroyl oxokadsurane)	R ₁ = H, R ₂ = O iso-V aleroyl, R ₃ = H	<i>K. sp, K. coccinea</i>	[29, 13]
115	heteroclitin D	R ₁ = H, R ₂ = OAng, R ₃ = H	<i>K. heteroclita</i>	[11]
116	benzoyl oxokadsurane	R ₁ = H, R ₂ = OBen, R ₃ = H	<i>K. coccinea</i>	[30]
117	acetoxyl oxokadsurane	R ₁ = H, R ₂ = OAc, R ₃ = H	<i>K. coccinea</i>	[30]
118	isovaleroyl oxokadsuranol	R ₁ = OH, R ₂ = O iso-V aleroyl, R ₃ = H	<i>K. coccinea</i>	[30]
119	heteroclitin E	R ₁ = OH, R ₂ = OAng, R ₃ = H	<i>K. heteroclita</i>	[11]
120	schiarisanrin A	R ₁ = R ₂ = H, R ₃ = O iso-V aleroyl	<i>S. arisanensis</i>	[6]
121	schiarisanrin B	R ₁ = R ₂ = H, R ₃ = OAc	<i>S. arisanensis</i>	[6]
122	schiarisanrin C	R ₁ = R ₂ = H, R ₃ = OBen	<i>S. arisanensis</i>	[6]
123	schiarisanrin D	R ₁ = R ₂ = H, R ₃ = OCinnamoxyl	<i>S. arisanensis</i>	[6]
124	kadsulignan C	R ₁ = Ac, R ₂ = Ben	<i>K. longipedunculata</i>	[31]
125	kadsulignan D	R ₁ = R ₂ = Ang	<i>K. longipedunculata</i>	[31]
126	kadsulignan A	R= H	<i>K. coccinea</i>	[32]
127	kadsulignan B	R= OAc	<i>K. coccinea</i>	[32]
128	heteroclitin F		<i>K. heteroclita</i>	[33]
129	kadsulignan C (heteroclitin G)		<i>K. heteroclita, K. sp</i>	[29, 33]

不同学者报道的 kadsulignan I(113)和 propoxyl oxokadsurane, kadsulignan J (114)和 isovalero l oxokadsurane, kadsulignan C (129)和 heteroclitin G 的结构完全相同。

3 4-芳基四氢萘木脂素

已发现 9 个这类化合物(见图 3; 表 3: 130~ 138), 除 schizandriside (138)为木脂素木糖甙外, 其余均为游离木脂素, 其结构母核是 2, 3-二甲基-4-芳基四氢萘, 在芳核 6, 7 位上有亚甲二氧基、甲氧基或羟基取代, 除 schizandriside 外, 1 位均为酮基取代。

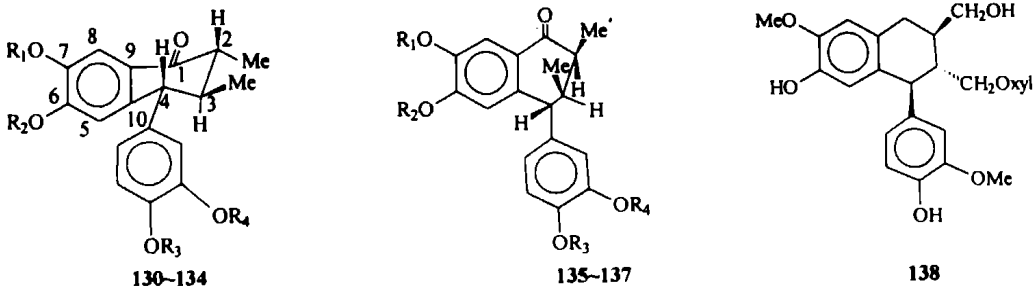


图 3 五味子科植物中新 4-芳基四氢萘木脂素的结构
Fig. 3 Structures of new 4-aryltetralin lignans from plants of Schisandraceae

表 3 五味子科植物中的新 4-芳基四氢萘木脂素
Table 3 New 4-aryltetralin lignans from plants of Schisandraceae

No.	化合物 Compounds	结构 Structures	植物来源 Plant sources	参考文献 References
130	epienschicine	R ₁ + R ₂ = CH ₂ , R ₃ = H, R ₄ = Me	<i>S. henryi, S. propinqua var sinensis</i>	[1]
131	epienschicinemethylether	R ₁ + R ₂ = CH ₂ , R ₃ = R ₄ = Me	<i>S. henryi</i>	[34]

续表 3

No.	化合物 Compounds	结构 Structures	植物来源 Plant sources	参考文献 References
132	epischisandrone	$R_1 = H, R_2 \sim R_4 = Me$	<i>S. henryi</i>	[1]
133	epiwulignan A ₁	$R_1 = R_3 = H, R_2 = R_4 = Me$	<i>S. henryi</i>	[1]
134	wulignan A ₂	$R_1 = R_4 = Me, R_2 = R_3 = H$	<i>S. henryi</i>	[1]
135	schisandrone	$R_1 = H, R_2 \sim R_4 = Me$	<i>S. henryi, S. spheanthera</i>	[1]
136	enshicine	$R_1 + R_2 = CH_2, R_3 = H, R_4 = Me$	<i>S. henryi, S. propinqua</i> var <i>sinensis</i>	[1]
137	wulignan A ₁	$R_1 = R_3 = H, R_2 = R_4 = Me$	<i>S. henryi</i>	[1]
138	schizandriside		<i>S. nigra</i>	[35]

4 2, 3-二甲基-1, 4-二芳基丁烷木脂素

在五味子科植物中发现 7 个这类化合物(见图 4; 表 4: 139~ 145), 在生物合成过程中它们是其它类型木脂素的生源前体。通常在芳环间位、对位有甲氧基、亚甲二氧基或羟基取代。

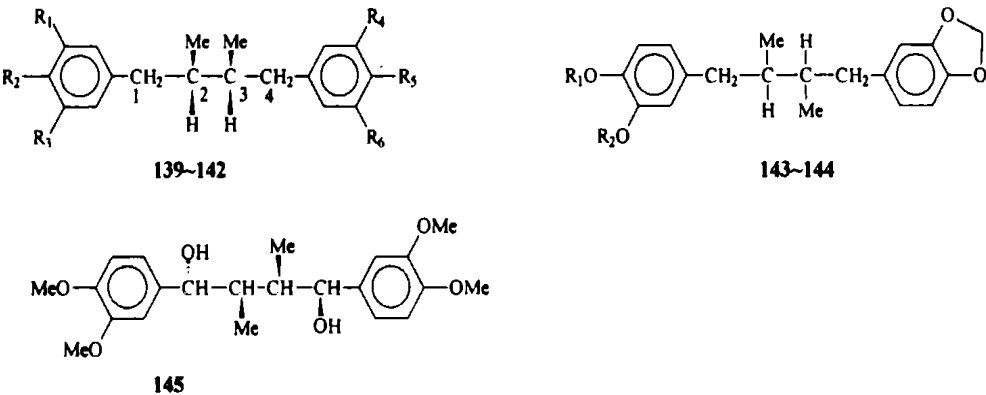


图 4 五味子科植物中新 2, 3-二甲基-1, 4-二芳基丁烷木脂素的结构
Fig. 4 Structures of new 2, 3-dimethyl-1, 4-diarylbutane lignans from plants of Schisandraceae

表 4 五味子科植物中的新 2, 3-二甲基-1, 4-二芳基丁烷木脂素
Table 4 New 2, 3-dimethyl-1, 4-diarylbutane lignans from plants of Schisandraceae

No.	化合物 Compounds	结构 Structures	植物来源 Plant sources	参考文献 References
139	pregomisin	$R_1 = R_4 = OH, R_2 = R_3 = R_5 = R_6 = OMe$	<i>S. chinese, S. rubriflora, S. propinqua</i> var <i>intemedial</i>	[1, 7]
140	(+)-anwulignan	$R_1 = R_4 = OH, R_2 = OH, R_3 = OMe, R_5 + R_6 = CH_2$	<i>K. longipedunculata</i>	[36]
141	dianwulignan	$R_1 = R_4 = OH, R_2 = OH, R_3 = OMe, R_5 + R_6 = CH_2$	<i>S. spheanthera</i>	[1]
142	preschisanthrin	$R_1 = R_3 = R_4 = R_6 = OMe, R_2 = R_5 = OH$	<i>S. propinqua</i> var <i>intemedial</i>	[37]
143	isoanwulignan	$R_1 = Me, R_2 = H$	<i>S. viridis</i>	[21]
144	3-methoxy-4-hydroxy-3', 4'-methenedioxyllignan	$R_1 = H, R_2 = Me$	<i>K. coccinea</i>	[38]
145	lignandiol		<i>S. rubriflora</i>	[39]

5 四氢呋喃类木脂素

在五味子科植物中发现 5 个这类化合物(见图 5; 表 5: 146~ 150), 其基本母核为 2, 5-二芳基-3, 4-二甲基四氢呋喃, 2 位芳基与 3, 4 位甲基均为顺式。

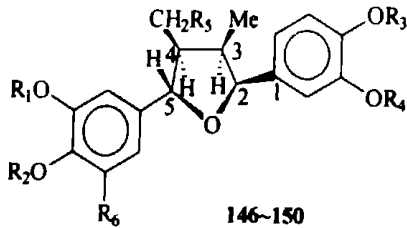


图 5 五味子科植物中新四氢呋喃类木脂素的结构

Fig. 5 Structures of new 2, 5-diaryl tetrahydrofuran lignans from plants of Schisandraceae

表 5 五味子科植物中的新四氢呋喃类木脂素

Table 5 New 2, 5-diaryl tetrahydrofuran lignans from plants of Schisandraceae

No.	化合物 Compounds	结构 Structures	植物来源 Plant sources	参考文献 References
146	chicanine	$R_1 + R_2 = CH_2, R_3 = R_5 = R_6 = H, R_4 = Me$	<i>S. sp., S. sphenanthera</i>	[36]
147	d-epigalbacine	$R_1 + R_2 = R_3 + R_4 = CH_2, R_5 = R_6 = H$	<i>S. sphenanthera, K. longipedunculata</i>	[36]
148	ganschisandrine	$R_1 \sim R_4 = Me, R_5 = R_6 = H$	<i>S. sphenanthera</i>	[40]
149	henricine	$R_1 = R_2 = Me, R_3 + R_4 = CH_2, R_5 = H, R_6 = OMe$	<i>S. henryi</i>	[1]
150	enshizhisu	$R_1 + R_2 = CH_2, R_3 = R_6 = H, R_4 = Me, R_5 = OH$	<i>S. henryi</i>	[1]

6 结语

五味子为著名传统中药,在临床上得到广泛的应用。对五味子科植物进行的广泛研究,虽已分离鉴定 150 余个木脂素化合物,但由于类型广、结构变化大、立体异构多,其结构与合成研究仍然受到有机化学家的重视;从药理研究方面看,五味子木脂素的生理活性不仅仅限于以前发现的保肝降酶,而且近年来也发现本科植物三萜成分具有重要的生物活性。因此继续深入研究五味子科植物的成分及活性,对阐明五味子在传统中医应用中的功效包括镇静、安神、滋补强身的物质基础具有重要的意义。

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