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Naturally Occurring Pterocarpanoids and Related Compounds

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Abstract. In the present review, an effort has been made to list all pterocarpanoids and coumestans which have been isolated from various plants belonging to the plant family Leguminosae (Fabaceae) up to mid-1998. The antimicrobial activities as well as the biosynthetic pathways of these compounds are briefly included.

Introduction

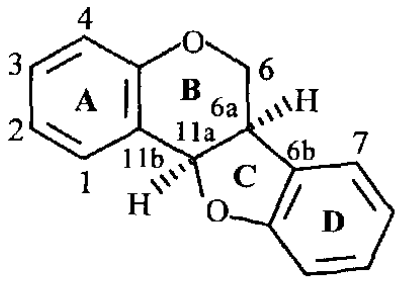
Pterocarpanoids and isoflavones represent the most abundant classes of isoflavonoid phytoalexins produced by leguminous plants. These natural compounds probably play an important role in the disease resistance of such plants. In continuation of our interest in literature survey of natural phenolics [1-4] we present, herein, a survey of ptercapanoids and the structurally related coumestans.

Pterocarpanoids

Pterocarpanoids are a group of naturally occurring heterocycles having a 6a, 11a-dihydrofurobenzopyran nucleus (a) which has two assymmetric centers. Formula (a) shows the absolute configuration of the majority of the naturally occurring pterocarpans [5] which is currently indicated as 6a*R* , 11 a*R*. This designation is consistent with those pterocarpans which have no substituents at carbons 6a and 11a.

The majority of natural pterocarpans have large negative $[\alpha]_D$ values and consequently are considered to have the same absolute stereochemistry which is consistent with the results from ORD curves [6 - 8].

Literature survey revealed that the pterocarpanoids are limited in their occurrence to plants of many genera of Leguminosae (Fabaceae). However, the plant species of the



(a)

Erythrina, Glycine, Sophora and *Swartzia,* constitute the major source of this class of natural compounds. The structures of these natural compounds are shown in Figs. 1-5, while their botanical sources are given in Table 1. These compounds bear hydroxy , methoxy, methylenedioxy or prenyl substituents as illustrated in Figs. 1-5, and all of them are oxygenated at 3 and 9 positions. These compounds occur in nature mainly as aglycones. Pterocarpans are found mainly in the heartwood of tropical genera of the Leguminosae. However, these natural phenolics are often found in the roots of other leguminous plants such as *Neorautanenia, Lonchocarpus, Sophora* and *Tephrosia* (Table 1).

Table 1. Distribution of pterocarpanoids in leguminous plants

Plant species	Compd. no.	M.p.°C	Plant parts	Reference(s)
Andira inermis (Wright) H.B.K	30	179-80	heartwood	[132]
Albizzia procera	1		heartwood,bark	[137]
Astragalus mongholicus	16	136-37	roots	[9]
	114		roots	[57]
Baphia nitida	31		heartwood	[138]
Calopogonium caeruleum	55		leaves	[120]
Calopogonium muconoides	72			[120]
Cladrastis platycarpa (Maxim.)	2,30		heartwood	[6]
Makino	32	amorphous	heartwood	[6]
Cicer species	114,115		roots	[183]
	2,30		roots	[183]
Crotalaria barbata	98	75°	aerial parts	[172]
Dalbergia decipularis Rizz. et Matt.	2	127-28		[106]
D. ecastophyllum	2		wood	[77]
D. odorifera T. Chen	2,10,23,25			[167]
	26	amorphous		[167]
D . spruceana Betith.	33,34,36			[11]
D . variabilis	45		leaves	[186]
Derris amazonica	2	127-28	aerial parts	[166]
Derris uruca	109	179-80	aerial parts	[166]
Desmodium gangeticum	69		roots	[23]
	70	136-38	roots	[24]
	71	236-38	roots	[24]
Dolichos biflorus L.	53		leaves and stem	[88,142]

Table 1. (Contd.).

Plant species	Compd. no.	M.p.°C	Plant parts	Reference(s)
Erythrina abyssinica	61		bark	[121]
E. burana Chiov.	53,73		bark	[49]
E. burttii	55	amorphous	stem-bark	[176]
	68	amorphous	stem-bark	[176]
E. crista-galli	53,73		stem-bark	[70]
	54	88.5-89.5	stem-bark	[89]
	61	152-53	stem-bark	[89]
	62	120-21	stem-bark	[89]
	107		roots	[44]
	80	oil	wood	[178]
	81	oil	wood	[178]
	99	oil	wood	[178]
	79	oil	wood	[178]
	53	oil	wood	[178]
	73		wood	[178]
E. eriotricha, E. sigmoida	55	180°	stem,root bark	[177]
	70	224°	stem,root bark	[177]
E. mildbraedii	61,72		roots	[50]
	86-88		roots	50]
E. orientalis	48	amorphous	wood	[179]
	49	246-48	wood	[180]
	56	oil	roots	[181]
	57	oil	roots	[181]
	78	oil	roots	[181]
	61	160-62	roots	[181]
E. sandwicensis	53,73		bark	[90]
	54			
	1,108			
	74			
E. variegata	61			[122]
Eysenhardtia polystachya (Ortego) Sarg.	37		stems and bark	[74]
Flemingia chapper Buch-Ham	109	179-80	whole plant	[41]
Gliricidia sepium	2	28-29	heartwood	[184]
Glycine canescens	90,91		infected leaves	[97,123]
	105	164-67		[25]
G. clandestina	106			[25]
G. max L.	40		seeds	[91]
	108			[92,97]
	41		seeds	[52,67,68]
	42		seeds	[105]
	42		seeds	[52]
	2		[93]	
	90-91		leaves	[124,125]
	90			[94,95]
	75,76			[94]
	93			[17,99]
	94			[96]
	95-97		leaves	[96,97]
	40,90-92		leaves	[97]

Table 1. (Contd.).

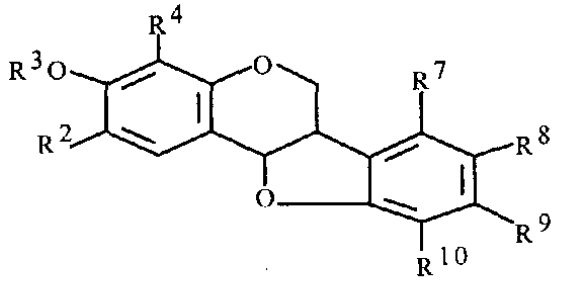
Plant species	Compd. no.	M.p.°C	Plant parts	Reference(s)
Lonchocaipus laxiflorus	14,15		roots	[20]
Lonchocarpus species	four pterocarpans			[126]
Machaerium vestitum Vogel	8		heartwood	[107]
Maackia amunensis	30		heartwood	[133,136]
Medicago sativa L	2, 7		hay	[98-100]
	9		hay	[101]
Melilotus alba	2		aerial parts	[102]
Melilotus alba Desr.	20	48-51	aerial parts	[18]
	21	173-75.5	aerial parts	[18]
	22	160-62.5	aerial parts	[18]
	23	161-62.5	aerial parts	[18]
	25	197-99	aerial parts	[18]
Millettia pulchra Benth	30	177-77.5	aerial parts	[16]
	31	164-64.5	aerial parts	[16]
	46,47		aerial parts	[16]
Mundulea striata Baker	63	amorphous	aerial parts	[36]
Neorautanenia amboensis Schinz.	102	244-46	roots	[26]
N. amboensis	64-67,82,83		root bark	[27]
N. edulis	100	222-23		[27,31]
	66		root bark	[27,29]
	84		root bark	[28]
	68		root bark	[30]
	103			[32,33]
N. ficifoli	101		root bark	[34]
	52		root bark	[35]
Ononis viscosa L.	45	-	aerial parts	[185]
	110	-	aerial parts	[15, 185]
	50, 51	-	aerial parts	[187]
	2, 4, 30, 31		aerial parts	[187]
Pachyrrhizus erosus	1,103		leaves	[33]
	55		leaves	[174]
	100		seeds	[182]
Pericopsis angolensis L.	4,30,31		heartwood	[103]
Phaseolus vulgaris L.	75-77			[37,85]
	53	177-78		[38,39]
Pisum sativum L.	30			[12,69]
	41			[52,67,104,127]
	42			[52]
	17	146-48		[13]
	18	122-24		[13]
	19	141-45		[13]
Platymiscium trinitatis Bth.	2,8		wood	[128]
Psophocarpus tetragonolobus	53		winged bean pods	[108]
	3,53,60		winged bean pods	[21]
Pterocarpus. dabergoides	31		heartwood	[134]
P.macrocarpus	31		heartwood	[134]
P.santalinus	4	86	heartwood	[129]
	3,4		heartwood	[135]
	31		heartwood	[138,139]
P. soyauxii	11		heartwood	[129]
	12	129	heartwood	[129]

Table 1. (Contd.).

Plant species	Compd. no.	M.p.°C	Plant parts	Reference(s)
	4			[134]
Pueraria phaseoloides	55		leaves	[175]
Pueraria tuberosa DC.	109	213	tubers	[130,131]
Sophora flavessens var.*angustifolia*	30,114		roots	[110]
S. fiavescens var. *angustifolia*	115		callus cultures	[111,112]
S.flavescens Aiton	10	230-32	roots	[109]
S. franchetiana Dunn	89	149	roots	[113]
S. franchetiana Dunn	36	159-61	roots	[114]
S. japonica	31,101, 114,116,117		roots	[46]
S. prostrata	58	oil	roots	[173]
	59	oil	roots	[173]
	30,52, 61, 72			[173]
S. subprostrata	31	158	roots	[46]
	101		roots	[46]
Spartium junceum	13		roots	[115]
Swartzia laevicarpa Amsh.	26	178-80	trunkwood	[19]
(= *S. benthamiana* Bth.)	27	126-27		
	28	196-98		
	29	188-90		
S. leiocalycina	38		trunkwood	[116]
	111,113		trunkwood	[116]
S. madagascariensis	2,4, 7, 31,37		heartwood	[103]
	100 , 110			
S. ulei Harms	112		trunkwood	[117]
Taverniera abyssinica	2,6		roots	[168,169]
Tephrosia bidwilli	30,31,36,44		aerial parts	[22]
Tephrosia candida	109	178-79	stems & leaves	[42]
Tephrosia hildebrandtii Vatke	43		roots	[54]
T. hildebrandtii Vatke	104		roots	[56]
T. hamiltonii	109	180	roots	[43]
T. maxima	30			[164]
T. purpurea	30		roots	[118]
T.vulgaris	76		roots	[165]
Tetragonolobus maritimus	108		detached leaves	[119]
Trifolium pratense	5			[102]
	41		infected	[15]
	114	142-44		[45]
Trigonella foenum-graecum	2 (6a*R*, 11a*R*)			[71]
Ulex parviflorus	39	165-66	aerial parts	[170]
	2, 35, 36		aerial parts	[170]

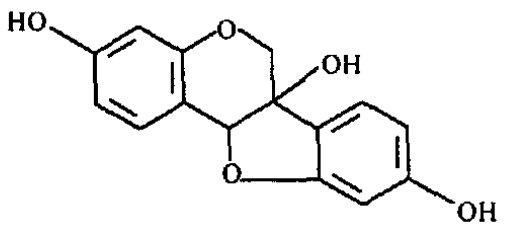
Simple pterocarpans: The pterocarpans 5 and 16 have been recently isolated from the roots of *Astragalus mongholicus* [9]. The heartwood extractives of *Cladrastis platycarpa* yielded the 8,9-methylenedioxy pterocarpan 3 [6,10],while the structurally related compounds 7-9 were obtained from *Dalbergia spruceana* [11]. We prefer this term to those pterocarpans which are not prenylated. Their structures are shown in Figs. 1 and 2. A total of forty-four nonprenylated pterocarpans have been obtained from different legnminous plants. Among these, the compounds, medicarpin (2), maackiain (30) and pterocarpin (31) repeatedly occur in plants belonging to various genera as is noted from Table1. However, pterocarpin (31) is widely obtained from the heartwood of different *Pterocarpus* plants (Table 1). Medicarpin (2) and its 4-hydroxy derivative(6) were isolated from the root extracts of *Taverniera abyssinica*[168,169]. On the other hand, maackiain (30) and its methoxylated derivatives 35 and 36 were obtained from *Ulex parviflorus*[170]. Medicarpin (2) and maackiain (30) have been obtained as phytoalexins from the fungus-inoculated stems of 15 *Cicer* species[47,171] (-)(6a*R*, 11a*R*)-maackiain (29)[12] as well as the simple pterocarpans 17-19[13] were identified in infected *Pisum sativum* (Pea) tissue. The latter three pterocarpanoids were thought to be microbial transformation products of other pea metabolites [14]. Bilton *et al* [15] demonstrated that red clover *(Trifolium pratense)* leaves infected by nonpathogenic *Botrytis cinerea* produced pisatin (41). (-) Maackiain (30) and medicarpin (2) were metabolized by *Sclerotinia trifoliorum* to yield hydroxylated products identical to those isolated from the infected tissues of *Trifolium pratense* [15].

(-) Maackiain (30) and pterocarpin (31) as well as the two pterocarpanoids of a new type (46 , 47) have been obtained from the extracts of the aerial parts of *Mellettia pulchra* [16]. The absolute configurations of (-) 30 and (-) 31 are 6a*R*, 11a*R* , as confirmed by X-ray analysis [17]. The simple pterocarpan 4 was also reported in five plant species as is noted in Table 1. Five new pterocarpans, namely melilotocarpans A-E(20-23,25), have been obtained from the aerial parts of *Melilotus alba* [18]. Besides the common pterocarpans 4,30,31, several nonprenylated pterocarpans were obtained from the trunkwood of four *Swartzia* species (Table 1) and all possess the 6a*R* , 11a*R* configuration [19]. Among these, compounds 27-29 (Fig. 1) are considered to be highly oxygenated particularly at ring D. Such highly substituted pterocarpans are also represented by compounds 14 and 15 which occur in the *Lonchocarpus* species [20]. 9-Hydroxy-3-methoxypterocarpan 3 has been isolated in 1977 [21] from the winged been pods of *Psophocarpus tetragonolobous* and this is its single occurrence in nature. Acanthocarpin (44, Fig.2) is the only characterized pterocarpan with a methylenedioxy substitution in rings A and D, and was isolated from *Tephrosia bidwillii* [22]. The remaining pterocarpans and the plants from which they have been isolated are given in Table 1.

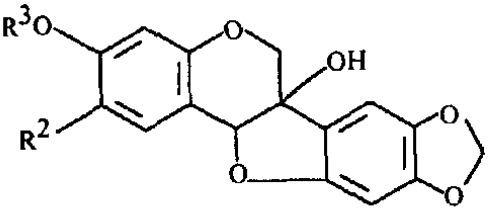


1	H	H	H		H	H	OH	H	Demethylmedicarpin
2	H	H	H	*S,S*	H	H	OMe	H	Medicarpin
3	H	Me	H		H	H	OH	H	
4	H	Me	H	*R,R*	H	H	OMe	H	Homopterocarpin
5	H	H	H	*R,R*	H	H	OH	OMe	Nissolin
6	H	H	OH		H	H	OMe	H	4-Hydroxymedicarpin
7	H	H	OMe		H	H	OMe	H	4-Methoxymedicarpin
8	H	H	H	*S,S*	H	H	OMe	OH	Vesticarpin
9	H	H	H	*R,R*	H	H	OMe	OMe	Methylnissolin
10	H	H	H	*R,R*	H	OMe	OH	H	Kushenin
11	H	H	H	*R,R*	H	OH	OMe	H	
12	H	Me	H	*R,R*	H	OH	OMe	H	
13	OMe	Me	H		H	H	OH	H	Sparticarpan
14	H	H	H		OMe	H	OH	OMe	
15	H	H	H		OMe	H	OMe	OMe	
16	H	Me	H	*R,R*	H	H	OMe	OMe	
17	OMe	H	H	*R,R*	H	H	OMe	H	
18	OMe	Me	H	*R,R*	H	H	OMe	H	
19	OMe	Me	OH	*R,R*	H	H	OMe	H	
20	H	Me	OH	*R,R*	H	H	OH	H	Melilotocarpan A
21	H	Me	OH	*R,R*	H	H	OMe	H	Melilotocarpan B
22	H	Me	OH	*R,R*	H	H	OMe	OMe	Mehiotocarpan C
23	H	Me	OH	*R,R*	H	H	OMe	OH	Melilotocarpan D
24	H	Me	OMe	*R,R*	H	H	OH	OMe	Odoricarpin
25	H	Me	OH	*R,R*	H	H	OH	OMe	Melilotocarpan E
26	OH	Me	H	*R,R*	H	OH	OMe	H	
27	OH	Me	H	*R,R*	H	OH	OMe	OMe	
28	H	Me	OMe	*R,R*	H	OH	OMe	OMe	
29	OH	Me	OMe	*R,R*	H	OH	OMe	OMe	
30	H	H	H		H	O-CH_2-O		H	Maackiain =Demethylpterocarpin
31	H	Me	H	*R,R*	H	O-CH_2-O		H	Pterocarpin
32	OH	H	H		H	O-CH_2-O		H	
33	H	H	OH	*R,R*	H	O-CH_2-O		H	
34	H	Me	OH	*R,R*	H	O-CH_2-O		H	
35	OMe	H	H		H	O-CH_2-O		H	(-)-2-Methoxymaackiain
36	H	H	OMe	*R,R*	H	O-CH_2-O		H	(-)-4-Methoxymaackiain
37	H	Me	OMe		H	O-CH_2-O		H	
38	OH	Me	H		H	O-CH_2-O		H	
39	OMe	Me	OMe		H	O-CH_2-O		H	

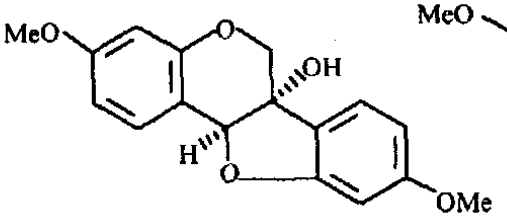
Fig. 1. Simple pterocarpans.



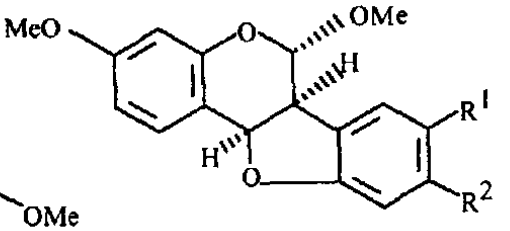
40. (-) glycinol



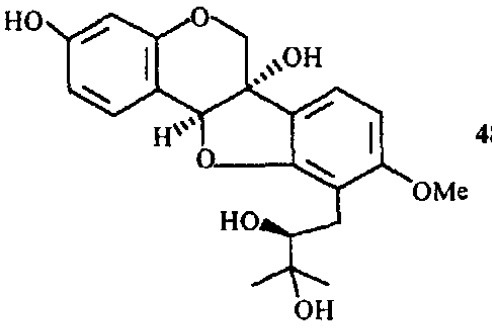
	R^2	R^3	
41.	H	Me	Pisatin (6a*R*, 11a*R*)
42.	OH	Me	(6a*R*, 11a*R*)
43.	OMe	H	Hildecarpin(6a*S*,11a*S*)
44.	OH	Me	Acanthocarpin



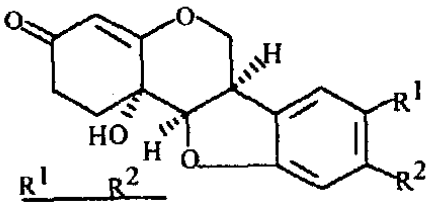
45. Variabilin



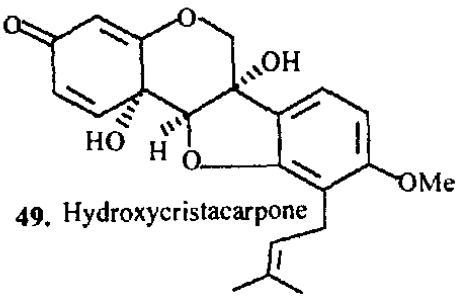
	R^1	R^2	
46.	O-CH_2-O,		6-Methoxypterocarpin (6*S*,6a*S*, 11a*R*)
47.	OMe	H,	6-Methoxyhomopterocarpin (6*S*,6a*S*,11a*R*)



48. Orientanol A



	R^1	R^2
50.	H	OMe
51.	O-CH_2-O	



49. Hydroxycristacarpone

Fig. 2. 6-Hydroxylated pterocarpans.

Prenylated pterocarpans: The structures of these compounds are shown in Figs. 3a-d. The root extracts of *Desmodium gangelicum* [23,24] yielded the prenylated compounds (69-71). Several 6a-hydroxypterocarpans are synthesized as phytoalexins by *Glycine max* (Soybean). These *Glycine* pterocarpanoids are all prenylated (6a*S*, 11a*S*)-6a-hydroxypterocarpans (Fig. 3d) with the exception of the nonprenylated parent, glycinol 40. The infected leaves of other two *Glycine* species found to contain isoprenyl 6a-hydroxypterocarpanoids include two novel compounds 105 and 106 [25]. The new pterocarpan, barbacarpan (98) has been isolated from the chloroform soluble fraction of the alcoholic extract of the dried aerial parts of *Crotalaria barbata* [172]. Prenylated pterocarpans, 89 and 101, were obtained from the roots of two species. Further investigation of the phenolic constituents in the roots of *Sophora prostrata* gave fourteen phenolic compounds, including the prenylated pterocarpans 24, 61, 72, 58 and 59 [173].

Examination of the root bark extracts of three *Neoraulanenia* species led to the isolation of the prenylated pterocarpanoids 52,72,64-67,82-84,68 and 100-103 [26-35]. The extract of the seeds of *Pachyrrhizus erosus* gave nine isoflavonoids, including the ptrocarpan, neodulin 100 [182]. Recently, the new prenylated compound 63 was isolated from *Mundulea striata,* a plant used locally in Madagasear as fish poison [36]. Phaseollidin (53) and the structurally related pterocarpanoids 75 and 76 occur in *Phaseolus vulgaris* [37-40]. However, 53 was isolated from other plants (Table 1) accompanied occasionally by prenylated pterocarpans like 60 (1-methoxyphaseollidin) from *Psophocarpus tetragonolobous* [21] and compounds 53, 73 from *Erythrina crista-galli* (Table 1). Calocarpin (55) has earlier been reported from *Pachyrrhizus erosus* [174] and later from *Calopogonium* species[120]. This prenylated pterocarpan accumulates as a major phytoalexin in leaves of *Pueraria phaseoloides*[175]. Recently, compound (55) has been obtained from the stem bark exudates of *Erythrina burtii* [176] together with pterocarpan 68. Tanaka *et al.* [177] have also reported compound (55) from the stem and root bark of another *Erythrina* species(Table 1). Pterocarpanoids 1,53,54,61,62,72-74,87-89,107 and 108 have been isolated from various *Erythrina* species (Table 1) and are all prenylated with the exception of the pterocarpanoids 1 and 108. More recently, the new pterocarpans, erystagallins A-C(80, 81, and 99) were isolated from the wood of *Erythrina crista-galli* [178] together with three other prenylated pterocarpans, 79, 53 and 73. The absolute stereochemistry at C-6α and C-11α was *R* [178], which was confirmed by the CD spectrum which displayed a negative cotton effect at 236 nm. Further, prenylated pterocarpans, 48, 49, 56, 57 and 78 were isolated from the wood extracts of *E. orientalis* [179 - 181].

Pterocarp-6(11)-enes: This group is represented by six compounds and their structures are given in Fig. 4. Flemichapparin-B(109) was first isolated from *Flemingia chapper* [41] and was recently found in the roots of two *Tephrosia* species [42,43]. Erycrystagallin (107) has been recently obtained [44] from the roots of *Erythrina crista-galli* as the main antimicrobial constituent of this plant. In fact, this compound is the only prenylated representative of the group. Pterocarpenes 110-112 have been isolated from the extracts of three *Swartazia* species (Table 1).

Pterocarpan glucosides: These compounds are very limited in their numbers. Trifolrhizin (1-maackiain-mono-β-D-glucoside) (114) was first obtained from *Triofolium pratense* [45] and its structure was confirmed by spectroscopic methods[104]. This glucoside is also reported from the root extracts of two *Sophora* species (Table 1) and more recently, it was detected in nine *Cicer* species [183], together with its corresponding malonyl-glucoside(115). The latter compound was reported from *Sophora flavescens* [111, 112]. d-Maackiain o no- β-D-glucoside (sophojaponicin)(116) and dl-maackiain mono-β-D-glucoside (117) have been reported to occur in the roots of *Sophora japonica* [46].

Bioactivity

Phytoalexins are defense substances with antimicrobial properties that are produced by plants in response to fungal infection. A number of pterocarpans are phytoalexins [47,48]. For example, pisatin (41), phaseollin (75) and 6a-hydroxyphaseollin(76) are important phytoalexins of leguminous plants. Pterocarpans 53 and 73 have exhibited moderate but selective activity towards DNA repair-deficient yeast mutants, whereas only 53 was found to be cytoxic [49]. Simple pterocarpans 2 and 6 showed nematocidal activity[169]. Besides these nematocidal effects, cytotoxic and antimicrobial activities were observed. The chloroform soluble extract of the seeds of *Pachyrrhizus erosus* was reported to exhibit a very intense cytotoxic activity on P-388 lymphocytic leukemia cells [182]. A systematic study of phytoalexin production in the genus *Lathyrus* (Leguminosae) has shown that almost all of the species examined produce isoflavonoid phytoalexins in response to fungal infection. The pterocarpin, pisatin(41), was the major phytoalexin produced in most species, but other simple pterocarpans, like 2, 3, 5 and 45, were observed in some cases[55].

Antimicrobial activity is a common feature of pterocarpans, whether they are present in the healthy plant or are formed postinfectionally. Five pterocarpans, erythrabyssin- II(61), erybraedins A-C(87-89) and isoneorautenol (72), which were isolated from *Erythrina mildraedii* [50], have shown antimicrobial potency. In particular, (61) was more potent than the others. The antimicrobial potency of another *Erythrina* species has been shown to be due to the presence of pterocarpans [50]. (+) Pisatin (41), the first known phytoalexin has been shown to have a broad spectrum of antimicrobial activity and has an important role in disease resistance [51]. Pisatin (41) was also found to inhibit spore germination of some microorganisms [52], while 2-hydroxypisatin was not active at higher concentrations.

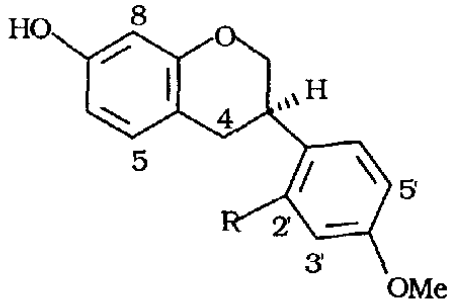
Some pterocarpans are known to be fungitoxic (e.g. (+) pisatin), although fungal degradation of these phytoalexins has been reported [53]. The profile of degradation of pisatin, and its regulation of production within the plant is not thoroughly understood. The pterocarpans isolated from the fungus inoculated parts of *Glycine max* have been shown to possess antifungal activity [25,91]. However, the unsubstituted (-) glycinol(40) is reported to be inactive [17]. The simple pterocarpan, medicarpin (2) is known to be antifungal [54].

6a-Hydroxypterocarpans have show insect antifeedant and antifungal properties [56]. The extracxts of *Tephrosia candida* are reported to possess significant insecticidal and antifeeding properties against some insects [42]. Toxic effects have also been reported form *Mundulea striata* [36].

Biosynthetic pathways

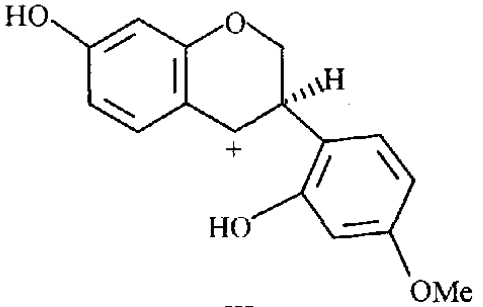
Pterocarpans are smoothly converted into the corresponding 2'-hydroxyisoflavans on hydrogenolysis [58] and they may be produced by DDQ oxidation of 2'-hydroxyisoflavans. This process has been postulated as a chemical analogy for the biosynthetic relationship [59].

2'-Hydroxyisoflavones are precursors of pterocarpanoids. Feeding experiments in $CuCl_2$ -treated lucerne *(Medicago sativa)* have shown that the 2',7-dihydroxy-4'-methoxyisoflavone (Me -^{14}C) and the corresponding isoflavanone are efficient precursors of the phytoalexins demethylhomopterocarpin (1) and the two isoflavans vestitol (I) and sativan (II).



I. Vestitol, R = OH
II. Sativan, R = OMe

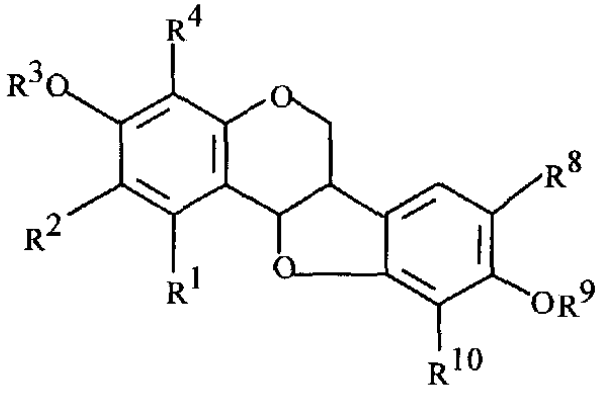
Similar feeding experiments have also shown that the pterocarpan 1 was incorporated into the isoflavans I and II. Vestitol (I) was also incorporated into 1 and II. Accordingly, the pterocarpan (1) and the 2'-hydroxyisoflavan (I) are interconvertible in *M. sativa.* These incorporation studies [60,61] as well as the results of kinetic feeding experiments with L. phenylalanine [61] suggested that these compounds are synthesized simultaneously from a common intermediate which was proposed to be the intermediate carbonium ion (III).



(III)

Similar investigations [62 - 64, 84] of medicarpin (2) of *Trifolium pratense* with labelled precursors have suggested that the biosynthetic pathway of the pterocarpan 5 proceeds via the 7-hydroxy 4'-methoxyisoflavan (Formononetin) followed by 2'-hydroxylation and the reduction to the corresponding isoflavanone. The latter is probably reduced further to the isoflavanol, which in turn can be cyclized to 5.

Isoflavone ⟶ Isoflavonone ⟶ Isoflavonol ⟶ Pterocarpan nucleus

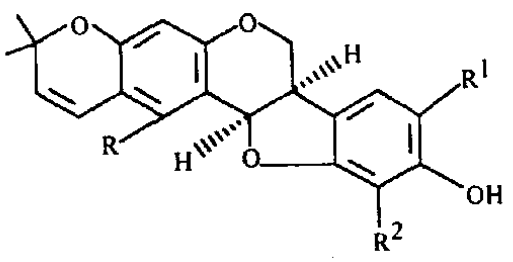


	R¹	R²	R³	R⁴	R⁸	R⁹	R¹⁰	
52.	H	*	H	H	*	H	H	Ficifoliol
53.	H	H	H	H	H	H	*	Phaseollidin(6a*R*,11a*R*)
54.	H	H	H	H	H	Me	*	Sandwicensin (6a*R*,11a*R*)
55.	H	*	H	H	H	H	H	Calopocarpin
56.	H	*	Me	H	H	H	H	Orientanol B
58.	H	H	H	H	*	Me	H	Prostratrol A
59.	H	H	H	H	***	Me	H	Prostratrol B
60.	OMe	H	H	H	H	H	*	
61.	H	*	H	H	H	H	*	Erythrabysiin-II
62.	H	*	H	H	H	Me	*	Erycristin
63.	H	**	H	H	H	H	*	Striatine (6a*R*,11a*R*)
64.	OMe	*	H	H	H	H	H	Edudiol
65.	H	*	Me	OMe	O-CH_2-O		H	Neuraucarpan
66.	OMe	*	H	H	H	Me	H	Edulenol
67.	H	*	H	OMe	O-CH_2-O		H	Neuraucarpanol

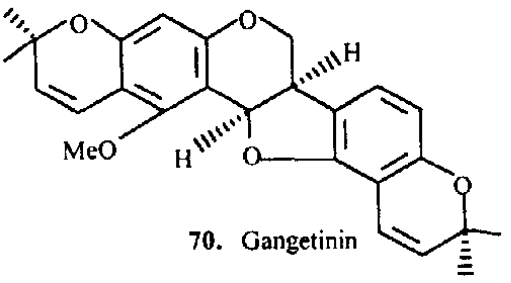
* $(CH_3)_2C = CHCH_2$ - , ** $(CH_2 = CH\text{-}C(CH_3)_2$, *** (geranyl moiety)

Fig. 3a. Prenylated pterocarpans.

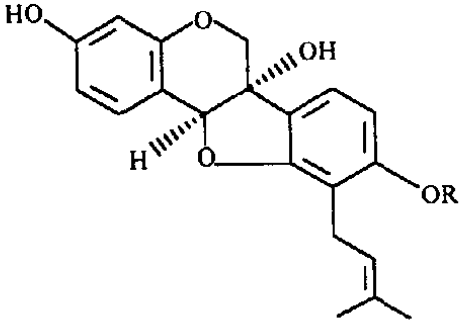
Several 6a-hydroxypterocarpan are formed as phytoalexins by *Glycine max* (soybean) tissues on treatment with a variety of biotic or abiotic agents. These pterocarpans are mainly prenylated (6a *S*, 11a *S*)6a-hydroxypterocarpans and include the major phytoalexins goyceollins I-IV (90-93) and glyceollidins (94,95). Incorporation of the daidzein (7,4'-Dihydroxyisoflavone, 7,2' ,4'-trihydroxyisoflavone, 3,9-dihydroxypterocarpan (1) and glycinol (40) into glyceollins I - III (90-92) are all sufficiently large [65]. Thus, it was assumed that these compounds may be natural precursors of the phytoalexins 90-95 (Fig. 3d). The two pterocarpans 1 and 40 were particularly well incorporated. The incorporation of all precursors tested suggests that



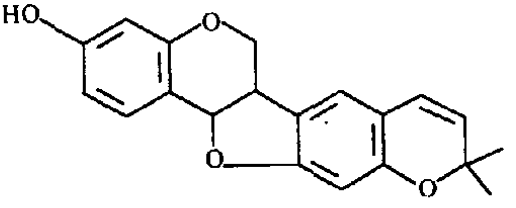
	R	R^1	R^2	
68.	H	H	H	Neorautenol
57.	H	H	*	Orientanol C
69.	OMe	H	*	Gangetin
71.	OMe	OMe	*	Desmodin



70. Gangetinin

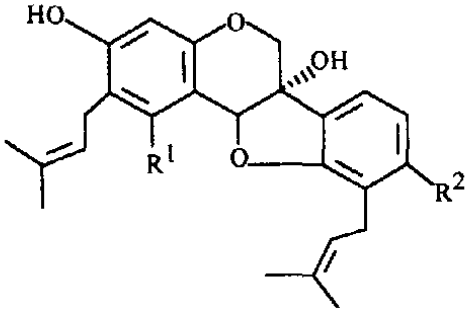


73. Cristacarpin (R = Me)
(6a *S*, 11a *S*)
74. Sandwicarpin (R = H)

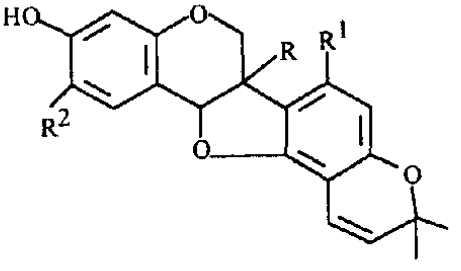


72. Isoneorautenol

(6a *S*, 11a *S*)

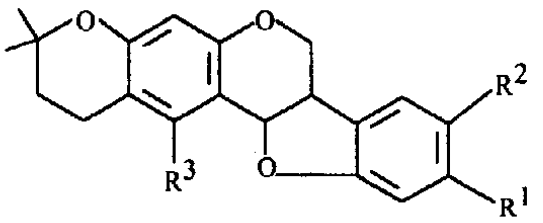


	R^1	R^2	
79.	H	H	
80.	H	OMe	Erystagallin A
81.	OMe	OH	Erystagallin B (6a*S*, 11a *S*)



	R	R^1	R^2	
75.	H	H	H	Phaseollin
76.	OH	H	H	
77.	OH	OH	H	
78.	H	H	*	

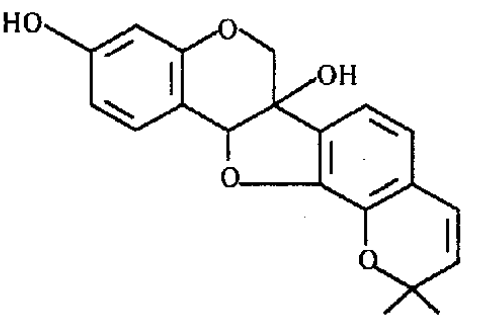
Fig. 3b. Prenylated pterocarpans.



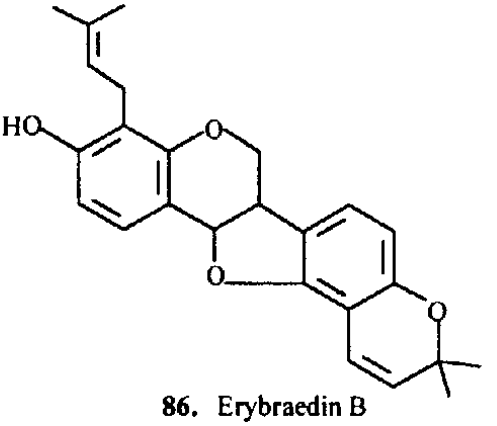
82. Edulane, $R^1 = R^3 = OMe$, $R^2 = H$

83. Neurautanin $R^1R^2 = OCH_2O$, $R^3 = OMe$

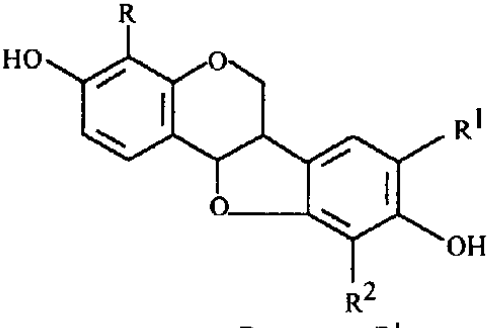
84. (-) Neorautane R^1 $R^2 = OCH_2O$, $R^3 = H$



85. Tuberosin



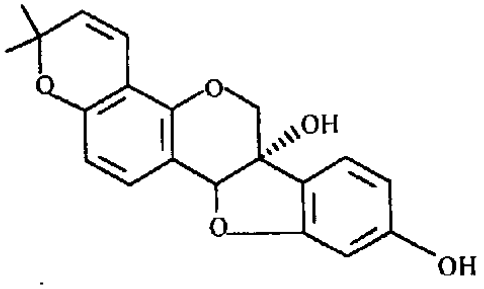
86. Erybraedin B
(6a*R*, 11a*R*)



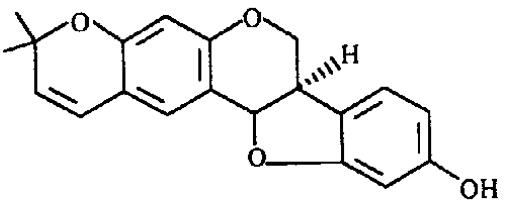
		R	R^1	R^2
87.	Erybraedin A (6a*R*,11a*R*)	*	H	*
88.	Erybraedin C (6a*R*,11a*R*)	OMe	*	H
89.	(6a*R* , 11a*R*)	H	*	H

* $(CH_3)_2 C = CHCH_2$ -

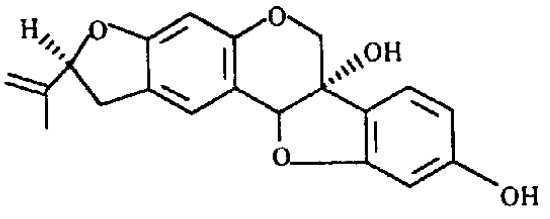
Fig. 3c. Prenylated pterocarpans.



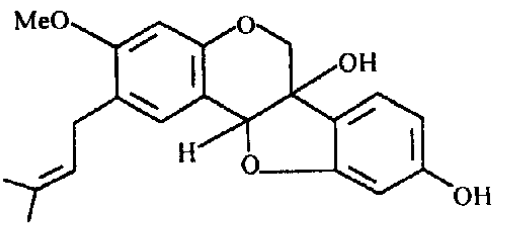
90. Glyceollin I
(6a*S*,11a*S*)



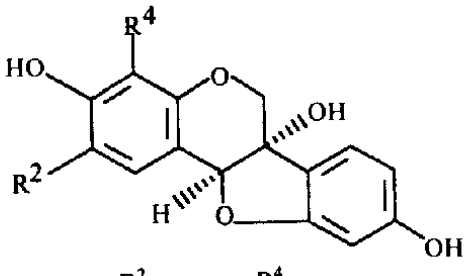
91. Glyceollin II
(6a*S*,11a*S*)



92. Glyceollin III
(6a*S*,11a*S*)

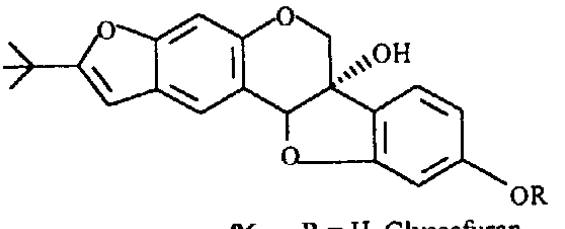


93. Glyceollin IV
(6a*R*,11a*R*)



	R^2	R^4	
94.	H	$(CH_3)_2C{=}CHCH_2$	Glyceollidin I (6a*S*,11a*S*)
95.	$(CH_3)_2C{=}CHCH_2$	H	Gluceollidin II (6a*S*,11a*S*) (=Glyceocarpin)

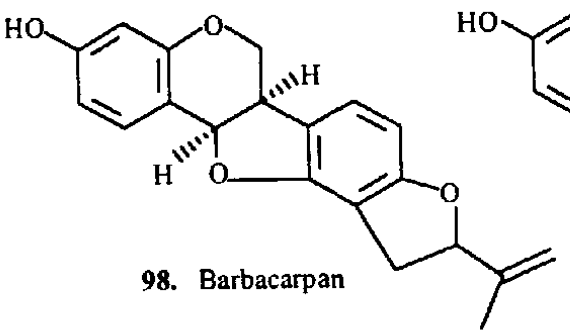
Glyceofuran(6a*S*,11a*S*)



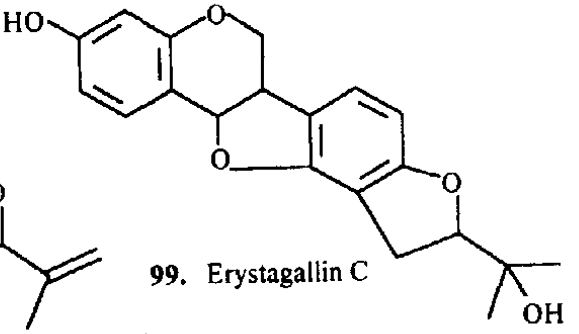
96. R = H, Glyceofuran
(6a*S*,11a*S*)

97. R = Me,

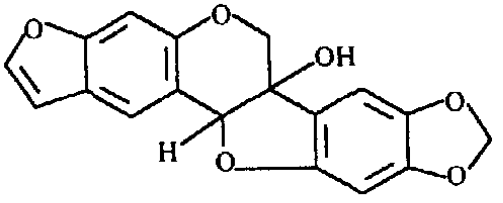
Fig. 3d. Major pterocarpanoids of *Glycine max*.



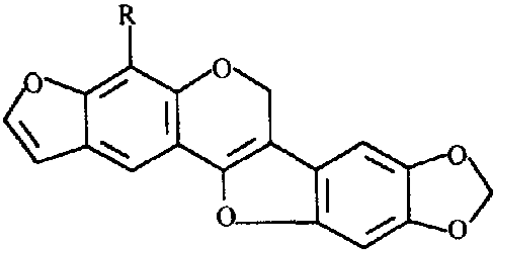
98. Barbacarpan



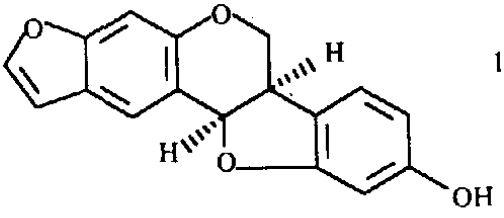
99. Erystagallin C



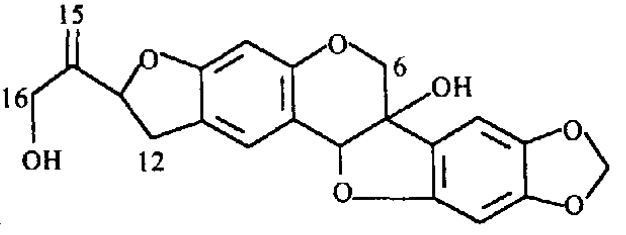
102. Neobanol
(6a*R* , 11a*R*)



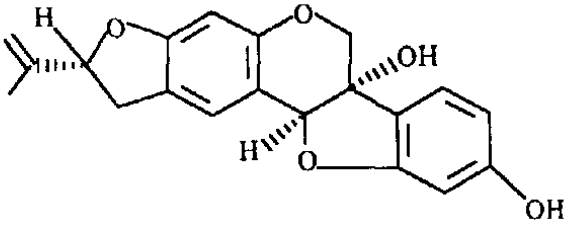
100. R = H, Neoduleen
101. R = OMe, Ficinin



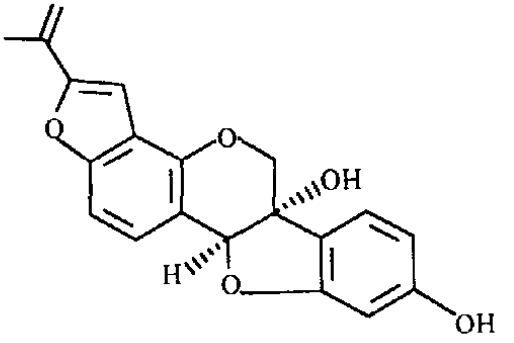
103. Neodunol



104. Hildecarpidin
(6a*S* , 11a*S*)

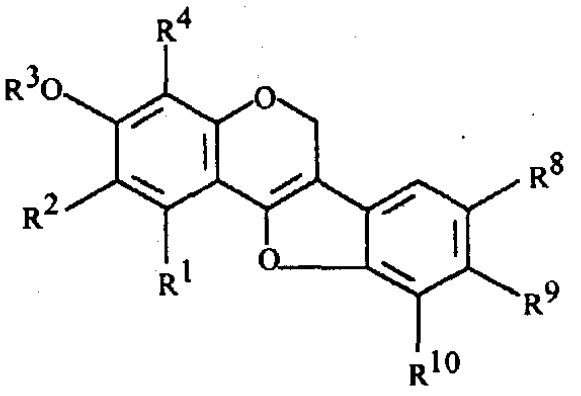


105. Canescacarpin (6a*S*,11a*S*)



106. Clandestacarpin(6a*S*,11a*S*)

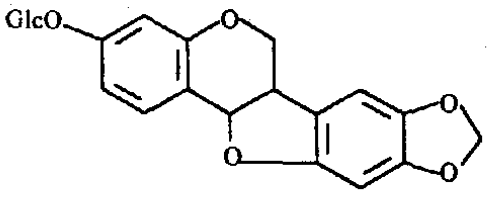
Fig. 3e. Prenylated pterocarpans.

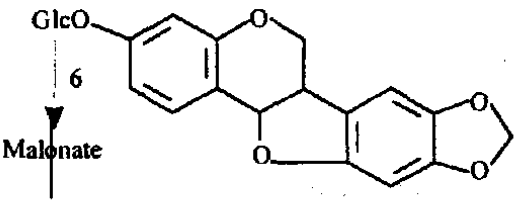


	R^1	R^2	R^3	R^4	R^8	R^9	R^{10}	
107.	H	*	H	H	H	OH	*	Erycrystagallin
108.	H	H	H	H	H	OH	H	Anhydroglycinol
109.	H	H	Me	H	O -CH_2 -O		H	Flemichapparin-B
110.	H	H	Me	H	H	OMe	H	
111.	OMe	OH	Me	H	O -CH_2-O		H	
112.	H	H	H	OMe	O -CH_2-O		H	
113.	H	OH	Me	H	O -CH_2-O		H	

* $(CH_3)_2C{=}CHCH_2$ -

Fig. 4. Some 6a, 11a anhydropterocarpanoids.





114. Trifolrhizin

115. Trifolrhizin-6-O-malonate

(=1-Maackiain-mono-β-D-glucoside

116. d-Maackiain- mono-β-D-glucoside

117. dl-Maackiain- mono-β-D-glucoside

Fig. 5. Maackiain (29) glucosides.

the basic 6a-hydroxypterocarpan (glycinol) is synthesized before any prenylation occurs. This is in agreement with data obtained with phaseollin (75), where prenylation is also delayed until the basic pterocarpan skeleton has been constructed [66]. Glycinol (40) arises from daidzein, which is hydroxylated in the 2' position, then successfully reduced via the corresponding isoflavanone and isoflavanol to give 3,9-dihydroxypterocarpan.

Feeding experiments in $CuCl_2$ treated *Pisum sativum* pods and seedling have indicated excellent incorporation into eight isoflavanoids including the pterocarpan phytoalexins (+) pisatin (41) and (+) maackiain (30) [67].

The biosynthetic pathways of glycinol(40) from *Glycine max* [65] and pisatin(41) from *Pisum sativum* [67] were initially believed to involve direct hydroxylation at 6a , most likely by an oxygenase. However, recent studies on the biosynthesis of phytoalexins of soybean has concluded that the molecular oxygen is the source of the 6a oxygen of glycinol synthesized by soybean [92]. Although, the phytoalexin (+)-(6a*R*,11a*R*)-pisatin are synthesized on treatment of *Pisum sativum* tissues with aqueous $CuCl_2$, significant quantities of (-) - (6a *S*, 11 a*S*)-pisatin are produced by supplying (-) - (6a*R*, 11a*R*)-maackiain, during the induction process [69]. This study demonstrated that the 6a-hydroxylation of maackiain during the biosynthesis of pisatin, must proceed with retention of configuration at 6a [69] which has also been confirmed in some other instances [70].

The biological reduction sequence is stereospecific. Labelling studies in *Trigonella foenumgæcum* [71] have established that the pterocarpan 2 (6a*R*, 11a*R*) was synthesized from 2' ,7-dihydroxy-4' -methoxy isoflavone via an overall *E* addition of hydrogen to the double bond. Pea *(Pisum sativum)* plants appear to have reductive enzymes capable of producing (3*R*) and (3*S*) isoflavanones via *E* and *Z* addition of hydrogen, respectively, [12,69] during the biosynthesis of medicarpin (2). Several other plants are known to constitutively accumulate enantiomeric pterocarpans 70 and 40 [67].

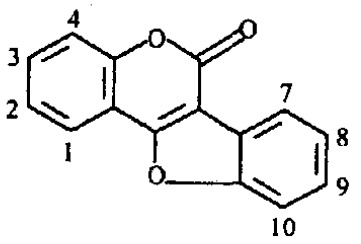
Coumestans

Coumestans are structurally similar to pterocarpans and often co-occur in the same natural sources. The structures of natural coumestans are depicted in Figs. 6 and 7, while their botanical sources are given in Table 2. Like pterocarpans, all these compounds are oxygenated at positions 3 and 9 as can be seen from Figures 6 and 7. Coumestrol (1) has been repeatedly isolated from various plants (Table 2). All natural coumestans are characterized by high melting points with the exception of plicadin 23 which has been recently isolated [72] from *Psoralea plicata,* a plant used in traditional medicine for the treatment of various diseases [73]. Flemichapparin C (9) has been isolated from the roots of *Flemingia chappar* [41] and *Tephrosia hamiltonii* [43]. This coumestan (9) was also reported from the stems of *Eysenhardlia polystachia* [74]. The coumestans 1, 3,12-16 were obtained from five *Phaseolus* species (Table 2) either by infection with fungi or treatment with $CuCl_2$.

Table 2. Distribution of coumestans in plants of Leguminosae and Astraceae

Plant species	Compd. No.	M.p. °C	Plant parts	Reference(s)
Leguminosae				
Cladrastis platycarpa (Maxim.) Makino	8		heartwood	[6]
Cicer arietinum	2,8		roots	[162]
Dolichos biflorus L.	1, 12		leaves & stems	[88,142]
Eysenhardtia polystachya (Ortego) Sary.	9	272	stems and bark	[74]
Flemingia chapper Buch-Ham.	9	272	roots	[41]
Glycine max L.	1			[143-145]
Lotus criticus	15	285-87	roots	[147]
Medicago sativa	1,2,8		seedlings	[63]
	8			[76]
	11	292-294	infected lucerne	[75]
	2			[61,161]
	5	303		[73]
	4	>350		[73]
Pachyrrhizus erosus	24	>350		[160]
Phaseolus aureus	1,3,13,16			[149,150]
P. calcaratus	1			[149]
P. coccineus	1,3,14			[151]
P. lunatus	1,12			[149]
P. vulgaris	1			[149]
Psoralea corylifolia	17	300-301*		[154]
	19	242-243	seeds	[154]
	20	236-238*		[154]
	21	232-234*	seeds	[155]
	22	349-351	seeds	[156]
	12		seeds	[159]
Psoralea plicata Del.	23	127		[72]
Sophor afranchetiana Dunn	17	>300	roots	[113]
	18	>300	roots	[114]
Tephrosia hamiltonii	9	272	roots	[43]
	6	318-320	roots	[43]
Tephrosia villosa L.	10		roots	[163]
Trifolium repens	1			[157]
	7	332		[158]
Asteraceae				
Eclipta alba (L) Hassk	25	>310	aerial parts	81]
	26			83]
Wedelia calendulacea (= synonyms *Eclipta erecta Linn.)*	25,26		fresh leaves	81]
	25	327-330		79,80]
Mutisia acuminata var. hirsuta	27	298-300	aerial parts	[86]

*Characterized as their corresponding acetates.



No.	1	2	3	4	7	8	9	10	Trivial name
1	-	-	OH	-	-	-	OH	-	Coumestrol
2	-	-	OH	-	-	-	OMe	-	9-O-Methylcoumestrol
3	OH	-	OH	-	-	-	OH	-	Aureol
4	-	OH	OH	-	-	-	OH	-	Sativol
5	-	-	OMe	OH	-	-	OH	-	Lucrenol
6	-	OMe	OH	-	-	-	OH	-	Tephrosol
7	-	-	OH	-	OH	-	OMe	-	Trifoliol
8	-	-	OH	-	-	-	$O\text{-}CH_2\text{-}O$-	-	Medicagol
9	-	-	OMe	-	-	-	$O\text{-}CH_2\text{-}O$-	-	Flemichapparin-C
10	-	OMe	OH	-	-	-	$O\text{-}CH_2\text{-}O$-	-	Tephrol
11	-	-	OH	-	OMe	-	OMe	-	Wariol
12	-	-	*		-	OH	-		Psoralidin
13	-	-	OH	*	-	OH	-		Phaseol
14	-	-	OH	-	-	-	OH	*	Isosojagol
15	OH	-	OH	-	-	*	OH	-	
25	OH	-	OMe	-	-	OH	OH	-	Wedelolactone
26	OH	-	OH	-	-	OH	OH	-	Desmethylwedelol lactone

* $(CH_3)_2C{=}CHCH_2$ -

Fig. 6. Simple coumestans.

The new coumestan 11 was isolated from fungal infected Lucerne foliage *(Medicago sativa)* [75]. Compounds 7 and 11 are the only representative coumestans having a substituent at position 7. Simple coumestans (1 and 8), in addition to some other coumestans, were also reported from *M. sativa* [63,76,77]. Recent feeding experiments [61,63,78] have demonstrated that the pterocarpan, medicarpin, (2) and the coumestan (2) are closely related in their biosynthesis and share common flavone and isoflavone precursors.

The first natural coumestan was reported by Govindachari *et.al.*[79] in 1956. These researchers have isolated wedelolactone (25) from the fresh leaves of *Wedelia calendulacea (synonyms:Eclipta erecta* Linn). The coumestan (25) was also reported later from the same natural source [80]. Wedelolactone (25) and its demethylated

derivative (26) were recently reported from *W. calendulacea* and *Eclipta alba* [81] , both plants belong to the family, Asteraceae. The two plants are reported to be widely used in India in hepatic enlargement, for jaundice and for other ailments of the liver and gall bladder [80,82]. Furthermore, the glucoside of desmethylwedelolactone(26) was isolated from the leaves of *E. alba* [83]. In fact, the main active principles of the two plants are the coumestans (25) and (26). It has been mentioned that *Eclipta alba* is the best drug for the treatment of the liver cirrhosis and infective hepatitis [81]. Six phenolic compounds were recently reported from *Mutisia acuminata* [86] of the family, Asteraceae. Among these phenolics was the coumestan (27). The latter is abnormal since it lacks the substitution at position 3.

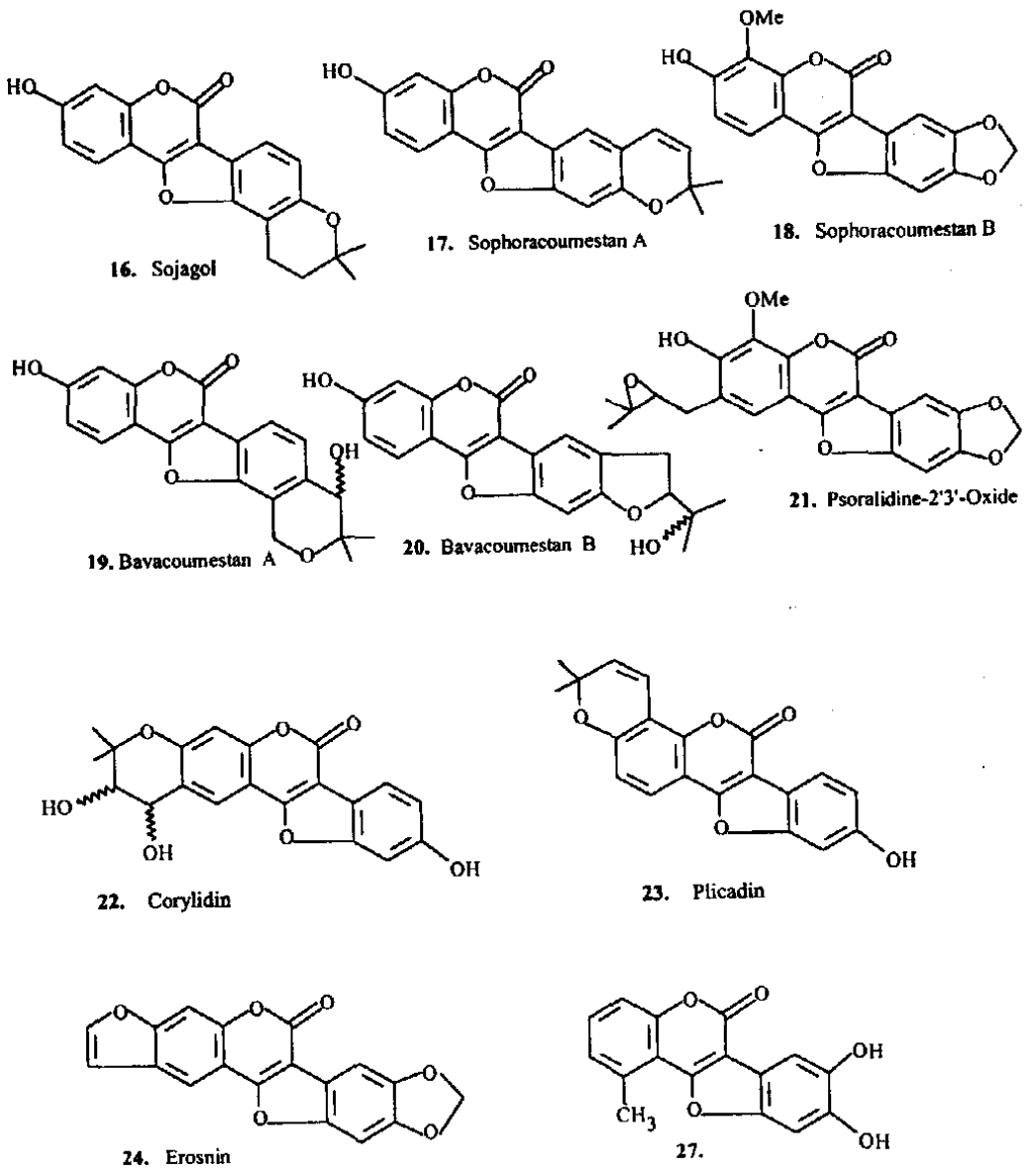


Fig. 7. Some natural coumestans.

Conclusion

It seems that the occurrence of pterocarpanoids in higher plants is restricted to the plants of Leguminosae. This feature may be of chemotaxonomic interest. However, literature survey revealed that the two racemic pterocarpans 3 and 30 occur in the wood of *Osteophelum platyspermum* (DC) Warb.,a plant belonging to the plant family Myristicaceae[87]. Natural coumestans (Figs. 6 and 7) were isolated from various leguminous plants (Table 2) with the exception of compounds 25-27.

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مركبات البتروكاربان الطبيعية ومشابهاتها النباتية

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الرياض ١١٤٥١، المملكة العربية السعودية

(قدم للنشر في ١٤٢٠/٦/٤هـ، وقبل للنشر في ١٤٢٠/١١/١٥هـ)

ملخص البحث. تم في هذا المقال حصر لجميع البتروكاربان والكومستان التي سبق فصلها من نباتات مختلفة للعائلة البقلية. وبالإضافة إلى ذلك فقد تمت الإشارة إلى كل من فعالية هذه المركبات الطبيعية ضد الميكروبات وكذلك مسار الاصطناع الحيوي لها.