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THE DISTRIBUTION OF LIGNANOIDS IN THE ORDER CONIFERAE

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Key Word Index—Order Coniferae; Podocarpaceae; Araucariaceae; Cupressaceae; Taxodiaceae; Pinaceae; lignans; cyclolignans; neolignans; norlignans.

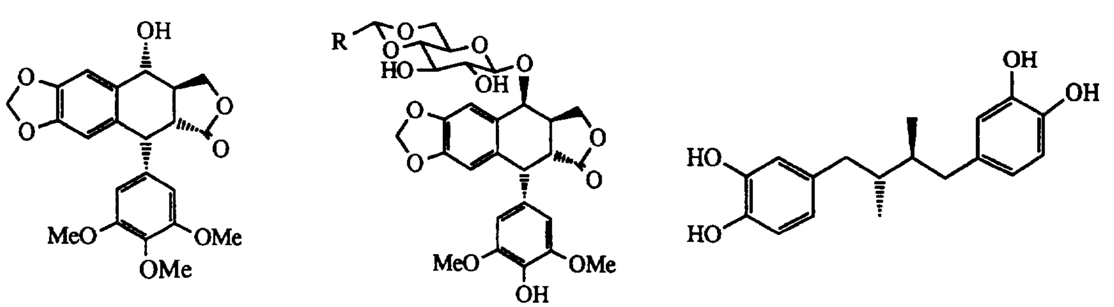
Abstract—Lignan distribution in the Coniferae order, which includes six families, has been reviewed from 1967 to 1994. The occurrence of lignanoids in five of the six families of this order has been reported and the predominant lignan type is different for each one.

INTRODUCTION

Lignanoids are secondary metabolites constituted by two phenylpropane units, biosynthesized through the shikimic acid pathway and widely distributed in the plant kingdom. They have been isolated from different parts of plants: roots, rhizomes, woody parts, stems, leaves, fruits and seeds [1]. These natural products have attracted much attention due to the great variety of biological activities they show [2]. The therapeutical use of several cyclolignanolides should be mentioned and among them is podophyllotoxin (**22**), which is valued for its antiviral properties and used for the treatment of condiloma acuminata and other types of warts [3]. Another therapeutic lignan is masoprocol (Fig. 1), a useful topical agent for the prevention and treatment of pre-malignant skin lesion induced by actinic processes; it is also under clinical evaluation for the treatment of other neoplastic processes [4].

In several cases, these natural bioactive lignans have become lead compounds for the development of new drugs as is the case for podophyllotoxin. Two derivatives, etoposide and teniposide (Fig. 1), have improved pharmacological activity over the parent compound and are being used in the treatment of different types of cancer [1].

Lignans have been detected, with varying levels of abundance, in species belonging to up seventy plant families [5, 6]. They are the main secondary metabolites in



Podophyllotoxin

R
Me Etoposide

Teniposide

Masoprocol

Fig. 1. Structures of lignan derivatives with clinical therapeutic use.

Table 1. The distribution of lignanoids in the Podocarpaceae

Compound type	No.	Name(s)	References: *Podocarpus* Pd. s.	*Podocarpus* Pd. sl.	*Dacrydium* (Dc. i.)
1. Lignans					
1.1. Dibenzylbutanediol derivatives					
	1	Secoisolariciresinol	21		
1.2. Tetrahydrofurans					
	6	α-Intermedianol			22
	7	Iso-α-intermedianol			22
	8	β-Intermedianol			22
	9				22
	10				22
1.4. Lignanolides					
	37	Matairesinol	21		
	57	Methyl-thujaplicatin		23	
2. Cyclolignans					
2.1. Non-lactone naphthalene derivatives					
	82	Methyl-α-conidendral diacetate			24
	84	Ethyl-α-conidendral			22
	86	Formosanol			22
	87	Methyl-α-conidendral (tsugacetal)			22
	88	Methyl-β-conidendral			24
	89	Ethyl-β-conidendral			24
	100	α-Conidendrin	21		

Table 2. The distribution of lignanoids in the Araucariaceae

Compound type	No.	Name(s)	References: Ag. a.	Ar. a.
1. Lignans				
1.1. Dibenzylbutanediol derivatives				
	1	Secoisolariciresinol		25, 26
	2	Methyl-secoisolariciresinol		27
1.2. Tetrahydrofurans				
	19	Lariciresinol		28
	20	Methyl-lariciresinol		27
1.3. Furofurans				
	31	Pinoresinol		25
	32	Dimethyl-pinoresinol		25
	33	Methyl-pinoresinol		25, 26
2. Cyclolignans				
2.1. Non-lactone naphthalene derivatives				
	71	Ciclogalgravin		27
	72	Galbulin		27
	73	Galcatin		27
	74	Isogalcatin		27
	75	Isolariciresinol		25, 26
	76	Methyl-isolariciresinol		26, 28
4. Norlignans				
	134	Agatharesinol	29	
	135	Hinokiresinol	29	25, 26
	140	Sugiresinol (sequirin A)	29	
	145	Cryptoresinol		26
	146			26

Table 3. The distribution of lignanoids in the Cupressaceae

Compound type	No.	Name(s)	References														
			Juniperus					*Thuja*						*Libocedrus*			
			Jn.c.	Jn.f.	Jn.p.	Jn.t.	Jn.s.	Th.s.	Th.p.	Th.o.	Cl.f.	Ch.o.	As.c.	Lb.b.	Lb.y.	Ft.c.	Tj.d.
1. Lignans																	
1.1. Bibenzylbutanediol derivatives																	
	1	Secoisolariciresinol														30	
	3	Dimethyl-secoisolariciresinol				18											
	4	Meso-secoisolariciresinol	31														
1.2. Tetrahydrofurans																	
	5	Shonanin									32						
	21	Dihydrosesamin				17	14										
	22	7-β-Hydroxydihydrosesamin				18											
	23	Acuminatin					15										
1.3. Furofurans																	
	34		31														
	35	Sesamin				17					32	33					
	36	(+)-Epipinoresinol					15										
1.4. Lignanolides																	
	37	Matairesinol									34						
	38	Pluviatolide									5						
	44	Thujaplicatin						5	5								
	45	Methyl-thujaplicatin						35	35								
	46	Methyl-hydroxythujaplicatin						35	35								
	47	Dihydroxythujaplicatin						35	35								
	48	Methyl-dihydroxythujaplicatin						35	35								
	49	Thujastandin						35									
	50	Podorhizol				17, 18	14										
	51	Podorhizol acetate					14										
	52	Epipodorhizol				17											
	53	Yatein				17, 18	13			36	32				37		
	54	3′-Demethylyatein					15										
	55	Hinokinin				17					5, 34	33					

Table 3. *Continued*

Compound type	No.	Name(s)	References														
			Juniperus					*Thuja*						*Libocedrus*			
			Jn.c.	Jn.f.	Jn.p.	Jn.t.	Jn.s.	Th.s.	Th.p	Th.o.	Cl.f.	Ch.o.	As.c.	Lb.b.	Lb.y.	Ft.c.	Tj.d.
	56	7-Acetyloxyhinokinin	31														
	57	7-Hydroxyhinokinin (sventenin)	31														
	58	7-Oxohinokinin	31								34						
	59		31														
	61	Isohibalactone	31														
	62	γ-Thujaplicatene							38								
	63	Calocedrin									39						
	64										34						
	65										34						
	66	Savinin(hibalactone)*	31	40		17	41				34, 39	42					
	67	Anhydropodorhizol				17, 18	14										
2. Cyclolignans																	
2.1. Non-lactone naphthalene derivatives																	
	69	Junaphthoic acid					15										
	70	Thuriferic acid				16											
	75	Isolariciresinol														30	
	77	Isotaxiresinol														30	
	78	Methyl-isotaxiresinol														30	
	79	Plicatic acid							43								
	80	Methyl deoxypodophyllotoxinate				18											
	81	Podophyllotoxinic acid				18											
	86	Formosanol		44													
	87	Tsugacetal (methyl-α-conidendral)		44													
2.2. Cyclolignanolides																	
	91	Detetrahydroconidendrin		44													
	96	Plicatinaphthalene							45								
	97	Plicatinaphthol							46								
	98	Dehydropodophyllotoxin					15										
	99	β-Apoplicatitoxin							47								
	101	Formosalactone		40													
	102	Plicatin							43								

Table 3. *Continued*

			References														
			Juniperus					*Thuja*						*Libocedrus*			
Compound type	No.	Name(s)	Jn.c.	Jn.f.	Jn.p.	Jn.t.	Jn.s.	Th.s.	Th.p	Th.o.	Cl.f.	Ch.o.	As.c.	Lb.b.	Lb.y.	Ft.c.	Tj.d.
	103	β-Peltatin															48
	104	β-Peltatin A methyl ether			19, 49	17	13							50			
	105	2′-Methoxypodophyllotoxin					14										
	106	Deoxypodophyllotoxin†			19, 49	17, 18	13			36			51	50			48
	107	Podophyllotoxin‡				17, 18	41										
	108	Epipodophyllotoxin					14										
	109	Epipodophyllotoxin acetate					13										
	110	Deoxypicropodophyllin			19	17, 18	13		52								
	111	Picropodophyllin				17, 18	13										
	112	Epipicropodophyllin				18	14										
	113	Epipicropodophyllin acetate				17	13										
	114	β-Peltatin B methyl ether				18	14										
	115	2′-Methoxypicropodophyllin					14										
	116	2′-Methoxyepipicropodophyllin					14										
	117	Picropodophyllone					14										
3. Neolignans																	
	122	Dihydrodehydrodiconiferyl alcohol	31														
	128		31														
	129		31														
	131		31														
	132		31														
4. Norlignans																	
	133	Yateresinol													37		
	135	Hinokiresinol											53		37		
	136	Dehydroagatharesinol													37		

*Also isolated from *Jn. communis* and *Ch. pisifera* [33].

†Also isolated from *Jn. bermudiana* [54], *Jn. foetidissima*, *Jn. silicicola*, *Ch. lawsoniana* [33] and *Callitris cullumellaris* [5].

‡Also isolated from *Jn. lucayana*, *Jn. pseudosabina*, *Jn. scopulorum*, *Jn. seravschanica*, *Jn. silicicola*, *Jn. virginiana* and *Callitris drummondi* [33].

Table 4. The distribution of lignanoids in the Taxodiaceae

			References					
Compound type	No.	Name(s)	At.s.	Tw.c.	Cr.j.	Sq.s.	Mt.g.	Sd.g.
1. Lignans								
1.4. Lignanolides								
	66	Savinin		55				
	68	Taiwanin A		56				
2. Cyclolignans								
2.2. Cyclolignanolides								
	90	Taiwanin E		57				
	92	Taiwanin C (justicidin E)		58				
	93	Taiwanin H		59				
	94	Diphyllin		57				
	95	Helioxanthin		57				
4. Norlignans								
	133	Yateresinol			61			
	134	Agatharesinol	60		61	62	63	62
	135	Hinokiresinol			61			
	137	Sequirin C			61	62		
	140	Sugiresinol (sequirin A)			61	62		
	145	Cryptoresinol			64			
	141	Sequirin B (hydroxysugiresinol)			61	62		
	142	Permethyl-sequirin E						62
	143	Permethyl-sequirin F						62
	144	Permethyl-sequirin G						62
	138	Metasequirin A					63	
	139	Hydroxymetasequirin A					65	
	147	Sequirin D				62		
	148	Athrotaxin	66				63	
	149	Hydroxyanthrotaxin					65	
	150	Metasequirin B					65	

species of Podophyllaceae, but with a few exceptions these natural sources do not provide commercially useful quantities. However, the wound resins of trees are better sources of lignans, which, although occurring in mixtures with other natural products, are easily separated [1].

This review on lignan distribution in the Coniferae includes the literature covered by *Chemical Abstracts* from January 1967 to June 1994 and could be considered complementary to previous reviews on distribution, structural and synthetic aspects of lignans [5–12].

The botanic order of Coniferae includes several species very rich in lignans, as in the case of genus *Juniperus*, on which our group has been interested in the last years. We have studied the chemical composition of several species of the section *sabina* of this genus, which has considerable amounts of cyclolignans [13–19].

The Coniferae order includes numerous species used in folk medicine and distributed, according to Dallimore and Jackson [20], into six families: Cephalotaxaceae (one genus), Podocarpaceae (seven genera), Araucariaceae (two genera), Cupressaceae (21 genera and 130 species), Taxodiaceae (10 genera) and Pinaceae (10 genera and 225 species). Lignans have been isolated not only from leaves, but also from wood of species belonging to five of these families. No lignans have been reported from any species of the Cephalotaxaceae. The genera and species of conifers producing lignans and the abbreviations used in the tables of this review are shown in the following list:

1. Podocarpaceae (Table 1): *Podocarpus spicatus* (Pd. s.); *P. salignus* (Pd. sl.); *Dacrydium intermedius* (Dc. i.).
2. Araucariaceae (Table 2): *Agathis australis* (Ag. a.); *Araucaria angustifolia* (Ar. a.).
3. Cupressaceae (Table 3): *Juniperus chinensis* (Jn. c.); *J. formosana* (Jn. f.); *J. phoenicea* (Jn. p.); *J. thurifera* (Jn. t.); *J. sabina* (Jn. s.); *Thuja standishi* (Th. s.); *T. plicata* (Th. p.); *T. occidentalis* (Th.o.); *Calocedrus formosana* (Cl. f.); *Chamaecyparis obtusa* (Ch. o.); *Austrocedrus chilensis* (As. c.); *Libocedrus bidwillii* (Lb. b.); *L. yateensis* (Lb. y.); *Fitzroya cupressoides* (Ft. c.); *Thujopsis dolabrata* (Tj. d.).
4. Taxodiaceae (Table 4): *Athrotaxis selaginoides* (At. s.); *Taiwania criptomerioides* (Tw. c.); *Cryptomeria japonica* (Cr. j.); *Sequoia sempervirens* (Sq. s.); *Metasequoia glyptostroboides* (Mt. g.); *Sequoiadendrom giganteum* (Sd. g.)
5. Pinaceae (Table 5): *Abies pinsapo* (Ab. p.); *A. sachalinensis* (Ab. s.); *A. sibirica* (Ab. sb.); *A. nephrolepis*

Table 5. The distribution of lignanoids in the Pinaceae

Compound type	No.	Name(s)	References																			
			Abies				*Pinus*				*Tsuga*			*Larix*				*Picea*				
			Ab.p.	Ab.s.	Ab.sb.	Ab.n.	Pn.a.	Pn.m.	Pn.p.	Pn.t.	Ts.c.	Ts.h.	Cd.d	Lr.d.	Lr.l.	Lr.s.	Lr.dh.	Pc.a.	Pc.k.	Pc.o.	Pc.ab.	Pc.j.
1. Lignans																						
1.1. Dibenzylbutanediol derivatives																						
	1	Secoisolariciresinol			67						68			5	69	70	70					
	4	Meso-secoisolariciresinol											71									
1.2. Tetrahydrofurans																						
	5	Shonanin			67	72										74	74	73	73	73	5	
	11	Liovil			67	72							5	5		70	70	73	73	73	75	
	12		76																			
	13	Todolactol A	76	77																		
	14														69							
	15			78																		
	16				79	79																
	17				79	79																
	18				79	79																
	19	Lariciresinol	76	77, 78	67								81	5	69	74	70	73	73	73	5	
	24														69							
	25	Olivil			67												70					
	26	Massoniresinol						83														
	27	9-Hydroxylariciresinol	76																			
	28	7*R*-Hydroxylariciresinol	76																			
	29	7*S*-Hydroxylariciresinol	76																			
	30			77, 78																	84	
1.3. Furofurans																						
	31	Pinoresinol		78	67	72		85		86				30	69	74	70	73	73	73	5	
	36	(+)-epipinoresinol																			5	
1.4. Lignanolides																						
	37	Matairesinol*	76		67	72				86	68	87				70	70	73	73	73	75	
	39	Hydroxymatairesinol†			67	72					68	87						73	73	73	75	88
	40	Pinopalustrin							89													
	41				79	79																

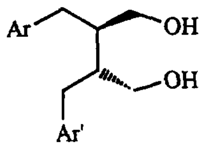
Table 5. *Continued*

Compound type	No.	Name(s)	References																			
			Abies				*Pinus*				*Tsuga*			*Larix*				*Picea*				
			Ab.p.	Ab.s.	Ab.sb.	Ab.n.	Pn.a.	Pn.m.	Pn.p.	Pn.t.	Ts.c.	Ts.h.	Cd.d	Lr.d.	Lr.l.	Lr.s.	Lr.dh.	Pc.a.	Pc.k.	Pc.o.	Pc.ab.	Pc.j.
	42				79	79																
	43	Oxomatairesinol									68	5						73	73	73	5	
	60	Nor-trachelogenin						85														
2. Cyclolignans																						
2.1. Non-lactone naphthalene derivatives																						
	75	Isolariciresinol	76	77, 78	70						68		81		69	70	70	73	73	73	5	
	83	Todolactol B		77, 80																		
	84	Todolactol D		77, 80																		
	85						90															
	87	Todolactol C (tsugacetal)		77, 80							68											
2.2. Cyclolignanolides																						
	100	α-Conidendrin		77, 78							68	87				74	70	73	73	73	75	88
2.3. Dibenzocyclooctene																						
	118	Kadsuranin													91							
3. Neolignans																						
	119			82																		
	120	Cedrusinin											71									
	121	Cedrusin						92	85				81									
	122	Dihydrodehydrodiconiferyl alcohol							85				81		93							
	123														94							
	124														94							
	125			82											69							
	126	Dehydrodiconiferyl alcohol											81									
	127														94							
	130			78																		

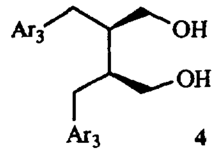
*Also isolated from *Ab. amabilis*, *Ab. concolor*, *Ab. grandis*, *Ab. procera* and *Ts. mertensiana* [5].
†Also in *Picea glauca* [5].

1.- LIGNANS

1.1.- Dibenzylbutanediol derivatives



Ar	Ar'	
Ar_3	Ar_3	**1**
Ar_4	Ar_4	**2**
Ar_4	Ar_4	**3**



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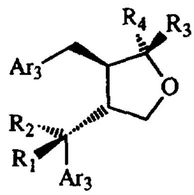
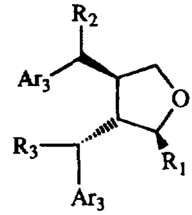
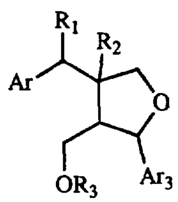
1.2.- Tetrahydrofurans



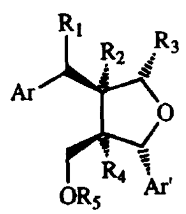
R_1	R_2	R_3	R_4	
H	H	H	H	**5**
OMe	H	H	OMe	**6**
H	OMe	H	OMe	**7**
OMe	H	OMe	H	**8**
OEt	H	H	OMe	**9**
OMe	H	H	OEt	**10**



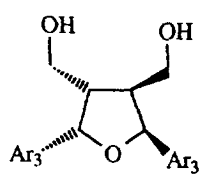
R_1	R_2	R_3	
H	OH	OH	**11**
OH	H	H	**12**
OH	OH	H	**13**



R_1	R_2	R_3	Ar	
H	H	H	Ar_1	**14**
=O	H	H	Ar_3	**15**
H	OH	coumaroyl	Ar_3	**16**
H	OH	feruloyl	Ar_3	**17**
H	H	vanilloyl	Ar_3	**18**



R_1	R_2	R_3	R_4	R_5	Ar	Ar'	
H	H	H	H	H	Ar_3	Ar_3	**19**
H	H	H	H	H	Ar_4	Ar_3	**20**
H	H	H	H	H	Ar_5	Ar_5	**21**
OH	H	H	H	H	Ar_5	Ar_5	**22**
H	H	H	H	H	Ar_3	Ar_5	**23**
H	H	H	H	coumaroyl	Ar_3	Ar_3	**24**
H	OH	H	H	H	Ar_3	Ar_3	**25**
H	OH	H	OH	H	Ar_3	Ar_3	**26**
H	H	OH	H	H	Ar_3	Ar_3	**27**
αOH	H	H	H	H	Ar_3	Ar_3	**28**
βOH	H	H	H	H	Ar_3	Ar_3	**29**



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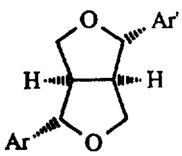
(Ab. n.); *Pinus armandii* (Pn. a.); *P. massoniana* (Pn. m.); *P. palustris* (Pn. p.); *P. tadea* (Pn. t.); *Tsuga chinensis* (Ts. c.); *T. heterophylla* (Ts. h.); *Cedrus deodara* (Cd. d.); *Larix decidua* (Lr. d.); *L. leptolepis* (Lr. l.); *L. sibirica* (Lr. s.); *L. dahurica* (Lr. dh.); *Picea ajanensis* (Pc. a.); *P. koraiensis* (Pc. k.); *P. obovata* (Pc. o.); *P. abies* (Pc. ab.); *P. jezoensis* (Pc. j.).

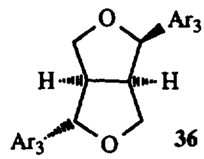
Lignanoids found in Conifers are classified into the following groups:

1. Lignans
   1.1. Dibenzylbutanediol derivatives
   1.2. Tetrahydrofurans
   1.3. Furofurans
   1.4. Lignanolides

1.3.- Furofurans



Ar	Ar'	
Ar_3	Ar_3	**31**
Ar_4	Ar_4	**32**
Ar_3	Ar_4	**33**
Ar_5	Ar_3	**34**
Ar_5	Ar_5	**35**



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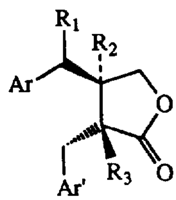
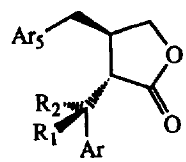
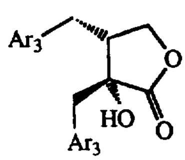
1.4.- Lignanolides



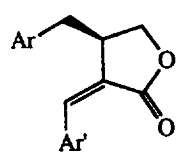
R_1	R_2	R_3	Ar	Ar'	
H	H	H	Ar_3	Ar_3	**37**
H	H	H	Ar_5	Ar_3	**38**
OH	H	H	Ar_3	Ar_3	**39**
H	H	OH	Ar_3	Ar_3	**40**
O-vanilloyl	H	H	Ar_3	Ar_3	**41**
O-benzoyl	H	H	Ar_3	Ar_3	**42**
=O	H	H	Ar_3	Ar_3	**43**
H	H	H	Ar_3	Ar_6	**44**
H	H	H	Ar_3	Ar_7	**45**
H	H	OH	Ar_3	Ar_7	**46**
H	OH	OH	Ar_3	Ar_6	**47**
H	OH	OH	Ar_3	Ar_7	**48**
H	OH	OH	Ar_3	Ar_3	**49**



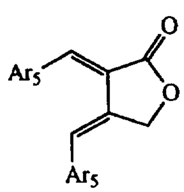
R_1	R_2	Ar	
OH	H	Ar_9	**50**
OAc	H	Ar_9	**51**
H	OH	Ar_9	**52**
H	H	Ar_9	**53**
H	H	Ar_8	**54**
H	H	Ar_5	**55**
H	OAc	Ar_5	**56**
H	OH	Ar_5	**57**
=O		Ar_5	**58**
H	H	Ar_4	**59**



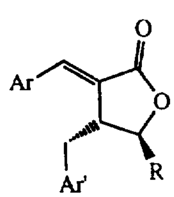
60



Ar	Ar'	
Ar_5	Ar_5	**61**
Ar_3	Ar_6	**62**



68



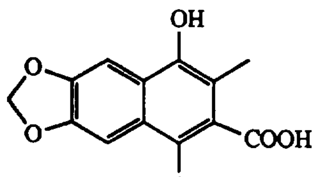
R	Ar	Ar'	
OH	Ar_5	Ar_5	**63**
H	Ar_8	Ar_3	**64**
H	Ar_7	Ar_3	**65**
H	Ar_5	Ar_5	**66**
H	Ar_9	Ar_5	**67**

2. Cyclolignans
   2.1. Non-lactone naphthalene derivatives
   2.2. Cyclolignanolides
   2.3. Dibenzocyclooctene derivatives
3. Neolignans
4. Norlignans

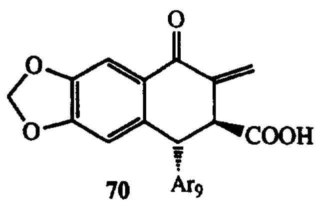
The distribution of lignans in the above plants is listed in Tables 1–5. As can be seen in the tables, the Cupressaceae and Pinaceae, which are those having the two largest number of species in the order Coniferae, are also the best studied and have been shown to contain lignanoids of all the types mentioned in this

2.- CYCLOLIGNANS

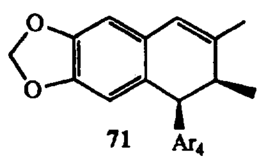
2.1.- Non-lactone naphthalene derivatives



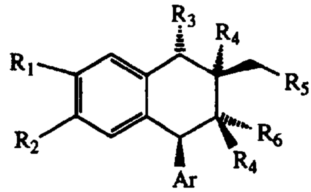
69



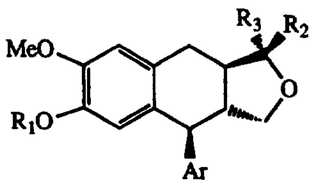
70



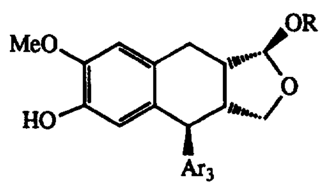
71



R_1	R_2	R_3	R_4	R_5	R_6	Ar	
OMe	OMe	H	H	H	CH_3	Ar_4	**72**
O-CH_2-O		H	H	H	CH_3	Ar_4	**73**
OMe	OMe	H	H	H	CH_3	Ar_5	**74**
OMe	OH	H	H	OH	CH_2OH	Ar_3	**75**
OMe	OMe	H	H	OH	CH_2OH	Ar_3	**76**
OMe	OH	H	H	OH	CH_2OH	Ar_2	**77**
OMe	OMe	H	H	OH	CH_2OH	Ar_2	**78**
OMe	OH	H	OH	OH	COOH	Ar_6	**79**
O-CH_2-O		H	H	OH	COOMe	Ar_9	**80**
O-CH_2-O		OH	H	OH	COOH	Ar_9	**81**

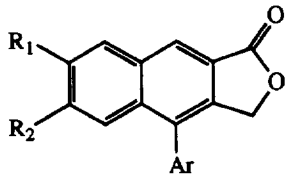


R_1	R_2	R_3	Ar		
Ac	OMe	H	Ar_3	Acetate	**82**
H	OH	H	Ar_3		**83**
H	OEt	H	Ar_3		**84**
Ac	OAc	H	Ar_3	Acetate	**85**
H	OMe	H	Ar_3		**86**
H	H	OMe	Ar_3		**87**

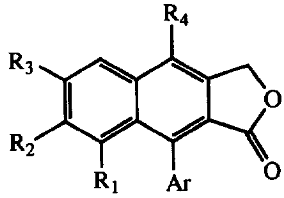


R	
Me	**88**
Et	**89**

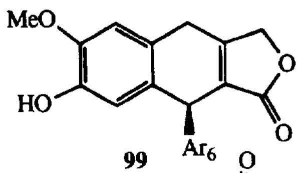
2.2.- Cyclolignanolides



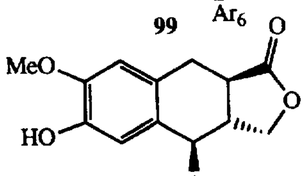
R_1	R_2	Ar	
-O-CH_2-O-		Ar_5	**90**
OMe	OH	Ar_3	**91**



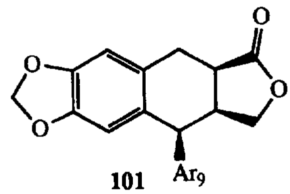
R_1	R_2	R_3	R_4	Ar	
H	O-CH_2-O		H	Ar_5	**92**
H	OMe	OMe	OH	Ar_2	**93**
H	OMe	OMe	OH	Ar_5	**94**
O-CH_2-O		H	H	Ar_5	**95**
H	OH	OMe	H	Ar_6	**96**
H	OH	OMe	OH	Ar_6	**97**
H	O-CH_2-O		OH	Ar_9	**98**



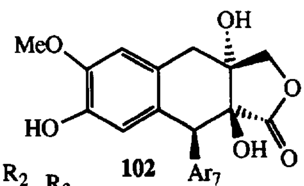
99



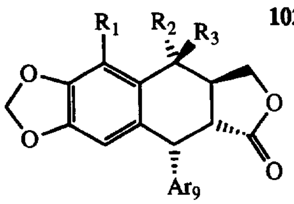
100



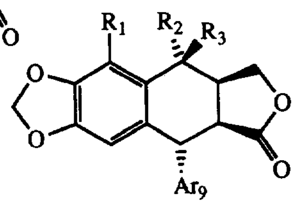
101



102

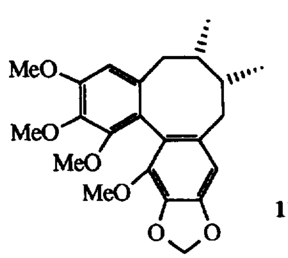


R_1	R_2	R_3	
OH	H	H	**103**
OMe	H	H	**104**
OMe	OH	H	**105**
H	H	H	**106**
H	OH	H	**107**
H	H	OH	**108**
H	H	OAc	**109**



R_1	R_2	R_3	
H	H	H	**110**
H	OH	H	**111**
H	H	OH	**112**
H	H	OAc	**113**
OMe	H	H	**114**
OMe	OH	H	**115**
OMe	H	OH	**116**
H	=O		**117**

2.3.- Dibenzocyclooctene derivative

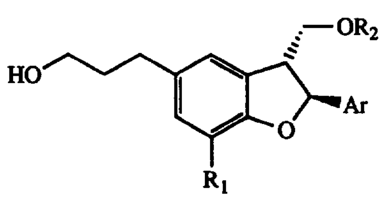


118

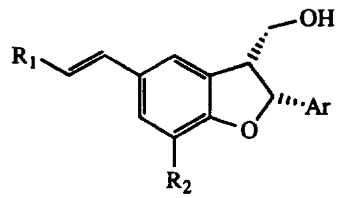
work, except that norlignans are absent from the Pinaceae.

Other aspects that can be noted are the following. Dibenzylbutanediols occur in all the families except the Taxodiaceae, in which norlignans are the common components. *Taiwania cryptomerioides*, from which only lignanolides and cyclolignanolides have been isolated, is exceptional and shows a close parallelism with the

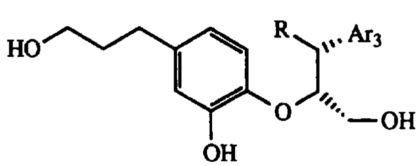
3.- NEOLIGNANS



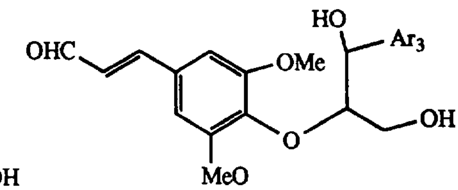
R_1	R_2	Ar	
OH	coumaroyl	Ar_3	**119**
H	H	Ar_3	**120**
OH	H	Ar_3	**121**
OMe	H	Ar_3	**122**
OH	H	Ar_1	**123**
OMe	H	Ar_1	**124**



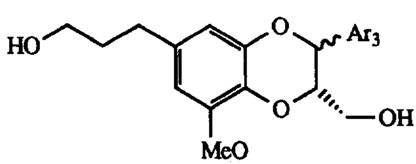
R_1	R_2	Ar	
CHO	OH	Ar_3	**125**
CH_2OH	OMe	Ar_3	**126**
CHO	OH	Ar_4	**127**



R	
OH	**128**
H	**129**



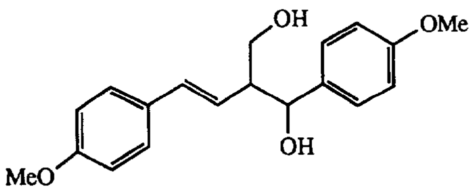
130



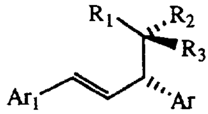
cis **131**
trans **132**

species of Cupressaceae. The occurrence of kadsuranin (**118**) in *Larix leptolepis* represents the only case of the presence of a dibenzocyclooctene in conifers up to the present. Neolignans have been reported only in the Pinaceae and Cupressaceae. Trivial names, if known, are also included in the tables. Structures are given for all the compounds, and the aryl groups used in the structural formulae throughout this review are shown in Fig. 2.

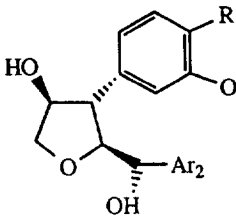
4.-NORLIGNANS



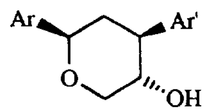
133



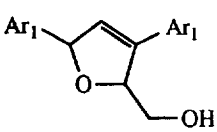
R_1	R_2	R_3	Ar	
CH_2OH	OH	H	Ar_1	**134**
H	$=CH_2$		Ar_1	**135**
CH_2OH	$=O$		Ar_1	**136**
CH_2OH	H	OH	Ar_2	**137**



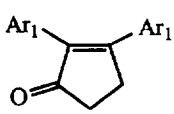
R	
H	**138**
OH	**139**



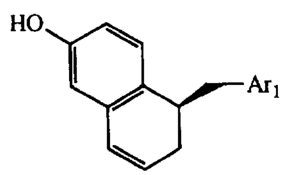
Ar	Ar'	
Ar_1	Ar_1	**140**
Ar_1	Ar_2	**141**
Ar_4	Ar_1 Me-ether	**142**
Ar_4	Ar_4	**143**
Ar_4	Ar_9	**144**



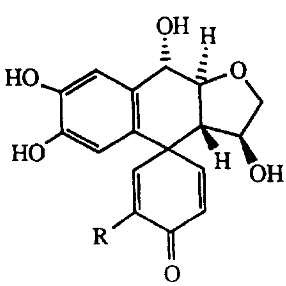
145



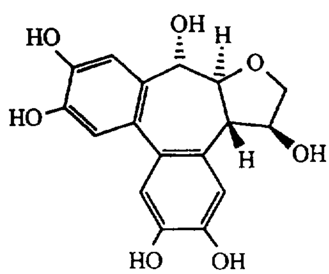
146



147



R	
H	**148**
OH	**149**



150

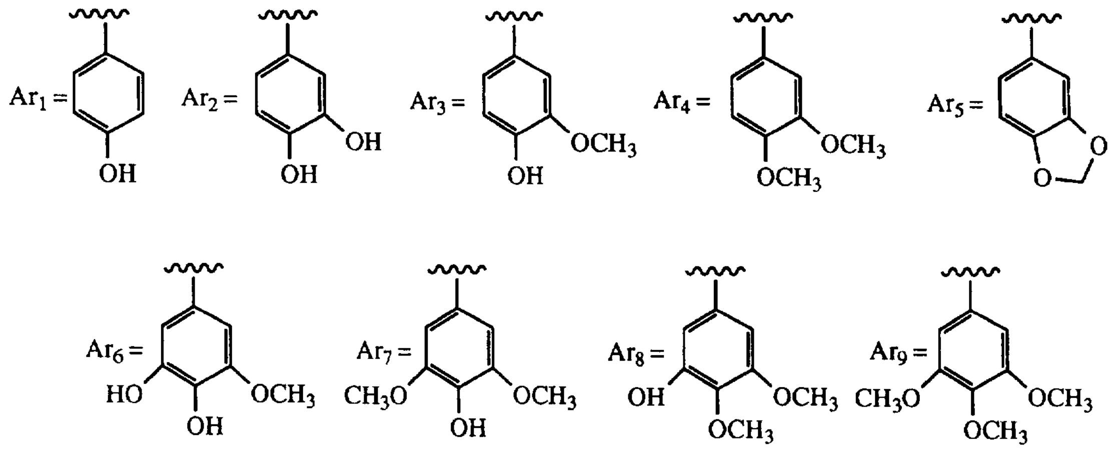


Fig. 2. Structures of aryl substitutes.

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