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Stilbenes and Bibenzyls in Higher Plants

Hassan M.G. Al-Hazimi and Hamad Z. Alkhathlan
Department of Chemistry, College of Science, King Saud University
P.O. Box 2455, Riyadh 11451, Saudi Arabia

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Abstract. Stilbenes and their dihydroderivatives, bibenzyls, which have been isolated from higher plants up to the end of 1994 are reviewed.

Introduction

Phenolic compounds are widely distributed in plants and appear to perform a variety of functions. Continuing our literature survey of these important natural compounds [1-3], we now review stilbenes and their dihydroderivatives (bibenzyls).

Stilbenes

Stilbenes are of interest as chemotaxonomic agents and as extractives in wood used for pulping. They are a group of organic compounds which are produced by woody plants as metabolites and also as constitutive defence agents [4]. These compounds occur in nature as aglycones and glucosides.

Aglycones. As can be seen from Table 1. Stilbene aglycones are distributed among seventeen families of flowering plants. The Pinaceae, cupressaceae and Gnetaceae are the only families in the Gymnospermae reported to contain stilbenes. However, stilbenes have also been identified in members of Malvaceae [5].

Most of the natural stilbenes were isolated as trans isomers. Although trans-stilbene itself **(1)** has only been reported from *alnus* species (Table 1), its existence has previously been suggested in Perubalsam oil [6] on the basis of its melting point. Studies on the chemical constituents of the male flowers of two other *Alnus* species showed the presence of three simple stilbenes. Stilbene aglycones possessing a carboxyl group at position 2 are only represented by three compounds (**28**,**29** and **35**).

The stilbene, trans-resveratrol (**4**) was first isolated in 1940 from the roots of *Veratrum grandiflorum* [7]. This compound has been obtained frequently from various species of nine plant families (Table 1), being accompanied by oxyresveratrol (**22**) in gymnosperms, Lilaceae, Moraceae and Myrtaceae. Cis and trans-Resveratrol have been reported from *Arachis hypogea* (Fabaceae) and from *Eucalyptus* species of Myrtaceae. The dihydroxystilbene (**2**) and the tetrahydroxystilbene (**21**) frequently occur in nature. Prenylated stilbenes have been reported only from Leguminous plants. Similarly, only two prenylated stilbenes have been obtained from *Chlorophlora excelsa* of the plant family Moraceae.

The South African tree *Combretum caffrum* (Combretaceae) has been found to contain a large number of closely related phenolic compounds, namely phenanthrenes, stillbenes and bibenzyls. These products were mainly isolated from the root bark of this productive tree. Stilbenes of this natural source are represented by compounds **30-34** (Table 1) which are designated combretastatins, and all of them are in the cis configuration except combretastatin A-6 (**34**). Stilbene **30** is hexaoxygenated while **31-34** are pentaoxygenated. Such highly oxygenated stilbenes have only been reported from *Eucalyptus sideroxylon* (Myrtaceae). The latter plant showed the presence of the pentaoxygenated compound **7** along with the less substituted stilbenes **5** and **6**. Compounds **5**,**7** were originally isolated as glycosides but they are subsequently identified as aglycones.

Stilbene oligomers. Literature survey has revealed that stilbene oligomers are limitd to six plant families. The occurrence of this new class of oligomeric stilbenols in these families seems to be of chemotaxonomic importance.

Oligomers of 3,5,4'-trihydroxystilbene (resveratrol, **4**) were obtained from a variety of species belonging to five plant families [8]. Resveratrol units are coupled together to produce compounds containing aryl dihydrobenzofuran units in most known stilbene oligomers. Such polymerized derivatives occur as dimers, trimers or tetramers. However, resveratrol dimers are predominant, as can be noted from Table 2 and Fig. 3. The grapevine (*Vitis venifera* L.) has been shown to produce a range of compounds termed viniferins; all of them are resveratrol oligomers. ε-Viniverin also occurs in *Vatica affinis* [9] and in the barks of two *Shorea* [Table] of Dipterocarpaceae and it is the only dimer found in the latter family. The latter compound was also obtained from the rhizomes of some *Carex* species of Cyperaceae and from exudates of two plants of gnetaceae and Fabaceae. Pallidol, which bears structural similarities (Fig. 3) to ε-viniverin, was obtained from a member of Vitaceae (Table 2). Recently, the resveratrol dimer tricuspidatol-A, has been reported in other species belonging to the latter family

[10]. Five novel oligomers named ampelopsins were obtained from the roots of *Ampelopsis* species of Vitaceae (Table 2).

Copalliferol A was first isolated from *Vateria copallifera* [11] of the family Dipterocarpaceae. This trimer was also reported from two genera of the same plant family (Table 2). The bark of *Vateria copallifera* was also found to contain another trimer named copalliferol **B** [12]. Canaliculatol, a resveratrol trimer, was isolated from the bark of another member of tis plant family [13]. Stemonoporol, which is isomeric with copalliferol A, was also isolated from several *Stemonoporus* species [14]. This phenolic oligomer was also reported by Sotheeswaran *et al.* [15] from other dipterocarp species (Table 2).

Hopeaphenol was the first polyphenol isolated from the bark of *Hopea odorata* [55]. This compound was regarded as a tetramer of resveratrol and its presence in other dipterocarps was confirmed by Madhev *et al.* [16]. Vaticaffinol, a stilbene tetramer, was islated from the bark of two genera of Dipterocarpaceae (Table 2).

The ethanolic extract of the woody parts of the *Gnetum leyboldi* gave five novel compounds, designated gnetins A-E. The gnetins A and B were bicyclocatanoid dimers, while gnetins C-E were the typical dihdrobenzofuran oligomers (Fig. 3) which are structurally similar to the constituents of Dipterocarpaceae and Vitaceae. Gnetins A-E were also isolated from the fruit of other *Gnetum species* (Table 2). Four other gnetins were also obtained from *Welwitschia mirabilis* of the same plant family of the genus *Gnetum*. Extracts of the lianas of *G. parvifolium gave* ε-viniferin together with two dimers called gnetifolins. Studies on the root extractives of some *Care* species (Cyperaceae) revealed the presence of resveratrol oligomers in large amounts, particularly tetramers [17-20].

Recent investigations of two *Sophora* species (Fabaceae) yielded nine oligomers [21-25], four of which contain a flavone moiety. Occurrence of these stilbenols was restricted to the roots of the investigated plants. A new dimer of the stilbene oxyresveratrol **(22)** has been isolated from the extract of the woods of *Chlorophora excelsa* of Moraceae [26]. Furthermore, two derivatives of **22** with a fused dihydrochalcone partial moiety were also reported from the roots [27] and from the shoots of the plant *Morus Ihou* (Ser.) of the later family.

Stilbene glucosides. These phenolics were isolated from various plants belonging to four plant families (Table 3), with the majority of their occurrence in species of the genus *Picea* of Pinaceae. Stilbene glucosides astringin and isorhapontin (Fig. 2) were present in high levels in the bark of most of the seven investigated *picea* species [28]. Their levels in other parts of these plants such as sapwood and roots were relatively low.

The most notable feature of Table 3 is that astringin and isorhapontin are restricted only to the genus *Picea*. Rhapontin (Fig. 2), the first known glucoside, was reported from *Rheum rhaponticum* [29].

The resveratrol glucoside piceid occurs in members of three plant families, while the glucoside of piceatannol **(21)** has been reported only from the genus *Picea*. A few other stilbene glucosides are known from genera *Gaylussacia* and ***Polygonum*** (Table 3).

Bibenzyls

Bibenzyls and phenanthrenoids occur sporadically [3] in botanical sources and they are structurally similar to stilbenols. The structures of these natural compounds are shown in Figs. 4 and 5, while their botanical sources are given in Table 4. Although naturally occurring bibenzyls are very limited in their numbers, they are distributed among eleven plant families (Table 4). Most of them have been isolated from species of the two families Dioscoraceae and Orchidaceae. It can be also seen from Figs. 4 and 5 that most of these natural compounds are tetraoxygenated. Batatasin I (a phenanthrene derivative) and the bibenzyls, batatasins II-IV, were originally found in *Dioscorea opposita* (*D. batata*) [30-35], while one or more batatasins have been found [35] in either tubers or bulbils of most *Dioscorea* examined. The occurrence of batatasin III **(8)** is restricted to the plants of ***Dioscoreaceae*** and ***Orchidaceae***. The structure of batatasin II has not yet been elucidated.

Bioactivity

Naturally occurring stilbenes are known for their wide range of biological activities, including toxicity to fungi, termites, insects, fish and mice [36, 37]. Resveratrol **(4)**, the most widely distributed stilbenol, has been found to have antifungal activity and the formation of its dimers and trimers in *vitis vinivera* leaves has been correlated with disease resistance [37]. In *Arachis*, *Veratrum* and *Vitis* genera, **(4)** is considered to be a phytoalexin whose synthesis can be induced by antimicrobial infection [38]. Simple stilbenes such as pinosylvin **(2)** and its methyl ether have been considered to be phytoalexins in the heartwood of *Pinus* trees [39]. Resveratrol may also serve as a phytoalexin in some grasses (Poaceae) [40]. Stilbenes are considered as the possible inhibitors of some forest pathogens, the control of which plays an important role in the economic cultivations of spruce (*picea*) forests [41].

Stilbenols are also reported as inhibitors of photosynthesis [42]. These natural compounds tested in the absence of wood substrate exhibit singnificant bioactivity against many fungal species [36, 43, 44].

Silbene oligomers with high bioactivities have been isolted from many plants. Such polymerized derivatives were reported to have more antifungal activity than the coresponding monomers. A number of oligostilbenes show antimicrobial and various physiological activities from Dipterocarpaceae [9, 12-15], Vitaceae [45-47] and Cyperaceae [17, 18]. The oligomers of Cyperaceae species have shown moderate antibacterial activity and their extremely high content suggested a physiological role as defensive agents [18]. The major stilbene glucosides astringin and isorhapontin (Fig. 3) in the bark of *Picea* species have shown some antifungal properties.

Many naturally occurring stilbenes were tested against fungi and bacteria. Takasugi *et al.* [32] have examined the antimicrobial activity of some phenanthrenes and the bibenzyls **1,3,6** and **10** from *Dioscorea batata* against 24 species of fungi and 6 genera of bacteria. It was found that fungi were affected more than bacteria, and the bibenzyls appeared to be more active than the phenanthrenes. The bibenzyl **(1)** showed complete inhibition of microbial growth of some fungi at a low concentration, although it did not show any significant antibacterial activity even at higher concentration. Similarly, the antimicrobial activity of the bibenzyls amorfrutins **20** and **21** and related substances has been reported and is limited to Gram positive bacteria [48]. The chloroform fraction of an EtOH extract of *Cymbidium aloifolium* roots exhibited antifungal activity against *Trichophyton melangrophytes* at moderate concentration [49]. This extract contained the two new bibenzyls **16** and **17**.

Many stilbenols isolated from the South African tree, *Combretum caffrum* have been found to be potent antimitotic agents, inhibiting tubulin polymerisation [50-54]. The agents of this tree are of particular interest for their antineoplastic potential, especially in the two most active compounds, combretastatins A-2 and A-4 [50, 55]. A series of combretastatins, including some natural compounds, have been prepared [56] and evaluated as potential antimitotic agents on the basis of their abilities to inhibit *in vitro* tubulin polymerisation. Cushman *et al.* [57] have also prepared many stilbenes and tested them for cytotoxicity in five human cancer cell lines. These researchers found that the prepared cis-stilbenes proved to be cytotoxic in all five cancer cell lines, with potencies compatible to that of combretastatin A-4. Thus, all cis-stilbenes were potent inhibitors of tubulin polymerisation. However, it has been found [57] that coresponding trans isomers were inactive as tubulin polymerisation inhibitors and were less cytotoxic in all five cancer cell lines.

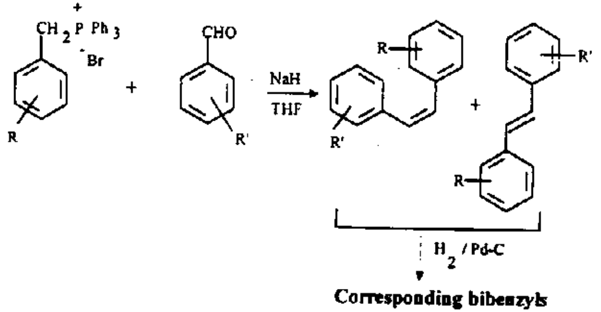
Synthesis of Stilbenes and Bibenzyls

Although many methods have been employed for the synthesis of stilbenes and bibenzyls, the following two methods are the most effective and widely applicable for the preparation of unsymmetrical stilbenes. The first is the Wittig reaction of an arylaldehyde with an arylmethylenephosphorane (Scheme I). This method usually leads to a mixture of (E)- and (Z)- isomers, with predominance of the latter.

The second method is a modification of a Perkin condensation in which a sodium (hydroxy) phenylacetate and a benzaldehyde derivative are heated (6-10 hr) with Ac_2O to give cis and trans isomers of the stilbene -α-caboxylic acid. The next step is the decarboxylation, which produces the stilbene. Reduction of the latter with H_2 in the presence of Pd/C yields the benzyl derivatives (Scheme II).

A number of stilbenoid derivatives, both naturally occurring and synthetic, have been synthesised by adopting the above methods [50, 56, 58, 59]. Symmetrical (*E*)-stilbenes are readily prepared in high yield by reductive coupling of arylaldehydes [60]. A new method for isomerisation of (*Z*)-stilbenes into the (*E*)-isomers catalysed by diaryl disulphides has been developed recently by Mohammad Ali and Yoshisuke Tsuda [61].

Scheme I.



Scheme II.

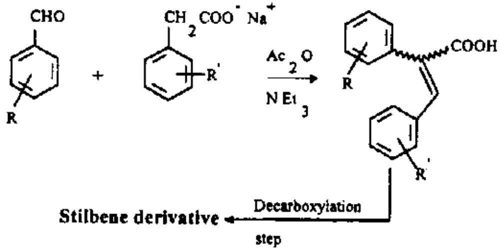


Table 1. Stilbene aglycones in higher plants

Plant Species	Compound Isolated	Plant Parts	Reference(s)
Basellaceae			
Clarisia racemosa	**4b**	wood	[62]
Betulaceae			
Alns firmau	**1**	young shoots	[6]
A.pendulo	**2 , 3**	male flowers	[63]
A.sieboldiana	**1, [illegible], 3**		[64,65]
A.viridis (Chaix) DC	**8**	bud excretion	[66]
Combretaceae			
Combretum caffrum	**30 ***	root bark	-
	31 *	root bark	-
	32 *	root bark	[50]
	33 *	root bark	[50]
	34	root bark	[50]
Cupressaceae			
Juniperus macropoda Bioss	**4**	leaves	[67]
Cyperaceae			
Scirpus fluviatilis	**4,21**	rhizoma	[17]
Euphorbiaceae			
Euophorbia laga scae	**21**	seeds	-
Fagaceae			
Nothofagus fusca	**4**	bark	[68]
Gnetaceae			
Gnetum ula	**10**	stemwood	[69]
	20		[70]
	23		[69]
	24	whole plant	[71]
G. parvifolium (Warb.) C.W.	**4,26,36**	lianas	-
	2,20	lianas	[72]
Leguminosae			
Arachis hypogaea L.	**4, 4***	seeds	[73]
	4		[74,75]
	12,13	seeds	[76]
	14,15,16	seeds	[77]
	17	kernels	[75]
Cajanus cajan	**28, 29**	leaves	[78]
Cassia garretiana Craib.	**21, 27**	heart wood	[79,80]
	21	heart wood	[81]

Table 1 . con.

Derris floribunda (Benth.) Duke	11, 13	roots	[82]
D. rariflora (Mart.) Macbr.	11		[83]
Liliaceae			
Veratrum grandiflorum	4	roots	[7]
Moraceae			
Chlorophlora excelsa (B.H.)	18, 19	wood	[84]
	18, 19, 22	wood	[26]
Maclura pomifera	4 , 22	heartwood	[85]
Morus rubra	4 .	heartwood	[86]
Toxylon pomiferum	4 , 22	heartwood	[85,87]
Myristicaceae			
Knema austrosiamensis	4b,4c	wood	[88]
Virola cuspidata	9	bark	[89]
Myrtaceae			
Eucalyptus sideroxylon	5, 6, 7	leaves	[90]
Eucalyptus species	4, 4*	heartwood and leaves	[91,92]
Melaleuca leucadendron	21, 22	fruits	[93]
Polygonaceae			
Polygonum cuspidatum Sieb. et Zucc	4	roots	[94]
Rheum webbianus	4b		[95]
Pinaceae			
Picea mariana (Mill) B.S.P.	26		[28]
Picea species	4, 21,26	bark	[96]
	21	cortex	[97]
	21	bark	[28]
Pinus bauksiana	3a	bark	-
Pinus excelsa	3	heartwood	[98]
P. monticola	3	heartwood	[99]
P. radiata	2 , 3	sapwood	[100]
P. resinosa	2, 3	sapwood	[39,101]
P. taeda	2, 3	sapwood	[39]
Poaceae			
Festuca arundianacea	4	seeds, forage	[40]
Festuca versuta	4	seeds	[40,102]
F. argentina	4		[103]
Hordeum bogdani	4	seeds, forage	[40]
H. brevisubulatum	4	seeds, forage	[40]
Lolium species (5)	4	seeds	[40]
Poa alsodes	4	seeds, forage	[40]
Saccharum sp.	21		[104]
Stipa rabusta	4		[40]
Saxifragaceae			
Hydrangea macrophylla	35		[105]
Vitaceae			
Vitis vinifera	4a	leaves	[106]

*** cis isomers**

Table 2. Naturally occurring resveratrol oligomers

Plant Species	Resveratrol Oligomer Dimer	 Trimer	 Tetramer	Plant Parts	Reference(s)
Cyperaceae					
Carex fedia var. miyabei			Miyabenol A	roots	[19]
	ε-Viniferin	Miyabenol C	Miyabenol B	roots	
Carex kobomugi	ε-Viniferin	Miyabenol C	Kobophenol A	roots	[19,20]
Carex pumila Thunb	ε-Viniferin	Miyabenol C	Kobophenol A	roots	[18]
	ε-Viniferin		Kobophenol B	roots	--
		Miyabenol C	Miyabenol A		-
			Hopeaphenol		[44]
Scirpus fluviatilis	Scirpusin A				[17]
	Scirpusin B				[17]
Dipterocarpaceae					
Balanocarpus zeylanicus	Balanocarpol				[107]
		Copalliferol A			[15]
			Hopeaphenol		[123]
Hopea brevipetiolaris (Thw.)		Copalliferol A		bark	[15]
H. cordifolia (Thw.) Trimen		Copalliferol A		bark	[15]
H. jucunda	Balanocarpol				[107]
H. odorata			Hopeaphenol	bark	[108]
Shorea disticha	ε-Viniferin	Distichol			-
S. robusta			Hopeaphenol	bark	[16]
S. stibularis (Thw.)	ε-Viniferin	Copalliferol A		bark	[15]
		Stemonoporol		bark	[15]
S. talura			Hopeaphenol	bark	[16]
Stemonoporus sp. (*S. affinis, S. elegans, S. kanneliensis, S. lancifolius, S. oblongifolius)*		Stemonoporol and Copalliferol A		bark	[14]
S. canaliculatus		Canaliculatol		bark	[13]
S. cordifolius			Vaticaffinol	bark	[14]
S. lancifolius			Vaticaffinol	bark	[14]
Vateria copallifera (Retz.) Aston		Copalliferol A		bark	[15,11]
		Copalliferol B		bark	[12]
		Stemonoporol		bark	[15]
Vatica affinis	ε-Viniferin		Vaticaffinol	bark	[9]
			Vaticaffinol	bark	[125]
Vatica affinis Thw.			Vaticaffinol	bark	[109]
Vatica affinis Thw.	ε-Viniferin		Vaticaffinol	bark	[9]

Table 2 : con.

Gnetaceae					
Gnetum leyboldii Tull.	Gnetin A			wood	[110]
	Gnetins A-D	Gnetin E		wood	[111]
G.schwackeanum Taub.	Gnetins C	Gnetin E		fruits	[111] [112]
G.Parvifolium (Warb)	Gnetifolins C,D			lianas	[72]
	ε-viniferin			lianas	[72]
Welwitschia mirabilis	Gnetin F	Gnetin H			-
	Gnetin G	Gnetin I			-
Fabaceae(Leguminosae)					
Cassia garrettiana	Cassigerol A				[24]
Sophora leachiana		Leachianols A,B		roots	[22]
	Pallidol			roots	[22]
	Leachianone I*			roots	[25]
	ε -Viniferin		Hopeaphenol	roots	[25]
	Sphoraflavanone*			roots	[23]
	Leachianone C*			roots	[23]
S.moorcroftiana	Sophoraflavanone*			roots	[21] [24]
Vitaceae					
Ampelopsis brevipedunculata var. hancei	Ampelopsins A,B	Ampelopsin C		roots	-
	Ampelopsin D	Ampelopsin E		roots	[113]
	Pallidol	Miyabenol C		roots	[113]
Cissus palloa	Pallidol			wood	[114]
Parthenocisss tricuspidata	Tricuspidatol-A			stemwood	[10]
Vitis vinifera	ε -Viniferin	α-Viniferin	β-Viniferin	leaves	[46]
	ε-Viniferin	α -Viniferin		leaves	[45,47,115]

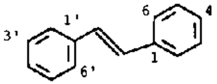
* contains flavonoid moiety.

Table 3. Natural stilbene glucosides in higher plants

Plant species	Compound	Plant Parts	Reference(s)
Cupressaceae			
Juniperus macropoda Bioss	Piceid	leaves	[67]
Ericaceae			
Gaylussacia baccata	Gaylussacin	leaves	[116]
G. Frondosa	Gaylussacin	leaves	[116]
Gnetaceae			

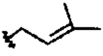
Table 3. con.

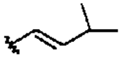
Gnetum parvifolium (Warb.) C.W.	Gnetifolin E Isorhapontin	lianas	[72]
Myrtaceae			
Eucalyptus species	Piceid, cis-Piceid	heartwood	[104]
Pinaceae			
Picea sp.	Piceatannol glucoside	bark	[110]
	Resveratrol glucoside	bark	[110]
	Isorhaponigenin glucoside	bark	[110]
P. engelmannii (Parry)	Isorhapontigin glucoside	inner bark	[144]
	Astringin ,		
	Isorhapontin	bark	[28]
	Isorhapontigin glucoside	bark	[28]
P. glauca	Astringin ,		
	Isorhapontin	bark	[28]
	Isorhapontigin glucoside		
P. mariana (Mill)B.S.P.	Isorhapontigin glucoside	bark	[144]
	Astringin	bark	
	Isorhapontin	bark	[28]
p . obovata	Isorhapontigin glucoside	bark	[145]
P. rubens	Isorhapontigin glucoside	bark	[144]
	Astringin	bark	[28]
	Isorhapontin	bark	[28]
	Isorhapontigenin glucoside	bark	[28]
P. sitchensis (Bong.) Carr.	Piceid, Astringin	bark	[41]
	Isorhapontin	bark	[41]
	Astringin, Isorhapontin	bark	[146,147]
	Astringin, Isorhapontin	stems	[149]
Polygonaceae			
Polygonum cuspidatum Sieb. et Zucc.	Piceid	roots	[94]
P. multiflorum	2,3,5,4-tetrahydroxy-2-O-β--D-glucopyranoside	roots	-
	2-O-monogalloyl ester of 2,3,5,4-tetrahydroxystilbene 2-O-β -glucopyranoside	roots	[148]
	3-O-monogalloyl ester of 2,3,5,4-tetrahydroxystilbene 2-O-β-glucopyranoside	roots	[148]
Rheum rhaponticum L.	Rhapontin	fresh roots	[29]
	3,5-Dihydroxy-4 -methoxy stilbene-3- β-D-glucoside	fresh roots	[29,58]
Vitaceae			
Ampelopsis brevipendunculata	Piceid	roots	[113]
	cis-Piceid	roots	[113
	resveratroloside	roots	[113]

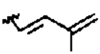


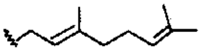
	2	3	4	5	2'	3'	4'	5'	
1.	-	-	-	-	-	-	-	-	
2.	-	OH	-	OH	-	-	-	-	Pinosylvin
3.	-	OMe	-	OH	-	-	-	-	
4.	-	OH	-	OH	-	-	OH	-	trans-Resveratrol
4a.	-	OMe	-	OMe	-	-	OH	-	Pterostilbene
4b	-	OH	-	OH	-	-	OMe	-	
4c	-	OMe	-	OH	-	-	OMe	-	
5.	-	OH	OH	OH	-	-	-	-	
6.	-	OH	-	OH	-	OH	OMe	-	
7.	-	OH	-	OH	-	OH	OH	OH	
8.	-	OMe	OH	OH	-	-	-	-	
9.	-	OMe	-	OMe	-	-	OMe	-	Gnetin
10.	-	O-CH$_2$-O		-	-	-	OMe	-	
11.	-	OMe	A	OMe	-	-	-	-	
12.	-	OH	A	OH	-	-	OH	-	
13.	-	OMe	A	OMe	-	-	OMe	-	
14.	-	OH	A	OH	-	-	OMe	-	
15.	-	OH	B	OH	-	-	OH	-	
16.	-	OH	B	OH	-	OH	OH	-	
17.	-	C	OH	-	-	OH	-	OH	
18.	-	OH	D	OH	-	-	OH	-	
19.	-	OH	D	OH	OH	-	OH	-	Chlorophorin
20.	OH	-	-	-	-	OH	-	OH	(6-OH) Gnetol
21.	-	OH	OH	-	-	OH	-	OH	Piceatannol(Astringinin)
22.	-	OH	-	OH	OH	-	OH	-	oxy-Resveratrol
23.	-	OH	OH	-	-	OMe	-	OH	
24.	-	OH	-	-	OMe	OH	OH	-	
25.	-	OH	-	OH	-	OH	OMe	-	Rhapontiginin
26.	-	OH	-	OH	-	OMe	OH	-	Isorhapontiginin
27.	-	O-C(Me)$_2$-O		-	-	OH	-	OH	
28.	COOH	OH	-	OMe	-	-	-	-	(6-A)
29.	COOH	OH	A	OMe	-	-	-	-	
30. *	-	OMe	OMe	OMe	OH	OH	OMe	-	Combretastatin A-1
31 .*	-	OMe	O- CH$_2$- O		-	OH	OMe	-	Combretastatin A-2
32 .*	-	OMe	OMe	OMe	-	OH	OMe	-	Combretastatin A-4
33 .*	-	OMe	OMe	OH	-	OMe	OMe	-	Combretastatin A-5
34 .	-	OMe	OMe	OH	-	OMe	OMe	-	Combretastatin A-6
3 5.	COOH	OH	-	-	-	-	OH	-	Hydrangeol
36.	see Fig. 1a								

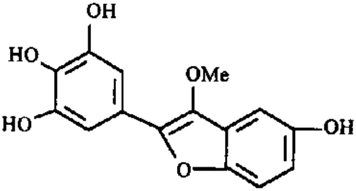
Fig. 1 . Natural Stilbene Aglycones (* cis isomers)


A , isopentenyl

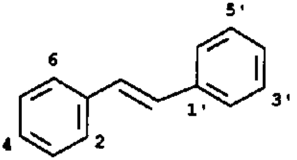

B


C, isopentadienyl


D , geranyl

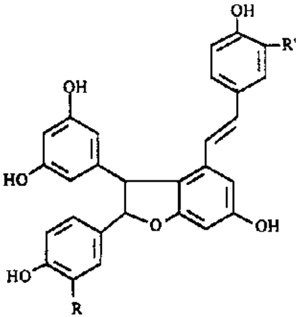


36. Gnetifolin A
(Fig. 1a)

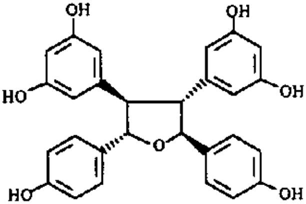


2	3	5	3'	4'	
-	OGlu.	OH	-	OH	Piceid
-	OGlu.	OH	-	OMe	3,5-Dihydroxy-4'-methoxy stilbene-3-β -glucopyranoside
-	OGlu.	OH	OH	OH	Astrinigin
-	OGlu.	OH	OH	OMe	Rhapontin
-	OGlu.	OH	OMe	OH	Isorhapontin
-	OH	OH	OMe	OGlu.	Gnetifolin E
OGlu.	OH	OH	-	OH	2,3,5,4'-Tetrahydroxystilbene 2-O-β -D-glucopyranoside
COOH	OH	OGlu.	-	-	Gaylussacin

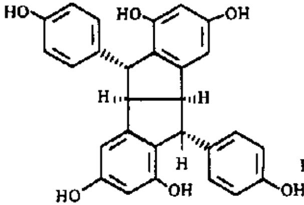
Fig. 2 . Some Stilbene Glucosides



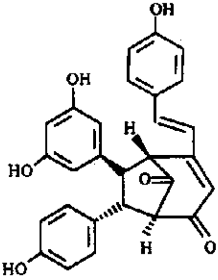
ε- Viniferin (R=R'=H)
Scirpusin A (R=OH, R'=H)
Scirpusin B (R=R'=OH)



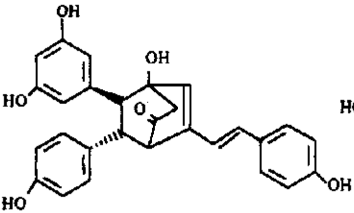
Tricuspidatol A



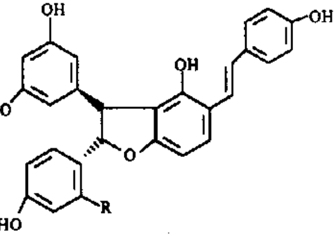
Pallidol



Gnetin A

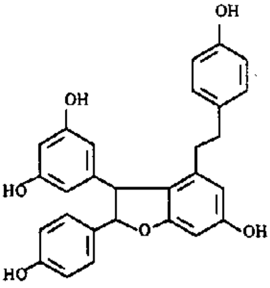


Gnetin B

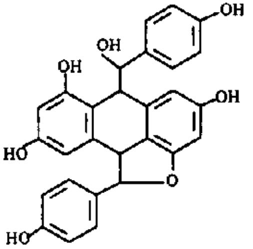


Gnetin C (R=H)
Gnetin D (R=OH)

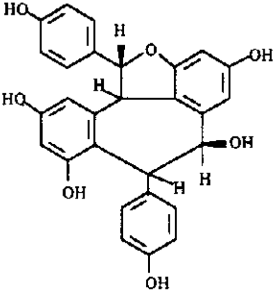
Fig. 3a . Some resveratrol dimers



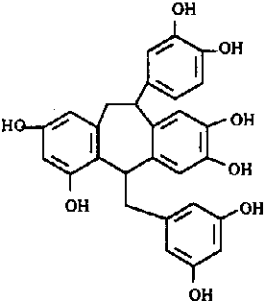
Gnetin F



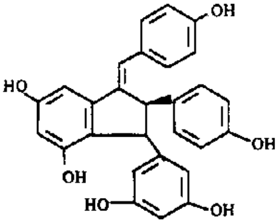
Gnetin G



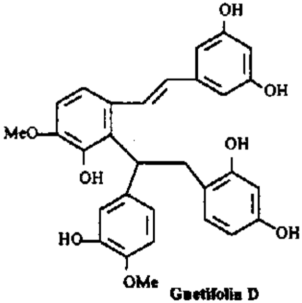
Balanocarpol



Cassigerol A



Ampelopsin D



Gnetifolin D

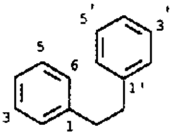
Fig. 3b . Some *resveratrol* dimers .

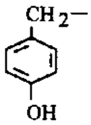
Table 4. Distribution of Natural Bibenzyls in Higher Plants

Plant species	Compound	Reference(s)
Alliaceae		
Allium chinense G.Don.	**45**	[117]
Berberidaceae		
Epimedium grandiflorum	**31**	[118]
Cannabidaceae		
Cannabis sativa	**25-28**	[119]
Combretaceae		
Combretum caffrum (Eckl. Zeyh.) Kuntze	**33**	[52]
	15,36-39	[51]
Combretum mole	**15**	[120,121]
C. psidioides	**12,13,15**	[120,121]]
Compositae (Astraceae)		
Helichrysum umbraculigerum	**22,23**	[122]
Dioscoreaceae		
Dioscorea batatas L.	**1,9,11**	[32]
	3	[32,33]
D. bulbifera	**5a**	[123]
D. domentorum	**8**	[35]
	9a	[123]
D. floribunda Mart.	**14**	[35]
D. opposita Thumb.	**8,10,12**	[30,35]
D. preusii Pax.	**14**	[35]
D. rotundata	**18**	[34]
	1,7,10,9a	[124]
Fabaceae (Leguminosae)		
Amorpha fruticosa	**20,21**	[48]
Cassia garrettiana Craib.	**2,5,11**	[125]
Glycyrrhiza lepidota	**22**	[126]
Liliaceae		
Chlorophytum arundinaceum	**29**	[127]
Orchidaceae		
Anthogonium gracile	**8**	[128]
Arundina bambusifolia	**8**	[129-132]
	40,41	[129]
	42	[129,133]
	43,44	[134]
Bletilla striata	**4,8,9,24,34,35**	[31,135,136]
Bulbophyllum fuscopurpureum	**8**	[128]
B. guttulatum	**8**	[128]

Table 4 : contin.

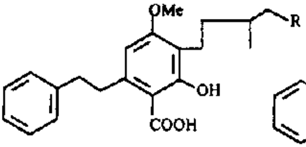
B. triste	**48**	[137]
	5a, 5b	
Calanthe masuca	**8**	[128]
Cymbridum aloifolium	**8,16,17,19**	[49]
C. giganteum	**19**	[138]
Coelogyne ovalis	**8,10**	[130]
Coelogyne (7 species)	**8**	[128]
Dendrobium (10 species)	**8**	[128]
Dendrobium crepidatum	**30**	[139]
D. cumulatum	**49**	[137]
Eria carinata	**32**	[140]
Pholidota imbricata	**8**	[128]
Pinaceae		
Pinus albicaulis	**3**	[38,168.169]
P. aramandii	**1,4**	[141]
P. morrisonicola	**4**	[141]
Saxifragaceae		
Hydrangea macrophylla Seringe	**46**	[58]
	46,47	[142,143]



A=


	2	3	4	5	2'	3'	4'	
1.	-	OH	-	OH	-	-	-	Dihydropinosylvin
2.	-	OH	-	-	-	OH	-	
3.	-	OH	-	OMe	-	-	-	
4.	-	OMe	-	OMe	-	-	-	
5.	-	OH	OH	-	-	OH	-	
5a	-	OH	-	OH	-	-	OH	Dihydroresveratrol
5b	-	OH	-	OMe	-	-	OH	
6.	-	OMe	-	OMe	OH	-	-	
7.	-	OH	-	OMe	OMe	-	-	
8.	-	OH	-	OMe	-	OH	-	Batatasin III
9.	-	OH	-	OMe	-	OMe	-	
9a	-	OH	-	OH	OH	-	-	Demethylbatatasin IV
10.	-	OH	-	OMe	OH	-	-	Batatasin IV
11.	-	OH	-	OH	-	OH	OH	
12.	-	OMe	OH	OMe	-	-	OH	
13.	-	OH	OMe	OMe	-	-	OH	
14.	-	OMe	OMe	OMe	OH	-	-	
15.	-	OMe	OMe	OMe	-	-	OH	
16.	-	OMe	OH	OMe	-	OH	-	Aloifol I
17.	-	OMe	OH	OMe	-	OMe	OH	Aloifol II
18.	-	OMe	OH	OMe	-	OMe	-	(5-OH)
19.	-	OH	-	OMe	-	OMe	OH	Gigantol
25.	-	OMe	-	OH	-	-	OH	
26.	-	OMe	-	OH	-	OH	OMe	
29.	O-Xyl.	-	OH	-	OH	-	OH	
30.	-	OMe	OMe	OMe	-	OMe	OH	Crepidatin
31.	-	OGlu.	OMe	OMe	-	OH	OMe	Icariside A6
32.	-	OMe	OMe	OMe	-	OH	OMe	Erianin
34.	A	OMe	-	OH	-	OH	-	(6-A)
35.	A	OMe	-	OH	-	OMe	-	(6-A)
36.	-	OMe	OMe	OMe	-	OH	OH	Combretastastin B-3
37.	-	OMe	-	OMe	-	OH	OH	Combretastastin A-4
38.	-	OMe	-	OMe	-	OH	OMe	
39.	-	OMe	-	OMe	-	-	OH	
40.	-	OH	A	OMe	-	OH	-	Arundinin
41.	A	OH	-	OMe	-	-	-	(6-A),Arundin
42.	A	OH	-	OMe	-	OH	-	(6-A)
43.	A	OMe	-	OH	-	OH	-	Isoarundinin-I
44.	A	OH	-	OMe	-	OH	-	Isoarundinin-II
48.	-	OH	-	OH	-	OMe	OH	Tristin
49.	-	OH	OMe	OMe	-	OH	OMe	(5-OMe) Cumulatin

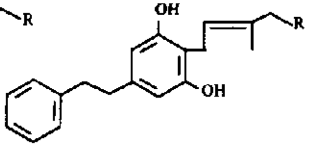
Fig. 4 . Natural Bibenzyl Derivatives.



R

20. H, Amorfrutin A

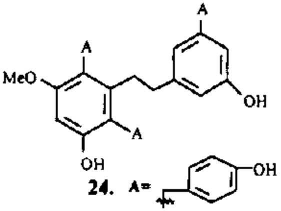
21. $CH_2CH=C(CH_3)_2$



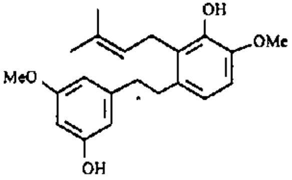
R

22. H

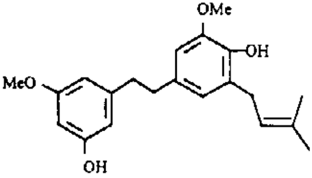
23. $CH_2CH=C(CH_3)_2$



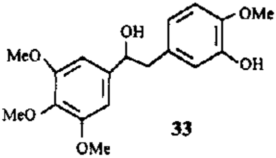
24. A=



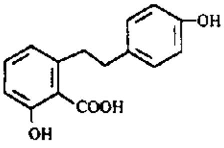
27.



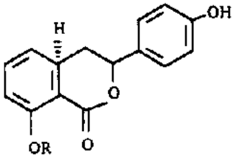
28



33



45. Lunularic acid



46. R=H, Hydrangenol

47. R= glucoside

Fig. 5 . Natural bibenzyls .

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ستلبينات وثنائيّة البنزيل في النباتات الراقية

حسن بن محمد الحازمي و حمد بن زيد الخثلان
قسم الكيمياء، كلية العلوم، جامعة الملك سعود، ص.ب ٢٤٥٥،
الرياض ١١٤٥١، المملكة العربية السعودية

(استلم في ٢٦/ ١١/ ١٤١٦هـ، وقبل للنشر في ١٧/ ٦/ ١٤١٧هـ)

ملخص البحث. تعتبر المركبات الفينولية من المركبات الواسعة الانتشار في النباتات حيث تقوم بوظائف مختلفة. واستمراراً لاهتمامنا بحصر المركّبات الطبيعية المهمة فقد قمنا في هذا البحث بحصر مكتبي لجميع ما نشر في المجلات العلمية عن مركبات ستلبينات ومشتقّاتها ثنائية الهيدروجين (ثنائيّة البنزيل) التي تم فصلها من النباتات الراقية حتى نهاية عام ١٩٩٤م.