Stilbenoids from *Leguminosae* and their Bioactivities

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Abstract Stilbenoids, usually found in *Leguminosae*, are a class of compounds with the skeleton of stilbene or their polymers, existing mostly in the xylem of plants. Till now, one hundred and seventy-six stilbenoids have been isolated from plants of *Leguminosae*. Herein, stilbene compounds and their derivatives in *Leguminosae* and their biological activities including anti-neoplastic, anti-bacterial, anti-inflammation are reviewed.

Keywords *Leguminosae*, stilbene, stilbenoids, bioactivities

Introduction

Leguminosae family is one of the largest families in the plant kingdom, which contains thousands of species. There are three subfamilies of the *Leguminosae* family, which are *Fabaceae* (*Papilionoideae*), *Caesalpinioideae* and *Mimosaceae*.^[1] The latest research shows that, 33 families, 183 genera and 1859 species (including naturalized and cultivated species) of *Leguminosae* are distributed in China. The plants in this family can be trees, shrubs, subshrubs or herbs, erect or climbing, often with nitrogen-fixing nodules.^[2] By 2014, more than 70 species of plants in at least 20 families and 30 genera have been reported to have stilbenoids.^[3,4] Stilbenoids can be categorized into diphenylethyl, phenanthrene, stilbene monomers, and polymers. In addition to the antibacterial activity found at an early age, some stilbenes have also been found to have anti-tumor, insecticidal, antiviral, anti-inflammatory, anti-senile dementia, coronary vasodilation, antihypertensive, anti-allergic, hepatocytes protecting and blood lipid reducing activities.^[3] In this minireview, we summarize the stilbenes from *Leguminosae* and their bioactivities.

Stilbenes isolated from *Leguminosae*

Up to now, stilbenes have been found in many genera of *Leguminosae*, such as *Cajanus*, *Caragana*, *Castanopsis*, *Deguelia*, *Lysidice*, *Arachis*, and so on. Li *et al.*^[5] isolated a pair of new enantiomers stilbene dimer (+)- and (–)-Cajanusine [(+)-1 and (–)-1] with unique coupling patterns from the leaves of pigeon pea (*Cajanus Cajan*) (1–2). Two stilbene compounds, longistylin A and C (3–4) were isolated from the leaves of pigeon pea by Duker-Eshun *et al.*^[6] According to the investigation and research of Tao and others, there were 44 stilbene compounds in *Leguminosae* from 1995 to 2008,^[7] cicerfuran (5),^[8] pawhuskins A–C (6–8),^[9] 5-methoxy-*E*-resveratrol-3-*O*-rutinoside (9),^[10] 2'-*O*-demthylbidwillol B, addisofurans A–B (10–12),^[11] burttionil D (13),^[12] (*E*)-3,4'-dimethoxy-5-rutinosyl-stilbene (14),^[13] 3,5-dimethoxy-4'-*O*-(β-rhamnopyranosyl)-(1→6)-β-glucopyranoside stilbene (15),^[14] lespedeazavirgatal (16),^[15] chiricanines A–E (17–21),^[16] 4-hydroxy-5'-methoxy-6",6"-dimethylpyran[2",3",3',4"]stilbene (22), 3,5-dimethoxy-4-hydroxy-6",6"-dimethylpyran[2",3",3',4"]-

stilbene (23), 3,4,5-trimethoxy-6",6"-dimethylpyran[2",3",3',4"]-stilbene (24),^[17] macheariols A–B (25–26),^[18] *trans*-4-[2-(3,5-dimethoxyphenyl)ethenyl]-1,2-benzenediol (27),^[19] cararosinol A (28),^[20] (+)-isoampelopsin F (29) and (–)-isoampelopsin F (30), caraphenols A–C (31–33),^[21] carasinols A–C (34–36),^[22] caragaphenol A (37),^[23] tibeticanol (38),^[24] T-epi,8'-epi,11-de-*O*-methyl-5'-methoxygnetifolin F (39),^[25] leachianols C–G (40–44),^[26] davidiols A–C (45–47),^[27] stenophyllol B (48).^[28] In recent years, scholars have done a lot of research on the chemical constituents of pigeon pea. Cai *et al.*^[29] isolated a new natural halogen-containing stilbene derivative from the leaves of *Cajanus cajan* (L.) Millsp. and named cajanstilbene H (49). Zhang *et al.*^[30,31] reported the isolation, structural elucidation, and cytotoxicities of cajanstilbenoid A, cajanstilbenoid B, cajanotone, cajanamide A (50–53), and other four known stilbenes (54–57). Wu *et al.*^[32] carried out phytochemical research on the plant *Cajanus cajan* and resulted in the isolation of four new stilbenes, determined as cajanusins A–D (58–61). Stilbene compounds are also the characteristic components of the genus *Caragana*. Jeong *et al.*^[33] isolated a new oligostilbene from the roots of *Caragana sinica*. The structure of caragasinin C (62) was established on the basis of spectroscopic techniques, including HRESIMS, 1D and 2D-NMR. Lan *et al.*^[34] summarized 33 stilbene compounds, *i.e.*, *Caragan*, resveratrol (63),^[35] piceatannol (64),^[24] isorhontigenin (65),^[24] pinosylvin (66),^[36] 2-(4-hydroxyphenylacetyl)-4-methoxy-6-hydroxy benzoic acid (67),^[35] cassigarol E (68), cassigarol G (69), maackin (70), cararosinol C–D (71–72), *cis*-scirpusin A (73), scirpusin A–B (74–75),^[24] pallidol (76),^[35] kompasinol A (77),^[24] caragasinin A (78),^[37] caragasinin B, miyabenol C, leachianol C, kobophenol A, carasiphenol D (79–83),^[38] (+)-α-viniferin, carasiphenol B, and carasiphenol C (84–86),^[39] (+)-stenophyllol B, carasinols A–C, carasinol D, carasinasurone, carasiphenol A (87–93),^[35] cararosinol B (94),^[40] cararosin (95).^[41] Ngoupayo *et al.*^[42] reported the isolation and structure elucidation of compounds from the stems of *Erythrophleum suaveolens*, including a new stilbenoid, suaveolensone A (96). Nguyen *et al.*^[43] isolated a new stilbenoid (97) from the soluble extract of EtOAc from the root bark of *Erythrina addisoniae*. Currently, Marques reported that 18 stilbenes (98–115) and their derivatives had been isolated

from the *Deguelia* genus.^[44-51] New prenylated stilbene derivatives, 3-hydroxy-4-prenyl-5-methoxy-stilbene acid (**116**) and 5,4'-dihydroxy-3-methoxy-2-prenyl-stilbene (**117**) had been isolated from methanol extract of *Cajanus cajan* (L.) Millsp.^[52] At present, a number of resveratrol derivatives have been isolated and extracted from peanuts, *trans*-resveratrol, *cis*-resveratrol, *trans*-piceid, *cis*-piceid, arachidin I, arachidin II, arachidin III (**118–124**),^[53] cudrastilbene, 3,5,3'-trihydroxy-4'-methoxy-5'-isopentenylstilbene, arahypin B, arahypin-13, arahypin-14, arahypin-15, arahypin-6, arahypin-7, arahypin-11, arahypin-12 (**125–134**).^[54] Seven stilbene compounds (**135–141**) were isolated from *Maackia hupehensis* (**135–141**).^[55] Compound **142** was isolated from *C. chinensis*.^[56] Four stilbene compounds (**143–146**) have been isolated from the genus *Amorpha* of Leguminosae.^[57-59] Stilbene is one of the most abundant components in the genus *Euphorbia*, especially in the *Lysidice rhodostegia* Hance of short calyx.^[60] Gao^[61] isolated the compounds **147–149** from the *Lysidice rhodostegia* Hance. Gao *et al.*^[62] isolated the compounds **157** and **164** from *n*-butanol fraction of the *Lysidice rhodostegia* Hance. Hu^[63] isolated eight stilbene compounds **150–156**, **163** from the *Lysidice rhodostegia* Hance of by high performance liquid chromatography-electrospray tandem mass spectrometry. Compounds **158–167** were isolated from the *Lysidice rhodostegia* Hance by Hu *et al.*^[64,65] Qu^[66] obtained compound **168** from *Lysidice brevicalyx*. Compounds **170–176** were also isolated from the *Lysidice rhodostegia* Hance.^[67-69]

All structures of stilbenes from *Leguminosae* are shown in Figure 1.

Bioactivities of stilbenes from Leguminosae

In addition to the early-reported antibacterial activity, some stilbene compounds have been found to also have antineoplastic activity, anti-insect effect, anti-inflammatory and analgesic effect, antimalarial, hypoglycemic, antioxidant, estrogenic and other physiological activities.

Antineoplastic activity

(+)-Cajanusine and (–)-cajanusine (**1–2**) exhibited inhibitory activities on the growth of human hepatocellular carcinoma cells.^[5] Cajanstilbene (**49**) showed a moderate inhibitory effect on cell proliferation, with IC₅₀ values of 21.42–25.85 μmol·L⁻¹.^[29] Cajanstilbenoid A (**50**) showed strong cytotoxicity against HepG2, MCF-7, and A549 cells (IC₅₀ values: 2.14–2.56 μM). However, Cajanstilbenoid B (**51**) showed strong toxicity only against HepG2 (IC₅₀ value: 5.99 μM) and A549 cells (IC₅₀ value: 6.18 μM).^[31] Cajanotone (**52**) and Cajanstilbene acid (**54**) showed strong cytotoxicity against A549 cells (with IC₅₀ values of 5.9 and 4.4 μM, respectively), but moderate cytotoxicity against HepG2 and MCF-7 cell lines (with IC₅₀ values from 12.2 to 17.9 μM), pinosylvin monomethyl ether (**55**) showed strong cytotoxicity against MCF-7 (with an IC₅₀ value of 8.8 μM) and A549 (with an IC₅₀ value of 7.4 μM) cell lines and moderate activity against HepG2 cells, with an IC₅₀ value of 15.5 μM.^[30] miyabenol C (**80**) exerted an inhibitory effect on protein kinase in a non-competitive inhibition mode.^[70] Miyabenol C (**80**) kobo-phenol A (**82**) and (+)-α-viniferin (**84**) could significantly inhibit the growth of A549 cells, and the effects of these compounds on the activities of egg autokinase c and isozymes in two human lung cancer cell lines (CA549 and HCl-H446) were studied. The results (**80**) showed they could inhibit the activity of PKc and decrease the content of PKc-a in the granule fraction, thus hindered the membrane translocation of A549 cells.^[71]

Antimalarial activity

Longistylin A and C (**3–4**) showed a moderately high

in vitro activity against the chloroquine-sensitive Plasmodium falciparum strain 3D7,^[6] machaeriol B (**26**) demonstrated *in vitro* antimalarial activity (IC₅₀ = 120 ng/mL) against Plasmodium falciparum W-2 clone.^[18]

Antimicrobial activity

Cicerfuran (**5**) showed potent antifungal activity against spores of *F. oxysporum* f. sp. *ciceri*,^[8] and chircanine A (**17**) was the only prenylated stilbene to demonstrate antifungal effects against *Cladosporium cucumerinum*.^[16] The preliminary antimicrobial activities of the crude extracts/fractions and the IC₅₀ values of machaeriols A–B (**25–26**) were determined by using a modified 96-well microplate assay protocol.^[18] The antimicrobial activity of amorfrutins A–B (**144–145**) was limited to Gram-positive and acid-fast microorganisms and compounds (**144–145**) were essentially equipotent.^[58]

Hypoglycemic activity

2'-O-Demthylbidwillol B (**10**), addisofuran A (**11**), addisofuran B (**12**) inhibited PTP1B activity with IC₅₀ values of 13.6±1.1, 17.5±1.2, and 15.7±1.6 μM.^[11]

Antioxidant activity

Lespedezavigatol (**16**) showed strong oxygen radical

Figure 1 The structures of stilbenes from *Leguminosae*.

absorbance capacity and potent inhibition toward lipid peroxidation in both plasma and kidney homogenate of renal failure rats.^[15] Tibeticanol (**38**) showed the highest antioxidant activity since it possesses two catechol groups in a molecule and a well-conjugated structure.^[24] Caragasinin A (**78**), caraphenol B (**32**), caragasinin B (**79**) have good antioxidant effects ($IC_{50} = 34.70 \pm 1.98.10 \pm 2.30 \mu\text{mol/L}$),^[39] 3,3',4',5-tetrahydroxystilbene (**135**), maackiasin (**136**) had strong antioxidant activity.^[55]

Insect-resistant activity

Chiricanines B—E (**18—21**) showed toxic properties against larvae of the yellow fever-transmitting mosquito *Aedes aegypti*.^[16]

Estrogenic activity

It was found that (+)-isoampelopsin F (**29**), (–)-isoampelopsin F (**30**), and caraphenols A—C (**31—33**) had the effects of stimulating the proliferation (the reproduction rates of cultured osteoblasts were raised 11%—37% in different concentration (10^{-10} — 10^{-4} g/mL) than that of the control group (0 g/mL), enhancing the ALP activities and increasing the number of mineral nodes of cultured osteoblasts. MTT method was used to observe the activity of stimulating the growth of osteoblasts.^[21] Carasinol A (**34**) and carasinol C (**36**) had the effects of stimulating the proliferation of cultured osteoblasts,^[22] cajanstilbene H (**49**) distinctly promoted osteoblast differentiation in HMSC (human mesenchymal stem cell) in dose and time-dependent manners,^[29] leachianol C (**81**), kobophenol A (**82**), and compounds (**88—91**) could stimulate the proliferation of osteoblasts to a certain extent.^[35]

Anti-inflammatory and analgesic activity

(+)- α -Viniferin (**84**) can inhibit the release of free radicals in blood and inhibit prostaglandin H2 synthase ($IC_{50} = 7.00 \mu\text{M}$), which is about three times that of resveratrol.^[72]

Conclusions and Perspectives

In recent years, researchers have conducted in-depth studies on the chemistry and biological activity of stilbene compounds and found some stilbene with strong activity, all of which have a strong ability to scavenge free radicals. The distribution of stilbene is limited, and it is only found in more than 30 plant families. Due to the diversity of oligomer structure, degree of polymerization and stereochemistry, the range of oligomer is very wide. This paper reviews hydroquinone and its anti-tumor, antibacterial, anti-inflammatory and antimalarial activities in 13 genera of Leguminosae. Stilbenes are rich sources of lead compounds in the search for new drugs. Resveratrol, a representative compound, has been tested in clinical trials as a drug for the treatment of Alzheimer's disease and tumors, and has shown satisfactory therapeutic effects. However, most of the chemical constituents in the pharmacological analysis are still unclear and should attract the attention of phytochemists and pharmacologists, some of which have potential for development.

Acknowledgement

This work was supported by the National Natural Science Foundation of China (Nos. 81860612, 81703793), the Social Development Supportive Program of Science & Technology Department of Guizhou Province (No. [2018]2767), the Joint Fund by Science & Technology Bureau of Guiyang and Guizhou Medical University (No. [2017]30-37).

Conflict of Interest

The authors declare no conflict of interest.

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Received February 5, 2020

Accepted February 15, 2020