Abstract: *Cajanus cajan* (aka pigeon pea) is a terrestrial medicinal plant native to Asian and African countries before being introduced to the American continent. This protein-rich legume species, belonging to the Fabaceae family, has been traditionally used to cure various ailments in many traditional medicines. Recent works have highlighted it as a rich source of a wide array of flavonoids and other phenolic compounds. The major biological activities that are currently reported on are mainly focused on antioxidant and anti-inflammatory activities which are relevant for the cosmetic field. For example, hydroalcoholic extract from *C. cajan* has been highlighted as a particularly effective antioxidant in various scavenging assays for both reactive oxygen or nitrogen species. One of its constituents, cyanidin-3-monoglucoside, has been reported to suppress inflammatory cytokine production (e.g., TNF-α, IL-1β, and IL-6 in murine RAW264.7 macrophages). The present review provides an overview on the flavonoids and phenolics from *C. cajan* as well as their biological activities that can be applied for cosmetic applications. In addition, the botanical data including taxonomic description, flowering season, distribution, synonyms and traditional uses are illustrated, so as to provide an overview of pigeon pea’s cosmetic/cosmeceutical potentials.

Keywords: *Cajanus cajan*; pigeon pea; flavonoids; phenolic acids; coumarins; antioxidant; anti-inflammatory

1. Introduction

*Cajanus cajan* (L.) Millsp is a protein-rich legume species belonging to the Fabaceae family. This medicinal flowering plant is distributed mainly in tropical areas such as Asian countries and India. *C. cajan* is also known as its common name, pigeon pea [1–3]. This medicinal species is also called different things depending on its location of growth [1,2]. Due to being rich in protein and interesting flavonoid and phenolic compounds, it is continuously studied and reported on nowadays. This work aims to update the literature on the reported flavonoids and phenolics and their biological activities that can be applied for cosmetic applications. In addition, the botanical data including taxonomic description, flowering season, distribution, synonyms as well as the traditional uses are illustrated, so as to provide an overview of pigeon pea’s cosmetic/cosmeceutical potential.
This paragraph provides a complete botanical description of *C. cajan* (Figure 1). Perennial shrubs, **stem**: erect, 1–3.5 m, branchlets green to gray with pubescent. **Leaf**: stipulate, pinnately 3-foliolate, ovate to lanceolate, abaxial densely pubescent with inconspicuous yellow glands, adaxial pubescent, apex acute or acuminate; petiole 1–5 cm long. **Inflorescence**: raceme 3.5–8 cm long; peduncle 1.5–4 cm; bracts ovate or ovate-elliptic. **Flowers**: calyx campanulate, 5–7 mm, green, pubescent; corolla papilionaceous form, yellow, standard suborbicular with auricle, wings obovate with auricle; keel apex obtuse. **Ovary**: pubescent; style slender, linear, glabrous; stigma capititate, ovule numerous. **Fruit**: Legume, oblong or linear-oblong. **Seeds**: subspherical, 3–6 mm in diameter, gray with brown spots.

![Figure 1](https://example.com/fig1.png)  
*Figure 1. Cajanus cajan* (L.) Millsp: (A) habitat; (B) leaves; (C) Inflorescence and fruits. The photos were taken by D.T. on 13 January 2019, in North-Eastern Thailand.

**Flowering season**: Between June and November (according to our preliminary survey in the natural habitats, some years its flowering season finishes in January).

**Distribution**: Tropical regions, especially Thailand, China, India.


### 3. Traditional Uses

Pigeon pea is a terrestrial medicinal plant native to Asian and African countries before being introduced to the American continent. This species, a member of the Fabaceae family, has been used for protein-rich food and medicines since prehistoric times in Asia, Egypt and African regions [2–6]. This herbal species was also called the meat of poor people because of its seeds that consist of high protein content. In the past, *C. cajan* has been used mainly as food and traditional medicines. For example, people in some areas of Tamil Nadu, India use young stems, leaves and seeds to cure gingivitis, stomatitis and also as a toothbrush [7]. In addition, the leaf of pigeon pea is also applied to treat oral ulcers and inflammations [2]. For the traditional use in Oman, people use *C. cajan* seeds for treatment of various chronic diseases [8]. Interestingly, ancient people used juice from the leaves of pigeon pea to treat various skin problems even inside the human mouth [1,4,5]. This may be the fundamental evidence to reveal the potential of *C. cajan* in skin care research and development. Nowadays, the research interest in flavonoids and other phenolics from this medicinal plant is
increasing, suggesting that more potential biological activities from these phytochemical compounds are waiting to be investigated.

4. Phytochemical Characterization of the Main Phenolics from Pigeon Pea

4.1. Metabolic Origins of the Pigeon Pea Phenolics

Pigeon pea is a rich source of different classes of phenolic compounds, including flavonoids, stilbenes and coumarins. These three classes derive from the common precursor p-coumaroyl-CoA, originating from the general phenylpropanoid pathway (Figure 2).

Figure 2. Biosynthetic relationship between the main groups of phenolic compounds (flavonoids, stilbenoids and coumarins) accumulated in various organs of pigeon pea. Their biosynthesis starts with the deamination of L-phenylalanine by L-phenylalanine ammonia lyase (PAL) into trans-cinnamic acid, followed its hydroxylation by cinnamic acid4-hydroxylase (C4H) to form the p-coumaric acid, then the p-coumarate. Coenzyme A ligase (4CL) converts it into p-coumaroyl-CoA, the common precursor of flavonoids, stilbenoids and coumarins. Flavonoids and stilbenoids are formed from the condensation of one molecule of p-coumaroyl-CoA and three molecules of malonyl-CoA but with different cyclization patterns catalyzed by two distinct enzymes: chalcone synthase (CHS) for the flavonoids vs stilbene synthase (STS) for the stilbenoids. The p-coumaroyl-CoA is also the precursor of coumarin biosynthesis starting with the hydroxylation step at position 6′ (ortho) catalyzed by feruloyl-CoA ortho-hydroxylase 1 (F6′H1), then followed by the trans > cis isomerization step of the exocyclic double bond, and a lactonization/cyclization reaction.

L-Phenylalanine, formed by the shikimate biosynthetic pathway, is converted into trans-cinnamic acid by the L-phenylalanine ammonia lyase (PAL), a branch-point enzyme between primary (shikimate pathway) and secondary (phenylpropanoid pathway) metabolism in the plant. The activity of this enzyme is essential for controlling the entry flux toward the different classes of phenylpropanoids. The cytochrome P450 monooxygenase and cinnamic acid4-hydroxylase (C4H) catalyze the hydroxylation in position 4 to form p-coumaric acid, and then p-coumarate: coenzyme A ligase (4CL) converts the latter into p-coumaroyl-CoA, an activated high-energy ester intermediate at the branch point between flavonoids, stilbenoids and coumarins [9].

Flavonoids and stilbenoids are formed from the condensation of one molecule of p-coumaroyl-CoA and three molecules of malonyl-CoA but with different cyclization patterns [9]. Two distinct enzymes belonging to the type III polyketide synthase superfamily are responsible for the cyclization reaction: (i) chalcone synthase (CHS), the first enzyme committed to the biosynthetic pathway of plant flavonoid synthesizing the production of chalcononaringenin and (ii) stilbene synthase (STS), the key enzyme leading to biosynthesis of resveratrol and other stilbenoids [10]. Both enzymes present a high degree of similarity based on sequence homology and on the comparison of their crystallographic
structures [11]. In particular, the region surrounding their active sites is well conserved. The presence of the conserved residue of cysteine in the central section of these proteins has been shown to be essential for the catalytic activity of both STS and CHS enzymes and for the binding of the p-coumaroyl-CoA substrate [12]. CHS is ubiquitous, while the occurrence of STS is restricted to stilbene-producing plants only, including the pigeon pea Fabaceae family.

Alternatively, p-coumaroyl-CoA can affect the biosynthesis of coumarins starting with the hydroxylation step at position 6′ (ortho) catalyzed by feruloyl coA ortho-hydroxylase 1 (F6′H1), 2-oxoglutarate-dependent dioxygenase, followed by a trans > cis isomerization step of the exocyclic double bond and then a final lactonization/cyclization reaction [13].

Methylation, glycosylation and prenylation reactions, which are all effectively observed in pigeon pea, can further process flavonoids, stilbenoids and coumarins.

To date, there is little information available on the regulations of these biosynthetic pathways in pigeon pea and, in particular, on how p-coumaroyl-CoA is directed towards these different branches, but there is no doubt that there will be an increasing interest in these compounds and their biosynthetic regulations due to their biological interest and application in cosmetics.

4.2. Flavonoids from Pigeon Pea

In pigeon pea, different classes of flavonoids have been reported. From a chemical viewpoint, flavonoids are C6-C3-C6 backbone phenylpropanoids consisting of two phenyl rings (rings A and B) paired with one heterocyclic ring (ring C). Depending on the carbon of the C ring connected to the B ring and the degree of unsaturation and oxidation of the C ring, flavonoids can be subdivided into different subgroups. On the basis of the structural features of the C ring, those in which the B ring is connected in position 2 can be further subdivided into several subgroups: chalcones, flavones, flavonols, flavanones, flavanols and anthocyanins. Flavonoids in which the B ring is connected to position 3 of the C ring are called isoflavones (Figure 3).

4.2.1. Chalcones

Characterized by the lack of ring C of the basic structure of the flavonoid skeleton, chalcones are known as open-chain flavonoids. Accumulating in leaves, 2′,6′-dihydroxy-4′-methoxycalcone is the only chalcone mentioned to date in pigeon pea [14,15]. Its antimicrobial and photo-protective roles have been proposed [14,15].

4.2.2. Flavones

Flavones have a double bond between positions 2 and 3 as well as a ketone at position 4 of their C ring. Most flavones present a hydroxy group in position 5 of the A ring, while hydroxylation in other positions, often in position 7 of the A ring or positions 3′ and 4′ of the B ring, can differ depending on the taxonomy. Leaves are the only part of pigeon pea that contains flavones. Flavones described in pigeon are: apigenin (both aglycone and glycosides: apigenin-8-C-glucoside or vitexin, apigenin-6-C-glucoside or isovitexin as well as apigenin-6,8-di-C-α-L-arabinopyranoside) and luteolin (both aglycone and its 8-C-glucoside derivative, also known as orientin) [14,16–20]. The most abundant are orientin and vitexin with reported concentrations of 18.82 mg/g and 21.03 mg/g of dried leaves, respectively [20]. The presence of these flavones is likely to be associated with their role in UV photoprotection, as has been found in a variety of other plant species, which is in good agreement with their observed increase in response to post-harvest exposure to UV [14]. The results from the study of this research team that evaluated the effect of UV-A, UV-B, and UV-C on phytochemical compounds and antioxidant property of C. cajan indicated that UV-A induced lower levels of phytochemicals and antioxidant activity in C. cajan leaves compared with UV-B and UV-C, and UV irradiation of its leaves help to increase this active compound as well as antioxidant activity [14]. Accordingly, the photoprotective actions have been described as a function of these compounds in plants which could be also relevant for potential cosmetic applications as sun protective compounds.
pea leaves, while cajaflavanone has been reported in roots and root barks. Prenylation reactions also occurred with isoflavonoids in pigeon pea as leaves, stems and seeds. Formononetin in stem and leaves, 4'-O-methylcajanin in roots and stems, cajanol in roots, root barks, leaves, stems and seeds, formononetin in stem and leaves, 4'-O-methylcajanin in stems and cajanin in seeds and stems. Prenylation reactions also occurred with isoflavonoids in pigeon pea as isoprenylated-genistein has been reported in seedlings. Note that isoflavonoids were among the

**Figure 3.** (a) Classical C6-C3-C6 chemical backbone and atom numbering of flavonoids. (b) Structures of the flavonoids identified in pigeon pea as a function of their subgroups: (i) chalcone: 2',6'-dihydroxy-4'-methoxychalcone; (ii) flavones: apigenin (R1=H, R2=H, R3=H), apigenin-6,8-di-C-1-arabinose (R1=H, R2=1-arabinose, R3=1-arabinose), vitexin (apigenin-8-C-glucoside, R1=H, R2=H, R3=Glucose), isovitexin (apigenin-6-C-glucoside, R1=H, R2=glucose, R3=H), luteolin (R1=OH, R2=H, R3=H) and orientin (luteolin-8-C-glucoside, R1=OH, R2=H, R3=glucose); (iii) flavonols: quercetin (R1=H, R2=H), quercetin-3-O-glucoside (R1=glucose, R2=H), quercetin-3-methylether (R1=CH3, R2=H), quercetin 3-O-xyllosyl-(1-2)-galactoside (R1=xyllosyl(1,2)-galactoside, R2=H), quercetin-3-O-glucuronic acid (R1=glucuronic acid, R2=H) and isorhamnetin (R1=H, R2=CH3); (iv) flavanones: naringenin (R1=H, R2=OH, R3=OH) and pinostrobin (R1=OCH3, R2=H, R3=H); (v) isoflavonoids: daidzein (R1=H, R2=H, R3=OH, R4=H, R5=H), genistein (R1=H, R2=OH, R3=OH, R4=H, R5=H), 2'-hydroxy-genistein (R1=H, R2=OH, R3=OH, R4=OH, R5=H), genistein-7-O-glucoside (R1=glucose, R2=OH, R3=OH, R4=H, R5=H), isogenistein-7-O-glucoside (R1=glucose, R2=OH, R3=H, R4=OH, R5=H), formononetin ((R1=H, R2=H, R3=OCH3, R4=H, R5=H), biochanin A (R1=H, R2=OH, R3=OCH3, R4=H, R5=H), cajanin (R1=CH3, R2=OH, R3=OH, R4=OH, R5=H), 4'-O-methylcajanin (R1=CH3, R2=OH, R3=OCH3, R4=OH, R5=H) and cajanol (R1=CH3, R2=OH, R3=OH, R4=OH, R5=OCH3, R6=H); vi) anthocyanins: chrysanthemin (R1=H) and peonidin-3-O-glucoside (R1=CH3). (c) Structures of the prenylated flavonoids identified in pigeon pea as a function of their subgroups: (i) prenylated flavanones: cajaflavanone; (ii) prenylated isoflavonoids: 3'-prenylgenistein, cajaisoflavone, 2'-O-methyl-cajanone and cajanone.

### 4.2.3. Flavanones

The C ring of flavanones is fully saturated, therefore, unlike flavones, the double bond between positions 2 and 3 is saturated, and this is the only structural distinction between these two flavonoid subgroups. The flavanones naringenin and pinostrobin have been reported in pigeon pea leaves [14,19–24], while cajaflavanone has been reported in roots and root barks [25,26].

### 4.2.4. Isoflavonoids

In isoflavonoids, the position of the phenyl group is linked to carbon 3 instead of carbon 2 for flavones. They are a large and very distinctive subgroup with a limited distribution in the plant kingdom, mainly found in soybeans and other leguminous plants such as pigeon pea. A large variety of isoflavonoids were found in different pigeon pea organs: cajaflavone, isogenistein 7-O-glucoside, cajanone, genistin (genistein 7-O-β-D-glucoside) and 2'-O-methylcajanone in roots, biochanin A in roots and leaves, genistein and 2'-hydroxygenistein in roots and stems, cajanol in roots, root barks, leaves, stems and seeds, formononetin in stem and leaves, 4'-O-methylcajanin in stems and cajanin in seeds and stems [19,22,26–38]. Prenylation reactions also occurred with isoflavonoids in pigeon pea as isoprenylated-genistein has been reported in seedlings [26]. Note that isoflavonoids were among the
main bioactive phytochemicals accumulated in pigeon pea with reported concentrations ranging from 0.022 mg/g of 4′-O-methylcajanin in stems [28] to 0.405 mg/g of biochanin A in leaves [19].

4.2.5. Flavonols

Flavonols are ketone-containing flavonoids. They are the most common and largest subgroup of flavonoids, presenting various patterns of hydroxylation, methylation and glycosylation. In particular, flavonols have a hydroxyl group in position 3 of the C ring. They are also the building blocks of proanthocyanins. In pigeon pea, flavonols quercetin and its derivatives have been identified on the surface of pods (isoquercitrin (quercetin-3-O-glucoside) and quercetin-3-methyl ether) [39], and bark (quercetin, isoquercitrin, quercetin 3-O-xylosyl-(1-2)-galactoside and quercetin 3-O-glucuronide) [40], as well asisorhamnetin and quercetin in leaves [18]. The highest concentration reaching 0.082 mg/g of dried leaves has been reported [18].

4.2.6. Anthocyanins

Anthocyanins are pigments that are responsible for plant, flower and fruit colors, which may vary depending on the methylation or acylation of the hydroxyl groups on the A and B rings but also the pH. Chrysanthemin (cyanidin-3-O-glucoside) and peonidin-3-O-glucoside have been detected in pigeon pea, but without any indication on their exact localization in plants [41].

4.3. Stilbenoids from Pigeon Pea

Stilbenoids present a C6-C2-C6 carbon skeleton, namely the trans- and cis-1,2-diphenylethylene structures of (E)-stilbenes and (Z)-stilbenes, respectively (Figure 4). Commonly hydroxylated, their derivatives provide a wide range of polymerization and oligomeric construction to this group. Various prenylated stilbenoids have been reported in pigeon pea, with cajaninstilbene acid at the surface of pods [23,41], cajaninstilbenoids A-B and cajanins A-D in leaves [42,43], and longistylin A and C in leaves but also in roots [22,33].

![Figure 4](https://example.com/figure4.png)

**Figure 4.** (a) Classical C6-C2-C6 chemical backbone and atom numbering of stilbenoids (here trans-stilbenoids are represented). (b) Structures of the different prenylated stilbenoids identified in pigeon pea: cajaninstilbene acid, cajaninstilbenoids A-B, cajanins A-D and longistylin A and C.

4.4. Coumarins from Pigeon Pea

Coumarins are benzopyrone derivatives (Figure 5) (1,2-benzopyrones or 2H-1-benzopyran-2-ones) widely distributed in nature. Their name originates from a French term for the Tonka bean (*Dipteryx odorata*, Fabaceae) “coumarou” from which coumarin was at first isolated by Vogel in 1820 [44].
They are classified in various subgroups: simple coumarins, furocoumarins, dihydrofurocoumarins, pyranocoumarins (linear and angular), phenylcoumarins, and biscoumarins. In pigeon pea leaves the accumulation of cajanuslactone, a prenylated 4-phenylcoumarin with anti-bacterial activity, has been reported [45]. Furthermore, the Scientific Committee on Consumer Safety (SCCS) [46] pointed out in their regulations that the concentration of active ingredients belonging to the group of furocoumarins should be below 1 mg/kg. This important point should be taken into account for potential sun protective formulations utilizing C. cajan leaf extracts for future study and/or product development.

Figure 5. (a) Classical 1,2-benzopyrones chemical backbone and atom numbering of coumarins. (b) Structure of cajanuslactone, a prenylated 4-phenylcoumarin, accumulated in pigeon pea leaves.

Figure 6 summarizes the localization of these different bioactive flavonoids, stilbenoids and coumarins in pigeon pea.

Figure 6. Localization of the flavonoids (blue), stilbenoids (green) and coumarin (red) accumulated in the different organs of pigeon pea. Notes: “*” isoprenylated-genistein was detected in seedlings only; “?” the localization of chrysanthemin and peonidin-3-O-glucoside was not mentioned by the authors.
5. Biological Activities of Flavonoids and Phenolics from Pigeon Pea

Flavonoids and phenolics are commonly known as potential natural bioactive molecules which offer various biological activities for cosmetic and/or cosmeceutical applications [47,48]. In this section, the biological activities of flavonoid and phenolic phytochemical compounds from C. cajan which have been reported in this recent decade and that have cosmetic potential for future product development will be illustrated. The major biological activities that are currently reported are mainly focused on antioxidative and anti-inflammatory activities. However, other activities, such as anti-aging from key enzymes, are still waiting to be discovered.

5.1. Antioxidant Activity

Sarkar and Mandal [49] investigated the antioxidant properties of hydroalcoholic extract from C. cajan and many Indian medicinal species using scavenging assays for reactive oxygen species (ROS) e.g., nitric oxide, superoxide, hypochlorous acid, and so on. The authors observed that flavonoid and phenolic contents of the studied plants correlated to their individual antioxidant activity [49]. The antioxidant capacity of pigeon pea was also reported by Lai et al. [41], who found, using 50% aqueous ethanol pigeon pea’s extracts, the major components cyanidin-3-monoglucoside and anthocyanin on the activity of antioxidant enzymes. Wei et al. [50] researched leaf extracts from 6 cultivars of pigeon pea and determined the appropriate harvesting time that provided the highest antioxidant potential; this team also investigated flavonoid glycosides orientin, apigenin-6,8-di-C-α-L-arabinopyranoside, vitexin and 2′,6′-dihydroxy-4′-methoxychalcone, as well as stilbenoids longistyline C and cajaninstilbene acid in each extract. The results revealed that the best harvesting time when the antioxidant properties reached higher values was 135 days after sowing [50]. Mahitha et al. [51] also investigated in vitro antioxidant activity of pigeon pea leaf extracts, comparing aqueous and ethanol solvents in various assays. Their results showed that aqueous solvents possessed the highest antioxidant potential in all the tested assays and suggested that the antioxidants observed in leaf extracts occurred because of the presence of polyphenol phytochemical compounds. Furthermore, the antioxidant potential of pigeon pea seeds was also reported with plants grown in Egypt using DPPH radical scavenging, inhibition of lipid peroxidation and total reduction capability of butanol fraction [52]. Moreover, in addition, Uchegbu and Ishiwu [53] reported antioxidant activity from germinated pigeon pea extract in an in vivo animal model. Vo et al. [54] determined the antioxidant potential of C. cajan root extracts from 50%, 95% ethanol and hot water extracts. This team reported that root extract from 95% ethanol offered the higher polyphenol content, especially cajanol, daidzein and genistein, and also provided the most potent antioxidant activity.

5.2. Anti-Inflammatory Activity

It is commonly known that chronic inflammation causes various disorders and undesirable effects on the skin and the body system. Chemopreventive activities against various chronic inflammatory conditions are currently investigated using natural plant species, and pigeon pea has also been investigated to fight against this inflammation. Lai et al. [41] conducted their research on 50% aqueous ethanolic extracts of pigeon pea, as well as the major phenolic components on murine RAW264.7 macrophages. These results trended to the prevention of reduction in antioxidant enzyme activity and lipid peroxidation-treated murine RAW264.7 macrophages by pigeon pea extracts, and cyanidin-3-monoglucoside suppressed the inflammatory cytokine production (TNF-α, IL-1β, and IL-6, inside these RAW264.7 macrophages). Hassan et al. [52] also assessed anti-inflammatory potential of pigeon pea seed extracts and found that hexane extract can inhibit carrageenan-induced inflammation, accompanied by decreased levels of TNF-α and IL-6. Furthermore, Vo et al. [54] determined the anti-inflammatory activity of root extract from pigeon pea in lipopolysaccharide-stimulated RAW 264.7 cells. These results suggested that 95% ethanol extracts from
pigeon pea root significantly boosted superoxide dismutase and catalase activities, and also proposed isoflavone genistein as the main compound in this mechanism [54].

6. Conclusions and Future Perspectives

*Cajanus cajan* is a widely distributed terrestrial medicinal plant belonging to the Fabaceae family, native to Asian and African countries before being introduced to American continent. It has been traditionally used to cure various ailments in many traditional medicines. This plant is a rich source of diverse flavonoids, phenolic acids and coumarins. Major biological activities, in particular antioxidant and anti-inflammatory activities, have been reported making it an attractive ingredient for cosmetic applications. Some future perspectives have emerged in the light of this short literature survey:

- According to continuous reports on new flavonoid and other phenolic compounds from pigeon pea, more biological activities, such as anti-aging, anti-wrinkle and other activities that are valuable to cosmetic developments, should be explored in future research.
- Various flavonoids and other phenolic compounds have been detected in various parts of pigeon pea which may not be equivalent in the consistency and quantity of these phytochemicals, so a preliminary analysis to identify the best part of this plant to be used as a raw material for cosmetic and/or cosmeceutical applications is a necessary and indisputable step.
- The new innovative extraction method to enrich flavonoids and other phenolic phytochemical compounds from different plant material has been developed; these modern extraction methods are interesting to use with pigeon pea to minimize the cost and time of extraction.
- Cosmetic companies based in different countries can consider the local pigeon pea cultivar for research and development of their products.

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