We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Flavonoids: Classification, Biosynthesis and Chemical Ecology

Erica L. Santos, Beatriz Helena L.N. Sales Maia,
Aurea P. Ferriani and Sirlei Dias Teixeira

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/67861>

Abstract

Flavonoids are natural products widely distributed in the plant kingdom and form one of the main classes of secondary metabolites. They display a large range of structures and ecological significance (e.g., such as the colored pigments in many flower petals), serve as chemotaxonomic marker compounds and have a variety of biological activities. Therefore, they have been extensively investigated but the interest in them is still increasing. The topics that will be discussed in this chapter describe the regulation of flavonoid biosynthesis, the roles of flavonoids in flowers, fruits and roots and mechanisms involved in pollination and their specific functions in the plant.

Keywords: flavonoids, biosynthesis, pollination, allelochemicals, chemical ecology

1. Introduction

Flavonoids represent a highly diverse class of polyphenolic secondary metabolites, which are abundant in spermatophytes (seed-bearing vascular land plants: gymnosperms (cycades, conifers, ginkos and gnetophytes) and angiosperms) [1–3] but have also been reported from primitive taxa, such as bryophytes (nonvascular land plants, including liverworts, hornworts and mosses) [4, 5], pteridophytes (seedless vascular land plants, i.e., lycophytes, horsetails and all ferns) [6, 7] and algae [8, 9]. Overall, about 10,000 flavonoids have been recorded which represent the third largest group of natural products following the alkaloids (12,000) and terpenoids (30,000) [1, 10].

Flavonoids are essential constituents of the cells of all higher plants [11]. Plants have evolved to produce flavonoids to protect themselves against fungal parasites, herbivores, pathogens

and ultraviolet (UV) radiation [10]. They resemble in their regulatory properties most of the lipid-soluble vitamins but serve, in addition, due to their color, as communicators with the environment. Flavonoids are recognized by pollinators, for example, insects, birds and animals, which contribute to the dispersion of seeds [11]. They act as symbionts, as allelochemicals, as antimicrobial and antiherbivory factors [10, 12]. Many studies have shown that flavonoids exhibit biological and pharmacological activities, including antioxidant, cytotoxic, anticancer, antiviral, antibacterial, anti-inflammatory, antiallergic, antithrombotic, cardioprotective, hepatoprotective, neuroprotective, antimalarial, antileishmanial, antitrypanosomal and antiamebial properties [13–15].

The topics that will be discussed in this chapter describe the regulation of flavonoid biosynthesis, the roles of flavonoids in flowers, fruits and roots and mechanisms involved in pollination and their specific functions in the plant.

2. The classification and biosynthesis of flavonoids

Flavonoids can be classified according to biosynthetic origin. Flavonoids are characterized by the presence of 15 carbon atoms in their basic skeleton, arranged in the form C₆-C₃-C₆, which corresponds to two aromatic rings A and B linked by a unit of three carbon atoms, which may or may not give rise to a third ring. The rings are labeled A, B and C [15, 16]. The initial step in the biosynthesis of most flavonoids is the condensation of one *p*-coumaroyl-CoA molecule (shikimate derived, B ring) with three molecules of malonyl-CoA (polyketid origin, A ring) to give chalcone (2', 4', 6', 4-tetrahydroxychalcone). This reaction is carried out by the enzyme chalcone synthase (CHS) [14–16]. Chalcone is subsequently isomerized by the enzyme chalcone flavanone isomerase (CHI) to flavanone. From these central intermediates, the pathway diverges into several side branches, each yielding a different class of flavonoids (Figure 1) [14, 16, 17].

Although the central pathway for flavonoid biosynthesis was conserved in plants, depending on the species, a group of enzymes, such as isomerases, reductases, hydroxylases, modifies the basic flavonoid skeleton, leading to the different flavonoid classes [1, 16], including chalcones and flavanones which are intermediary compounds in biosynthesis and final products present in various parts of the plant. Anthocyanins, proanthocyanidins, flavones and flavonols are other classes only known as end products of biosynthesis. The other important class is the isoflavonoids, which are formed by migration reaction of 2-aryl side chain to 3-position mediated by isoflavone synthase [1, 16, 18].

The retrochalcones are unusual flavonoids and have reversed A and B rings. The biosynthesis is not yet clearly defined but is likely to be derived from the common C₁₅ intermediate of general flavonoid biosynthesis, more specifically from the reduction of dibenzoylmethanes [19–21] or by 2-hydroxylation of a flavanone [22, 23]. These compounds are restricted to relatively few plant species and have been isolated from some species of the families Leguminosae [24], Annonaceae and Basellaceae [25–28].

Figure 1. A diagram of the flavonoid biosynthetic pathway. Key enzymes catalyzing some reactions: PAL, phenylalanine amonialyase; C4H, cinnamate 4-hydroxylase; 4CL, 4-coumaroyl-coenzyme A ligase; CHS, chalcone synthase; CHI, chalcone flavanone synthase; F3H, flavanone 3 β -hydroxylase; DFR, dihydroflavonol 4-reductase; FLS, flavonol synthase; IFS, isoflavanoid synthase; AS, anthocianin synthase and UF3GT, UDP glucose: flavonoid 3-O-glucosyltransferase. Adapted from Ref. [17].

Several species reported the presence of chalcone dimers bound by a cyclobutane (**Figure 2**) [29–35]. The phytochemical study of the roots of *Dahlstedtia grandiflora* was observed, and for the first time, the occurrence of dimerization in retrochalcones was noted [24]. The mechanisms of [2 + 2] cycloaddition involved in the formation of these compounds are suggested [30, 35]. In spite of the lack of biosynthetic studies of these natural products, much effort has been made in elucidating the biosynthetic pathways of flavonoids from a genetic perspective.

Figure 2. Chalcone dimmers isolated from *Combretum albopunctatum* [31], *Helichrysum zivojinii* [29] and *Agapanthus africanus* [30].

Flavonoids occur naturally as compounds associated with sugar in conjugated forms (glycosides), without attached sugar as aglycones [1, 36]. They are often hydroxylated in positions 3, 5, 7, 3', 4' and 5'. Some of these hydroxyl groups are frequently methylated, acetylated or sulfated. Prenylation usually occurs directly at a carbon atom in the aromatic rings, but O-prenylation has also been found [11]. When glycosides are formed, the glycosidic linkage is normally located in position 3 or 7, and the carbohydrates are commonly L-rhamnose, D-glucose, glucose rhamnose, galactose or arabinose [1, 11]. These changes often alter their solubility, reactivity and stability. The majority of flavonoids are present in the form of glycosides under natural conditions [1].

2.1. The chemical structure of flavonoids

The chemical nature of flavonoids varies according to the hydroxylation pattern, conjugation between the aromatic rings, glycosidic moieties, methoxy groups and other substituents [37–39]. Flavonoids contain conjugated double bonds and groups (hydroxyl or other substituents) that can donate electrons through resonance to stabilize the free radicals, which originate in the electronic spectra of flavonoids [40].

Studies on flavonoids by UV spectroscopy have shown that most flavonoids consist of two major absorption maxima: band II (240–285 nm) which corresponds to the benzoyl system of the A ring, while band I (300–400 nm) represents the cinnamoyl system of the B ring (**Figure 3**) [36, 41].

Functional groups attached to the flavonoid skeleton may cause a shift in absorption. The application of standardized UV (or UV-Vis) spectroscopy has for years been used in analyses of flavonoids [11].

Flavonoids have the ability to sequester free radicals, are natural antioxidants derived from plants and are commonly found in foods and beverages [40]. The main structural features of flavonoids required for antioxidant activity can be determined by three fundamental factors: (1) a 3',4'-dihydroxy (catechol) structure in the B ring favors the electron delocalization (**A**), (2) an unsaturated 2-3 bond in conjugation with a 4-keto group provides electron delocalization from the B ring (**B**) and (3) hydroxyl groups at positions 3 and 5 form intramolecular hydrogen bonding to the keto group (**C**) (**Figure 4**). These effects lead to the increases of the radical scavenging by delocalization of electrons or by donation of hydrogen [42].

Figure 3. Band II absorption (originated from A-ring benzoyl system) and band I (from the B-ring cinnamoyl system). Adapted from Ref. [41].

Figure 4. Structural groups for radical scavenging [42].

Flavonoids have different activity mechanisms such as free radical scavenging, inactivation of peroxides and other reactive oxygen species, chelation of metals and quenching of secondary

lipid oxidation products [40]. The radical scavenging properties associated with the structure of flavonoids defend against oxidative stress and in doing so reduce heart disease, prevent cancer and slow down the aging processes in cells responsible for degenerative diseases [40, 42].

3. Ecology chemicals

3.1. Pigments and pollination

Plant compounds that are perceived by humans to have color are generally referred to as “pigments.” The three main classes of pigments for coloration in plants are: betalains, carotenoids and flavonoids (anthocyanins) [43, 44]. All three classes of pigments act as visible signals to attract insects, birds and animals for pollination and seed dispersal [11, 43].

The pigments that color most flowers, fruits and seeds are flavonoids, which have the widest color range, from pale-yellow to blue [12]. Anthocyanins occur in all plant tissues and provide a wide range of colors ranging from orange/red to violet/blue [44]. They are formed by glycosides that may have several sugars in position 3; when there are no glycosides, the pigments are called anthocyanidins [12]. In addition to various modifications to their structures, their specific color also depends on pH, copigments and metal ions [11, 45].

The basic chromophore of anthocyanins is the flavylium ion [45, 46]. In acidic medium (pH below 2.5), anthocyanins show intensely reddish coloration or orange due the presence of flavylium cation form. When the pH increases from 2.5 to 4–6, the violet anhydrobase is formed first, but it decolorizes rapidly due the predominance of pseudobase carbinol formed by hydration (**Figure 5**) [11, 39, 47].

Since the flower cell sap is usually weakly acidic, in this pH region, most of the anthocyanins are in colorless form Ref. [47]. Hydration of the flavylium cation, which causes decoloration, may be prevented by formation of a complex between this ion and other substances. This phenomenon is called copigmenting [11, 47]. Such complexes are formed by intermolecular, intramolecular rearrangements and self-association, with organic molecules such as flavonoids, tannins, aromatic acids or metal for chelation [46, 47]. The copigmentation has a stabilizing effect as well as a bathochromic effect on anthocyanins [47]. Various flavonols and flavones act as copigments, with anthocyanins leading to an intensification of flower color [32, 45, 46]. So far, the main pigments targeted for flower and fruit color modifications are anthocyanins that contribute to a variety of colors such as red, pink and blue [44].

Humans recognize the color of a compound by perceiving reflected or transmitted light of wavelengths between 380 and 730 nm, while insects recognize light of shorter wavelengths [43]. Anthocyanins contribute to the UV patterns that are visible to insects and serve to signal flowers and fruits that are attractive to pollinators [45]. The light absorption of anthocyanins extends over most of the spectrum. Particularly, anthocyanins have an intense absorption in the 450–560 nm region (visible region), attributed to the hydroxyl cinnamoyl system of the B ring, while the absorption in the 240–280 nm region (UV region), characteristic of all flavonoids, corresponds to the A ring [32, 39].

Figure 5. A change in the structure of an anthocyanin in aqueous solution as a function of pH [47].

The different colors produced by pigments are visible only to animals with the right photoreceptors, and many insects have limited color vision at the red end of the spectrum [40]. Due to the structural diversity of anthocyanins, the presence of one determined anthocyanin in the flower might affect the type of pollinators visiting the plant. The color preferences are different for different pollinators, and blue anthocyanins, for example, appear to attract bees more than red ones. Some butterfly and birds species visit red flowers, suggesting that both groups of animals are attracted to red anthocyanins [12, 40, 48].

A study of anthocyanins in two species of the genus *Schizanthus* Ruiz & Pav (Solanaceae) showed that the hummingbird-pollinated red flowers of *S. grahamii* contained a higher proportion of delphinidin 3-O-rutinoside (anthocyanin), whereas the bee-pollinated bluish-pink flowers of *S. hookeri* contained a higher proportion of petanin-derivatives (anthocyanin) [48].

Flavones and flavonols also contribute to flower color hue. Both groups of compounds comprise unpigmented or pale yellow flavonoids and are mostly invisible to the human eye [43, 44]. Studies on flavonoids by spectroscopy have revealed that most flavones and flavonols exhibit two major absorption bands: band I (320–385 nm) represents the B ring absorption, while band II (250–285 nm) corresponds to the A ring absorption [39]. As they absorb UV, which insects recognize, they give color and patterns to flowers to attract insects [43].

Chalcones and aurones, which provide yellow pigmentation in the flowers of several ornamental species, are relatively rare types of flavonoids [49]. The UV spectra of both compounds are characterized by an intense band I and diminished band II absorption [50]. The major absorption band in chalcones (band I) usually occurs in the range 340–390 nm. Band II is usually a minor peak in the 220–270 nm region, while the long wavelength absorption band in aurones is usually found in the 370–430 nm region. They produce the strongest yellow colors owing to their absorbance at longer wavelengths compared to the other types [50, 51]. Chalcones, flavonols, flavones or anthocyanins usually accumulate in sex organs of flowers, including the pollen. In contrast to man, some insects, especially bees, can perceive in the near ultraviolet (340–380 nm) as well as in the visible region. However, insects are possibly attracted to pollen whose color contrasts against petals due to UV reflective or absorptive flavonoids [46].

Pollination is an essential step in the reproductive process of the world's nearly 300,000 species of flowering plants because it is usually required for the production of seeds. Pollination can result from the action of abiotic forces such as wind and water, but 80% of the Angiosperms rely on animals, including bats, flies, butterflies, beetles and other insects [52]. Such diversity is acquired through evolutionary processes to ensure successful reproduction [44].

3.2. Allelopathy

The interactions between organisms are fundamental for the determination of plant abundance and distribution pattern in the community, of the productivity of several cultivated species and of the degree of interference on weeds [53]. Weeds are one of the most important factors that impose limitations on the development of agricultural activity in the world and are difficult to eradicate. The success of weeds in different cropping systems is associated, in part, with their ability to produce, store and release to the environment chemicals with allelopathic properties [54].

Allelopathy can be defined as a process by which compounds from the metabolism of a plant are released, preventing the germination, growth and development of other neighboring plants [55]. These compounds are involved in plant-plant interactions or allelopathy [56] and may influence, for example, in the vegetation of a local, in the succession of plants, in the germination of seeds and in the cultures productivity, among others [57]. Among the main groups of compounds with allelopathic potential are highlighted the benzoquinones, coumarins, flavonoids, terpenoids, glycosides, phenolic acids, alkaloids, rotenoids, catechins and tannins [58, 59].

Although flavonoids have many roles in plants, in relation to their role in allelopathy and the inhibition of seedling root growth [56], the activity of flavonoids in plant-plant interactions can be positive or negative [60]. The negative relations are mainly based on inhibiting germination and growth of other plants seedlings [56], as depicted in **Table 1**.

Some flavonoids present a level of phytotoxicity, indicating that allelopathy could be a beneficial function of the flavonoids to the producing plant [65]. Although the relative role of flavonoids in allelopathic interference has been less well-characterized than of some secondary metabolites, some examples of their involvement in autotoxicity and allelopathy are reported

Plant organism	Flavonoid	Function	References
<i>Oryza sativa</i> L.		Allelopathic inhibitor of weeds and pathogens	[61]
-		Allelopathic inhibitor of seed germination	[62]
<i>Helianthus annuus</i>		Inhibitor of seedling growth	[63]
-		Allelopathic inhibitor of seedling growth	[64]

Table 1. Flavonoids of different classes with allelopathic potential.

[56]. In a previous study, see [65], presented flavonoids as are at least partly responsible for the strong phytotoxic effects of *Stellera chamaejasme* L. The potential allelopathic behavior may facilitate this weed to become a good competitor against other plant species in the environment.

Allied to the need for understanding the mechanism action of flavonoids, the importance of the study of allelopathy gains more and more attention in agriculture because these interactions could be employed for reducing weed growth.

Biopesticides based on flavonoids displaying allelopathic properties against weeds can potentially be an efficient natural defense against them [62]. In the study [63], the inhibiting activity against weeds of the species *Echinochloa crus-galli*, *Cyperus difformis* and *Cyperus iria* using the 5,7,4'-trihydroxy-3',5'-dimethoxyflavone is shown.

4. Conclusion

Flavonoids are found in most plant tissues, provide a range of colors that attract pollinators, and, in fruit, they probably serve to attract frugivores that assist in seed dispersal. All of these pigments also function as antioxidants and sunscreens, absorbing wavelengths of ultraviolet. Their biosynthesis appears to be ubiquitous in plants and evolved early during land plant (from primitive green algae) evolution, aiding in plant protection and signaling. The precise mechanism by which flavonoids participate in allelopathy is still unknown, but the significance of allelopathy has gained more attention in agriculture, for example. Plant-plant interactions can influence or determine diversity, productivity and reproduction of a plant community beyond reduction or inhibition of weed growth.

Author details

Erica L. Santos^{1*}, Beatriz Helena L.N. Sales Maia¹, Aurea P. Ferriani¹ and Sirlei Dias Teixeira²

*Address all correspondence to: ericaquimica@gmail.com

1 Federal University of Paraná, Curitiba, Paraná, Brazil

2 Technological Federal University of Paraná, Pato Branco, Paraná, Brazil

References

- [1] Martens S, Preuss A, Matern U. Multifunctional flavonoid dioxygenases: flavonols and anthocyanin biosynthesis in *Arabidopsis thaliana* L. *Phytochemistry*. 2010;**71**:1040-1049.
- [2] Jiang C, Schommer CK, Kim SY, Suh D-Y. Cloning and characterization of chalcone synthase from the moss, *Physcomitrella patens*. *Phytochemistry*. 2006;**67**:2531-2540.
- [3] Oh H, Kim DH, Cho JH, Kim YC. Hepatoprotective and free radical scavenging activities of phenolic petrosins, flavonoids isolated from *Equisetum arvense*. *Journal of Ethnopharmacology*. 2004;**95**:421-424.
- [4] Imperato, F. A new flavonoid glycoside from the fern *Dryopteris villarii*. *Natural Product Communications*. 2008;**3**:1709-1712.
- [5] Vassao D, Kim KW, Davin LB, Lewis NG. Lignans (neolignans) and allyl/propenyl phenols: biogenesis, structural biology, and biological/human health considerations. In: Mander L, Liu H-WB, editors. *Comprehensive natural products II* (1st ed.). Oxford: Elsevier; 2010, pp. 815-928.
- [6] Iwashina T. The structure and distribution of the flavonoids in plants. *Journal of Plant Research*. 2000;**113**:287-299.
- [7] Markham KR. Distribution of flavonoids in the lower plants and its evolutionary significance. In: Harborne JB, editor. *The flavonoids: advances in research since 1980* (1st ed.). London: Chapman & Hall; 1988, pp. 427-464.
- [8] Markham KR, Porter LJ. Flavonoids in the green algae (chlorophyta). *Phytochemistry*. 1969;**8**:1777-1781.
- [9] Feld H, Zapp J, Becker H. Secondary metabolites from liverwort *Tylimanthus renifolius*. *Phytochemistry*. 2003;**64**:1335-1340.
- [10] Dixon RA, Pasinetti GM. Flavonoids and isoflavonoids: from plant biology to agriculture and neuroscience. *Plant Physiology*. 2010;**154**:453-457.
- [11] Havsteen BH. The biochemistry and medical significance of the flavonoids. *Pharmacology & Therapeutics*. 2002;**96**:67-202.

- [12] Harborne JB, Williams CA. Advances in flavonoid research since 1992. *Phytochemistry*. 2000;**55**:481-504.
- [13] Tapas AR, Sakarkar DM, Kakde RB, Beydemir S. Flavonoids as nutraceuticals: a review. *Tropical Journal of Pharmaceutical Research*. 2008;**7**:1089-1099.
- [14] Alzand KI, Mohamed M. Flavonoids: chemistry, biochemistry and antioxidant activity. *Journal of Pharmacy Research*. 2012;**5**:4013-4020.
- [15] Ferreyra F, Rius SP, Casati P. Flavonoids: biosynthesis, biological functions, and biotechnological applications. *Frontiers in Plant Science*. 2012;**3**:1-15.
- [16] Mierziak J, Kostyn K, Kulma A. Flavonoids as important molecules of plant interactions with the environment. *Molecules*. 2014;**19**:16240-16265.
- [17] Koes RE, Quattrocchio F, Mol JNM. The flavonoid biosynthetic pathway in plants: function and evolution. *BioEssays*. 1994;**16**:123-132.
- [18] Cushnie TPT, Lamb AJ. Antimicrobial activity of flavonoids. *International Journal of Antimicrobial Agents*. 2005;**26**:343-356.
- [19] Shin-ichi A, Tsutomu F. Biosynthesis of a retrochalcone, echinatin: a feeding study with advanced precursors. *Tetrahedron*. 1981;**22**:2097-2098.
- [20] Shin-ichi A, Tsutomu F. Studies on plant tissue cultures. Part 36. Biosynthesis of a retrochalcone, echinatin, and other flavonoids in the cultured cells of *Glycyrrhiza echinata*. A new route to a chalcone with transposed A- and B-rings. *Journal of the Chemical Society, Perkin Transactions I*. 1982:2725-2734.
- [21] Shin-ichi A, Kumiko I, Tsutomu F. Stress-induced formation of echinatin and a metabolite, s-prenyl-licodione, in cultured *Glycyrrhiza echinata* cells. *Phytochemistry*. 1986;**25**:2803-2806.
- [22] Nakamura K, Akashi T, Aoki T, Kawaguchi K, Ayabe S. Induction of isoflavonoid and retrochalcone branches of the flavonoid pathway in cultured *Glycyrrhiza echinata* cells treated with yeast extract. *Bioscience Biotechnology and Biochemistry*. 1999;**63**:1618-1620.
- [23] Kajiyama K, Hiraga Y, Takahashi K, Hirata T, Kobayashi S, Sankawa U, Kinoshita T. Flavonoids and isoflavonoids of chemotaxonomic significance from *Glycyrrhiza pallidiflora* (Leguminosae). *Biochemical Systematic and Ecology*. 1993;**21**:785-793.
- [24] Nepel A, Marques FA, Tozzi AMGA, Silva M, Maia BHLNS. Retrochalcones and its dimmers from roots of *Dahlstedtia grandiflora* – Fabaceae. In: 5th Brazilian Conference on Natural Products – BCNP and XXXI Annual Meeting on Micromolecular Evolution, Systematics and Ecology – RESEM, 26-29 October 2015, Atibaia. São Paulo; 2015.
- [25] Furuya T, Matswnoto K, Hikichi M. Echinatin, a new chalcone from tissueculture of *Glycyrrhiza echinata*. *Tetrahedron Letters*. 1971;**27**:2567-2569.
- [26] Calzada F, Mata R, Byes R, Linares E. A retrochalcone from *Anredera scandens*. *Phytochemistry*. 1990;**29**:2737-2738.

- [27] Colegate LB, Ghisalberti EL, Latiff A. Tepanone, a retrochalcone from *Ellisya cuneifolia*. *Phytochemistry*. 1992;**31**:2123-2126.
- [28] Haraguchi H, Ishikawa H, Mizutani K, Tamura Y, Kinoshita T. Antioxidative and superoxide scavenging activities of retrochalcones in *Glycyrrhiza inflata*. *Bioorganic & Medicinal Chemistry*. 1998;**6**:339-347.
- [29] Aljancic IS, Vuckovic I, Jadranin M, Pesic M, Dordevic I, Podolski-Renic A, Stojkovic S, Menkovic N, Vajs VE, Milosavljevic SM. Two structurally distinct chalcone dimers from *Helichrysum zivojinii* and their activities in cancer cell lines. *Phytochemistry*. 2014;**98**:190-196.
- [30] Kamara BI, Manong DTL, Brandt EV. Isolation and synthesis of a dimeric dihydrochalcone from *Agapanthus africanus*. *Phytochemistry*. 2005;**66**:1126-1132.
- [31] Katerere DR, Gray AI, Kennedy AR, Nash RJ, Waigh RD. Cyclobutanes from *Combretum albo punctatum*. *Phytochemistry*. 2004;**65**:433-438.
- [32] Kumar M, Rawat P, Rahuja N, Srivastava AK. Antihyperglycemic activity of phenylpropanoyl esters of catechol glycoside and its dimers from *Dodecadenia grandiflora*. *Phytochemistry*. 2009;**70**:1448-1455.
- [33] Seidel V, Bailleul F, Waterman PG. (*Rel*)-1 β ,2 α -di-(2,4-dihydroxy-6-methoxybenzoyl)-3 β ,4 α -di-(4-methoxyphenyl)-cyclobutane and other flavonoids from the aerial parts of *Goniothalamus gardneri* and *Goniothalamus thwaitesii*. *Phytochemistry*. 2000;**55**:439-446.
- [34] Zhang LIL, Wang S, Que S, Yang W, Zhang F, Gong N, Cheng W, Liang H, Ye M, Jia Y, Zhang Q. Oxyfadi-chalcones A–C: three chalcone dimers fused through a cyclobutane ring from Tibetan medicine *Oxytropis falcate* Bunge. *Tetrahedron*. 2013;**69**:11074-11079.
- [35] Yang C, Wang X, Wang J, Luo J, Kong L. A [2 + 2] cycloaddition dimer and a diels-alder adduct from *Alpinia katsumadai*. *Organic Letters*. 2011;**13**:3380-3383.
- [36] Fossen T, Andersen ØM. Spectroscopic techniques applied to flavonoids. In: Andersen OM, Markham KR, editors. *Flavonoids chemistry, biochemistry and applications* (1st ed.). New York: Taylor & Francis Group; 2006, pp. 100-118.
- [37] Heim KE, Tagliaferro AR, Bobilya DJ. Flavonoid antioxidants: chemistry, metabolism and structure-activity relationships. *Journal of Nutritional Biochemistry*. 2002;**13**:572-584.
- [38] Kumar S, Pandey AK. Chemistry and biological activities of flavonoids: an overview. *The Scientific World Journal*. 2013;**2013** 1-16.
- [39] Eugster CH, Marki-Fischer E. The chemistry of rose pigments. *Angewandte Chemie International Edition in English*. 1991;**30**:654-672.
- [40] Gupta J, Gupta A, Gupta AK. Flavonoids: its working mechanism and various protective roles. *International Journal of Chemical Studies*. 2016;**4**:190-198.

- [41] Markham KR, Mabry TJ. Ultraviolet-visible and proton magnetic resonance spectroscopy of flavonoids. In: Harborne JB, Mabry TJ, editors. The flavonoids (1st ed.). London: Chapman & Hall; 1975, pp. 45-77.
- [42] Croft KD. The chemistry and biological effects of flavonoids and phenolic acids. *Annals of the New York Academy of Sciences*. 1998;**854**:435-442.
- [43] Tanaka Y, Sasaki N, Ohmiya A. Biosynthesis of plant pigments: anthocyanins, betalains and carotenoids. *The Plant Journal*. 2008;**54**:733-749.
- [44] Nishihara M, Nakatsuka T. Biosynthesis of plant pigments: anthocyanins, betalains and carotenoids. *Biotechnology Letters*. 2011;**33**:433-441.
- [45] Bueno JM, Sáez-Plaza P, Ramos-Escudero F, Jiménez AM, Fett R, Asuero AG. Analysis and antioxidant capacity of anthocyanin pigments. Part II: chemical structure, color, and intake of anthocyanins. *Critical Reviews in Analytical Chemistry*. 2012;**42**:126-151.
- [46] Gould KS, Lister C. Flavonoid functions in plants. In: Andersen OM, Markham KR, editors. *Flavonoids chemistry, biochemistry and applications* (1st ed.). New York: Taylor & Francis Group; 2006, pp. 397-425.
- [47] Goto T, Kondo T. Structure and molecular stacking of anthocyanins-flower color variation. *Angewandte Chemie International Edition in English*. 1991;**30**:17-33.
- [48] Sasaki K, Takahashi T. A flavonoid from *Brassica rapa* flower as the UV-absorbing nectar guide. *Phytochemistry*. 2002;**61**:339-343.
- [49] Davies KM, Bloor SJ, Spiller GB, Deroles SC. Production of yellow colour in flowers: redirection of flavonoid biosynthesis in *Petunia*. *The Plant Journal*. 1998;**13**:259-266.
- [50] Mabry T, Markham KR, Thomas MB. The ultraviolet spectra of chalcones and aurones spectroscopy of flavonoids. In: Mabry T, Markham KR, Thomas MB, editors. *The systematic identification of flavonoids* (1st ed.). New York: Springer-Verlag; 1970. pp. 227-230.
- [51] Molitor C, Mauracher SG, Pargan S, Mayer RL, Halbwirth H, Rompel A. Latent and active aurone synthase from petals of *C. grandiflora*: a polyphenol oxidase with unique characteristics. *Planta*. 2015;**242**:519-537.
- [52] Calderone NW. Insect pollinated crops, insect pollinators and US agriculture: trend analysis of aggregate data for the period 1992-2009. *PLoS One*. 2012;**7**:1-27.
- [53] Trezzi MM. Avaliação do potencial alelopático de genótipos de sorgo[tese]. Porto Alegre: Universidade Federal do Rio Grande do Sul; 2002.
- [54] Inoue MH, Santana DC, Souza Filho APS, Possamai ACS, Silva LE, Pereira MJB, Pereira KM. Potencial alelopático de *Annona crassiflora*: efeitos sobre plantas daninhas. *Planta Daninha*. 2010;**28**(3):489-498.
- [55] Alves MCS, Medeiros Filho S, Innecco R, Torres SB. Alelopatia de extratos voláteis na germinação de sementes e no comprimento da raiz de alface. *Pesquisa Agropecuária Brasileira*. 2004;**39**:1083-1086.

- [56] Weston LA, Mathesius U. Flavonoids: their structure, biosynthesis and role in the rhizosphere, including allelopathy. *Journal of Chemical Ecology*. 2013;**39**:283-297.
- [57] Demuner AJ, Barbosa LCA, Chinelatto Junior LS, Reis C, Silva AA. Sorção e persistência da sorgoleona em um latossolo vermelho-amarelo. *Química Nova*. 2005;**28**:451-455.
- [58] Vyvyan JR. Allelochemicals as leads for new herbicides and agrochemicals. *Tetrahedron*. 2002;**58**:1631-1646.
- [59] Wang Q, Li Z, Ruan X, Pan C, Jiang D. Phenolics and plant allelopathy. *Molecules*. 2010;**15**:8933-8952.
- [60] Almeida LFR. Composição química e atividade alelopática de extratos foliares de *Leonurussibiricus* L. (Lamiaceae). 2006, 105 p. Tese (Doutorado em Ciências Biológicas) – Instituto de Biociências, Universidade Estadual Paulista, Botucatu, 2006.
- [61] Kong C, Xu X, Zhou B, Hu F, Zhang C, Zhang M. Two compounds from allelopathic rice accession and their inhibitory activity on weeds and fungal pathogens. *Phytochemistry*. 2004;**65**:1123-1128.
- [62] Chang CF, Akinori S, Sumio K, Saburo T. Chemical studies on clover sickness. II. Biological functions of isoflavonoids and related compounds. *From Agricultural and Biological Chemistry*. 1969;**33**:398-408.
- [63] Macías FA, Molinillo JMG, Torres A, Varela RM, Castellano D. Bioactive flavonoids from *Helianthus annuus* cultivars. *Phytochemistry*. 1997;**45**:683-687.
- [64] Levizou E, Karageorgou P, Petropoulou Y, Grammatikopoulos G, Maneta SY. Induction of a geotropic response in lettuce radicle growth by epicuticular flavonoid aglycons of *Dittrichia viscosa*. *Biologia Plantarum*. 2004;**48**:305-307.
- [65] Yan Z, Zeng L, Jin H, Qin B. Potential ecological roles of flavonoids from *Stellera chamaejasme*. *Plant Signaling & Behavior*, 2015;**10**:e1001225-1–e1001225-3.