Progress in the Chemistry of Organic Natural Products

A. Douglas Kinghorn · Heinz Falk ·
Simon Gibbons · Jun'ichi Kobayashi ·
Yoshinori Asakawa · Ji-Kai Liu *Editors*

112

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Volume 112

With contributions by

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Contents

Allelopathy: The Chemical Language of Plants

Francisco A. Macías, Alexandra G. Durán, and José M. G. Molinillo

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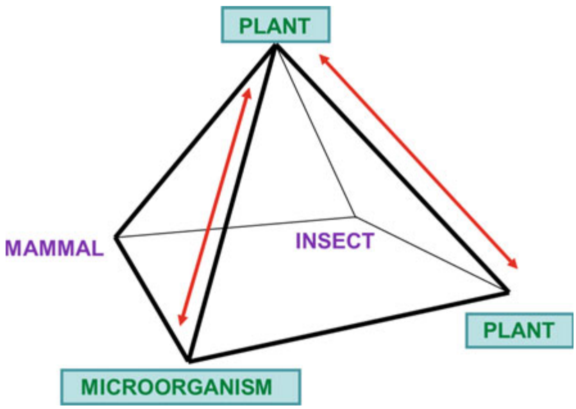
1 Introduction

In Nature, the oldest method of communication between living systems is the chemical language. Plants in particular, due to their lack of mobility, have developed the most sophisticated way of chemical communication, which is mainly based on specialized metabolites belonging to secondary metabolism [1, 2]. The most relevant aspects regarding the chemical language of plants will be described in this chapter. Only those examples with a growing body of evidence of allelopathic phenomena will be discussed and these will be categorized by plant families and listed in alphabetical order.

The term allelopathy (Greek: ἀλλήλων, allelon = each other, πάθος, pathos = suffering, mutual interaction) was introduced for the first time by Hans Molisch (1937) to refer to biochemical interactions (both inhibitory and stimulatory) between plants, including microorganisms [3, 4]. This definition was slightly modified by Rice (1974) to any direct or indirect, beneficial or destructive effect by one plant (including microorganisms) on another through the production of chemical compounds (allelochemicals) released into the environment [5]. The most commonly accepted definition is described by the International Allelopathy Society (IAS) (1996), which recommended the term allelopathy to mean the science that concerns any process involving mainly secondary metabolites, produced by plants, algae, bacteria, and fungi, that influence the growth and development of agricultural and biological systems (Fig. 1) [6–8].

Allelochemicals can be released into the environment by four main pathways: (i) exudation from roots, (ii) leaching from aerial parts by rain, fog, or dew, (iii) volatilization, and (iv) decomposition of plant remains [9, 10] (Fig. 2). These compounds can affect the development of neighboring plants, mainly on germination and root or shoot growth.

Fig. 1 Different interactions encompassed by allelopathy



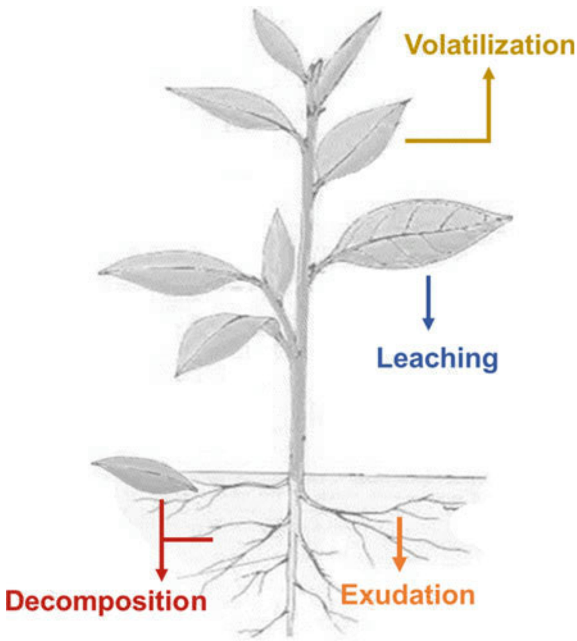


Fig. 2 The main pathways for the release of allelochemicals

2 Exudation

The most widely known allelochemicals have been identified in root exudates. The synthesis and exudation of allelochemicals in root exudates is typically enhanced by abiotic and biotic stress conditions encountered by the plant, which include plant competitors, extreme temperature, drought, and UV exposure [11]. These exudates play a key role in the rhizosphere and some of the most relevant aspects are described below.

2.1 Plant–Plant Interaction

2.1.1 Asteraceae

Centaurea diffusa Lam.

Centaurea diffusa (Asteraceae), also known as diffuse knapweed, is native to the eastern Mediterranean Eurasian range and it is an exotic invasive species and a prominent threat in North American grasslands [12]. This plant has invaded more than 1.4 million ha since its introduction as a seed contaminant prior to 1907 [13]. This species is one of the main examples in the field of allelopathy, and it has been

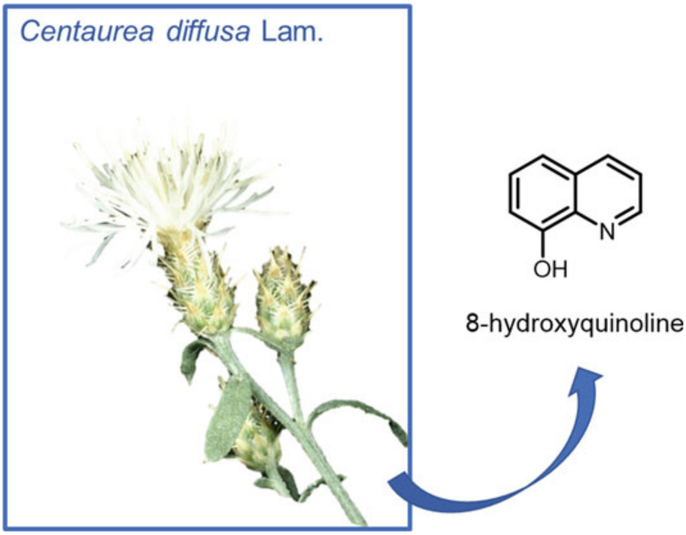


Fig. 3 Structure of 8-hydroxyquinoline (**1**), a putative allelochemical from *C. diffusa* roots. Image adapted from USDA APHIS PPQ, Bugwood.org

suggested that the allelochemicals exuded or leached from this weed might explain its invasion success [14]. It has been reported that 8-hydroxyquinoline (**1**) (Fig. 3) is exuded from its roots, and this compound has shown phytotoxic activity on neighboring species [15]. The concentration of this compound was three times higher in *C. diffusa*-invaded North American soils than in its native Eurasian soils. Furthermore, it has a strong affinity for divalent and trivalent cations such as aluminum, magnesium, and iron. Since this species mostly invades alkaline calcareous soils, the relationship between this compound and nutrition uptake was investigated. Studies carried out by Tharayil and co-workers [16] demonstrated that 8-hydroxyquinoline is used by the plant to facilitate iron uptake (a nutrient deficient in most of its invaded soils) in its complexed form. This represents a possible adaptive mechanism that confers a competitive advantage over native species in alkaline soils. This compound can be released from the roots of *C. diffusa* following a diurnal rhythm. The authors indicated that this temporal pattern is similar to the exudation of phytosiderophores by the roots of graminaceous species to enhance their uptake of metals. The phytotoxicity of 8-hydroxyquinoline was influenced by the presence of metals and it was significantly reduced when complexed with metal ions, including copper and iron [17].

However, in subsequent studies clear evidence was not found that this species produces this compound at ecologically meaningful concentrations. For instance, Norton et al. were unable to detect 8-hydroxyquinoline (**1**) in experimental or field collected soils infected by *C. diffusa*, and Quintana et al. did not detect it in root exudates or root extracts of in vitro growth [13, 14]. Additional studies are required to establish the role of this putative phytotoxin, to corroborate its presence in a soil environment and to ascertain how soil factors and microorganisms mediate its allelopathic activity [18].

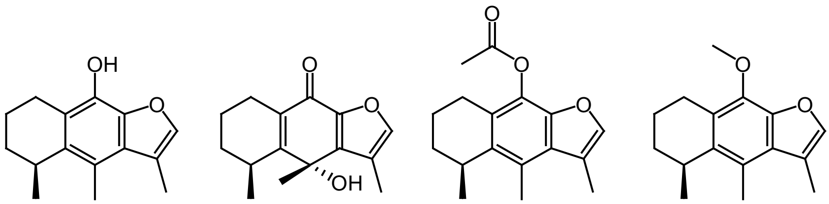
Flaveria bidentis (L.) Kuntze

Flaveria bidentis (Asteraceae) is an annual herb that is native to South America and was discovered as an exotic plant in China. It is also known as "eco-killer" due to its high adaptation to new environments, high rate of germination, and well-developed root system, as well as the production of large amounts of allelochemicals that inhibit the growth of surrounding plants. Despite this potential allelopathic activity, there are very few studies on its root exudates [19]. Recently, Xing and co-workers [20] identified by GC/MS a large variety of compounds suggested as allelochemicals.

Psacalium decompositum (Gray) Rob. ex Brett.

Psacalium decompositum (Gray) (Asteraceae) is a shrub that is native to northern Mexico and southern North America and it is called locally "matarique" or "maturin" [21]. The infusion of both the roots and rhizomes of this plant has been used for the treatment of rheumatism, pains, diabetes, snakebites, and renal, hepatic, and gastrointestinal ailments [22]. Phytochemical studies have revealed that the most abundant constituents in the hexane extract of its roots are two sesquiterpene compounds (furanoeremophilanes), namely, cacalol (**2**) and cacalone (**3**) [23] (Fig. 4). These particular compounds possess an unusual tetrahydronaphthofuran structure and their isolation led to the first report of this kind of backbone in Nature [21]. Cacalol is an unstable compound that forms a homodimer upon exposure to UV radiation and it is also oxidized by oxygen and light [24]. Additionally, these sesquiterpenes and related structures have been found in aqueous decoctions of the roots and rhizomes, thus explaining the pungent odor and bitter taste of the traditional infusions used for medicinal purposes. These compounds were detected by thin-layer chromatography using standards, after extraction of the aqueous infusion with chloroform and then ethyl acetate. Moreover, it has been reported that cacalol (**2**) inhibits ATP synthesis, proton uptake, and electron transport at the oxygen evolution level. A concentration of 60 μ*M* of cacalol completely inhibited the electron transport from water to 2,6-dichlorophenolindophenol (DCIP). This suggested that cacalol could act as an allelochemical agent to interfere with the growth of photosynthetic organisms [24].

The effect of the aqueous extract (obtained from 1 g of roots soaked with 100 cm^3 of distilled water for 4 h), *n*-hexane extract, and cacalol (**2**) on the germination and radicle growth of *Amaranthus hypochondriacus* L. and *Echinochloa crus-galli* L. was studied. Significant inhibition of the germination of *A. hypochondriacus* and on the radicle growth of both species was noted, especially by the aqueous extract and **2**. In previous studies it was suggested that the hydroxy group of **2** plays an important



2 (cacalol) **3** (cacalone) **4** (cacalol acetate) **5** (methyl cacalol)

Fig. 4 Structures of the main constituents of *Psacalium decompositum* (cacalol and cacalone) and synthetic derivatives (cacalol acetate and methyl cacalol)

role in the inhibition of oxygen evolution in photosynthesis. Therefore, two synthetic derivatives with higher lipophilicity (cacalol acetate (**4**) and methyl cacalol (**5**)) (Fig. 4) were prepared in order to evaluate their influence on the activity. The results showed that the methyl ether **5** was less active than the other compounds and a potent radicle growth inhibition of *E. crus-galli* was observed for the acetate **4**. However, significant effects were not observed in *A. hypochondriacus* for the latter compound. These results indicated that substitution of the free hydroxy group in the cacalol structure did not enhance the activity on radicle growth inhibition for either species, although greater selectivity was achieved. An enzymatic biotransformation of cacalol acetate (**4**) to cacalol (**2**) inside the seeds of *E. crus-galli* was proposed. Regarding *A. hypochondriacus*, this biotransformation would not occur and cacalol acetate would remain in its seeds without any effect [21, 25]. The typical pappus of the Asteraceae is shown in Plate 1.

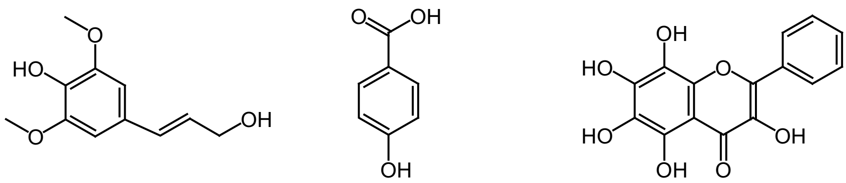
Plate 1 Asteraceae. Pappus (flower structure) of Asteraceae. Cabrera de Mar (Barcelona). Image from Creative Commons Attribution-Share Alike 3.0 Unported license. (https://commons.wikimedia.org/wiki/File:Papus_(Asteraceae).jpg)

2.1.2 Brassicaceae

Brassica napus L.

Brassica napus (Brassicaceae) (Plate 2), commonly known as canola, is one of the main crops for the production of vegetable oil for human consumption and animal nutrition worldwide. Recently, this plant has also been used for the production of biodiesel [26]. Asaduzzaman et al. [27] evaluated the allelopathic potential of this crop against annual ryegrass by comparing different canola genotypes (strongly and weakly competitive). Metabolomic analysis by LC-QTOF-MS of shoots, roots, and root exudates was performed. A greater number of secondary metabolites were found in the roots than in the shoot extracts, and a few of these compounds were identified in the root exudates. Previous research findings have also led to the same conclusion in the study of other species. It is suggested, therefore, that shoots and roots contain many metabolites, but only some of these are released into the soil environment in a process that depends on particular plant-soil conditions. Significant differences were observed between growth inhibition of annual ryegrass and the tested canola genotypes, including in chemical composition. Sinapyl alcohol (**6**), 4-hydroxybenzoic acid (**7**), and 3,5,6,7,8-pentahydroxyflavone (**8**) (Fig. 5) were found in the root exudates of the most suppressive genotypes, and it was suggested that these compounds were probably responsible for the allelopathic activity that was observed [27]. Furthermore, Uremis and co-workers [28] evaluated the allelopathic potential of different canola cultivars on the seed germination and shoot and root growth of several weed species. Root exudates showed inhibition of seed germination although root and shoot extracts had higher

Plate 2 Brassicaceae. *Brassica napus* L. Image from Tilo Hauke (http://commons.wikimedia.org/wiki/File:Brassica_napus_2.jpg)



6 (sinapyl alcohol) **7** (4-hydroxybenzoic acid) **8** (3,5,6,7,8-pentahydroxyflavone)

Fig. 5 Metabolites isolated from the root exudates of *Brassica napus* that are probably responsible for the allelopathic activity observed

inhibition potential. It was demonstrated that those cultivars with higher levels of benzyl and allyl isothiocyanate had stronger allelopathic effects.

2.1.3 Boraginaceae

Echium spp.

Isohexenylnaphthazarins (alkannin and shikonin derivatives) are found in the root periderm of several Boraginaceous plants, including *Echium* species (Fig. 6) [29].

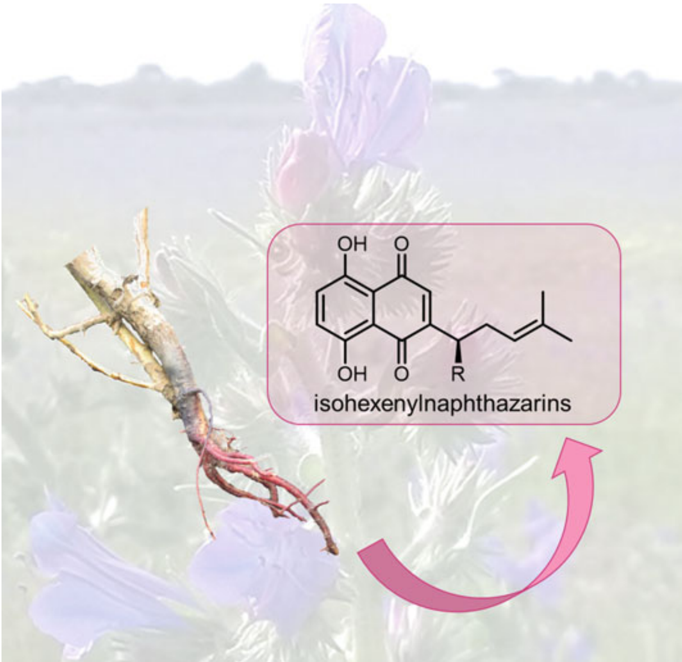
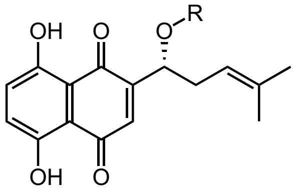


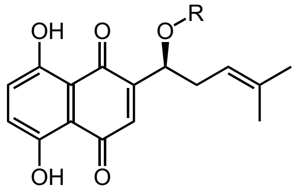
Fig. 6 Isohexenylnaphthazarins released from the roots of *Echium* spp.

Plate 3 Boraginaceae. Viper's bugloss (*Echium vulgare*) flower. Copyright Evelyn Simak and licensed for reuse under creativecommons.org/licenses/by-sa/2.0. (https://www.geograph.org.uk/reuse.php?id=5801578)

These compounds are characteristically red and are often light- and oxygen-labile, which makes their isolation difficult and methods for their separation rather few in number [30]. It has been suggested that in the soil the naphthoquinones released by *Echium vulgare* (Plate 3) roots may act as defense compounds and they are produced potentially as a result of plant stress [31, 32].

Durán and co-workers [33] quantified the content of these allelochemicals by LC-MS-MS from the periderm roots of two *Echium* spp., namely, *E. plantagineum* and *E. gaditanum*, to assess their impact on their native and invaded ranges. *E. plantagineum*, also known as Paterson's curse or Salvation Jane, is a successful invader in Australia that was introduced in the 1800s [34]. In contrast to the above, *E. gaditanum* is perennial and its toxicity does not have a major impact on agriculture in its native range. Phytochemical studies of this plant are uncommon and previously only the fatty acid composition of the seed oil has been reported [35]. The results highlighted that the abundance of certain pigments is closely related to climatic conditions. Thus, root extracts from both species collected in late spring were more inhibitory in the wheat coleoptile bioassay. Acetylshikonin (**9**) and acetylalkannin (**10**) versus dimethylacrylshikonin (**11**) and dimethylacrylalkannin (**12**) were present in the highest concentrations in extracts from both species.





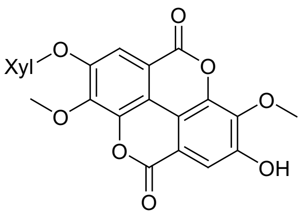
9 R = $COCH_3$ (acetylshikonin) **11** R = $COCH{=}C(CH_3)_2$ (dimethylacrylshikonin)

10 R = $COCH_3$ (acetylalkannin) **12** R = $COCH{=}C(CH_3)_2$ (dimethylacrylalkannin)

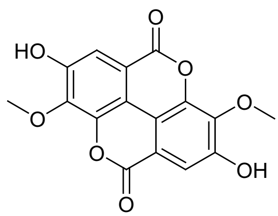
2.1.4 Euphorbiaceae

Euphorbia himalayensis (Klotzsch) Boiss.

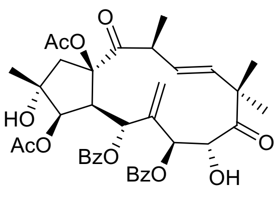
Euphorbia himalayensis is a noxious weed to livestock and humans, in addition to affecting the performance of crops in the Tibetan Plateau. Liu and co-workers [36] isolated three compounds from the root extracts, including 4-*O*-[*β*-D-xylopyranosyl]-3,3′-di-*O*-methylellagic acid (**13**), 3,3′-di-*O*-methylellagic acid (**14**), and esulone A (**15**) (Fig. 7). Furthermore, these compounds were also identified in the rhizosphere soil. Root exudates showed inhibitory growth activity on wheat seedlings at lower concentrations while an increase in plant growth was produced when the concentration



13 (4-*O*-[ß-D-xylopyranosyl]-3,3'-di-*O*-methylellagic acid)



14 (3,3'-di-*O*-methylellagic acid)



15 (esulone A)

Fig. 7 Possible allelochemicals from root exudates of *E. himalayensis*

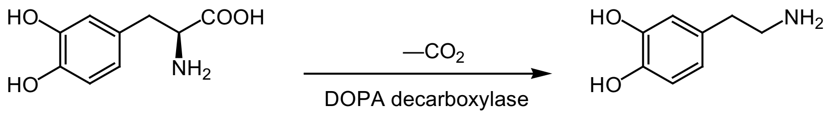
Plate 4 Euphorbiaceae. *Euphorbia milii* Des Moul. flowers. This file is licensed under the Creative Commons Attribution-Share Alike 3.0 Unported license. (https://commons.wikimedia.org/wiki/File:Euphorbia_Milii_flowers.jpg)

was higher. This finding suggests that the combination of these allelochemicals could provide a selective plant growth regulator. It was also proposed that these allelochemicals enable this species to become a successful competitor. To illustrate a typical Euphorbiaceae species, the flowers of *Euphorbia milii* are shown in Plate 4.

2.1.5 Fabaceae

Mucuna pruriens (L.) DC.

Mucuna pruriens (Fabaceae), also named velvet bean, is a popular Indian medicinal plant widely distributed throughout India and in other parts of the tropics, including Central and South America [37]. This plant has also been cultivated for intercropping with maize, sorghum, and millet in tropical regions to provide soil and crop benefits and for the management of various pests. In this way, the quantity of synthetic agrochemicals needed for the crops is reduced. The main allelochemical, which is exuded from the roots of this species, is the non-protein amino acid 3,4-dihydroxyphenyl-L-alanine [38] **16** (L-DOPA) (Fig. 8) and this reaches 1 ppm in water culture solution and 50 ppm in the vicinity of the roots. These concentrations are sufficient to affect the growth of surrounding plants by inhibition of seed and root growth. For instance, the growth of maize roots and the activities of phenylalanine ammonia-lyase (PAL), tyrosine ammonia-lyase (TAL), and peroxidase (POD) were reduced, while the contents of phenylalanine, tyrosine, and lignin were increased after exposure to L-DOPA (**16**) (39). These findings suggest that the inhibition of these activities could lead to a major incorporation of phenylalanine



16 (L-DOPA) **17** (dopamine)

Fig. 8 Detoxification of L-DOPA to form dopamine through the action of L-DOPA decarboxylase

and tyrosine levels into the cell wall and this would be followed by lignin deposition. Therefore, cell expansion is restricted and the root growth reduced.

Moreover, this allelochemical has also been found in large amounts in leaves and seeds from this species [40]. These phytotoxic effects are generally less damaging in Gramineae and Leguminosae species. It has been reported that some plants are able to detoxify L-DOPA (**16**) to form dopamine (**17**) or 3-*O*-methyldopa through the action of L-DOPA-decarboxylase and catechol-*O*-methyltransferase, respectively [41].

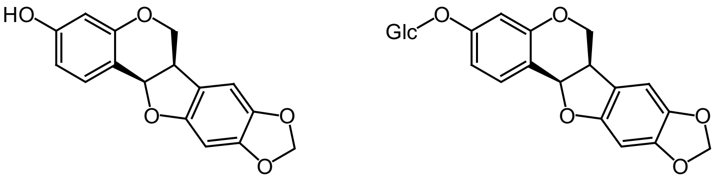
Dopamine (**17**) (Fig. 8) is an allelochemical that is widespread in animals and has also been detected in many plant families. For example, Wichers et al. [42] used HPLC coupled with mass spectrometry to identify **17** in 2–3-week-old leaves of *Mucuna pruriens*. The dopamine content of the leaves even exceeded the content of L-DOPA (**16**), the most abundant allelochemical in *Mucuna*. However, **17** could not be detected in the roots, stems, or seeds at any stage of development. Matsumoto [43] reported that *Mucuna* metabolizes **16** to **17** in leaves as a protective mechanism against the toxicity of **16**. Dopamine (**17**) has also been detected in numerous other plant families; for example, **17** is one of the major bioactive components of *Portulaca oleracea* L. [44], potato (*Solanum tuberosum*), the pulp of yellow banana (*Musa acuminata*), and fuerte avocado (*Persea americana*) [45, 46].

However, the role of dopamine (**17**) in plants has not been widely studied. In some studies, **17** has been proposed as a precursor for alkaloids and others revealed its allelopathic activity as it is involved in processes such as flowering, nitrogen fixation, and photophosphorylation of chloroplasts. For example, **17** has been shown to inhibit soybean root elongation [47].

Trifolium pratense L.

Trifolium pratense (Fabaceae) (Plate 5), also known as red clover, is a forage plant that is widely distributed worldwide and has a wide range of biological activities [48, 49]. Although its phytotoxicity on other plants has been reported, the identity of the responsible active metabolites has not been further explored. It was found in recent studies that isoflavonoids, namely, (6a*R*,11a*R*)-maackiain (**18**) and (6a*R*,11a*R*)-trifolirhizin (**19**), are the major components in root extracts of this species (Fig. 9). Furthermore, some of the compounds from the soil were identified as allelochemicals, showing remarkable phytotoxic activity on one of the most widely distributed weed species, *Poa annua* [50].

Plate 5 Fabaceae. *Trifolium pratense*. Photograph courtesy Ivar Leidus (https://reativecommons.org/licenses/by-sa/4.0)



18 ((6a*R*,11a*R*)-maackiain)

19 ((6a*R*,11a*R*)-trifolirhizin)

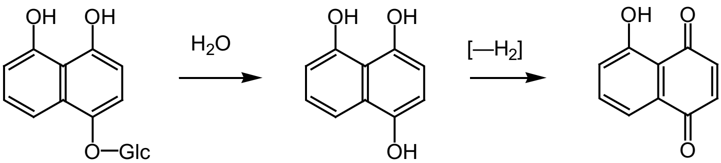
Fig. 9 Allelochemicals identified in *Trifolium pratense*

2.1.6 Juglandaceae

Juglans nigra L.

Juglans nigra (Juglandaceae) (Plate 6), also named black walnut, is one of the most notable and oldest examples in allelopathy since juglone (**20**) (5-hydroxy-1,4-naphthoquinone) was the first allelopathic agent to be described. Juglone (**20**) is mainly obtained from the leaves, roots, and husks of species belonging to this family and it has shown growth inhibitory effects for the whole plant on herbaceous and woody species, such as tomato, alfalfa, soy, and cucumber [51–54]. Pliny the Elder (23–79 AD) was the first to observe that "the shadow of walnut trees is poison to all plants within its compass" [55]. In living plant tissues, a colorless non-toxic reduced

Plate 6 Juglandaceae. *Juglans nigra*, Walnut tree. Photograph Georg Slickers, licensed under the Creative Commons Attribution-Share Alike 2.5 license. (https://es.m.wikipedia.org/wiki/Archivo:Walnut-tree_20041012_2599.JPG)



22 (glucoside) **21** (hydrojuglone or 1,4,5-trihydroxy-naphthalene) **20** (juglone)

Fig. 10 The presence of hydrojuglone in living tissues of walnut tree and subsequent formation of the allelopathic compound, juglone

form of this compound, hydrojuglone (**21**), is abundant—especially in the leaves, fruit hulls, and roots of walnut. When this compound is exposed to air or to an oxidizing compound, hydrojuglone is oxidized to its toxic form, juglone (**20**) (Fig. 10). Therefore, plants in the vicinity of the walnut tree are affected by absorbing **20** through their roots [53]. With respect to biosynthesis, juglone is presumed to be produced by hydrolysis of its glucoside **22**.

2.1.7 Poaceae

Avena fatua L.

Avena fatua (Poaceae) (Plate 7), or wild oat, is one of the worst annual grass weeds in the world (especially on wheat and other cereals). It has been reported that phenolic acids (such as *p*-coumaric (**93**), vanillic (**46**), and ferulic (**44**) acids) and

Plate 7 Poaceae. *Avena fatua* L. This file is licensed under Creative Commons Attribution—Partage dans les Mêmes Conditions 4.0 International. (https://fr.wikipedia.org/wiki/Fichier:Avena_fatua-Folle_avoine-20150527.jpg)

scopoletin are the major compounds released from its roots [56]. Additionally, it has been demonstrated that the concentration of these phenolic acids depends on the plant growth stage. The highest concentration of these allelochemicals in the rhizospheric soil was recorded at the stem extension and heading stages [57].

Oryza sativa L.

Rice*, Oryza sativa* (Poaceae or Gramineae), is one of the main food crops worldwide [58]. Previous studies have shown that the allelopathic activity of this species is varied and dependent on the origin. Large amounts of allelochemicals are released from rice plants under biotic and abiotic conditions for defense and protection [59]. Among these compounds, phenolic acids (vanillic (**46**) or benzoic (**47**) acids), diterpenoids, and momilactones have been described [60–63]. A study performed by Khanh et al. relied on the allelopathic responses of two rice varieties (Koshihikari and Jasmine) under abiotic stresses: temperature and complete submergence (one of the most harmful abiotic stresses). The results revealed that the total phenolic content was higher in extracts and root exudates from rice seedlings under the abiotic stresses evaluated, especially for the Koshihikari variety. Five phenolic acids were found to be involved in the allelopathic response, with syringic and benzoic acids being the most prominent. Moreover, root exudates of Koshihikari rice seedlings reduced the number of total weeds by up to 60% at 32°C [64]. Likewise, the secretion of the allelochemical momilactone B was increased by the presence of barnyardgrass seedlings or barnyardgrass root exudates [65].

Li and co-workers [66] investigated whether the phenomenon of rice allelopathy could be related to root fineness (roots ≤ 0.2 mm diameter). The results showed that allelopathic rice cultivars had higher length, a greater number of root tips of fine roots, and a direct correlation between the phenolic acids content in root exudates, and allelopathic activity was noted. These findings were not evident in roots with a diameter greater than 0.2 mm. It is believed that fine-root traits could accumulate more allelochemicals and release them into the environment. Moreover, the release of greater quantities of allelochemicals could be related to phytohormone regulation. It has been proposed that the phytohormones jasmonic acid and salicylic acid play a crucial role in the signaling pathway in rice-barnyard recognition [67, 68].

Phragmites australis (Cav.) Trin. ex Steud.

Phragmites australis (Poaceae) is one of the most invasive species in the world [69]. Several studies have shown that aqueous extracts of different parts of this plant (leaves, stems, rhizomes, and roots), as well as root exudates, have strong phytotoxic effects on the germination and growth of other plant species [70]. This activity has been related to the presence of phenolic compounds. Moreover, gallic acid was identified as the major compound in leaf extracts, which showed the highest activity, followed by the inflorescence, rhizomes, roots, and finally stems. Aqueous extracts caused oxidative stress through the production of reactive oxygen species, which resulted in cell death and inhibition of plant growth. A decrease in water uptake and a delay in total carbohydrate degradation were also noted, thus providing evidence of a negative effect on the overall germination process [71].

Secale cereale L. (rye)

Secale cereale became a crop about 2000 years ago. It is used as a grain, forage, green manure crop, or for hay, as well as a cover crop or mulch for allelopathic weed control. The major allelochemicals reported and identified for the first time in this species are benzoxazinoids [72]. Macías and co-workers described for the first time the allelochemical pathway of benzoxazinoids released by rye (donor plant) on *Avena fatua* L. (target plant) [73]. This kind of compound has been found in *S. cereale* as well as in other Gramineae crops. Glucosylated benzoxazinoids are found inside the plants and they are released into the environment without the sugar moiety [74]. These compounds can be classified into three categories: benzoxazolinones (**23, 24**), lactams (**25**), and hydroxamic acids (**26, 27**) [75] (Fig. 11). These metabolites have attracted great interest due to the wide spectrum of biological bioactivities and remarkable allelopathic effects reported [76]. Additionally, these compounds are transformed by soil microbiota into benzoxazolin-2-one (BOA) and 2-aminophenol derivatives, which are subsequently oxidized to 2-amino-3*H*-phenoxazin-3-one (**28**) (APO) and other related products (Fig. 12). These findings showed that, besides the allelochemicals released into the environment, the degradation products after biotic and abiotic stresses are also decisive.