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Review

Isolation and identification of allelochemicals and their activities and functions

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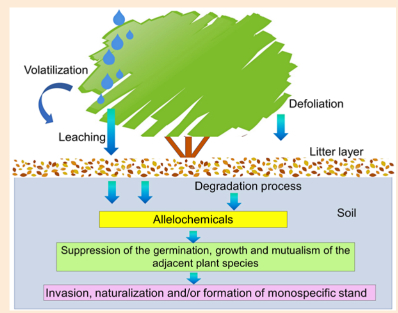
Allelopathy is the interaction between donor plants and receiver plants through allelochemicals. According to a great number of publications, allelopathy may be involved in several ecological aspects such as the formation of monospecific stands and sparse understory vegetation for certain plant species. Allelopathy also contributes to the naturalization of invasive plant species in introduced ranges. Autotoxicity is a particular type of allelopathy involving certain compounds. Many medicinal plants have been reported to show relatively high allelopathic activity. We selected plant species that show high allelopathic activity and isolated allelochemicals through the bioassay-guided purification process. More than 100 allelochemicals, including novel compounds have been identified in some medicinal and invasive plants, plants forming monospecific stands, plants with sparse understory vegetation, and plants showing autotoxicity. The allelopathic activity of benzoxazinones and related compounds was also determined.



Keywords: allelopathy, autotoxicity, invasive plant, medicinal plant, monospecific stand, phytotoxicity.

Introduction

Allelopathy is the chemical interaction between donor plants and receiver plants, and the compounds involved in the allelopathy are defined as allelochemicals.[1–3] The phenomenon of allelopathy can be found in several ecological aspects that have been documented in a great number of publications. Allelochemicals suppress the germination, growth, and regeneration process of the receiver plant species.[4–6] Some allelochemicals such as cinnamic acid, benzoic acid, and their derivatives disturb cell membrane permeability, water balance, and stomatal functions, and suppress the enzyme activities involved in the photosynthesis, protein synthesis, respiration, and the metabolism of some secondary metabolites including plant hormones.[7–9] The disruption of the metabolism and cell functions by allelochemicals may cause the inhibition of the germination, growth, and regeneration process of the receiver plant species.

Allelochemicals also disturb the mutualism of receiver plants with arbuscular mycorrhizal fungi and/or rhizobia.[10–12] Rhizobium nodulation occurs in legumes, and enhances the host plant performance through the supply of ammonium and nitrogen to the host plants.[13,14] Colonization of the arbuscular mycorrhizal fungi occurs in the most territorial plants, and enhances the host plant performance through the increasing the absorption of water and nutrients, photosynthesis of the host plants, and their defense functions against pathogen attacks and stress conditions.[15–17] Therefore, the disturbance of these mutualism by allelochemicals may reduce the competitive ability of the receiver plant species, resulting in the relative elevation of the competitive ability of donor plants.

Allelochemicals are released from the donor plants into the surrounding environments including the rhizosphere soil through volatilization, rainfall leachates, and root exudation from the donor plants, and decomposition processes of the donor plant litter and residues. Some plants possessing allelopathic potential synthesize allelochemicals and stored them in certain plant tissues until they are released into the surrounding environments.[1–3] Therefore, the extraction of the allelopathic plant species allows us the isolation and identification of the allelochemicals stored in the plant tissues. In addition, the extracts and residues of several plant species have shown significant

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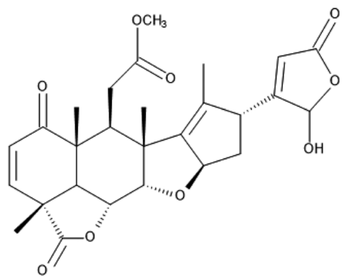

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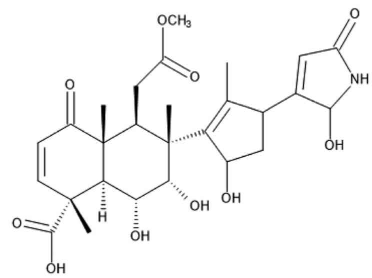

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Fig. 1. Allelochemicals of neem.

weed control ability as soil additives and mulch because of the allelochemicals.[3–6)]

We selected plant species through the following three-step evaluation process: 1) the selection of possible plant species that dominate in natural conditions, 2) investigate plant species in publications and websites, and 3) evaluate the allelopathic activity of the crude extracts of the plant species. After the selection, we extracted the plant species, separated the extracts through the bioassay-guided purification process: evaluate the allelopathic activity of all fractions obtained after each separation step, and apply most active fraction to the next separation step. We extracted plant species that showed high allelopathic activity and isolated and identified more than 100 of allelochemicals including novel compounds. The objective of this review is to describe some of identified allelochemicals and their activities, and to discuss the possible involvement of the allelochemicals in some ecological aspects such as the formation of monospecific stands and the naturalization of invasive plant species. The allelopathic activity of benzoxazinones and related degradative products is also discussed.

1. Allelochemicals in medicinal plants

Many of medicinal plants have shown relatively high allelopathic activity.[18,19)] Therefore, we surveyed the allelopathic activity of several medicinal plants and isolated the allelochemicals from plants that showed high allelopathic activity.

1.1. Neem

Neem (*Azadirachta indica*), belonging to the Meliaceae family, is native to the Indian subcontinent and Indochina, and is used as a traditional medicinal plant in the native ranges and in the Ayurvedic medicine system. Local people in the native ranges have also been used various parts of the plant and its extracts to control weeds and insects.[20–22)] Extracts of the neem leaves showed high allelopathic activity, significantly suppressing the growth of *Festuca myuros*, *Phleum pretense*, *Echinochloa crus-galli* and *Echinochloa colonum*.[23)] The extracts were then separated and two allelochemicals were isolated and characterized as novel compounds, nimbolide B (**1**) and nimbic acid B (**2**) (Fig. 1).[24)] More than 200 natural compounds have been isolated and identified from neem, with some showing biological activity.[25–28)] However, compounds **1** and **2** were isolated from the most active fraction with bioassay-guided purification process. Compounds **1** and **2** inhibited the growth of *Echinochloa crus-galli* at concentrations greater than 0.3 μM and 1 μM, respectively. The concentration of compounds **1** and **2** required for 50% inhibition, defined as IC_{50}, on the growth of *E. crus-galli* was 3.7 μM and 29 μM for compounds **1** and **2**, respectively, suggesting the allelopathic activity of compound **1** is 7.8-fold greater than that of compound **2**.

1.2. Aglaia odorata

Aglaia odorata is also a member of the Meliaceae family, and has been used as a traditional herb in Southeast Asia.[29–31)] Leaf powder of the species and its ethanol extracts have shown allelopathic activity against the emergence and growth of the weed species, *Digitaria adscendens* and *Trianthema portulacastrum* under the field conditions,[32,33)] and against the growth of *Phleum pretense*, *Lolium multiflorum* and *Echinochloa crus-galli* under the laboratory conditions.[34)] The extracts were then separated, and the most active allelochemical was isolated and identified as rocaglaol (**3**) (Fig. 2).[34)] Although the biological activity of this compound against human and animal cells has been reported,[35,36)] the allelopathic effect of the compound has not been reported. The compound suppressed the growth of *E. crus-galli* at concentrations greater than 0.03 μM, and its IC_{50} value on the growth of *E. crus-galli* was 0.09 μM.

1.3. Ginkgo

Ginkgo (*Ginkgo biloba*) is one of the oldest tree species, and the only surviving species in the family of *Ginkgoaceae* that

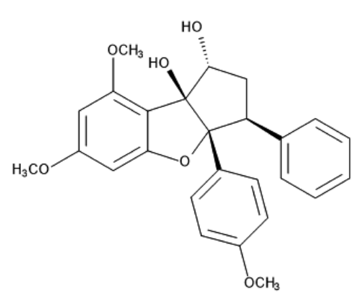

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Fig. 2. Allelochemical of *Aglaia odorata.*

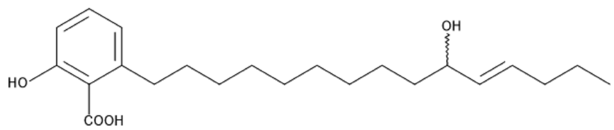

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Fig. 3. Allelochemical of ginkgo.

appeared in the Jurassic period.[37] The species has been used as a traditional herb in China, and its leaf extracts of Ginkgo such as EGb761 are sold worldwide as dietary supplement and phytomedicine.[38] Extract of the ginkgo leaves significantly suppressed the growth of *Phleum pratense* and *Lolium multiflorum*. The extracts were then separated, and a main allelochemical was isolated and characterized as a novel compound, 2-hydroxy-6-(10-hydroxypentadec-11-enyl)benzoic acid (**4**) (Fig. 3).[39] The compound suppressed the growth of *P. pretense* at concentrations greater than 3 μM, and its IC_{50} value on the growth of *P. pretense* was 17 μM. The compound was also found in the litter under the ginkgo trees, and the concentration of the compound was greater in the litter collected near the ginkgo trees than that from farther away.[40] Therefore, the growth inhibitory activity of the ginkgo litter layer against other plant species may be higher the closer the litter is to the ginkgo trees, which provides ginkgo with the advantage of increased acquisition of water and nutrients because the growth of other plants are suppressed. Its related compound, nonanoic acid (pelargonic acid) exists as esters in the oil of *Pelargonium* species. This compound suppressed the growth of *P. pretense* at concentrations greater than 30 μM, and its IC_{50} value on the growth of *P. pretense* was 265 μM.[39] Therefore, the inhibitory activity of the newly identified compound **4** was 10- to 16-fold greater than that of nonanoic acid.

1.4. Orthosiphon stamineus

Orthosiphon stamineus (syn. *Orthosiphon aristatus*), belonging to the Lamiaceae family, is known as Java tea, and is used widely in the herbal tea in Asia.[41,42] Extracts of the species inhibited the growth of lettuce (*Lactuca sativa*) and *Lepidium sativum*, and a novel compound, 13-*epi*-orthosiphol N (**5**), was isolated from the extracts (Fig. 4).[43] The compound inhibited the growth of lettuce and *L. sativum* at concentrations greater than 10 μM. The IC_{50} values of the compound **5** on the growth of lettuce and *L. sativum* were 41 μM and 39 μM, respectively.

1.5. Marsdenia tenacissima

Marsdenia tenacissima, belonging to the Asclepiadaceae family, has been widely used as a traditional household remedy in South Asia.[44,45] This plant exhibits many pharmacological activities such as anti-tumor, anti-diarrheal, anti-inflammatory and immunomodulatory activity.[46,47] Leaf extracts suppressed the growth of *Phleum pretense, Lolium multiflorum* and *Echinochloa crus-galli* in a concentration dependent-manner.[48,49] The extracts were then separated, and two novel steroidal glycosides, 5,6-dihydrogen-11α-*O*-acetyl-12β-*O*-tigloyl-17β-marsdenin (**6**) and 8-dehydroxy-11β-*O*-acetyl-12β-*O*-tigloyl-17β-marsdenin (**7**), and one known steroidal glycoside, 5,6-dihydrogen-11α,12β-di-*O*-tigloyl-17β-marsdenin (**8**), were isolated (Fig. 5).[48,49] The relative configuration of the compound **6** was deduced from the NOESY spectrum. Yield of compound **7** was not sufficient for the NOEST analysis. The compounds suppressed the growth of *Lepidium sativum* at concentrations greater than 0.03 mM, 0.03 mM and 0.1 mM for compounds **6**, **7** and **8**, respectively. Thus, the growth inhibitory activity of compounds **6** and **7** was greater than that of compound **8**.

1.6. Garcinia xanthochymus

Garcinia xanthochymus, belonging to the Clusiaceae family, has been widely used in folk medicine to the treatments for diarrhea, dysentery, and bilious conditions.[50] Extracts suppressed the growth of *Echinochloa crus-galli, Vulpia myuros*, *Lolium multiflorum* and *Phleum pratense*, and a novel compound, garcienone (**9**) was isolated (Fig. 6).[51] The compound suppressed the growth of *Lepidium sativum* at concentrations greater than 10 μM, and its IC_{50} value on the growth of *L. sativum* was 120 μM.

1.7. Wedelia chinensis

Wedelia chinensis (Asteraceae family) has been widely used as a traditional medicine to the treatments for jaundice, diarrhea, kidney dysfunction, fever, and wounds.[52,53] Extracts of the above-ground parts of the species suppressed the growth of *Vulpia myuros, Phleum pretense*, *Lolium multiflorum*, and *Echinochloa crus-galli*. The extracts were separated and a novel compound, wedelienone (**10**), was isolated (Fig. 7).[54] Wedelienone suppressed the growth of *P. pretense* at concentrations greater than 10 μM, and IC_{50} value of wedelienone on the growth of *P. pretense* was 85.1 μM.

1.8. Albizia richardiana and Elaeocarpus floribundus

Two other medicinal plants, *Albizia richardiana* (Fabaceae family) and *Elaeocarpus floribundus* (Elaeocarpaceae family) showed allelopathic activity, and two novel compounds, 3-hydroxy-4-oxo-β-dehydroionol (**11**) and elaeocarpunone (**12**) were isolated, respectively (Fig. 8).[55,56] These compounds suppressed the growth of *Lepidium sativum* at concentrations greater than 0.03 mM and 0.3 mM for compounds **11** and **12**, respectively, and the IC_{50} values on the growth of *L. sativum* were 0.06 mM

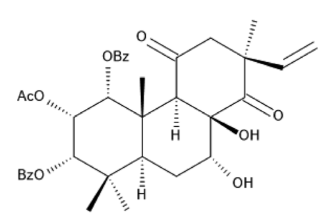

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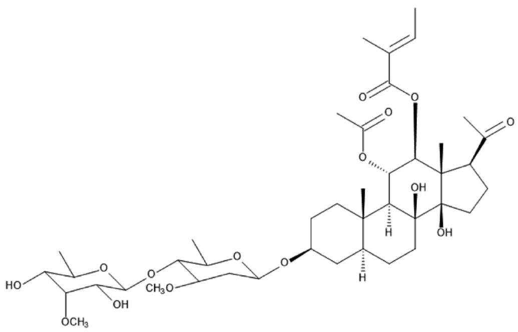
Fig. 4. Allelochemical of *Orthosiphon stamineus.*



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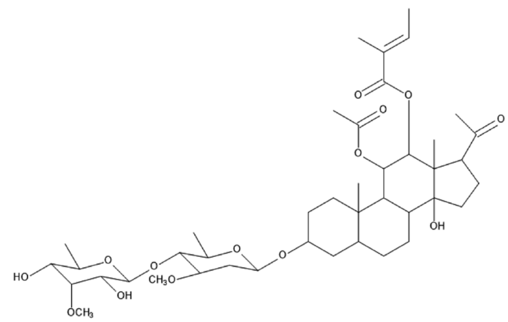

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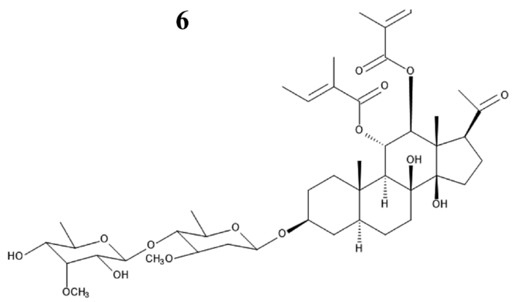

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Fig. 5. Allelochemicals of *Marsdenia tenacissima*.

and 0.5 mM for compounds **11** and **12**, respectively.

2. Allelochemicals involved in the formation of monospecific stands

Some plant species including moss and fern species outcompete other plant species because of high allelopathic activity, and form the monospecific stands, resulting in the elimination of other plant species from the areas.[57–60] We determined the allelopathic activity of such dominant species in the natural ecosystems and identified their allelochemicals.

2.1. Hypnum plumaeforme

The moss species *Hypnum plumaeforme* (syn. *Calohypnum plumiforme*) belongs to the Hypnaceae family and thrives in sunny places from the uplands to lowlands including wet lands in East Asia. The species outcompetes other plant species, and forms large monospecific stands (mats) on soils and rocks.[61,62] These observations suggest that the species possesses high allelopathic activity and releases allelochemicals into its rooting zones. The allelochemicals may suppress the growth of other plant species and contribute to the formation of the monospecific stands. Therefore, the species was selected, and the soil under the *H. plumaeforme* monospecific stands was collected for investigation. Extracts of the soil suppressed the growth of *Phleum pratense*, *Lolium multiflorum*, *Digitaria sanguinalis* and *Echinochloa crus-galli* in a concentration-dependent manner. The extracts were then separated, and two allelochemicals were isolated and identified as momilactone A (**13**) and momilactone B (**14**) (Fig. 9).[63] Compounds **13** and **14** were also identified in the moss tissues and growth medium. The concentration of compounds **13** and **14** was 58.7 and 23.4 μg/g dry weight in the moss tissues respectively, and 4.3 and 6.4 μg/g dry weight in the growth medium, respectively.[63] These results indicate the moss *H. plumaeforme* produces compounds **13** and **14**, and releases them into the growth medium. Considering the inhibitory activity and concentration in the medium, compounds **13** and **14** may contribute to the formation of the monospecific stands of the moss as allelopathic agents.

Compounds **13** and **14** were first isolated from the husks of

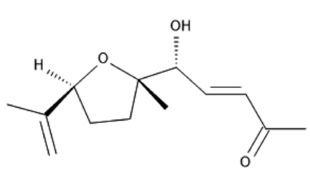

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Fig. 6. Allelochemical of *Garcinia xanthochymus.*

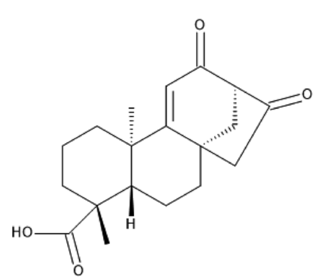

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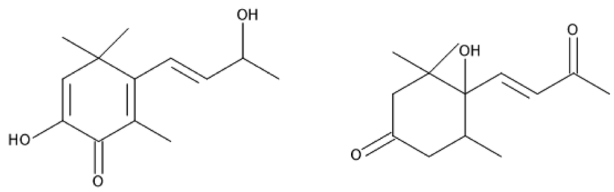
Fig. 7. Allelochemical of *Wedelia chinensis.*

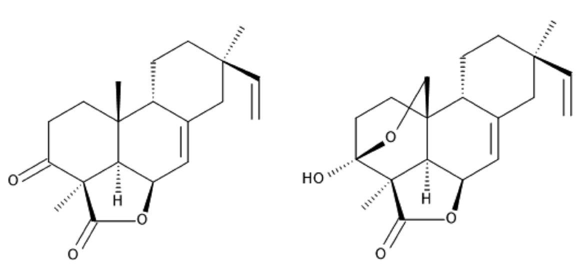


11 12

Fig. 8. Allelochemicals of *Albizia richardiana* and *Elaeocarpus floribundus.*

rice (*Oryza sativa*), and then identified in the rice straws, leaves, roots and root exudate.[64–66] Both compounds have also been identified in several other *Oryza* species such as *Oryza rufipogon, O, burthii, O. brachyatha*, *O. glumaepatula, O. glaberrima, O. meridionalis*, and *O. punctatas*,[67] and the moss species *H. plumaeforme* as described above. The compounds in rice plants showed defense functions against the fungal pathogen attacks, and allelopathy. Rice plants suppress the growth of neighboring plant species through the root exudation of the compounds into their rhizosphere. Pathogen attacks, and biotic and abiotic elicitors induced the production of momilactones through the jasmonic acid signaling pathway and jasmonic acid independent signaling pathway. Rice allelopathy was also induced by jasmonic acid, and the conditions of the nutrient competition with the neighboring plant species.[66,67] Momilactone-deficient rice mutants showed considerable reduction in the tolerance to the pathogen attacks, and lost the allelopathic activity. Momilactones are synthesized form geranylgeranyl diphosphate through cyclization steps. The genes involved in the synthesis, *OsCPS4, OsKSL4*, *CYP99A2, CYP99A3, OsMS1*, and *OsMS2* are located on chromosome 4 in plastids of rice cells.[68,69]

Biotic and abiotic elicitors, and jasmonic acid also induced momilactones in the moss *H. plumaeforme*.[70] In addition, momilactones are synthesized from geranylgeranyl diphosphate in the moss, and some of synthesis-related genes (*CpMS, CpCYP970A14*, *CpDTC1/HpDTC1*. and *CpCYP964A1*) are located on the same chromosome of the moss.[71] Although momilactones have been found in taxonomically quite distinct species, *H. plumaeforme* and *Oryza* species, momilactones may play an important ecological role in the evolution of the moss and *Oryza* because of the presence of a dedicated biosynthetic gene cluster in their genomes.[67,72]



13 14

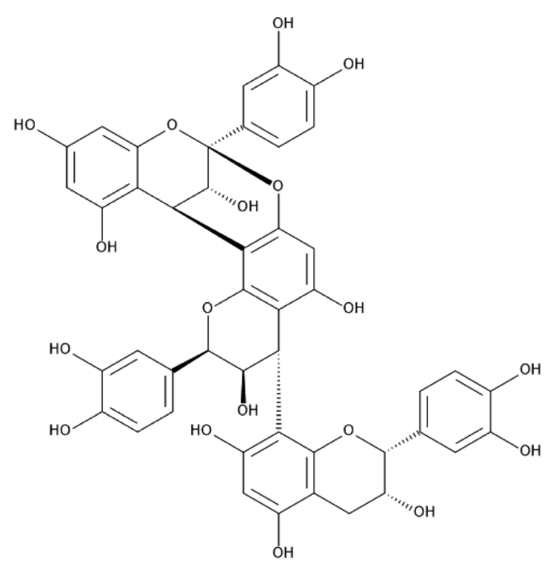
Fig. 9. Allelochemicals of *Hypnum plumaeforme.*

2.2. *Dicranopteris linearis*

The fern species *Dicranopteris linearis* (Gleicheniaceae family) thrives in sunny places, and is one of the most distributed fern species from the temperature to tropical regions of Asia, Europe and Africa. This fern also outcompetes other plant species and often forms large monospecific stands.[73] Extracts of the fern suppressed the growth of *Echinochloa colonum* and *Avena fatua*. The most active allelochemical was isolated from the extracts and identified as cinnamtannin B-1 (**15**) (Fig. 10).[74] Compound **15** was also found in the soil under the monospecific stands of the fern. The concentration of the compound was 4.3 mM and 14.5 mM in the soil collected from the edge of the stands and the soil collected from under the stands, respectively.[74] This finding suggests that the compound may be released into the soil either as an exudate from living plants or through the decomposition process of the plant residues. Compound **15** suppressed the growth of *A. fatua* and *E. colonum* at concentrations greater than 0.2 mM. The concentration of the compound in the soil exceeded the threshold, which caused the growth inhibition. Therefore, the compound may contribute to the formation of monospecific stands of the fern species.

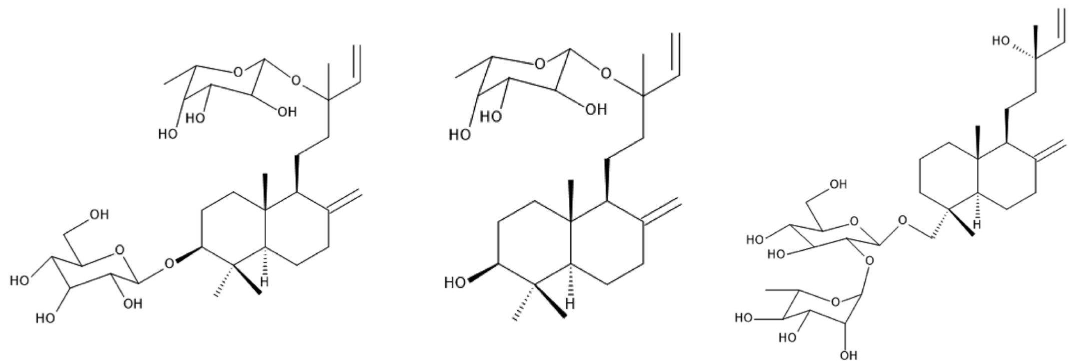
2.3. *Gleichenia japonica*

The fern species, *Gleichenia japonica*, belonging to the Gleicheniaceae family, thrives in sunny places, and is one of the most distributed ferns from South to East Asia. The fern also forms large monospecific stands.[75,76] Extracts of the fern suppressed the growth of *Phleum pretense* and *Lolium multiflorum*. Extracts of its litter obtained from the soil surface under the fern also suppressed the growth of *L. multiflorum* and *Echinochloa crus-galli*. The litter extract was then separated, and two novel



15

Fig. 10. Allelochemical of *Dicranopteris linearis.*



16 **17** **18**

Fig. 11. Allelochemicals of *Gleichenia japonica.*

compounds 3-*O*-β-allopyranosyl-13-*O*-β-fucopyranosyl-3β-hydroxymanool (**16**), and 13-*O*-β-fucopyranosyl-3β-hydroxymanool (**17**), and a known compound 18-*O*-β-L-rhamnopyranosyl-(1→2)-β-D-glucopyranosyl-13-epitorreferol (**18**) were isolated and identified (Fig. 11).[77,78] The IC_{50} values againstthe growth of *E. crus-galli* were 0.72 mM, 0.09 mM and 0.97 mM for compounds **16**, **17** and **18**, respectively. The concentration of those compounds in the soil under the fern species was 4.9 mM, 0.8 mM and 5.7 mM for compounds **16**, **17** and **18**, respectively, indicating that the concentration of these three compounds in the soil exceeded their IC_{50} values.[77,78] Therefore, these compounds may contribute to the allelopathy of *G. japonica*, and be involved in the formation of the monospecific stands of the species.

2.4. *Schumannianthus dichotomus*

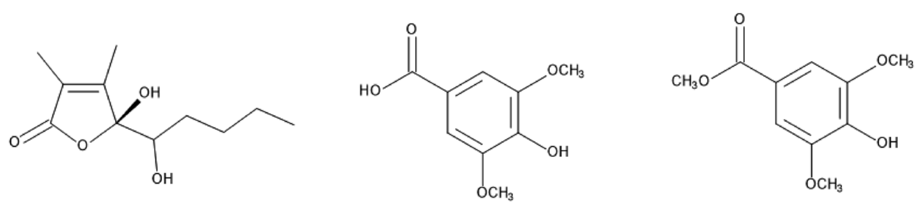
Schumannianthus dichotomus belongs to the Marantaceae family, and is known as cool mat. The plant is cultivated without the application of pesticides because of its significant ability to defend itself against insects and fungi, and is used for making traditional bed mats in Indian continental.[79] Extracts of the species suppressed the growth of *Lolium multiflorum*, *Phleum pretense*, and *Echinochloa crus-galli* in a concentration-dependent manner. A novel compound; schumannione (**19**), and two known compounds; syringic acid (**20**) and methyl syringate (**21**) were isolated form the extracts (Fig. 12).[80,81] These three compounds suppressed the growth of *Lepidium sativum* at concentrations greater than 10 μM, and the IC_{50} values on the growth of *L. sativum* were 109 μM, 61 μM and 32 μM for compounds **19**, **20** and **21**, respectively.

3. Allelochemicals involved in causing sparse understory vegetation

Some tree plant species are characterized by sparse understory vegetation because of their high allelopathic activity.[82] We determined the allelopathic activity of Japanese red pine and *Citrus junos*, and identified the allelochemicals involved in causing the sparse understory vegetation.

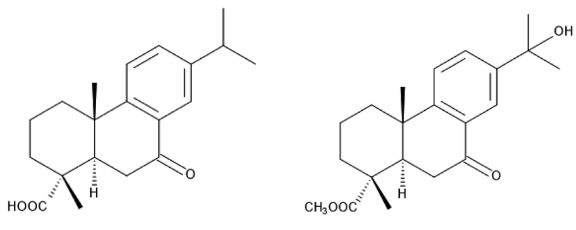
3.1. Japanese red pine

Japanese red pine (*Pinus densiflora*), belonging to the Pinaceae family, is native to Eastern Asia. The species is characterized by sparse understory vegetation even though sunlight at the forest floor levels is sufficient for the growth of other understory plant species.[1] This phenomenon was also written about in *Daigaku-Wakumon* by the Japanese Confucian Kumazawa Banzan in the 17 the century (the Edo period).[83] Soil obtained from the Japanese red pine forest floor showed allelopathic activity against *Lolium multiflorum*, which exists at the margin of the pine forests but not in the forests. Two allelochemicals were isolated from the soil, and characterized as 7-oxodehydroabietic acid (**22**) and 15-hydroxy-7-oxodehydroabietate (**23**) (Fig. 13).[84] These compounds may be formed by the degradation processes of abietic acid, which is abundant in the leaves of the species. The leaves were accumulated on the forest floor by the defoliation and decompose into the soil, where the compounds are generated. The



19 **20** **21**

Fig. 12. Allelochemicals of *Schumannianthus dichotomus.*



22 23

Fig. 13. Allelochemicals of Japanese red pine.

species is evergreen, but drops its old leaves in early spring.[85] The concentrations of compounds **22** and **23** in the soil under the pine trees was 397 μM and 312 μM, respectively. The IC_{50} values of compounds **22** and **23** against the growth of *L. multiflorum* were 34 μM and 137 μM, respectively. Therefore, the concentrations of both compounds in the soil on the pine forest floor were sufficient to cause growth inhibition. In addition, a mixture of both compounds showed a synergic effect on the growth inhibition. The compounds may contribute to the allelopathy of Japanese red pine and suppress the growth of undergrowth plant species of the pine forests, resulting in the establishment of sparse understory vegetation.

3.2. *Citrus junos*

Citrus junos, belonging to the Rutaceae family, is also characterized by sparse undergrowth vegetation compared with other *Citrus* species.[86] When the fruit peel of *C. junos* was incorporated into the soil, the soil, the growth of *Digitaria ciliaris*, *Alopecurus aequalis*, and *Sonchus oleraceus* was supressed.[86,87] The peel extracts also showed allelopathic activity.[88,89] An allelochemical was isolated from the peel extracts, and characterized as an abscisic acid-β-D-glucopyranosyl ester (ABA-GE; **24**) (Fig. 14).[90] The compound suppressed the seedling growth of lettuce and *Arabidopsis thaliana* at concentrations greater than 0.3 μM, and its IC_{50} values on the growth of lettuce and *A. thaliana* were 1.4 μM and 1.8 μM, respectively.[90,91] ABA-β-D-glucosidase was induced in *A. thaliana* seedlings after the application of ABA-GE, suggesting that exogenously applied ABA-GE may be hydrolyzed into abscisic acid (ABA) by apoplastic ABA-β-D-glucosidase in the root cortexes.[91,92] Liberated ABA may be loaded into the xylem through the parenchyma, transported to the target cells, and induce the growth suppression. Soil obtained from several crop fields, pastures, and forests has been reported to contain a significant amount of ABA, which was thought to be released from the roots of the previously existing plant species in those areas.[93]

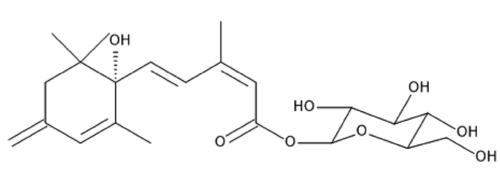


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Fig. 14. Allelochemical of *Citrus junos.*

4. Allelochemicals in the invasive plant species

Allelopathy also contributes to the naturalization of invasive plant species in the introduced ranges. The allelopathic activity of many invasive plant species is high, and some of the invasive plant species eliminate native plant species because of their allelochemicals.[94–96] The allelochemicals of the invasive plant species enable to suppress the regeneration process of the native plant species by inhibiting germination and growth, resulting in the expansion of invasive plant species in the introduced ranges.[97,98] We determined the allelopathic activity of some invasive plant species and identified the allelochemicals involved in the invasion.

4.1. *Pueraria montana*

Pueraria montana (syn. *Pueraria lobata*, *Pueraria thunbergiana*), belonging to the Fabaceae family, is a perennial climbing vine, and has been listed in the top 100 of the world's worst invasive alien species.[99,100] Sterilized quartz sand mixed with the leaf powder of *P. montana* suppressed the germination, and the growth of *Lepidium sativum, Phleum pretense* and *Lolium multiflorum*.[101] Two allelochemicals were isolated from the leaves, and identified as *cis,trans*-xanthoxin (**25**) and *trans,trans*-xanthoxin (**26**)(Fig. 15).[102] Compounds **25** and **26** suppressed the growth of *L. sativum* at concentrations greater than 0.3 μM and 3 μM, respectively. The IC_{50} values on the growth of *L. sativum* were 1.1 μM and 14 μM for compounds **25** and **26**, respectively. Therefore, xanthoxins may contribute to the allelopathy, and play an important role in the invasiveness of *P. montana*. In addition, compound **24** has been converted to ABA in cell free systems.[103–105]

4.2. *Imperata cylindrica*

Imperata cylindrica, belongs to the Poaceae family, and is a C_4 perennial rhizomatous grass species that has also been listed in the top 100 of the world's worst invasive alien species.[106,107] Three allelochemicals, 5-methoxyflavone (**27**), 5,2′-dimethoxyflavone (**28**), and methyl caffeate (**29**), were isolated from the rhizomes extracts of *I. cylindrica* (Fig. 16). These compounds suppressed the growth of *Lepidium sativum* at concentrations greater than 0.08 mM, 0.2 mM and 0.6 mM for compounds **27**, **28** and **29**, respectively, and the IC_{50} values on the growth of *L. sativum* were 0.08 mM, 1.1 mM and 0.23 mM for compounds **27**, **28** and **29**, respectively.[108] These compounds may contribute to

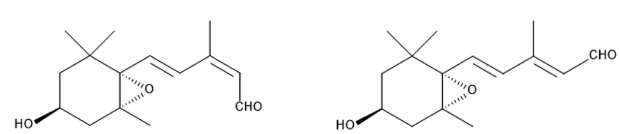

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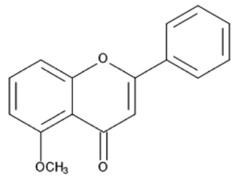
Fig. 15. Allelochemicals of *Pueraria montana.*



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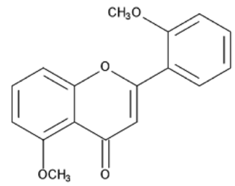

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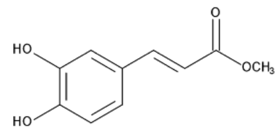

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Fig. 16. Allelochemicals of *Imperata cylindrica.*

the invasiveness of *I. cylindrica*.

4.3. Polygonum chinense

Polygonum chinense (syn. *Persicaria chinensis*), belonging to the Polygonaceae family, is native to South and South East Asia, and forms dense monospecific stands, and is listed a noxious invasive plant species.[109,110] Extracts of the plants suppressed the growth of *Phleum pretense*, *Lolium multiflorum*, and *Echinochloa crus-galli*, and two allelochemicals (3R)-3-hydroxy-β-ionone (**30**) and (3R)-3-hydroxy-7,8-dihydro-β-ionone (**31**), were isolated (Fig. 17).[111] These compounds suppressed the growth of *Lepidium sativum* at concentrations of 0.01 mM and 1 mM for compounds **30** and **31**, respectively, and the IC_{50} values on the growth of *L. sativum* were 0.05 mM and 0.42 mM for compounds **30** and **31**, respectively. The allelopathic activity of compound **30** was 8-fold greater than that of compound **31**.

4.4. Tithonia diversifolia

Tithonia diversifolia belongs to the Asteraceae family, and aggressively expands its population and habitats. The species is known as a noxious weed in agricultural fields, and disturbs native plant communities as an invasive plant species.[112,113] Extracts of *T. diversifolia* leaves suppressed the growth of *Phleum pretense, Lolium multiflorum* and *Echinochloa crus-galli*. Tagitinin C (**32**) was isolated from the extracts (Fig. 18), and inhibited the growth of *P. pretense, L. multiflorum* and *E. crus-galli* at concentrations greater than 0.1–0.3 mM in a concentration-dependent manner.[114] The IC_{50} values of the compound were 0.13 mM, 0.22 mM and 0.13 mM for *P. pretense*, *L. multiflorum* and *E. crus-galli*, respectively. This compound may contribute to the invasiveness of the species.

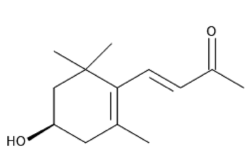
5. Compounds involved in autotoxicity

Some crop plants cannot be successively cultivated for a long time in the same fields because of their autotoxicity. Autotoxicity is a particular type of allelopathy, in which the compounds released by these crop plants suppresses their own growth and productivity.[1] We determined the autotoxic activity of asparagus and kiwifruit, and identified the compounds involved in the autotoxicity.

5.1. Asparagus

Asparagus (*Asparagus officinalis*; Asparagaceae family) is a widely cultivated perennial vegetable that can be harvested for more than 10 years. However, the yield and quality of asparagus decrease after several year' cultivation, known as "asparagus decline".[115,116] Although the senescent asparagus plants were replaced with juvenile asparagus plants in the same fields, the quality and yield of the juvenile asparagus remained low, known as the "asparagus replant problem".[117,118] The "asparagus decline" and "asparagus replant problem" were reported to be caused by a combination of pathogen infection such as by *Fusarium* species and autotoxicity.[119,120] However, the compounds involved in the autotoxicity of asparagus had not been reported.

Extracts of 10-year-asparagus cultivated soils suppressed the growth of asparagus seedlings in a concentration-dependent manner. The extracts were then separated, and a main autotoxic substance was isolated and determined to be *trans*-cinnamic acid (**33**) (Fig. 19).[121] The compound suppressed the growth of asparagus seedlings at concentrations greater than 10 μM, and the IC_{50} value of the compound on the growth of asparagus seedlings was 24.1 μM. The concentration of the compound in the 10-year-asparagus soils was 174 μM, which is enough to suppress the growth the asparagus. Compound **33** was also found in the shoots and roots of the asparagus and its growth medium.[121] Therefore, the compound **33** may be synthesized in the plants, and released into the medium and soil. Compound **33** is isomerized to *cis*-cinnamic acid (**34**) by sunlight and UV-



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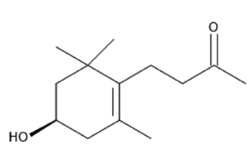

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Fig. 17. Allelochemicals of *Polygonum chinense.*

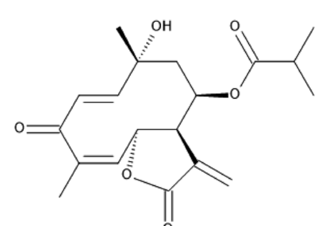

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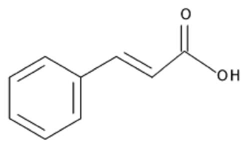
Fig. 18. Allelochemical of *Tithonia diversifolia.*



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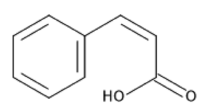

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Fig. 19. Autotoxic substances of asparagus.

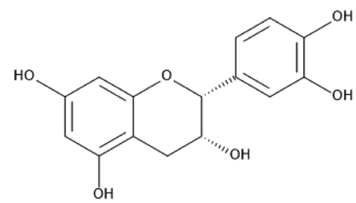

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Fig. 20. Autotoxic substance of kiwifruit.

light,[122,123] and the growth inhibitory activity of compound **34** was 10-fold greater than that of compound **33**.[122] Compound **34** inhibits growth because it disturbs cellular auxin transport and accumulation,[123] and compound **33** suppresses proton transport through plasma membrane H^+-ATPases.[124] Compound **33** in asparagus soil may be isomerized to compound **34** by sunlight during farm work. Therefore, both cinnamic acids may be involved in the autotoxicity of asparagus, and may be in partly responsible for the “asparagus decline” and the “asparagus replant problem”.

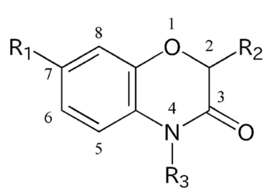
5.2. *Kiwifruit*

Kiwifruit (*Actinidia deliciosa*), belonging to the Actinidiaceae family, is cultivated worldwide. Reductions in the yield of kiwifruit occur in old orchards. When the old kiwifruit plants are replaced with juvenile plants in the same orchards, the growth and productivity of the juvenile plants are often lower than expected. This symptom is typical of the “replant problems” reported in several other fruit trees.[1,125,126] Kiwifruit leaf extracts showed autotoxic activity against the growth of kiwifruit seedlings. The compound involved in the autotoxicity was isolated and identified as (−)-epicatechin (**35**) (Fig. 20).[127] (−)-Epicatechin suppressed the growth of kiwifruit seedlings at concentrations greater than 3 mM, and the IC_{50} values of the compound on the growth of kiwifruit was 7.6 mM. Therefore, compound **35** may be involved in the autotoxicity of kiwifruit and be responsible for the “replant problems”.

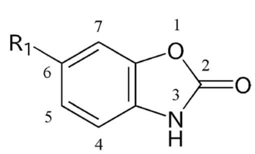
6. Allelopathic activity of benzoxazinones and related compounds

Several benzoxazinones have been found in some Poaceae species such as wheat, rye, and maize.[128] Benzoxazinones and their precursor hydroxamic acids showed plant defense functions against pathogenic fungi and herbivorous insects.[128–131] These compounds and their degradation products are also involved in the allelopathy.[131–135]

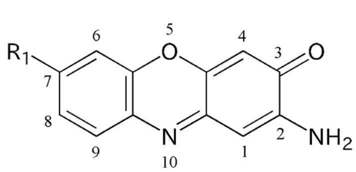
The main benzoxazinone of wheat and maize is 2,4-dihydroxy-7-methoxy-2*H*-1,4-benzoxazin-3(4*H*)-one (DIMBOA), while that of rye is the dimethoxylated analogue, 2,4-dihydroxy-2*H*-1,4-benzoxazin-3(4*H*)-one (DIBOA). DIMBOA and DIBOA exist in plant tissues as inactive glucoside esters, DIMBOA-*β*-*O*-D-glucopyranoside (DIMBOA-glucose) and DIBOA-*β*-*O*-D-glucopyranoside (DIBOA-glucose), respectively.[128,136,137] These glucosides are rapidly converted to the aglycones, DIMBOA and DIBOA by *β*-glucosidase upon plant cell disruptions, and show defense functions against attacks by fungal pathogens and herbivorous insects. DIMBOA and DIBOA are further degraded to MBOA and BOA, respectively.[128,137] These two degradation products, MBOA and BOA, have been found in the plant tissues and showed allelopathic activity.[134–137]



Benzoxazinone	Abbreviation	R_1	R_2	R_3
(2*H*)-1,4-Benzoxazin-3(4*H*)-one	D-HBOA	H	H	H
4-Hydroxy-(2*H*)-1,4-benzoxazin-3(4*H*)-one	D-DIBOA	H	H	OH
2-Hydroxy-(2*H*)-1,4-benzoxazin-3(4*H*)-one	HBOA	H	OH	H
2,4-Dihydroxy-(2*H*)-1,4-benzoxazin-3(4*H*)-one	DIBOA	H	OH	OH
7-Methoxy-(2*H*)-1,4-benzoxazin-3(4*H*)-one	D-HMBOA	OCH_3	H	H
4-Hydroxy-7-methoxy-(2*H*)-1,4-benzoxazin-3(4*H*)-one	D-DIMBOA	OCH_3	H	OH
2-Hydroxy-7-methoxy-(2*H*)-1,4-benzoxazin-3(4*H*)-one	HMBOA	OCH_3	OH	H
2,4-Dihydroxy-7-methoxy-(2*H*)-1,4-benzoxazin-3(4*H*)-one	DIMBOA	OCH_3	OH	OH



Benzoxazolinone	Abbreviation	R_1
Benzoxazolin-2(3*H*)-one	BOA	H
6-Methoxy-benzoxazolin-2(3*H*)-one	MBOA	OCH_3



Aminophenoxazinone	Abbreviation	R_1
2-Amino-phenoxazin-3-one	APO	H
2-Amino-7-hydroxyphenoxazine-3-one	AHPO	OH
2-Amino-7-methoxyphenoxazine-3-one	AMPO	OCH_3

Fig. 21. Benzoxazinones and related compounds.

After harvesting, the straw and roots of the plants are sometimes left in the fields. MBOA and BOA are produced during the degradation process of these straw and roots, and released into the field soil.[136–138] MBOA and BOA suppressed the germination and growth of several plant species, and the gibberellin-induced α-amylase activity.[139–143] α-Amylase triggers starch degradation in seed reserves, and enabling the seeds to germinate and grow.[144,145] Suppression of α-amylase induction by these compounds is one of the cause of the inhibition of germination and growth. Aminophenoxazinone (AMPO, AHPO and APO) were thought to be the final degradation products of DIMBOA and DIBOA because those compounds were found in the soil (Fig. 21).[136,137]

Natural benzoxazinones (DIMBOA and DIBOA), degradation products (MBOA, BOA, APO, AHPO and AMPO), and synthetic compounds (D-HBOA, D-DIBOA, HBOA, D-HMBOA, D-DIMBOA and HMBOA) were evaluated for their growth inhibitory and α-amylase suppression activity (Fig. 21). The IC_{50} values against the growth of *Lepidium sativum* were 0.13 mM, 0.15 mM, 0.16 mM, 0.19 mM, 0.47 mM, 0.54 mM, 0.62 mM, 0.81 mM, and 0.82 mM for DIMBOA, D-DIMBOA, DIBOA, D-DIBOA, MBOA, APO, BOA, D-HMBOA, and D-HBOA, respectively. The IC_{50} values againstα-amylase suppression activity were 0.07 mM, 0.09 mM, 0.11 mM, 0.14 mM, 0.32 mM, 0.38 mM, 0.61 mM, 0.65 mM, and 0.75 mM for DIMBOA, D-DIMBOA, DIBOA, D-DIBOA, MBOA, APO, BOA, D-HMBOA, and D-HBOA, respectively. The IC_{50} values against the growth of *L. sativum* and α-amylase suppression activity of HBOA, HMBOA, AHPO, and AMPO could not be determined because of their low activity. The inhibitory activity of these compounds was classified into three groups, high active group (DIMBOA, D-DIMBOA, DIBOA, and D-DIBOA), moderate active group (MBOA, APO, BOA, D-HMBOA, and D-HBOA), and low active group (HBOA, HMBOA, AHPO, and AMPO).[146] The structure–activity of these compounds suggests that the compounds with the benzoxazinone skeleton are the most active structure. A hydroxyl group at position N-4 on the benzoxazinone skeleton is essential for the inhibitory activity, whereas a hydroxyl group at position C-2 on the benzoxazinone skeleton may not affect the inhibitory activity.

Conclusion

The allelopathic activity of some medicinal plants was high, and several potent allelochemicals including novel compounds were isolated and identified. The allelopathic activity of the moss *Hypnum plumaeforme*, and the fern species *Dicranopteris linearis* and *Gleichenia japonica*, which form monospecific stands, were high, and the concentrations of the identified allelochemicals in the soil under their monospecific stands were sufficient levels to cause the growth inhibition. Therefore, those allelochemicals may contribute to forming the monospecific stands. Japanese red pine is characterized by sparse understory vegetation even though sunlight at the forest floor level is sufficient levels for the growth of other understory plant species. The allelochemicals found in the soil under the Japanese red pine trees may also contribute to causing the sparse understory vegetation. The invasive plants, *Pueraria montana, Imperata cylindrica, Polygonum chinense* and *Tithonia diversifolia* showed high allelopathic activity, and the identified allelochemicals may contribute to the invasiveness and naturalization of these species in the introduced ranges. Asparagus and kiwifruit show autotoxicity and cannot be successively cultivated for a long time in the same field soil. The identified compounds from the soil and/or plants may contribute to their autotoxicity. These investigations suggest the allelopathy and allelochemicals may be involved in several ecological aspects in the natural ecosystems.

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