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Table: 1, Figs : 9

Herbicidal activities of allelopathic and other compounds from *Oryza sativa*

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CONTENTS

ABSTRACT

We have reviewed the natural compounds present in rice (*Oryza sativa* L) plant. Several classes of compounds (diterpenoids, steroids and steroidal glycosides, aliphatic, anthracene derivatives, flavonoids and other classes of compounds) have been reported from the hulls and other plant parts of this genus. Many compounds identified from rice hulls, rice leaves and stems possess herbicidal activities. The rice hull is most abundant agricultural product in rice growing areas, possessing phytoalexin substances that could serve as natural herbicides to suppress weeds. Such information indicates that the inhibitory substances from rice hulls could potentially control weeds in an environmentally acceptable and sustainable manner.

Keywords: Allelochemicals, allelopathic natural substances, herbicidal agents, *Oryza sativa*, rice composition.

1. INTRODUCTION

Rice (*Oryza sativa* L.) is the principal cereal food in Asia and in many developing Countries (31,32). It has two types: white and colored hulled, with the white hull being the most common (85%). The compounds present in the seed coat (hull) influences the germination of rice (11,12,29,36). Momilactones A, B and C (diterpenoids)

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from the rice hulls inhibited the germination and growth of rice (39,40,72,76). They were later found in rice leaves and straw as phytoalexins (9,46). A putative growth inhibitor was isolated from rice root exudates and identified as momilactone B (43) and it was recently reported that rice seedlings release momilactone B into the environment (44). The methanol extracts (61) and *C*-glycosylflavonoid from rice hulls have antioxidant activity (62). The growth inhibitor sakuranetin, a flavonone phytoalexin from ultraviolet-irradiated rice leaves, has also been isolated (47). Hull extracts from 91 rice cultivars (*O. sativa* L.) were used to determine their allelopathic potential on seed germination and seedling growth of barnyardgrass (*Echinochloa crus-galli* P. Beauv. var. *oryzicola* Ohwi) (2).

The use of rice allelopathy for weed control is a new technology in agronomy. A laboratory bioassay using water extracts was conducted to determine the allelopathic potential of rice body parts on seed germination and growth of barnyardgrass (*E. crus-galli* P. Beauv. var. *oryzicola* Ohwi) and to develop a rapid and simple method for selecting allelopathic rice varieties (13). Song *et. al*. (70) reported that allelochemicals from root exudates of rice varieties at various growth stages were different and caused growth inhibition in barnyardgrass. These compounds may be used to control barnyardgrass, to reduce labour cost and use of synthetic agricultural chemicals.

Momilactone B was released into the neighboring environment from rice throughout its life cycle. The rate of momilactone B released from the rice increased until flowering initiation and then decreased. The release rate of momilactone B at onset of flowering was 2. 1 μg $plant^{-1}$ d^{-1} (44). On average, a single rice plant released about 100 μg of momilactone B into the neighboring environment over its life cycle. Since momilactone B is a growth inhibitor, it may serve as an allelochemical to inhibit the germination and growth of neighboring plants (45).

Rice hull ash (RHA) is a by-product of rice milling and is composed primarily of five bacteriocins (nisin, pediocin, leucocin, lactocin, and enterocin) with *Lactobacillus plantarum* showing the inhibitory effects of lactocin, enterocin and nisin. (37). Allelopathic potential and quantification of momilactone A, B from rice hull extracts and its inhibitory bioactivity on paddy field weeds has been reported (18). The use of synthetic herbicides is increasing world wide, but little information is available on the development of natural herbicides. It has been suggested that rice hulls, the most abundant agricultural products, could serve as natural herbicides by inhibiting seed germination and the growth of weeds. The use of agricultural residues could have implications in weed management because farmers in Korea have always left rice hulls in the field after harvesting. The inhibitory substances contained in rice hulls could be used as natural herbicides to control weeds. For example, cinmethylin and compounds from rice hulls have herbicidal activities.

Potentials for exploiting the allelopathy to enhance crop protection was reported by Einhelling *et al*. (30). The allelochemicals are released from allelopathic rice seedlings (51) and these compounds at low concentrations could inhibit the growth of weeds *E. crus-galli* and *Cyperus difformis* associated with rice. Especially, mixtures of compounds had stronger inhibitory activity than did individual compounds. Peters (60) reported the complex metabolic network underlying diterpenoid phytoalexin biosynthesis in rice and other cereal crop plants.

This paper reviews all compounds reported from rice hulls, leaves and stems. The compounds with inhibitory activity could have potential as natural herbicide for weed management.

2. ALLELOCHEMICALS PRESENT IN RICE PLANT

There are 62 allelochemicals in rice plant (Table 1). These belong to various groups viz., Diterpenoids, Steroids and Steroidal Glycosides, Aliphatic, Anthracene derivatives, Flavonoids and other classes.

Table 1. Allelochemicals present in rice plant

Compounds
Resistant rice stain
Phytocassane A to E (**13**-**17**)
Alleopathic rice accession
3-Isopropyl-5-acetoxycyclohexene-2-one-1 (**62**)
Rice husks, leaves, straw
Momilactone A (**1**)
Rice husks, leaves, straw, root and rice seedlings, alleopathic rice accession Momilactone B (**2**) **Rice husks** Momilactone C (**3**), Ineketone (**4**), Dehydrovomifoliol (**5**), Oryzalexin A to F,S (**6**-**12**), Orizaterpenol (**18**), Orizaterpenoid (**19**), Oryzasesterpenolide (**20**), Stigmastanol-3*β*-p-glyceroxydihydrocoumaroate (**21**), Stigmastanol-3*β*-p-butanoxydihydrocoumaroate (**22**), Lanast-7, 9 (11)-dien-3*α*, 15*α*-diol-3*α*-D-glucofuranoside (**23**), Sativasterolide (**24**), Stigmast-5-en-3α, 26-diol (**25**), Sativalanosteronylglycoside (**26**), 14-methyl stigmast-9(11)-en-3*α*-ol-3*β*-D-glucopyranoside (**27**) , Cholest-11-en-3*β*, 6*β*, 7*α*, 22*β*-tetraol-24-one-3*β*-palmitoleate (**28**), *β*-sitosteryl-3*β*-D-glucopyranosyl-6'-linoleiate (**29**), Orizalanasterolide A (**30**), Orizalanasterolide B (**31**), *β*-sitosterol-3-*O*-*β*-D-glucoside (**32**), *β*-sitosterol (**33**), 1-methoxyanthracen-2-ol (**34**), 1-hydroxy-2'',3'',4''-trihydroxy-5''-(hydroxymethyl)tetrahydro-2*H*-pyran-1-yloxy)anthracen-2-yl 3',7'-dimethyloctanoate (**35**), 1-hydroxy--2'',3'',4''-trihydroxy-5''-(hydroxymethyl) etrahydro-2*H*-pyran-1-yloxy)anthracen-2-yl-3',7',11',15',19'-pentamethyltricosanoate (**36**), 1-tetratriacontanol (**37**), *n*-octacos-9-en-yl propionate (**38**), 8'-cyclohexyl carboxylate-5'-hydroxy methylene cyclohexyl carboxylate-7-(cyclohexyl)-*n*-heptane-9-aldehyde (**39**), *n*-hentriacont-25-en-5*α*-ol (**40**), *n*-hexetriacont-9, 26-dien-8*α*, 11*β*, 23*α*-triol (**41**), *n*-tetracont-15*α*-ol (**42**), *n*-tritetracontan-5*α*-ol (**43**), *n*-hexacosanoic acid (**44**), *n*-hexadecanoic acid (**45**), Octacoasanoic acid (**46**), Isovitexin (**47**), 5,7,4'-trihydroxy-3',5'-dimethoxyflavone (**48**), Sakuranetin (**49**), Orizaterpenyl benzoate (**50**), Orizanor-diterpenyl benzoate (**51**), Orizaditerpenyl benzoate (**52**), 3,7-dimethyl-*n*-octan-1-yl benzoate (**53**), Hentriacontane (**54**), Dicyclohexanyl orizane (**55**), 4-hydroxymethylene-7-(9, 9, 13-trimethylcyclohexyl)-heptanyl-3', 7', 7'-trimethyl cyclohex-2', 4'-dien-1'-oate (**56**), 1-(n-hexadec-7-enoxy)-6-(n-octadecanoxy)-β-D-glucopyranoside (**57**), (Z)-12-hydroxy-9-octadecenoic acid-12-β-D-glucopyranoside (**58**), Oryzatriacontolide (**59**), Tritriaconta-4, 12-diene (**60**), 1-phenyl-2-hydroxy-3, 7-dimethyl-11-aldehydic-tetradecane-2-*β*-D-glucopyranoside (**61**),

3. DITERPENOIDS

Diterpenes are known to play diverse roles in plants (66). A series of closely related phytoalexins have been reported from rice (75). These compounds, the momilactone A [**1**], and momilactone B [**2**], are produced in response to the same organism as oryzalexins above or in response to ultraviolet light (8,9,75). The growthregulating substances momilactones A [**1**] and B [**2**] were reported from the seed husk of *O. sativa*, which inhibit the root growth of rice (39, 40). Momilactone C [**3**] was reported as a minor constituent from the rice husks (76). Three more growth and germination inhibitors were identified in rice husk (*O. sativa* L. cv Koshihikari), ineketone [**4**], dehydrovomifoliol [**5**] momilactone-C [**3**] and in addition to the previously known momilactones A [**1**] and B [**2**], especially the latter, inhibits the germination of lettuce seeds and growth of roots of rice (40). To establish the functional groups in the momilactones necessary for activity, several derivatives were prepared and assayed for inhibitory activity (40). It was found that all derivatives which inhibited lettuce seed germination had activity against the growth of rice roots. The inhibitory activity was strongest with 3-dihydromomilactone-A and acetyl momilactone B, while reduction of the vinyl group on ring C diminished the activity. The inhibitory activity of ineketone [**4**] and dehydrovomifoliol [**5**], toward the germination of lettuce seeds was less effective than as the momilactones and momilactone derivatives (40).

The functions of momilactones A and B as a phytoalexin have been extensively studied and they play an important role in rice defence system against pathogens (1,5,65,71,73). Although the growth inhibitory activity of momilactone B was much greater than momilactone A (40,72), but the function of momilactone B is still not known.

The inhibitory activities of momilactone B against the germination and growth of several plant species have been reported. For example, a solution of 5 μM of momilactone B inhibited the germination of *Amaranthus lividus* by 50 % and a 50 μM solution of momilactone B inhibited root and shoot growth of *Digitaria sanguinalis* and seed germination of *Poa annua* by more than 50 % (57). These compounds also inhibited the root and hypocotyl growth of cress seedlings at concentrations greater than 3 μM. The concentrations required for 30 % inhibition of cress roots and hypocotyls were 12 and 16 μM, respectively, and 36 and 41 μM, for 50 % inhibition of cress roots and hypocotyls, respectively (45,48). Judging from its inhibitory activity, momilactone B was considered to be a candidate for a rice allelochemical (63). Kong *et al.* (51) isolated and identified momilactone B (**2**) also from an allelopathic rice accession PI312777.

The diterpene compounds (momilactones A [**1**] and B [**2**]) from rice hulls showed potent inhibitory activity against duckweed (*L. paucicostata Hegelm 381*). In a germination assay of three weed species: *Leptochloa chinensis* L., *Amaranthus retroflexus* L. and *C. difformis* L. in culture tubes (GACT), the higher the concentration of compounds, the greater was the inhibitory effects on germination and fresh weight (14).

Momilactone A and B had high inhibitory activity against duckweed. Momilactone B was more active than momilactone A whereas the other compounds had lower or no inhibitory activity. Momilactone A and B at 10, 3.3, and 1 ppm concentrations reduced the chlorophyll content (85.8, 52.3, and 27.0%, and 98.3, 91.9, and 33.9%, respectively). At 100 and 33 ppm concentrations, momilactone A reduced the chlorophyll content by 98.9 and 95.6% respectively (14). Increasing concentrations of test compounds were correlated with increased inhibitory effects on germination and growth, with 100% inhibition at 20 ppm concentrations (14).

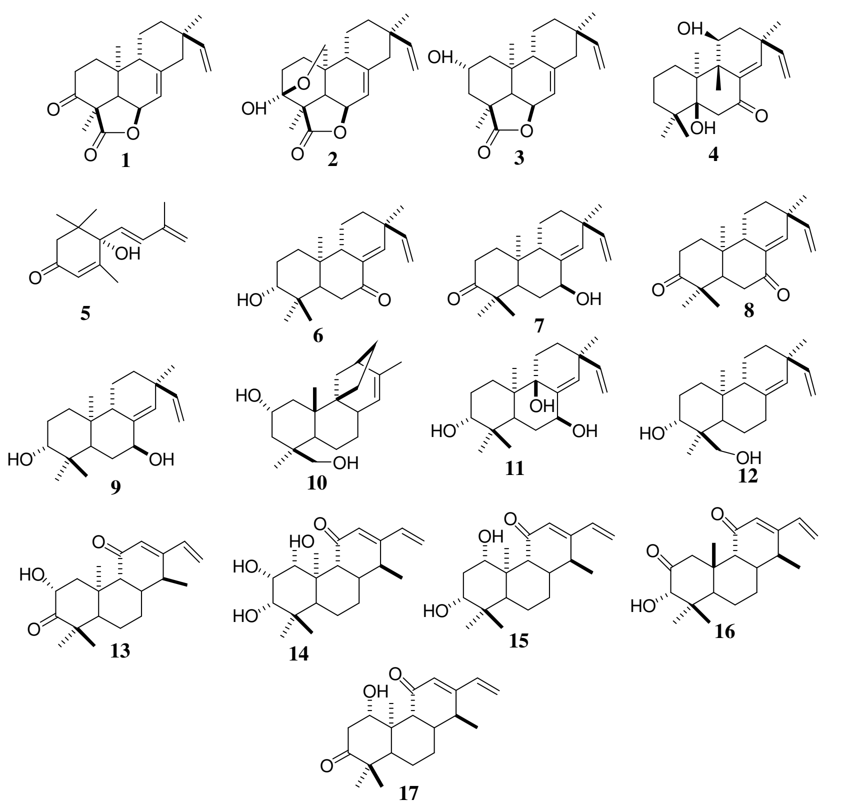


Figure 1. Terpenoids

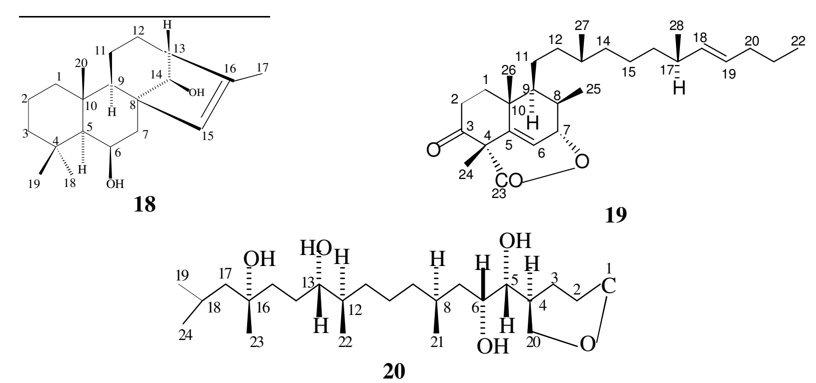


Figure 2. Terpenoids

There are many phytoalexins in rice plant (3,4), first a group of four compounds were isolated from *Magneporthe grisea* rice leaves, where the first, oryzalexin A [**6**] was suggested as pimarane diterpenoid (3). Further spectroscopic analysis showed that orizalexin A was configured with enantio-stereochemistry and thus, was an *ent*-pimarane diterpenoid (52). Oryzalexins B [**7**] and C [**8**] in *M. grisea* rice leaves were also identified as ent-pimarane diterpenoids (4, 53); likewise was oryzalexin-D [**9**] (69). All these four oryzalexins have been classified as rice phytoalexins. However, their production is localized in the rice blast disease lesions (4), rather than being systemic, which is consistent with the observed direct antifungal activity of these compounds, and further supports their physiologically role in plant disease resistance.

The compound was found to be the syn-stemarane diterpenoid oryzalexin S [**10**], which was classified as phytoalexin since it exhibited potent antifungal activity on *M. grisea* (48,74). Later, detailed fractionation of UV-irradiated leaves led to the identification of two more ent-pimarane diterpenoid phytoalexins, oryzalexins E [**11**] and F [**12**] (41,42).

Four antifungal natural products as phytoalexins were reported from *M. grisea* infected rice leaves or *Rhizoctonia solani* infected rice stems. These four compounds were initially identified as cassane diterpenoids: phytocassane A-D [**13**-**16**]. Interestingly, production of these compounds was not only induced by *M. grisea* infection, but seemed to correlate with the effectiveness of defensive response, as these phytoalexins accumulated to higher levels in *M. grisea* resistant rice stains than in susceptible ones. In addition, these compounds also exhibited antibiotic activity against *R. solanii,* suggesting that these and other identified rice phytoalexins, will prove to be broadly effective antifungal agents. An additional cassane diterpenoid was later identified as phytocassane E, [**17**] (49,50).

Chung *et*. *al*. (15) identified two compounds from rice hulls named orizaterpenol [**18]** and orizaterpenoid [**19]** including momilactones. Diterpenoids have been reported to show phytoalexins (7). Orizaterpenol [**18**] and orizaterpenoid [**19]** did not show any herbicidal activity (16). Further Chung *et al*. (17) isolated one more terpenoid named oryzasesterpenolide [**20**] and did not show any herbicidal activity.

4. STEROIDS AND STEROIDAL GLYCOSIDES

Although steroids related compounds are considered inactive plant constituents, but several compounds have pronounced physiological activity. Although phytosterols and triterpenoid compounds have been reported to possess growth inhibiting actvity (27,66). Toxic triterpenoids causes the poisoning of livestock (56). Ursolic acid plays a role in the allelopathic effects of several other types of secondary metabolites in sandhill vegetation. Dihydrocinnamic acid (derived from ceratiolin) from *Ceratiola ericoides* (Empetraceae), a series of monoterpenes including camphor, myrtenal, borneol, and carvone from *conradina canescens* (Lamiaceae) and the monoterpenes menthofuran, epievodone, and calaminthone from *Calamintha ashei* (Lamiaceae) all displayed biological activity. However, when these compounds were dissolved in a saturated aqueous solution of ursolic acid, allelopathic activity was greatly increased (8,33,34).

Three compounds stigmastanol-3*β*-p-glyceroxydihydrocoumaroate [**21**], stigmastanol-3*β*-p-butanoxydihydrocoumaroate [**22**], lanast-7, 9 (11)-dien-3*α*, 15*α*-diol-3*α*-D-glucofuranoside [**23**], identified from the methanol extract of hulls of *O. sativa* have herbicidal activity (19). Lanast-7, 9(11)-dien-3*α*,15*α*-diol-3*α*-D-glucofuranoside [**23**] was very inhibitory against duckweed (*L. paucicostata*), whereas, stigmastanol-3*β*-p-butanoxydihydrocoumaroate [**22**] had lower activity. Compounds [**22**] and [**23**] at 100 and 33 ppm concentrations reduced the chlorophyll content by 26.5, 16.6%**;** 79.4, 38.3%**;** respectively. At 10 and 3.3 ppm concentration compound [**23**] reduced the chlorophyll content by 18.9 and 9.8% respectively, while compound [**22**] did not decrease the chlorophyll content at 10 and 3.3 ppm concentrations (19). These results suggested that the allelopathic compounds in rice hulls specially, lanast-7, 9(11)-dien-3*α*,15*α*-diol-3*α*-D-glucofuranoside [**23**], proved to be potential natural herbicides.

Two compounds sativasterolide [**24**] and stigmast-5-en-3α, 26-diol [**25**], were reported from the methanol extract of rice hulls (20). Compound [**24**] had strong inhibition to the seed germination, growth of *Raphanus* at 500 ppm. At 200 ppm, shoot and root growth were reduced by 48.1% to 53.3%, respectively. It appears that the acetone dilution may contain phytotoxic substances that cause inhibition in radish seedlings growth.

Numerous rice allelochemicals belonging to chemical classes of resorcinol, flavone, hydroxamic acid, phenols, phenolic acids, indoles, terpenic acid, fatty acids, as well as momilactones (A and B) are responsible for rice's allelopathic activity (10,14,20,70). Allelochemicals exuded from the root of rice varieties at different growth stages exhibited variation and caused inhibition effects of this compound on barnyardgrass (70). These compounds may be used to reduce the weed interference and to reduce the dependency on synthetic agricultural chemicals, labour cost and enviromental contamination. The inhibitory effects of these compounds on *Raphanus* seeds were significantly inhibited at 100 ppm. However, decreased concentration at 50 ppm, growth of shoot and root length were slighly stimulated.

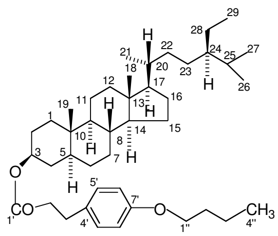
Chung *et al.* (24) identified one steroid glucoside as sativalanosteronylglycoside [**26**] from the rice hulls. Its activity compound is not reported in literature due to its little amount in rice hulls.

Two compounds, 14-methyl stigmast-9(11)-en-3*α*-ol-3*β*-D-glucopyranoside [**27**], cholest-11-en-3*β*, 6*β*, 7*α*, 22*β*-tetraol-24-one-3*β*-palmitoleate [**28**], along with one known compound *β*-sitosteryl-3*β*-D-glucopyranosyl-6'-linoleiate [**29**] were reported from the methanolic extract of hulls (25). Rice cultivated by water logging is susceptible to vigorous growth of weeds and algae. Algae growth reduces the water temperature and inhibits the photosynthesis by blocking the light. The growth inhibitory activity of the compounds [**27**-**29**] against blue-green algae (*Microcystis aeruginosa* UTEX # 2388) and duckweed (*L. paucicostata*) with the standard of momilactones A and B were reported (25).

The percentage of *M. aeruginosa* growth inhibition by compounds [**27**] and [**28**] was similar to that by momilactone A at 30 and 300 µM. Momilactone A inhibited growth the blue-green algae by 98.9 %, 98.1 %, 32.6 %, and 9.0 % at the concentrations of 300, 30, 3, and 0.3 µM, respectively. Therefore, momilactone A had a relatively higher inhibitory activity against *M. aeruginosa* than Momilactone B. On the other hand, momilactone B and compound [**29**] reduced inhibition of *M. aeruginosa* growth (25).

In *Lemna* assay, momilactone B showed the strongest inhibitory effects. At the concentrations of 300, 30, 3, and 0. 3 μM, momilactone B reduced the chlorophyll content (*L. paucicostata*) by 91.5 %, 86.3 %, 74.9 %, and 7.3 %, respectively. Momilactone A and compound [**28**] showed intermediate inhibition activity at 300 μM, whereas compound [**27**] did not inhibit *L. paucicostata* growth (25).

Momilactone B had a selective bioactivity with a higher inhibition of *L. paucicostata* than *M. aeruginosa*. In contrast, compound [**27**] showed a significant bioactivity against *M. aeruginosa*. Compound [**28**] and momilactone A had a slightly higher bioactivity against *M. aeuruginosa* and an intermediate inhibitory activity against *Lemna*. Compound [**29**] did not inhibit the growth of *M. aeruginosa* and *L. paucicostata* within the range of the tested concentrations.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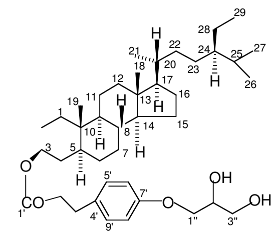
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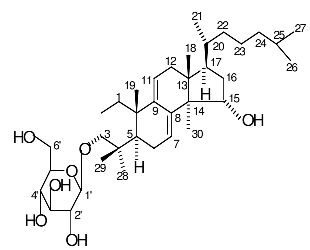
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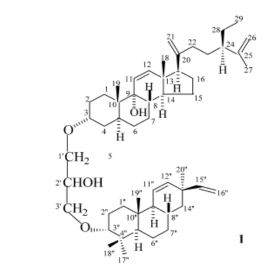
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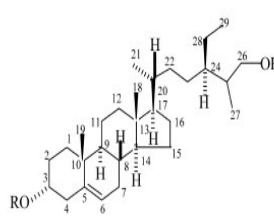
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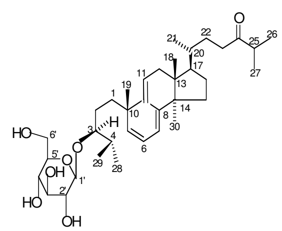
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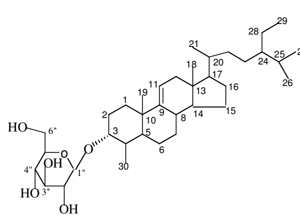
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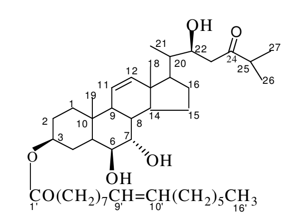
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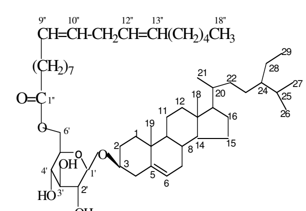
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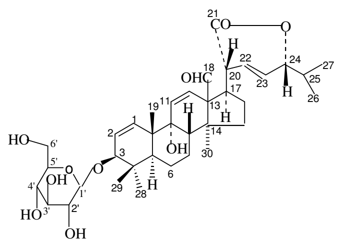
Figure 3. Steroids and Steroidal Glycosides



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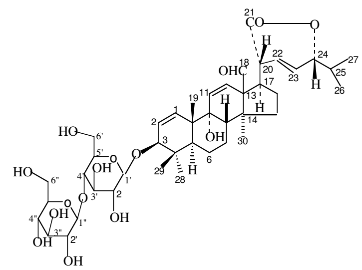

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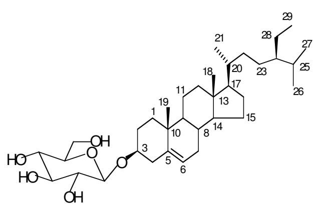

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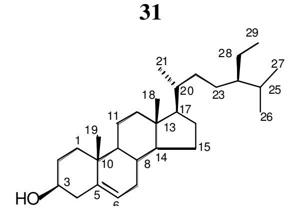

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Figure 4. Steroids and Steroidal Glycosides

The rice hulls contain many bioactive compounds such as phenols, long chain fatty acid, and benzene derivatives (70). In particular, momilactone A and B isolated from the rice husk suppressed the germination of lettuce seeds and the root growth of rice (39). Our results of momilactone A and B are similar to Chung *et al* (14,18). In addition, compounds [**27**] and [**28**] isolated from the rice hulls have a strong potential as algaecide and herbicide.

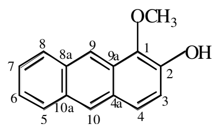
Four compounds [**1**,**2**, **27**-**28,**] displayed some species selectivity on the growth inhibition of *M*. *aeruginosa* and *L. paucicostata*. Further investigations are needed to evaluate the bioactivity of compounds in rice hulls on various plants. Compounds [**27**] and [**28**] exhibited excellent bioactivities against algae and duckweed, and thus can be used to reduce their interferences in water logged rice fields in a more environment-friendly way.

Two compounds orizalanasterolide A [**30**] and orizalanasterolide B (**31**) have been reported from the rice hulls (26), while the activities of these compounds are not available in literature due to their low quantity in rice hulls.

β-sitosterol-3-*O*-*β*-D-glucoside (14) [**32]** was identified for the first time in rice hulls. This compound showed 19.4%, 20.5%, and 21.3% inhibitory activity at 10, 33, and 100 ppm respectively, based on chlorophyll reduction (*L.paucicostata*), and *β*-sitosterol [**33]** did not show any herbicidal activity at concentrations of 10 and 100 ppm.

5. ANTHRACENE DERIVATIVES

Anthraquinones are toxic and known to be involved in biological interactions (28,35). Several types of woods that contain anthraquinone and related compounds are inhibiting activity (64,67).



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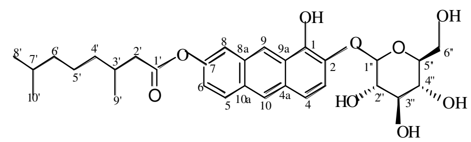

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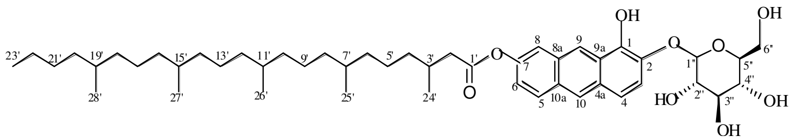

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Figure 5. Anthracene derivatives

Three compounds 1-methoxyanthracen-2-ol [**34]**, 1-hydroxy-2'',3'',4''-trihydroxy-5''-(hydroxymethyl)tetrahydro-2*H*-pyran-1-yloxy)anthracen-2-yl 3',7'-dimethyloctanoate [**35**] and 1-hydroxy--2'',3'',4''-trihydroxy-5''-(hydroxymethyl) etrahydro-2*H*-pyran-1-yloxy) anthracen-2-yl-3',7',11',15',19'-pentamethyltricosanoate [**36**] have been reported from the rice hulls (22). Compound [**34]** exhibited the most inhibitory with germination and growth of radish being reduced by 27 to 48%, and dry weight of shoot and root by 50 to 52%, respectively. The inhibitory activities of compounds [**35**, **36**] was weaker than compound [**34**]. These results are similar to (59), who observed that anthraquinoes, emodin, physcion, showed inhibitory activity against the seedling growth of lettuce, green amaranth and timothy grass bioassay at 50 ppm and 100 ppm (59). The toxicity of all these compounds was proportional to the concentrations and generally correlated with inhibitory effects on germination, growth of shoot, root and total dry weight. Furthermore, presence of anthraquinone, a derivative of anthrancene naturally occurring in some plants has growth inhibitory activities (55,59). At present, exploitation and utilization of allelopathy for controlling weeds could be either through directly using natural allelopathic interactions or by using the secondary compounds (allelochemicals) as natural herbicides. Allelochemicals are present in all types of plant tissues and are released into soil rhizosphere by a variety of mechanisms, including decomposition of residues, volatilization and root exudation (78). Especially the compound [**34**], was the first identified from rice hulls and exhibited greatest activity, hence, may be used for reducing weed interference and diminishing the dependence on synthetic agricultural chemicals, labour cost and environmental concern. However, for the practical utilization of those compounds, further studies are needed, in particular understanding the appropriate concentration that can suppress weeds in natural condition and whether those concentrations may induce environmental contamination with their toxicity.

6. ALIPHATIC ALCOHOLS, ESTERS AND ACIDS

Although similar in structure to common fatty acids and aliphatic alcohols are reported to biological activity (65). Cyclopropenoid fatty acids inhibit fatty acid

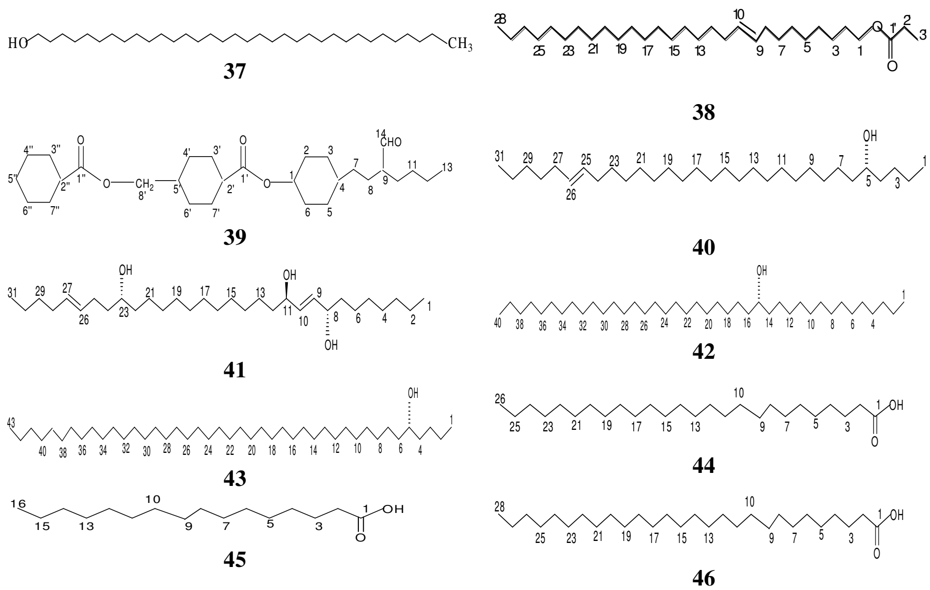


Figure 6. Aliphatic alcohols, esters and acids

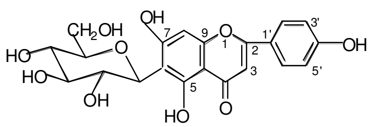
desaturation in several weed species and numerous types of deleterious with cyclopropenoid fatty acids have been observed (68). Chung *et al.* (14) identified 1-tetratriacontanol [**37**] in rice hulls and found that the compound reduced chlorophyll of *L. paucicostata* by 12.8, 13.1 and 14.3% at the concentration of 10, 33 and 100 ppm.

Six aliphatic alcohol and ester compounds (21) named as *n*-octacos-9-en-yl propionate [**38**], 8'-cyclohexyl carboxylate-5'-hydroxy methylene cyclohexyl carboxylate-7-(cyclohexyl)-*n*-heptane-9-aldehyde [**39**] *n*-hentriacont-25-en-5*α*-ol [**40**], *n*-hexetriacont-9, 26-dien-8*α*, 11*β*, 23*α*-triol [**41**], *n*-tetracont-15*α*-ol [**42**] *n*-tritetracontan-5*α*-ol [**43**] and two fatty acids (20),*n*-hexacosanoic acid [**44**], *n*-hexadecanoic acid [**45**] and octacoasanoic acid [**46**] (22,24) was obtained from rice hulls. The activities of these compounds are not reported in literature due to small amounts.

7. FLAVONOIDS

Flavonoids may serve as antioxidants, enzyme inhibitors, pigments for light absorbance and visual attractants for pollination, light screens, plant growth regulators, chemical signals in root modulation gene induction, phytoalexins and other functions (6,58).

Flavonoid substances were identified in methanol extract of rice hull from rice seeds. One of them exhibited antioxidant property as strong as α-tocopherol and was identified as isovitexin, a *C*-glycosyl flavonoid [**47**] (61). Kong *et al.* (51) was reported 5,7,4'-trihydroxy-3',5'-dimethoxyflavone (**48**) from an allelopathic rice accession



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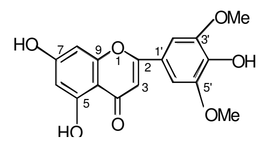

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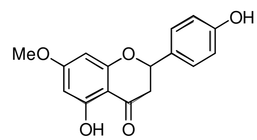

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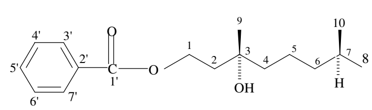
Figure 7. Flavonoids

PI312777. The compounds at low concentrations could inhibit the growth of weeds *E. crus-galli* and *C. difformis* associated with rice, especially mixtures of the compounds had stronger inhibitory activity than did individual compounds.

Tricin [**48**], a flavonoid found in rice hull did not show inhibition of chlorophyll or any visual injury symptoms at concentrations of 10 and 100 ppm and also did not inhibit germination/growth of 3 weeds (*L.chinensis, A. retroflexus, C. difformis*) at of 4, 20, 100 and 1000 ppm conc (14). In addition, the flavanone sakuranetin [**49**] was also found in UV-irradiated rice leaves, a rice phytoalexin, showed antibiotic activity to *M. grisea* (47).

8. BENZOIC ACID DERIVATIVES

Chung *et al.* (16,17) reported three benzoic acid derivatives orizaterpenyl benzoate [**50**], orizanor-diterpenyl benzoate [**51**], orizaditerpenyl benzoate [**52**] and compound 3,7-dimethyl-*n*-octan-1-yl benzoate [**53**], from the rice hulls.



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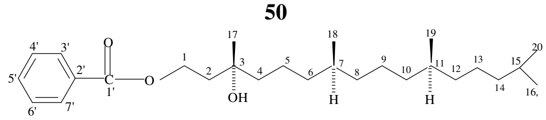

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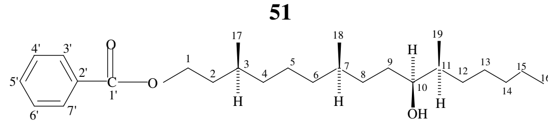

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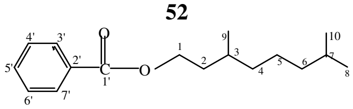

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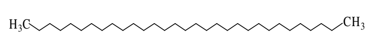
Figure 8. Benzoic acid derivatives

9. OTHER CLASSES OF COMPOUNDS

Methanol extracts of rice hull exhibited strong antioxidative activity than α-tocopherol and oryzanol, it could play a vital role in controlling the germination potentials of rice seeds during long storage (61).

Hentriacontane [**54**] (14) and dicyclohexanyl orizane [**55]** (15) identified from *O. sativa,* neither these inhibit the chlorophyll nor any visual injury symptoms of 10 and 100 ppm against duckweed (*L. paucicostata*). Chung, *et. al* (23 identified a range of chemicals from the rice hulls, including 4-hydroxymethylene-7-(9, 9, 13-trimethylcyclohexyl)-heptanyl-3', 7',7'-trimethyl cyclohex-2', 4'-dien-1'-oate [**56**], 1-(n-hexadec-7-enoxy)-6-(n-octadecanoxy)-β-D-glucopyranoside [**57**] (Z)-12-hydroxy-9-octadecenoic acid-12-β-D-glucopyranoside [**58**], and oryzatria-contolide (n-triacontan-1, 5-olide) [**59**], tritriaconta-4, 12-diene [**60**] (17). Chung *et al*. (19) further identified a compound from rice hulls as 1-



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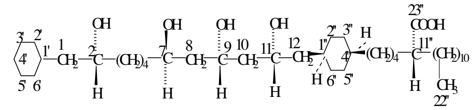

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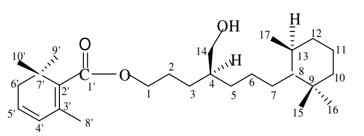

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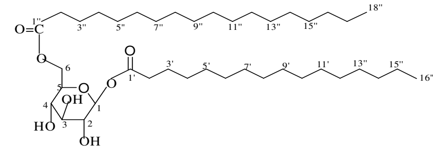

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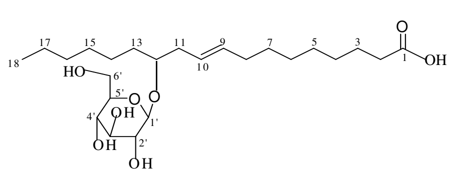

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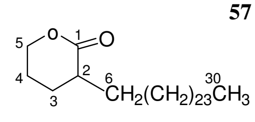

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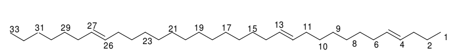

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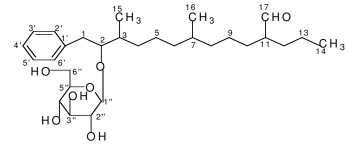

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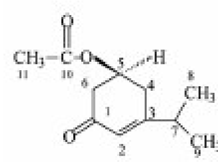

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Figure 9. Other class of compounds

phenyl-2-hydroxy-3, 7-dimethyl-11-aldehydic-tetradecane-2-β-D-glucopyranoside [**61**]. Compound (**61**) showed 34.1 and 27.3% reduction of chlorophyll content of *L. paucicostata* at concentrations of 100 and 33 ppm, respectively. Visual injury due to 1-phenyl-2-hydroxy-3, 7-dimethyl-11-aldehydic-tetradecane-2-β-D-glucopyranoside [**61**] was 20 and 10% at the concentration of 100 and 33 ppm.

Kong *et al*. (51) identified 3-Isopropyl-5-acetoxycyclohexene-2-one-1 (**62**) from an allelopathic rice accession PI312777. The compounds at low concentrations could inhibit the growth of weeds *E. crus-galli* and *C. difformis* associated with rice, especially mixtures of the compounds have more inhibitory activity than did individual compounds.

10. CONCLUSIONS

Rice (*O. sativa*) has a diversity of phytochemicals, which show inhibitory action against germination and suppression of weeds. This review provides knowledge about compounds from rice hulls and other parts of *O. sativa*. The inhibitory substances present in rice hulls should be tested as a potential natural herbicide resource. Further research can bring new and unexpected information in this field. Although literature in this area is not abundant, but its contribution is significant.

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