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RESEARCH PAPER

Production of Phytotoxic Metabolites with Bioherbicidal Activities from *Lasiodiplodia pseudotheobromae* Produced on Different Agricultural Wastes Using Solid-State Fermentation

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Abstract
This study was carried out to optimize and enhance the production of phytotoxic metabolites from *Lasiodiplodia pseudotheobromae* (C1136) for its herbicidal properties using solid-state fermentation with various agricultural wastes available in Nigeria. The results obtained showed that banana peel (10.12 ± 0.10 g/100 g) and wheat bran (9.89 ± 0.11 g/100 g) had the highest protein content. Banana peel was observed to have the highest value of phosphorus (0.30 ± 0.05 g/100 g), closely followed by wheat bran (0.23 ± 0.06 g/100 g). Higher values of arginine contents were obtained for rice bran (3.06 ± 0.06 g/100 g), groundnut wastes (2.98 ± 0.08 g/100 g) and wheat bran (2.38 ± 0.08 g/100 g). These values are significant ($p < 0.05$). Endoamylase (64 U/g), exoamylase (50 U/g), isoamylase (43 U/g), protease (15 U/g), xylanase (12 U/g), cellulose (4.8 U/g) enzymes that were obtained from groundnut waste showed the best activities when compared to other substrates. It was observed that as the concentration of the extract increases so also are the radicle length, shoot length and germination rate on the tested seeds. Leaf necrosis assay showed that the phytotoxic metabolite from strain C1136 produced the largest necrotic area (3.2 ± 0.2 mm) on *Amaranthus hybridus* leaves when grown on groundnut waste. In comparison, the necrotic area of (2.5 ± 0.2 mm) was observed for *Echinochloa crus-galli* leave from phytotoxic metabolites grown on pineapple waste. The efficacy of the phytotoxic metabolites produced from strain C1136 in this study potends a strong solution for the environmental and human health challenges alludes to chemical herbicides.

Keywords Agricultural wastes · Bioherbicides · Enzyme activities · Phytotoxic metabolite · Solid-state fermentation

1 Introduction

The environment in recent time has been subject to a lot of abuse from an anthropogenic activities such as pollution. Environmental pollution associated with agro-industrial wastes handling, expensive waste management system and increased need for land used has encouraged agricultural wastes bioconversion research. The recycling of resources and utilization of these wastes for economic benefits are major areas of attention because enormous amounts of agricultural residue are being wasted, especially in Nigeria due to poor waste handling. Improper wastes handling has caused various environmental and health hazards to many inhabitant (Taiwo and Osinowo 2013).

Solid-state fermentation (SSF) based on the utilization of agricultural by-products is an excellent low-cost option for efficient enzyme production. This type of fermentation is carried out by culturing filamentous fungi on solid renewable waste resources such as cereals, and various agricultural by-products for fungal colonization and sporulation. This technique is commonly used for the small-scale production of fungi that do not sporulate well in liquid media (Adetunji and Oloke 2013a).

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The major constituents in agricultural waste resources are basically macromolecules such as carbohydrates, protein, cellulose, hemicelluloses and lignin. When filamentous fungi are cultured on agricultural materials, they produce different enzymes that hydrolyze the macromolecular content. The sustainable utilization of agricultural by-products inspired the exploitation of all crude enzymes through SSF and fermentation media enriched with sugars such as glucose (Wang et al. 2009; Chen et al. 2010), fructose (Sirisansaneeyakul et al. 2007) and xylose (Vázquez et al. 2001), as well as many other micro- and macronutrients such as amino acids, phosphorus and minerals (Wang et al. 2010). These small molecules are easily metabolized by microorganisms during submerged fermentations to produce biofuels, microbial biopolymers and a wide spectrum of other important biologically important metabolites. Moreover, biomass quantification during solid-state fermentation has been proposed for the production of metabolites (Raimbault 1998).

Weeds have been listed as one of the significant constraints to agricultural production system. Considerable efforts have equally been put into studying and developing weed control methods as well as agents. However, the wide use of synthetic herbicides has raised some ecological problems such as environmental pollution, food safety challenges and biodiversity loss (Liu et al. 2001; Chen et al. 2003; Wu and Chen 2004).

Biocontrol is a scientific approach that uses natural enemies or their toxin to control or reduce the weed population. This method is fraught with advantages such as being easily adaptable, posing very minimal risk to non-target human and animal organisms and prevention of ecosystem. These pathogens can be isolated from diseased weed plants or tissues. There is an increasing interest in exploiting fungi as the control agents of pests, weeds and diseases (Whipps and Lumsden 2001).

Mycoherbicides are specifically formulated preparations of living inoculum of phytopathogens that are used for the control of weeds. They are usually applied in a manner similar to chemical herbicides by broadcasting of distinct doses of their inocula (Adetunji and Oloke 2013b). Among the most common limitations of mycoherbicides development is the one related to their mass production, good-quality active inocula. Large-scale production of fungal agents for weed biological control is by techniques of liquid, diphasic or solid fermentation (Jackson et al. 1996). Several works have been carried out involving the use of fungal derived from plant as bioherbicides in the management of weeds (Bailey 2014; Duke et al. 2015; Cordeau et al. 2016). The bioconversion potentials of fungal are attributed to their lignocellulolytic enzymes produced during solid-state fermentation (Haltrich et al. 1996; Bhat 2000; Pothiraj et al. 2006).

In view of the above, this present study aimed at exploiting agricultural wastes available in Nigeria for enhanced production of phytotoxic metabolites with bioherbicidal properties derived from strain C1136 under SSF techniques. Furthermore, the proximate composition, minerals, amino acid profile of the various agricultural wastes as well as the enzyme profile of strain C1136 were assay using standard procedures.

2 Materials and Methods

2.1 Source of the Fungus

The fungus used during this study, strain C1136, was isolated from *Tridax procumbens* (Adetunji and Oloke 2013a).

2.2 Inoculum Preparation and Solid-State Culture

The basal medium was made of (w/v) glucose 2.0%, malt extract 2.0% and peptone 0.1% for inoculum development. The pH was initially adjusted to 5 before autoclaving. Strain C1136 was transferred to the medium by punching out 0.7-mm-diameter agar disks from the culture grown on PDA plates. Thereafter, five disks were used to inoculate 100 mL of liquid media. The seed culture was grown in a 250-mL Erlenmeyer flask at 25 °C on a rotary shaker incubator at 100 rpm for 3 days.

Various agricultural wastes were prepared in 250-mL flasks containing 28 g of groundnut, wheat straw, rice bran, wheat bran, banana peel, watermelon peel, orange peel, pineapple waste, potatoes peel and yam peel. These wastes were inoculated with strain C1136 spores. Water content was maintained at 45%. After inoculating with 10% (v/v) seed cultures, the flasks were incubated at 25 °C for 14 days (Adetunji and Adejumo 2017).

2.3 Proximate, Mineral Analysis and Amino Acid Analyses

The combination of strain C1136 and various agricultural substrates was analyzed for chemical composition, mineral analysis and amino acids after fermentation. Chemical composition and amino acid profile of selected agricultural solid by-products were performed using DA 7250 NIR analyzer (Adetunji and Adejumo 2017). The mineral content of the various fermented agricultural substrates was determined using atomic absorption spectrophotometer by AOAC (1990). The mean values obtained for proximate composition, mineral content and amino acid profile were subjected to an analysis of variance using SPSS. Significant means were separated using Duncan's multiple range test. Each treatment was done in triplicate.

2.4 Extraction of Phytotoxic Metabolites and Determination of Biomass

In total, 50 mL of sterilized water was added to the fermented substrate and mixed thoroughly. Extractions were performed at 50 °C in an orbital shaker at the speed of 130 rpm for 24 h by centrifugation. After centrifuging, 50 mL of ethyl acetate was added to the resultant suspension and centrifuged again at 6000 rpm for 10 min; the ethyl acetate was removed from the supernatant extracts. It was then dried over sodium sulfate and evaporated at 40 °C on rota evaporator. The extracted content was then used for bioherbicidal activities (Chacon-Morales et al. 2013).

The biomass in SSF was directly determined by simple treatments as follows: The mycelia were obtained by boiling the cultures for about 0.5 h to separate the mycelia from the fermented substrate and filtered immediately with eight layers of gauze. The filter residues were washed three times with boiled water. The yield of biomass in SSF was determined gravimetrically after drying at 70 °C overnight to a constant weight (Bo-Bo et al. 2013).

2.5 Herbicidal Activity and Leaf Necrosis Assay

Thirty seeds of *Amaranthus hybridus* L. and *Echinochloa crus-galli* were immersed in 100 mL 5% sodium hypochlorite solution for 30 min for surface sterilization and then washed with sterilized water three times. The seeds were placed on previously sterilized (121 °C for 20 min) 7-cm-diameter Whatman No. I filter paper in 9-cm Petri dishes. The crude extract was then prepared into various concentrations of 1, 1.5, 2 and 2.5 mg/L, respectively.

The measurements of established seedlings in each flask were averaged before statistical analysis, while the germination rate, radicle inhibition rate and shoot inhibition rate were calculated according to the following equations:

$$\text{Germination rate } (\%) = (\text{number of germinated seeds in treatment} / \text{number of germinated seeds in control}) \times 100,$$

$$\text{Radicle inhibition rate } (\%) = [(\text{length of control} - \text{length of treatment}) / \text{length of control}] \times 100,$$

$$\text{Shoot inhibition rate } (\%) = [(\text{length of control} - \text{length of treatment}) / \text{length of control}] \times 100.$$

The leaves of *A. hybridus* and *E. crus-galli* were surface sterilized with ethanol and washed with sterile-distilled water. The leaf bioassay treated with the respective extracts was performed with different concentrations of 1, 1.5, 2 and 2.5 mg/L, respectively, by wounding them with a sterile needle. These were later transferred to Petri plate containing moistened cotton ball and filter paper. Thereafter, the plates were incubated at 25 °C for 1 week and observed for necrotic lesions (Amusa 2005).

2.6 Enzyme Extraction and Assay

The sample per flask was extracted with 30 mL sodium acetate buffer (50 mM, pH 4.5) and centrifuged (15 min at 4 °C, 9000 rpm) and then filtered through fine filter paper, and the filtrate was used for enzyme activities measurement (Wan and Li 2010). Assays exoamylase, endoamylase, isoamylase, protease, cellulose (CMCase) and xylanase activities were measured in the extraction supernatants using different substrates. All these substrates were supplied by Sigma-Aldrich (USA), except for soluble starch, which was provided by Vetec (Brazil). All activities were expressed as enzyme units (U) per dry mass at the sampling time. Endoamylase activity was performed using the protocol of Fernandes et al. (2007), with little modifications. The enzyme extract (10 µL) was incubated for 3 min with 90 µL of 0.5% (m/v) soluble starch solution, followed by addition of 90 µL of an iodine solution utilized in the quantification of the residual starch. The absorbance was measured at 640 nm. One U of endoamylase was defined as the amount of enzyme that catalyzes the liquefaction of 1 mg of starch per minute, under the assay conditions.

Exoamylase activity was performed on Riaz et al. (2007) by incubating 10 µL of enzyme extract with 90 µL of 1% (m/v) soluble starch solution for 10 min. Enzymes were then inactivated by incubation for 5 min using a boiling water bath. The glucose released was enumerated by a glucose assay kit, and the final absorbance was measured at 505 nm. One U of exoamylase was defined as the amount of enzyme that catalyses the liquefaction of 1 mg of starch per minute, under the assay conditions.

Protease activity was performed using Bendicho et al. (2002) with little modification. Enzyme extract (50 µL) was incubated with 500 µL of a 0.5% (m/v) azocasein solution, for 5 min. The reaction was stopped by adding 1 mL of a 1 M HCl solution. One U of the protease was defined as the amount of enzyme that supports an increase of one absorbance unit (at 345 nm) per minute, under the assay conditions.

Cellulase activity was performed using the method of Castro et al. (2010). Enzyme extract (10 µL) was incubated with 90 µL of a 2% (m/v) carboxymethylcellulose solution, for 10 min. The reaction was stopped by incubating the reaction tubes at 100 °C for 10 min. The glucose released was determined by the same assay kit used for the quantification of exoamylase activity. One U of cellulase was defined as the enzyme amount that catalyzes the release of

1 mol of glucose per minute, from their respective substrates, under the assay conditions.

Xylanase activity was evaluated by incubating 10 µL of enzyme extract with 90 µL of a 1% (m/v) Birchwood xylan solution, for 5 min. The reaction was stopped by adding 300 µL of 3,5-dinitrosalicylic acid (DNS) reagent (Castro et al. 2010). One U of xylanase was defined as the enzyme amount that catalyzes the release of 1 mol of xylose per minute under the assay conditions, and 1 U of the protease was defined as the amount of enzyme that promotes an increase of one absorbance unit (at 345 nm) per minute, under the assay conditions. All analyses were done in triplicate. They were subjected to one-way analysis of variance and analyzed using SPSS (version 21), while significant means were separated using Duncan's multiple range test. Data were expressed as a mean ± standard error (SE).

3 Results and Discussion

3.1 Proximate Mineral Analysis and Amino Acid Analyses

The proximate composition, mineral composition and amino acid profile of selected agricultural substrates are presented in Tables 1, 2 and 3, respectively. Dry matter content ranged from 84.67 ± 1.53 mg/g to 94.61 ± 0.10 mg/g (rice bran). Banana peel (10.12 ± 0.10 mg/g) and wheat bran (9.89 ± 0.11 mg/g) had the highest protein content followed by groundnut wastes (9.03 ± 0.03 mg/g). The least value of dry matter content was observed in yam peel (1.60 ± 0.10 mg/g). Banana peel (7.07 ± 0.07 mg/g), wheat bran (6.01 ± 0.01 mg/g) and watermelon peel (5.48 ± 0.02 mg/g) had higher values of ash than the other substrates which are significantly different ($p < 0.05$). Fat content was significantly ($p < 0.05$) lower for wheat straw (1.38 ± 0.08 mg/g), wheat bran (1.64 ± 0.01 mg/g), watermelon peel (1.83 ± 0.03 mg/g) and pineapple waste (1.88 ± 0.01 mg/g) when compared with other substrates. Fiber content and carbohydrate ranged from 34.68 ± 1.16 mg/g to 37.67 ± 1.53 mg/g for groundnut wastes to 14.16 ± 0.16 mg/g for banana peel and 7.36 ± 0.02 mg/g for yam peel, respectively. Rice bran obtained the highest value of calcium (0.34 ± 0.01 g/100 g), while the values obtained for other substrates were not statistically significant ($p = 0.05$). Banana peel had the highest value of phosphorus (0.30 ± 0.05 g/100 g), closely followed by wheat bran with value of 0.23 ± 0.06 g/100 g. Sodium was not detected in groundnut wastes, rice bran and wheat straw. Watermelon peel obtained the highest value for sodium (13.04 ± 0.04 mg/kg) and potassium (415.39 ± 2.13 mg/kg), respectively. The copper content was generally low in all the substrates except for wheat bran (0.57 ± 0.07 mg/kg).

Arginine content ranged from 1.81 ± 0.01 g/100 g to 3.06 ± 0.06 g/100 g rice bran. Higher values were obtained by rice bran (3.06 ± 0.06 g/100 g), groundnut wastes (2.98 ± 0.08 g/100 g) and wheat bran (2.38 ± 0.08 g/100 g). No values were obtained for cysteine in pineapple wastes and orange peel, while groundnut waste (3.66 ± 0.06 g/100 g) produced the highest value followed by rice bran (2.23 ± 0.06 g/100 g). Lower values of isoleucine were obtained by pineapple waste (0.08 ± 0.01 g/100 g), orange peel (0.36 ± 0.06 g/100 g) and yam peel (0.53 ± 0.03 g/100 g). Leucine content was lower for yam peel (0.34 ± 0.04 g/100 g), watermelon peel (0.07 ± 0.01 g/100 g), pineapple waste (0.00 ± 0.00 g/100 g) and orange peel (0.00 ± 0.00 g/100 g). Watermelon

Table 1 Proximate composition of selected agricultural substrates

Substrates	Dry matter (mg/g)	Protein (mg/g)	Ash (mg/g)	Fat (mg/g)	Fiber (mg/g)	Carbohydrates (mg/g)
Watermelon peel	86.05 ± 0.04^{g}	7.20 ± 0.36^{c}	5.48 ± 0.02^{c}	1.83 ± 0.03^{g}	18.73 ± 0.03^{f}	52.81 ± 1.23^{f}
Groundnut wastes	88.68 ± 0.02^{ef}	9.03 ± 0.03^{b}	4.52 ± 0.02^{f}	2.78 ± 0.02^{d}	37.67 ± 1.53^{a}	34.68 ± 1.16^{h}
Potato peelings	92.83 ± 0.21^{b}	1.93 ± 0.03^{g}	4.31 ± 0.01^{g}	2.16 ± 0.06^{e}	16.09 ± 0.09^{h}	68.34 ± 0.01^{b}
Rice bran	84.67 ± 1.53^{h}	4.75 ± 0.05^{d}	4.63 ± 0.03^{e}	3.09 ± 0.01^{c}	26.34 ± 0.04^{d}	45.86 ± 0.01^{g}
Carrot wastes	91.87 ± 0.13^{c}	3.85 ± 0.05^{e}	2.95 ± 0.05^{h}	2.02 ± 0.02^{f}	29.72 ± 0.03^{c}	53.33 ± 0.02^{ef}
Pineapple wastes	90.11 ± 0.10^{d}	3.22 ± 0.22^{f}	2.43 ± 0.03^{i}	1.88 ± 0.01^{g}	23.69 ± 0.10^{e}	58.89 ± 0.02^{c}
Wheat straw	89.00 ± 0.01^{e}	3.02 ± 0.12^{f}	1.78 ± 0.03^{j}	1.38 ± 0.08^{i}	36.34 ± 0.04^{b}	46.48 ± 0.01^{g}
Orange peel	92.67 ± 0.42^{bc}	9.17 ± 0.03^{b}	4.73 ± 0.05^{d}	2.75 ± 0.05^{d}	15.95 ± 0.05^{h}	60.05 ± 0.03^{c}
Banana peel	91.88 ± 0.11^{c}	10.12 ± 0.10^{a}	7.07 ± 0.07^{a}	4.07 ± 0.21^{a}	14.16 ± 0.16^{i}	56.46 ± 0.01^{d}
Yam peel	94.61 ± 0.10^{a}	1.60 ± 0.10^{h}	1.36 ± 0.06^{k}	3.67 ± 0.07^{b}	17.62 ± 0.02^{g}	70.36 ± 0.02^{a}
Wheat bran	88.02 ± 0.07^{f}	9.89 ± 0.01^{a}	6.01 ± 0.01^{b}	1.64 ± 0.01^{h}	16.08 ± 0.08^{h}	54.40 ± 0.01^{e}

Values are mean ± standard error. Means with different superscripts within the same column are significantly ($p < 0.05$) different

Table 2 Mineral composition of selected agricultural substrates

Substrates	Calcium (g/100 g)	Phosphorus (g/100 g)	Sodium (mg/kg)	Potassium (mg/kg)	Copper (mg/kg)
Watermelon peel	0.29 ± 0.03^{b}	0.15 ± 0.03^{cd}	13.04 ± 0.04^{a}	415.39 ± 2.13^{a}	0.07 ± 0.02^{c}
Groundnut wastes	0.93 ± 0.06^{a}	0.13 ± 0.02^{cde}	0.00 ± 0.00^{d}	33.30 ± 0.30^{j}	0.30 ± 0.10^{b}
Potato peelings	0.13 ± 0.01^{b}	0.09 ± 0.02^{de}	4.35 ± 0.05^{c}	108.97 ± 0.07^{g}	0.01 ± 0.01^{c}
Rice bran	0.34 ± 0.01^{ab}	0.20 ± 0.10^{bc}	0.00 ± 0.00^{d}	38.50 ± 0.50^{i}	0.02 ± 0.01^{c}
Carrot wastes	0.08 ± 0.02^{b}	0.05 ± 0.01^{e}	8.70 ± 0.70^{b}	128.00 ± 1.00^{e}	0.01 ± 0.00^{c}
Pineapple wastes	0.12 ± 0.01^{b}	0.06 ± 0.02^{e}	4.35 ± 0.05^{c}	215.39 ± 0.09^{c}	0.04 ± 0.01^{c}
Wheat straw	0.17 ± 0.01^{b}	0.05 ± 0.02^{e}	0.00 ± 0.00^{d}	75.00 ± 2.00^{h}	0.03 ± 0.01^{c}
Orange peel	0.14 ± 0.03^{b}	0.16 ± 0.01^{bcd}	8.70 ± 0.20^{b}	153.83 ± 0.05^{d}	0.06 ± 0.01^{c}
Banana peel	0.36 ± 0.01^{ab}	0.30 ± 0.05^{a}	8.70 ± 0.10^{b}	230.80 ± 0.41^{b}	0.01 ± 0.01^{c}
Yam peel	0.12 ± 0.02^{b}	0.15 ± 0.03^{cd}	4.35 ± 0.05^{c}	110.26 ± 0.06^{ef}	0.01 ± 0.01^{c}
Wheat bran	0.31 ± 0.01^{ab}	0.23 ± 0.06^{ab}	4.35 ± 0.03^{c}	38.70 ± 0.20^{i}	0.57 ± 0.07^{a}

Values are mean ± standard error. Means with different superscripts within the same column are significantly ($p < 0.05$) different

Table 3 Amino acid profile of selected agricultural substrates

Substrates	Arginine (g/100 g)	Cysteine (g/100 g)	Isoleucine (g/100 g)	Leucine (g/100 g)	Lysine (g/100 g)	Methionine (g/100 g)
Watermelon peel	2.26 ± 0.06^{c}	0.35 ± 0.05^{e}	0.65 ± 0.05^{e}	0.07 ± 0.01^{f}	3.51 ± 0.01^{a}	0.00 ± 0.00^{e}
Groundnut wastes	2.98 ± 0.08^{a}	3.66 ± 0.06^{a}	1.75 ± 0.05^{b}	1.13 ± 0.01^{c}	2.09 ± 0.09^{c}	0.00 ± 0.00^{e}
Rice bran	3.06 ± 0.06^{a}	2.23 ± 0.03^{b}	1.86 ± 0.06^{a}	2.28 ± 0.08^{b}	3.37 ± 0.07^{a}	0.00 ± 0.00^{e}
Pineapple wastes	2.13 ± 0.03^{d}	0.00 ± 0.00^{f}	0.08 ± 0.01^{h}	0.00 ± 0.00^{f}	3.39 ± 0.09^{a}	0.11 ± 0.01^{d}
Orange peel	2.02 ± 0.05^{e}	0.00 ± 0.00^{f}	0.36 ± 0.06^{g}	0.00 ± 0.00^{f}	2.12 ± 0.02^{c}	0.10 ± 0.01^{d}
Banana peel	2.18 ± 0.08^{cd}	0.67 ± 0.07^{d}	1.46 ± 0.06^{c}	2.59 ± 0.09^{a}	2.11 ± 0.01^{c}	0.76 ± 0.06^{a}
Yam peel	1.81 ± 0.01^{f}	1.13 ± 0.03^{c}	0.53 ± 0.03^{f}	0.34 ± 0.04^{e}	2.70 ± 0.70^{b}	0.36 ± 0.06^{c}
Wheat bran	2.38 ± 0.08^{b}	0.42 ± 0.02^{e}	0.88 ± 0.08^{d}	0.92 ± 0.02^{d}	3.51 ± 0.01^{a}	0.46 ± 0.06^{b}

Values are mean ± standard error. Means with different superscripts within the same column are significantly ($p < 0.05$) different

peel (3.51 ± 0.01 g/100 g), rice bran (3.37 ± 0.07 g/100 g), pineapple waste (3.39 ± 0.09 g/100 g) and wheat bran (3.51 ± 0.01 g/100 g) obtained highest values for lysine, while the least value was obtained by yam peel (2.70 ± 0.70 g/100 g). Watermelon peel, groundnut waste and rice bran obtained no values for methionine, while banana peel (0.76 ± 0.06 g/100 g) obtained the highest value followed by wheat bran (0.46 ± 0.06 g/100 g).

The result obtained during this study showed that all the agricultural wastes used have the potential for mass production of bioherbicidal agents through solid substrate fermentation. Although solid-state fermentation (SSF) technology has previously been used for culturing of fungal on solid agricultural wastes for the production of organisms and their by-products, it usage is more in bioherbicidal production (Prasad et al. 2002; Adetunji and Oloke 2013a).

3.2 Enzyme Activities of Strain C1136

The enzyme activities of strain C1136 are shown in Figs. 1, 2 and 3. Groundnut waste had the highest enzyme activities for endoamylase with 63 U/g, exoamylase with 50 U/g and isoamylase 43 U/g when compared to other substrates at 96 h after inoculation in SSF (Fig. 1). The highest protease was also found with groundnut waste with 35 U/g at 156 h, followed by wheat straw with 30 U/g at 132 h, while the least was found in orange peel with 25 U/g at 120 h. Orange peel had the highest cellulase activities with 20 U/g at 132 h. The highest xylanase activities were found on groundnut with 25 U/g at 120 h (Fig. 1) as well as the orange peel with 25 U/g at 132 h. The highest biomass was produced by strain C1136 at 156 h after SSF. The order of biomass production was groundnut (123.4 g/L) > wheat straw (114.6 g/L) > rice bran (113.6 g/L) > banana peel (77.3 g/L) > wheat bran (72.3 g/L) > orange peel (66.5 g/L), pineapple peel (65.4 g/L) > watermelon peel (63.5 g/L) > potatoes peel (52.5 g/L) > yam peel (Fig. 4).

Enzymatic assay of the various agricultural wastes showed the presence of some enzymes (endoamylase, exoamylase, isoamylase, protease, xylanase, cellulase) was produced during SSF. This is in line with Castro et al. (2010) who earlier discovered that the filamentous fungus

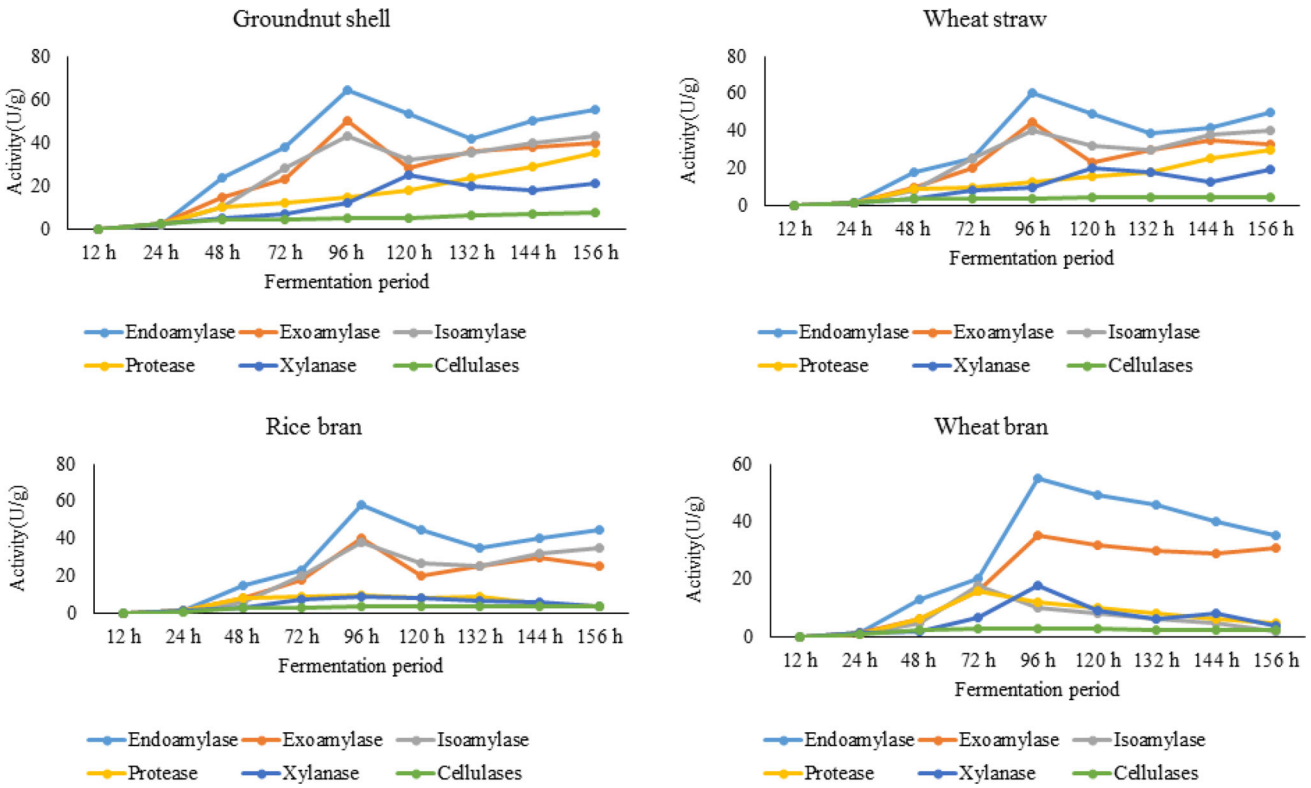

Fig. 1 Enzymes profile of *Lasiodiplodia pseudotheobromae* during solid-state fermentation of the groundnut shell, wheat straw, rice bran and wheat bran

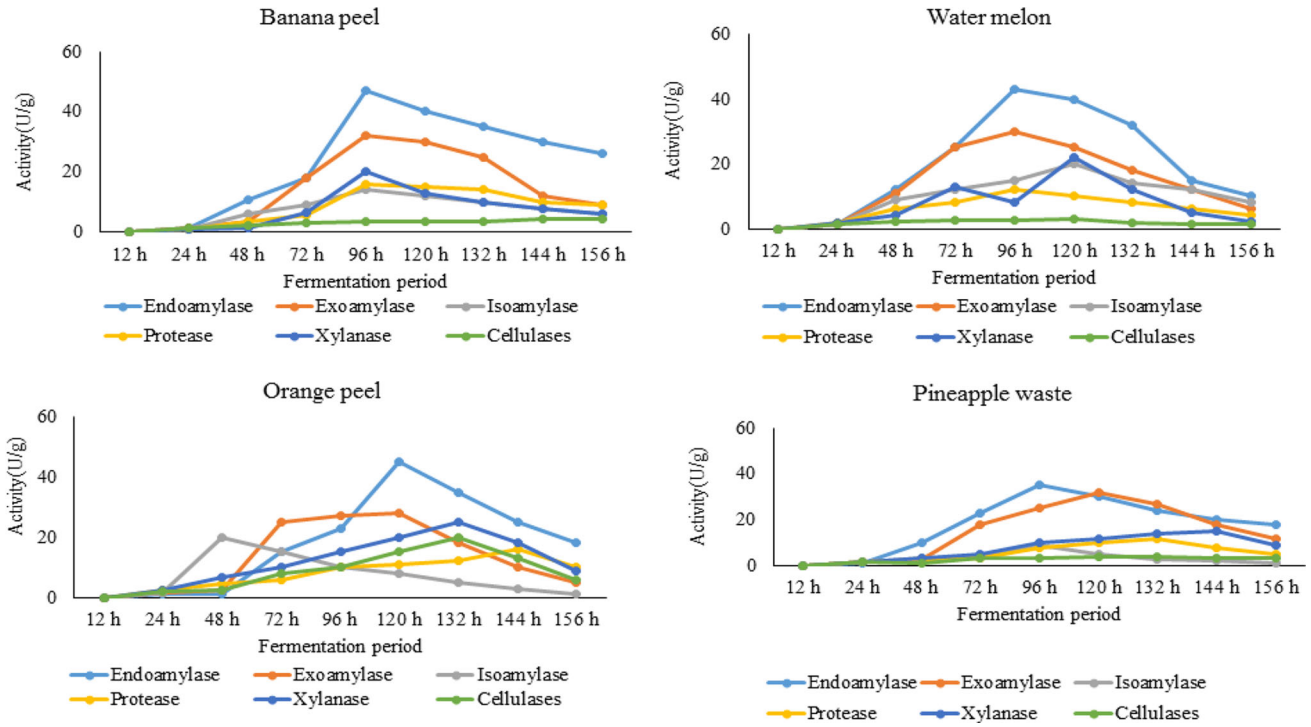

Fig. 2 Enzymes profile of *Lasiodiplodia pseudotheobromae* during solid-state fermentation of the banana peel, watermelon, orange peel and pineapple

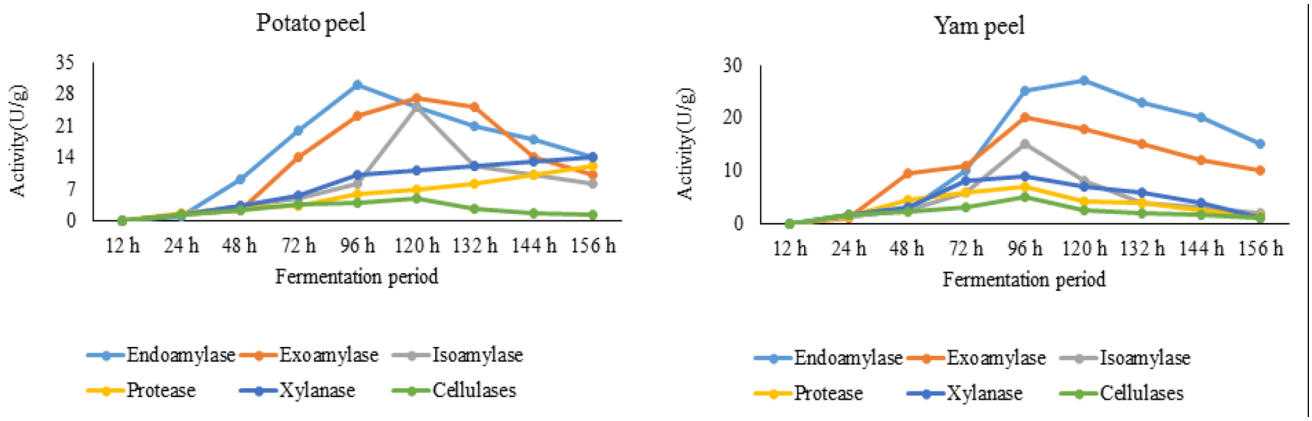

Fig. 3 Enzymes profile of *Lasiodiplodia pseudotheobromae* during solid-state fermentation of the potato and yam peels

Aspergillus awamori IOC-3914 produced relevant enzymes (amylases, cellulases, xylanases and proteases) which contain multiple industrially relevant hydrolases. Some authors have equally shown that raw enzyme pools could efficiently promote cold hydrolysis of complex agro-industrial raw materials such as canola (*Brassica napus*), sunflower (*Helianthus annus*) and castor bean (*Ricinus communis*) cakes (Castro et al. 2011), as well as of babassu (*Orbygnia phalerata*) flour (Lopez et al. 2013; Cinelli et al. 2014).

Furthermore, it was observed that endoamylase activity was high in all the different agricultural substrates used. This might be due to the fact that strain C1136 was able to hydrolyze and use the starch polysaccharides present in all the raw materials during solid-state fermentation as a carbon source (Castro et al. 2010, 2011). The result obtained is similar to the report of Matsubara et al. (2004) and Ertan et al. (2006).

3.3 Herbicidal Activity and Leaf Necrosis Assay

Table 4 shows the effects of crude extract obtained from SSF from strain C1136 on the germination, radicle length and shoot length of *A. hybridus* seeds. It was observed that as the concentration of the extract increased the radicle length, shoot length increased. The highest radicle inhibition was observed at the rate of 2.5 mg/L from groundnut waste with 100 ± 4.8% followed by wheat straw 98.0 ± 3.7%, while the least was found in yam peel with 60.0 ± 4.3%. Moreover, the highest shoot inhibition was found in yam peel 50 ± 4.5%, followed by groundnut waste with 48 ± 2.8%, while the least was found in orange peel 30 ± 1.8%. The result obtained from the germination showed that groundnut had 100 ± 3.7% followed by wheat straw with 95.0 ± 4.2%, while the least was found in yam peel with 67.0 ± 4.3%.

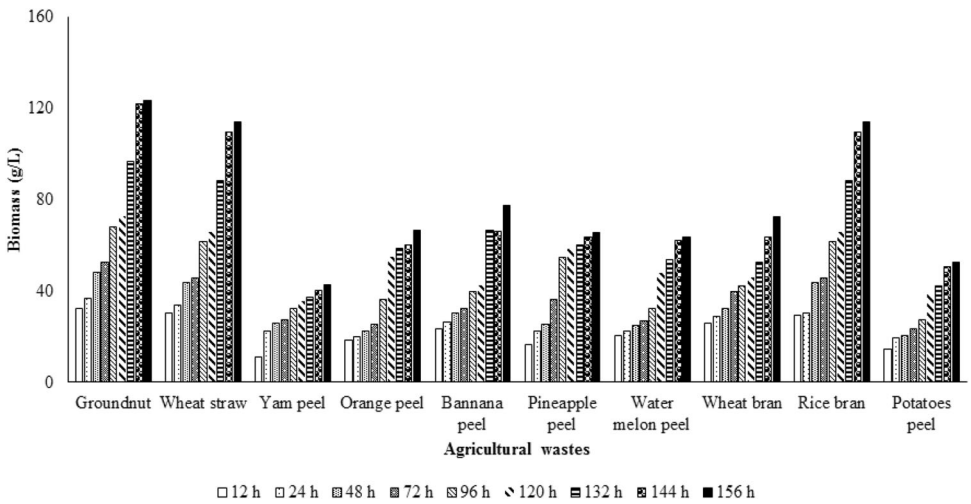

Fig. 4 Effect of biomass production of *Lasiodiplodia pseudotheobromae* during solid-state fermentation on the different agricultural wastes

Table 4 Effects of crude extract obtained from SSF from *Lasiodiplodia pseudotheobromae* on the germination, radicle length, shoot length of *Amaranthus hybridus* seeds

Concentrations (mg/L)	GN	WS	RB	WB	BP	WMP	OP	PW	PP	YP
Radicle length inhibition rate (%)										
1.0	25.0 ± 1.0^{d}	23.0 ± 2.0^{d}	20.0 ± 1.8^{d}	18.0 ± 0.5^{d}	15.0 ± 0.3^{d}	10.0 ± 2.0^{d}	8.0 ± 0.1^{d}	8.0 ± 0.4^{d}	15.0 ± 1.0^{d}	6.0 ± 0.3^{c}
1.5	53.0 ± 2.0^{c}	48.0 ± 2.3^{c}	45.0 ± 1.8^{c}	40.0 ± 1.6^{c}	39.0 ± 1.9^{c}	32.0 ± 1.2^{c}	30.0 ± 3.1^{c}	29.0 ± 1.2^{c}	40.0 ± 2.0^{c}	25.0 ± 2.5^{b}
2.0	78.0 ± 4.2^{b}	72.0 ± 2.4^{b}	68.0 ± 3.1^{b}	65.0 ± 1.5^{b}	62.0 ± 2.1^{b}	53.0 ± 1.4^{b}	49.0 ± 1.8^{b}	45.0 ± 1.3^{b}	65.0 ± 2.6^{b}	27.0 ± 1.4^{b}
2.5	100.0 ± 4.8^{a}	98.0 ± 3.7^{a}	90.0 ± 2.8^{a}	85.0 ± 1.6^{a}	80.0 ± 1.3^{a}	75.0 ± 5.0^{a}	70.0 ± 5.0^{a}	65.0 ± 2.3^{a}	85.0 ± 3.9^{a}	60.0 ± 4.3^{a}
Shoot inhibition rate (%)										
1.0	17.0 ± 1.5^{d}	15.0 ± 2.1^{d}	14.0 ± 1.3^{c}	11.0 ± 2.7^{c}	9.0 ± 1.6^{c}	7.0 ± 1.2^{c}	8.0 ± 1.5^{c}	9.0 ± 1.8^{c}	14.0 ± 2.4^{c}	15.0 ± 1.6^{c}
1.5	21.0 ± 3.2^{c}	18.0 ± 2.7^{c}	15.0 ± 1.8^{c}	13.0 ± 1.8^{c}	10.0 ± 1.2^{c}	8.0 ± 2.1^{c}	6.0 ± 0.8^{c}	7.0 ± 0.5^{c}	15.0 ± 1.3^{c}	17.0 ± 2.4^{c}
2.0	32.0 ± 2.8^{b}	27.0 ± 2.2^{b}	25.0 ± 2.8^{b}	21.0 ± 1.4^{b}	18.0 ± 1.6^{b}	15.0 ± 2.0^{b}	13.0 ± 1.4^{b}	14.0 ± 1.2^{b}	25.0 ± 2.1^{b}	28.0 ± 2.1^{b}
2.5	48.0 ± 3.5^{a}	43.0 ± 2.8^{a}	40.0 ± 1.9^{a}	38.0 ± 3.0^{a}	35.0 ± 1.7^{a}	32.0 ± 2.6^{a}	30.0 ± 1.8^{a}	35.0 ± 1.6^{a}	40.0 ± 2.9^{a}	50.0 ± 4.5^{a}
Germination rate (%)										
1.0	100.0 ± 4.3	90.0 ± 2.1^{c}	85.0 ± 2.5^{b}	70.0 ± 3.2^{c}	65.0 ± 2.5^{c}	60.0 ± 1.4^{b}	55.0 ± 0.8^{c}	55.0 ± 3.4^{c}	90.0 ± 2.2^{b}	45.0 ± 3.0^{c}
1.5	100.0 ± 2.6	92.0 ± 4.1^{bc}	86.0 ± 2.9^{b}	76.0 ± 2.6^{b}	73.0 ± 2.4^{ab}	74.0 ± 1.8^{a}	69.0 ± 2.3^{b}	65.0 ± 3.1^{b}	93.0 ± 2.8^{ab}	52.0 ± 3.6^{b}
2.0	100.0 ± 5.0	97.0 ± 3.2^{a}	95.0 ± 1.9^{a}	80.0 ± 2.8^{b}	75.0 ± 3.4^{a}	70.0 ± 2.8^{a}	72.0 ± 3.5^{ab}	70.0 ± 2.3^{a}	96.0 ± 3.4^{a}	63.0 ± 2.5^{a}
2.5	100.0 ± 3.7	95.0 ± 4.2^{ab}	98.0 ± 2.6^{a}	87.0 ± 2.3^{a}	70.0 ± 2.8^{b}	75.0 ± 2.1^{a}	75.0 ± 1.9^{a}	73.0 ± 3.2^{a}	98.0 ± 4.3^{a}	67.0 ± 4.3^{a}

Values are mean ± standard deviation. Means with different superscripts within the same column are significantly ($p < 0.05$) different

GN groundnut, *WS* wheat straw, *RB* rice bran, *WB* wheat bran, *BP* banana peel, *WMP* watermelon peel, *OP* orange peel, *PW* pineapple waste, *PP* potatoes peel, *YP* yam peel

Table 5 shows the effects of crude extract obtained from SSF from strain C1136 on the germination, radicle length and shoot length of *E. crus-galli* seeds. It was observed that as the concentration of the extract increased the radicle length, shoot length increased. The highest radicle inhibition was observed at the rate of 2.5 mg/L from groundnut waste with 100 ± 7.0% followed by wheat straw 98.0 ± 3.0%, while the least was found in yam peel with 43.0 ± 4.3%. Moreover, the highest shoot inhibition was found from 50 groundnut waste and pineapple waste with 35 ± 2.4% followed by wheat straw with 30.0 ± 1.9%, while the least was found in yam peel 12 ± 3.0%. The result obtained from the germination rate showed that groundnut had 98.0 ± 6.7% followed by wheat straw with 92.0 ± 6.0%, while the least was found in yam peel with 59 ± 2.4%.

The result obtained from the necrosis assay showed that strain C1136 was able to produce phytotoxic metabolite after solid-state fermentation after 14 days. When the phytotoxic metabolites were inoculated on *A. hybridus* leaves, the phytotoxic effect obtained from the groundnut had the highest with a necrotic area of 3.2 ± 0.2 mm, followed by wheat bran that had 2.7 ± 0.7 mm, while the least was obtained from yam peel 1.4 ± 0.4 mm. Increase in the production of phytotoxic metabolites for inducing necrotic area on *A. hybridus* leaves was in the following orders: groundnut wastes > wheat straw > rice bran > potatoes peel > banana peel > wheat bran > watermelon peel > orange peel > pineapple waste and yam peel, respectively (Table 6). Moreover, the phytotoxic metabolites from strain C1136 showed that necrotic area was induced on *E. crus-galli* leaves when inoculated with the phytotoxic metabolite. The highest necrotic region was obtained from pineapple waste with 2.5 ± 0.2 mm followed by groundnut with 1.9 ± 0.9 mm, while the least was obtained from yam peel with 0.3 ± 0.1 mm. Increase in the production of phytotoxic metabolites for inducing necrotic area on *E. crus-galli* leave was in the orders: pineapple waste > groundnut wastes > watermelon peel > wheat straw > rice bran > orange peel > potatoes peel > wheat bran > banana peel and yam peel, respectively (Table 6). The different agricultural substrates used for solid fermentation enhanced amount of phytotoxic metabolite being produced during the fermentation as a result of the necrotic area produced on the tested weeds. This also supports the findings of Stierle et al. (1992), who stated that culturing conditions, e.g., medium composition, aeration and light, under which a fungus is grown, are the most important factors affecting the production of phytotoxins. Comparatively, the phytotoxicity varying with different days and different concentrations has confirmed earlier studies (Shukla and Pandey 2006; Quereshi and Pandey 2007). The highest amount of phytotoxic metabolites produced by strain C1136 could be used as a bioherbicidal agent for the control of *A. hybridus* and *E. crus-galli* weeds. Similar results on detached leaf bioassay have been obtained by Sharma et al. (2004).

The inhibitory effects of phytotoxic metabolites from strain C1136 were more significant on shoots and the radicle of the tested weeds at higher concentration. This may be attributed to the presence of compound with high phytotoxicity or allochemical hormones capable of antagonizing tested weeds. Some researchers have demonstrated that plant could be inhibited in a bioassay, at high concentrations (Wang et al. 2006; Geng 2005; Jin et al. 2007). It is therefore logical to infer from this study that strain C1136 could be used in the biocontrol of *A. hybridus* L. and *E. crus-galli* weed. The use of fungal strains in the management of *Echinochloa crus-galli* has earlier been reported (Zhang and Watson 1997) as well as *Amaranthus* species (Ortiz-Ribbing and Williams 2006). Moreover, this study equally affirms that the presence of some amino acids in various agricultural wastes used during this study might have contributed to the radicle and shoot inhibition as well as the observed necrosis on the leaves of the tested weeds. Additionally, it may also be assumed that amino acid content may qualify the spent substrate for trial as animal feed (Adetunji and Adejumo 2017). It has been discovered by other scientists that certain amino acids applied in millimolar amounts can inhibit plants. This inhibition can be attributed to enzymes imbalance in a biosynthetic pathway (Galili 1995). Conversely, isoleucine is synthesized in plants through the branched chain amino acid pathways, and the end products of this pathway can generate leucine, isoleucine and valine. These have the ability to regulate the activity of acetolactate synthase. The lack of valine and leucine has been shown to disrupt essential; protein metabolism. It is not uncommon to discover that some modern chemical herbicides mimic this strategy. Therefore, the process may involve inhibiting a single biosynthetic enzyme in plants, thereby rendering treated plants incapable of producing a metabolite essential for plant growth. It has been reported that amino acid-producing plant pathogenic fungi and bacteria have an increased virulence of phytopathogenicity (Tiourebaer et al. 2011). Almost every plant is inhibited by at least one amino acid (Thompson et al. 2008), and the substrate used for bioherbicide production could enhance the potency of such formulations.

4 Conclusion

The efficacy of the produced bioherbicide may not only help to resolve the challenges of chemical herbicides, but will also help to resolve the rampart challenges of

Table 5 Effects of crude extract obtained from SSF from *Lasiodiplodia pseudotheobromae* on the germination, radicle length, shoot length of *Echinochloa crus-galli* seeds

Concentrations (mg/L)	GN	WS	RB	WB	BP	WMP	OP	PW	PP	YP
Radicle length inhibition rate (%)										
1.0	35.0 ± 1.0^{d}	32.0 ± 4.0^{d}	30.0 ± 1.5^{c}	25.0 ± 1.4^{c}	20.0 ± 2.0^{c}	25.0 ± 3.0^{d}	48.0 ± 3.0^{c}	32.0 ± 3.1^{c}	22.0 ± 2.1^{c}	12.0 ± 1.2^{c}
1.5	54.0 ± 4.0^{c}	50.0 ± 3.0^{c}	48.0 ± 4.0^{b}	40.0 ± 1.2^{b}	35.0 ± 1.5^{b}	32.0 ± 2.1^{c}	52.0 ± 1.8^{c}	46.0 ± 1.8^{b}	40.0 ± 1.4^{b}	30.0 ± 1.6^{b}
2.0	63.0 ± 3.0^{b}	57.0 ± 2.0^{b}	50.0 ± 5.0^{b}	45.0 ± 6.1^{b}	40.0 ± 4.0^{b}	43.0 ± 2.0^{b}	63.0 ± 3.0^{b}	46.0 ± 2.0^{b}	40.0 ± 1.8^{b}	30.0 ± 1.5^{b}
2.5	100.0 ± 7.0^{a}	98.0 ± 3.0^{a}	67.0 ± 3.0^{a}	60.0 ± 6.0^{a}	53.0 ± 2.8^{a}	50.0 ± 1.6^{a}	96.0 ± 4.0^{a}	53.0 ± 2.4^{a}	63.0 ± 3.1^{a}	43.0 ± 1.6^{a}
Shoot inhibition rate (%)										
1.0	14.0 ± 1.3^{d}	12.0 ± 1.3^{c}	10.0 ± 0.5^{d}	9.0 ± 0.6^{c}	5.0 ± 2.0^{c}	5.0 ± 1.1^{c}	15.0 ± 3.4^{c}	12.0 ± 3.1^{c}	10.0 ± 2.0^{d}	5.0 ± 1.2^{c}
1.5	21.0 ± 0.3^{c}	18.0 ± 0.5^{b}	15.0 ± 0.6^{c}	12.0 ± 0.1^{c}	10.0 ± 1.3^{b}	15.0 ± 0.2^{b}	25.0 ± 0.4^{b}	15.0 ± 0.2^{bc}	15.0 ± 0.8^{c}	7.0 ± 0.8^{bc}
2.0	28.0 ± 1.5^{b}	20.0 ± 2.0^{b}	18.0 ± 3.0^{b}	15.0 ± 3.0^{b}	14.0 ± 1.4^{a}	18.0 ± 3.0^{ab}	30.0 ± 4.0^{ab}	18.0 ± 2.0^{ab}	22.0 ± 1.6^{b}	10.0 ± 1.2^{ab}
2.5	35.0 ± 2.4^{a}	30.0 ± 1.9^{a}	25.0 ± 0.4^{a}	20.0 ± 0.8^{a}	8.0 ± 0.6^{b}	20.0 ± 1.0^{a}	32.0 ± 3.0^{a}	20.0 ± 1.4^{a}	35.0 ± 4.0^{a}	12.0 ± 3.0^{a}
Germination rate (%)										
1.0	55.0 ± 1.5^{c}	48.0 ± 1.53^{c}	35.0 ± 1.4^{d}	32.0 ± 0.8^{c}	30.0 ± 1.8^{d}	43.0 ± 1.5^{c}	45.0 ± 2.2^{d}	32.0 ± 1.8^{d}	56.0 ± 2.3^{c}	20.0 ± 2.0^{d}
1.5	85.0 ± 3.0^{b}	65.0 ± 4.0^{b}	60.0 ± 4.0^{c}	55.0 ± 4.0^{b}	50.0 ± 2.0^{c}	54.0 ± 1.8^{b}	63.0 ± 1.8^{c}	54.0 ± 2.1^{c}	83.0 ± 3.0^{b}	32.0 ± 3.0^{c}
2.0	87.0 ± 2.1^{b}	72.0 ± 2.1^{a}	70.0 ± 1.8^{b}	56.0 ± 3.0^{b}	56.0 ± 4.0^{b}	63.0 ± 2.0^{a}	75.0 ± 1.4^{b}	65.0 ± 3.0^{b}	84.0 ± 2.3^{b}	46.0 ± 1.7^{b}
2.5	98.0 ± 6.0^{a}	83.0 ± 4.0^{a}	75.0 ± 3.0^{a}	70.0 ± 1.4^{a}	63.0 ± 0.6^{a}	65.0 ± 1.7^{a}	85.0 ± 5.0^{a}	73.0 ± 3.0^{a}	92.0 ± 6.0^{a}	59.0 ± 2.4^{a}

Values are mean ± standard deviation. Means with different superscripts within the same column are significantly ($p < 0.05$) different

GN groundnut, *WS* wheat straw, *RB* rice bran, *WB* wheat bran, *BP* banana peel, *WMP* watermelon peel, *OP* orange peel, *PW* pineapple waste, *PP* potatoes peel, *YP* yam peel

Table 6 Effects of crude extract obtained from SSF of *Lasiodiplodia pseudotheobromae* on area of necrosis from *Amaranthus hybridus* and *Echinochloa crus-galli* leaves

Concentrations (mg/L)	GN	WS	RB	WB	BP	WMP	OP	PW	PP	YP
Area of necrosis on *Amaranthus hybridus* (mm)										
1.0	0.7 ± 0.1^{d}	0.5 ± 0.1^{c}	1.9 ± 0.2^{b}	1.6 ± 0.1^{c}	1.7 ± 0.1^{b}	1.5 ± 0.3^{c}	1.2 ± 0.1	1.0 ± 0.2	1.9 ± 0.1^{b}	0.2 ± 0.1^{b}
1.5	1.7 ± 0.1^{c}	1.4 ± 0.1^{b}	2.1 ± 0.1^{ab}	1.8 ± 0.2^{bc}	1.9 ± 0.3^{b}	1.7 ± 0.2^{bc}	1.4 ± 0.2	1.2 ± 0.1	2.1 ± 0.4^{ab}	0.4 ± 0.1^{b}
2.0	2.8 ± 0.2^{b}	2.5 ± 0.2^{a}	2.3 ± 0.3^{ab}	2.0 ± 0.2^{ab}	2.0 ± 0.1^{ab}	1.8 ± 0.3^{ab}	1.6 ± 0.1	1.4 ± 0.1	2.3 ± 0.3^{ab}	1.2 ± 0.5^{a}
2.5	3.2 ± 0.2^{a}	2.7 ± 0.7^{a}	2.4 ± 0.3^{a}	2.2 ± 0.3^{a}	2.3 ± 0.2^{a}	2.0 ± 0.2^{a}	1.8 ± 0.4	1.6 ± 0.8	2.4 ± 0.6^{a}	1.4 ± 0.4^{a}
Area of necrosis on *Echinochloa crus-galli* (mm)										
1.0	0.9 ± 0.1	0.5 ± 0.1^{c}	0.3 ± 0.1^{d}	0.1 ± 0.0^{c}	0.0 ± 0.0^{c}	0.4 ± 0.1^{c}	0.7 ± 0.1^{b}	0.2 ± 0.1^{c}	0.2 ± 0.1^{c}	0.0 ± 0.0^{c}
1.5	1.0 ± 0.2	0.9 ± 0.1^{bc}	0.9 ± 0.2^{c}	0.4 ± 0.2^{bc}	0.2 ± 0.2^{bc}	0.5 ± 0.2^{c}	1.5 ± 0.2^{a}	0.5 ± 0.2^{c}	2.5 ± 0.1^{a}	0.0 ± 0.0^{c}
2.0	1.4 ± 0.4	1.2 ± 0.2^{ab}	1.2 ± 0.2^{b}	0.9 ± 0.1^{b}	0.5 ± 0.3^{b}	1.3 ± 0.3^{b}	1.6 ± 0.6^{a}	1.6 ± 0.2^{b}	1.2 ± 0.2^{b}	0.1 ± 0.1^{b}
2.5	1.9 ± 0.9	1.5 ± 0.4^{a}	1.5 ± 0.1^{a}	1.3 ± 0.3^{a}	1.0 ± 0.1^{a}	1.7 ± 0.2^{a}	1.5 ± 0.1^{a}	2.5 ± 0.2^{a}	1.4 ± 0.4^{b}	0.3 ± 0.1^{a}

Values are mean ± standard deviation. Means with different superscripts within the same column are significantly ($p < 0.05$) different

GN groundnut, *WS* wheat straw, *RB* rice bran, *WB* wheat bran, *BP* banana peel, *WMP* watermelon peel, *OP* orange peel, *PW* pineapple waste, *PP* potatoes peel, *YP* yam peel

environmental pollution arising from agricultural wastes in Nigeria and other developing countries.

Compliance with Ethical Standards

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