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(54) Benævnelse: **Anvendelse af sarmentin og analoger deraf til bekæmpelse af ukrudt**

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DESCRIPTION

FIELD OF THE INVENTION

[0001] This invention relates to compositions and methods for controlling weeds using sarmentine or analogs thereof as an active ingredient.

BACKGROUND OF THE INVENTION

[0002] Utilization of synthetic herbicides not only prevents economic loss in food production, but also improves quality of crop products (Gianessi, L. P.; Reigner, N. P. The value of herbicides in U.S. crop production, Weed Technol. 2007, 21, 559-566). However, the use of synthetic herbicides may cause side-effects on environment and human health (Solomon, G. M.; and Schettler, T. Environment and health: 6. Endocrine disruption and potential human health implications, CMAJ, 2000, 163, 1471-1476. ; Stillerman, K. P.; Mattison, D. R.; Giudice, L. C.; Woodruff, T. J. Environmental exposures and adverse pregnancy outcomes: A review of the science. Reproductive Sci. 2008, 15, 631 - 650.) except that it also leads to an increasing resistance among many weed species (Whaley, C. M.; Wilson, H. P.; Westwood, J. H. A new mutation in plant ALS confers resistance to five classes of ALS-inhibiting herbicides, Weed Sci. 2007, 55, 83-90.). Therefore, it is very necessary to develop alternative means for weed management that are eco-friendly, cost-effective and bio-efficacious (Duke, S. O.; Dayan, F. E.; Rimando, A. M.; Schrader, K. K.; Aliotta, G.; Oliva, A.; Romagni, J. G. Chemicals from nature for weed management. Weed Sci. 2002, 50, 138-151).

[0003] The use of natural phytochemicals is one of these alternative means (Batish, D. R.; Setia, N.; Singh, H. P.; Kohli, R. K. Phytotoxicity of lemon-scented eucalypt oil and its potential use as a bioherbicide, Crop Protection, 2004, 23, 1209-1214).. Due to allelopathic properties, many of these chemicals are either released in air or soil to kill neighboring weeds or to inhibit their germination and/or growth. These phytotoxic chemicals include phenolic compounds (e.g., catechin, ellagic acid, sorgoleone, juglone, ceratiolin, usnic acid), terpenoids (e.g., 1,8-cineole, geranial, neral, cinmethylin, solstitiolide), quassinoids (e.g., ailanthone, chaparrine, ailanthinol B), benzoxazinoids (e.g., hydroxamic acids), glucoinolates (e.g., glucohirsutin, hirsutin, arabin), and some amino acids such as *meta*-tyrosine (Macias, F. A.; Molinillo, J. M. G.; Varela, R. M.; Galindo, J. C. J. Allelopathy - a natural alternative for weed control. Pest Manag Sci., 2007, 63, 327-348; Bertin, C.; Weston, L. A.; Huang, T.; Jander, G.; Owens, T.; Meinwald, J.; Schroeder, F. C. Grass roots chemistry: meta-Tyrosine, an herbicidal nonprotein amino acid. PNAS, 2007, 104, 16964-16969). Commercially available herbicides include products based on clove oil, lemongrass oil and d-limonene.

The Genus Piper

[0004] The genus *Piper* in the Piperaceae family contains approximately 2000 species found primarily in tropical regions. Plants of this genus are normally slender aromatic climbers with perennial woody roots. The fruits commonly known as "pippali" in India and "Bi Bo" in China are used as a spice and also as a preservative in pickles. They are also used as cattle feed.

[0005] In traditional medicinal practice, *P. longum* fruits have been advocated to be beneficial in treatment of diseases such as gonorrhea, menstrual pain, tuberculosis, sleeping problems, respiratory tract infections, chronic gut-related pain, and arthritic conditions (Krishnamurthi, A. 1969. The Wealth of India Raw Materials, vol. 8. CSIR, New Delhi, India, p. 96; Ghoshal, S.; Prasad, B. N. K.; Lakshmi, V. Antiamoebic activity of Piper longum fruits against Entamoeba histolytica in vitro and in vivo, J. Ethanopharmacol. 1996, 50, 167-170; Choi, E.M.; Hwang, J. K. Investigations of anti-inflammatory and antinociceptive activities of Piper cubeba, Physalis angulata and Rosa hybrid, J. Ethanopharmacol. 2003, 89, 171-175, Mata, R.; Morales, I.; Perez, O.; Rivero-Cruz, I.; Acevedo, L.; Enriquez-Mendoza, I.; Bye, R.; Franzblau, S.; Timmermann, B. Antimycobacterial compounds from Piper sanctum, J. Nat. Prod. 2004, 67, 1961-1968). Other reported beneficial effects of *P. longum* include analgesic and diuretic effects, relaxation of muscle tension, and alleviation of anxiety (Vedhanayaki, G.; Shastri, G. V.; Kuruvilla, A. Analgesic activity of Piper longum Linn. Root, Ind. J. Exp. Biol. 2003, 41, 649-651; Das, Biswanath, D.; Kashinatham, A.; Srinivas, K. V. N. S. Alkamides and other constituents of Piper longum, Planta Med, 1996, 62, 582). In addition, pipernonaline from *P. longum* has been found to possess mosquito larvicidal activity (Yang, Y. C.; Lee, S. G.; Lee, H. K.; Kim, M. K.; Lee, S. H.; Lee, H. S. A piperidine amide extracted from Piper longum L. fruit shows activity against Aedes aegypti Mosquito Larvae, J. Agric. Food Chem., 2002, 50, 3765-3767).

[0006] An alkaloid has been isolated from *Piper nigrum* (pepper) which is an alkenylene piperidine amide containing a C18 alkenylene with two or more double bonds. This compound has been found to inhibit mycotoxin biosynthesis. (US Patent No. 6825216).

Sarmentine

[0007] N-(2*E*, 4*E*-Decadienoyl) pyrrolidine (also called sarmentine) was originally separated from the fruit of *Piper sarmentosum* in 1987 [Likhitwitayawuid, K., Ruangrungsi, N, Lange, G and Decicco, C., Structural Elucidation and Synthesis of New Components isolated from Piper Samentosum, Tetrahedron 1987 (43) 3689-3694] and also from *Piper nigrum* in 1988 [Kiuchi, F., Nakamura, N., Tsuda, Y., Kondo, K and Yoshimura, H. Studies on Crude Drugs Effective on Visceral Larva Migrans. IV. Isolation and Identification of Larvicidal Principles in Pepper Chemical and Pharmaceutical Bulletin 1988(36):2452], and first synthesized in 1995 [Bernabeu, M., Chinchilla, R. and Najera, C., (2E,4E)-5-Tosyl-2,4-pentadienamides: New Dienic Sulfones for the Stereoselective Synthesis of (2E,4E)-Dienamides, Tetrahedron Letter, 1995 (36)3901-3904]. Sarmentine has been found to be *in vivo* skin antioxidant protecting photoaged skin [Cornacchione, S.; Sadick, N. S.; Neveu, M.; Talbourdet, S.; Lazou, K.; Viron, C.; Renimel, I.; de Quéral, D.; Kurfurst, R.; Schnebert, S.; Heusèle, C.; André, P.; Perrier E. In vivo skin antioxidant effect of a new combination based on a specific Vitis vinifera shoots extract and a biotechnological extract. J. Drugs in Dermatol. 2007, 6S, 8-13], display antiplatelet aggregation activity [Li, C.Y.; Tsai, W.; Damu, A.G.; Lee, E. J.; Wu, T. S.; Dung. N. X.; Thang, T. D.; Thanh, L. Isolation and identification of antiplatelet aggregatory principles from the leaves of Piper lolot, J. Agric. Food Chem. 2007, 55, 9436-9442], antiplasmodial and antimycobacterial activities [Tuntiwachwuttikul, P.; Phansa, P.; Pootaeng-on, Y.; Taylor, W. C. Chemical constituents of the roots of Piper Sarmentosum, Chem. Pharm. Bull. 2006, 54, 149-151] and antituberculosis activity [Rukachaisirikul, T.; Siriwattanakit, P.; Sukcharoenphol, K.; Wongvein, C.; Ruttanaweang, P.; Wongwattanavuch, P.; Suksamrarn, A. Chemical constituents and bioactivity of Piper sarmentosum, J. Ethnopharmacol., 2004, 93, 173-176]. Sarmentine is used as a solubilizer of hydrophobic compounds in cosmetics and pharmaceuticals (Stephen, T.; Andrew, H. Compositions comprising macromolecular assembles of lipid surfactant, PCT Publication No. WO/2008/065451).

[0008] Further prior art relates to Miyakado, Mazakazu et al (Chemical Abstracts, May 12 1984), which describes synthesis of pellitorine by an alkenyl-alkenyl cross-coupling reaction and insecticidal activities of its amide analogues. GB 2247621 describes herbicidal compositions comprising an aliphatic carboxylic acid, a salt thereof and an alcohol, wherein the acid and salts comprise a mixture of decanoic and nonanoic acids. Toshiake Matsuzaki et al (Agricultural and Biological Chemistry, 52, 8:1899, 1988) describe germination and growth inhibition of acylnornicotines from section repandae of the genus Nicotiana and synthetic acylnornicotines.

BRIEF SUMMARY OF THE INVENTION

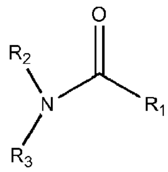
[0009] The invention is directed to a method for controlling a monocotyledonous, sedge, or dicotyledonous weed comprising applying to the weed an amount of a sarmentine or a sarmentine analog effective for controlling the weed, wherein said sarmentine analog is selected from N-(Decanoyl)pyrrolidine, N-(Decenoyl)pyrrolidine, N-(Decanoyl)piperidine, N-(*trans*-Cinnamoyl)pyrrolidine, N-(*trans*-Cinnamoyl)piperidine, (2E,4Z-Decadienoyl)pyrrolidine, N-(Decenoyl)piperidine, (2E,4Z-Decadienoyl)piperidine, (2E,4Z-Decadienoyl)hexamethyleneimine, N-(Decenoyl)hexamethyleneimine and N-(Decanoyl)hexamethyleneimine, wherein the sarmentine or the sarmentine analog is applied by foliar application.

[0010] The invention is further directed to a herbicidal composition comprising (a) sarmentine or a sarmentine analog, wherein said sarmentine analog is selected from N-(Decanoyl)pyrrolidine, N-(Decenoyl)pyrrolidine, N-(Decanoyl)piperidine, N-(trans-Cinnamoyl)pyrrolidine, N-(trans-Cinnamoyl)piperidine, (2E,4Z-Decadienoyl)pyrrolidine, N-(Decenoyl)piperidine, (2E,4Z-Decadienoyl)piperidine, (2E,4Z-Decadienoyl)hexamethyleneimine, N-(Decenoyl)hexamethyleneimine and N-(Decanoyl)hexamethyleneimine; and (b) one or more other herbicidal agents for use in modulating emergence of weeds.

[0011] In a particular embodiment, the sarmentine analog(s) which may be used in compositions and methods of the present invention has substantially the same activity as sarmentine. As defined herein "substantially the same activity as sarmentine" means that it has at least about 80% of the phytopathogenic and/or herbicidal activity of sarmentine and preferably at least about 90% of the phytopathogenic and/or herbicidal activity of sarmentine and even more preferably at least about 95% of the phytopathogenic and/or herbicidal activity of sarmentine.

[0012] The sarmentine analogs include N-(Decanoyl)pyrrolidine, N-(Decenoyl)pyrrolidine, N-(Decanoyl)piperidine , N-(*trans*-Cinnamoyl)pyrrolidine, (2E,4Z-Decadienoyl)pyrrolidine, N-(Decenoyl)piperidine, (2E,4Z-Decadienoyl)piperidine, (2E,4Z-Decadienoyl)hexamethleneimine, N-(Decenoyl)hexamethyleneimine, and N-(Decanoyl)hexamethyleneimine.

[0013] Disclosed herein are isolated sarmentine analogues having the structure:



Where R1 is an alkyl, alkenyl, alkynyl, heterocyclyl, aromatic, aryl group, NH-substituted, or N,N-substituted group, the length of R1 chain can be from 4 to 20 atoms, the preferred length will be from 6 to 12 atoms;

Wherein R2 and R3 are alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aromatic, arylalkyl, heterocyclyl or heteroaryl orR2 +R3+ N can be an N-containing heterocyclic or herteroaryl ring consisting of between 3-18 atoms and preferably between 5 to 8 atoms.

[0014] In a more particular embodiment, the isolated samentine analog includes but is not limited to: (2E,4Z-Decadienoyl)pyrrolidine; (2E,4Z-Decadienoyl)hexamethleneimine and N-(Decenoyl)hexamethyleneimine.

[0015] The compositions of the present invention further comprise one or more other herbicides or phytopathogenic modulating agents. The invention is also directed to uses of one or more sarmentine and/or its analogs for preparation of a composition for use as a pre or post emergent herbicide agent.

[0016] Also disclosed herein is a method for modulating phytopathogenic infection in a plant comprising applying to the plant and/or seeds thereof and/or substrate used for growing said plant an amount of a sarmentine and/or its analogs effective to modulate said phytopathogenic infection. The substrate for growing said plant in a particular embodiment may include but is not limited to soil, an artificial growth substrate, water or sediment.

[0017] In another particular embodiment, the invention is directed to a method for modulating emergence of monocotyledonous, or dicotyledonous weeds in a substrate comprising applying to the weeds an amount of a sarmentine and/or its analogs effective to modulate emergence of monocotyledonous or dicotyledonous weeds in the substrate. The substrate may include but is not limited to soil, an artificial growth substrate (e.g., rice growing system), water or sediment. The sarmentine and/or its analogs may be applied to the weed after emergence of said weed(s).The weeds may be broadleaved and/or grass weeds. In a particular embodiment, the weeds are in a rice growing system and the weed is a rice weed(s).

[0018] In a particular embodiment, the sarmentine and/or its analogs is applied in an amount of about 0.005 mg/ml to about 20mg/ml. In a more particular embodiment, the sarmentine and/or its analogs is applied in an amount of about 0.01 to about 15 mg/ml. In yet a more particular embodiment, the sarmentine and/or its analogs is applied in an amount of about 0.1 to about 10 mg/ml.

DETAILED DESCRIPTION OF THE INVENTION

[0019] Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limit of that range and any other stated or intervening value in that stated range is encompassed within the invention. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges is also encompassed within the invention, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either both of those included limits are also included in the invention.

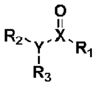
[0020] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present invention, the preferred methods and materials are now described.

[0021] It must be noted that as used herein and in the appended claims, the singular forms "a," "and" and "the" include plural references unless the context clearly dictates otherwise.

[0022] As defined herein, the term "modulate" is used to mean to alter the amount of phytopathogenic infection or rate of spread of phytopathogenic infection.

Sarmentine and its analogs

[0023] The sarmentine and/or its analogs disclosed herein may have the following structure:



[0024] Where X includes but is not limited to sulfur, phosphorus, boron or carbon; Y includes but is not limited to carbon, oxygen, nitrogen, sulfur, boron or phosphorous; R_1 includes but is not limited to hydrogen, hydroxyl, halogen, alkyl, alkoxy, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aromatic, arylalkyl, heterocyclyl and heteroaryl; R_2 includes but is not limited to hydrogen, hydroxyl, halogen, alkyl, alkoxy, alkenyl, alkynyl, cycloalkyl, aromatic, arylalkyl, heterocyclyl and heteroaryl; R_3 includes but is not limited to hydrogen, hydroxyl, halogen, alkyl, alkoxy, alkenyl, alkynyl, cycloalkyl, aromatic, arylalkyl, heterocyclyl and heteroaryl; wherein R_2 + R_3 + Y can be a cyclic or heterocyclyl ring containing 4-50 atoms. Each of these is optionally substituted.

[0025] As used herein, the term "alkyl" refers to a saturated hydrocarbon radical which may be straight-chain or branched-chain (e.g., ethyl, isopropyl, t-amyl, or 2, 5-dimethylhexyl, etc.). This definition applies both when the term is used alone and when it is used as part of a compound term.

[0026] The terms "cycloalkyl" and "cycloalkenyl" refer to a saturated hydrocarbon ring and includes bicyclic and polycyclic rings. Similarly, cycloalkyl and cycloalkenyl groups having a heteroatom (e.g., N, O, or S) in place of a carbon ring atom may be referred to as "heterocycloalkyl", "heterocyclyl," and "heterocycloalkylene," respectively.

[0027] The term "alkenyl" as used herein refers to an alkyl group as described above which contains one or more sites of unsaturation that is a double bond. Similarly, the term "alkynyl" as used herein refers to an alkyl group as described above which contains one or more sites of unsaturation that is a triple bond.

[0028] The term "alkoxy" refers to an alkyl radical as described above which also bears an oxygen substituent which is capable of covalent attachment to another hydrocarbon radical (such as, for example, methoxy, ethoxy, aryloxy, and t-butoxy).

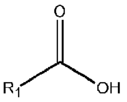
[0029] The term "aryl" refers to an aromatic carbocyclic substituent which may be a single ring or multiple rings which are fused together, linked covalently or linked to a common group such as an ethylene or methylene moiety. Similarly, aryl groups having a heteroatom (e.g., N, O, or S) in place of a carbon ring atom are referred to as "heteroaryl."

[0030] The terms "arylalkyl," "arylalkenyl," and "aryloxyalkyl" refer to an aryl radical attached directly to an alkyl group, an alkenyl group, or an oxygen atom which is attached to an alkyl group, respectively. For brevity, aryl as part of a combined term as above is meant to include heteroaryl as well.

[0031] The term "halo" or "halogen," by itself or as part of another substituent, means, unless otherwise stated, a fluorine, chlorine, bromine, or iodine atom. Additionally, terms such as "haloalkyl" are meant to include monohaloalkyl and polyhaloalkyl.

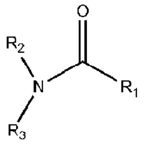
[0032] The term "hetero" as used in a "heteroatom-containing alkyl group" (i.e., a "heteroalkyl" group) or a "heteroatom-containing aryl group" (i.e., a "heteroaryl" group) refers to a molecule, linkage, or substituent in which one or more carbon atoms are replaced with an atom other than carbon, e.g., nitrogen, oxygen, sulfur, phosphorus, or silicon.

[0033] Disclosed herein are sarmentine analogues that have the following structure:



Where R_1 is an alkyl, alkenyl, alkynyl, herterocyclyl, aromatic, aryl group, NH-substituted, or N,N-substituted group. In a specific embodiment, R_1 is an alkyl or alkenyl moiety containing from 4 to 20 atoms and preferably from 6 to 12 atoms. In a more specific embodiment, R_1 is a C_{5-15} alkyl or C_{5-15} alkenyl group. In yet a very specific embodiment, R_1 is a C_{6-12} alkyl or C_{6-12} alkenyl group. Possible alkenyl include but are not limited to linear alkenyl fatty acids, branched alkenyl fatty acids, cycloalkenyl substituted fatty acids (e.g., cyclohexenylpropanoic acid, cyclohexenylbutanoic acid, cyclohexenylpentanoic acid and so on), heterocycloalkenyl (e.g., 4-[1,2, 3,4-tetrahydropyridinyl] butanoic acid).

[0034] Also disclosed are sarmentine analogues having the following structure:



Where R1 is an alkyl, alkenyl, alkynyl, herterocyclyl, aromatic, aryl group, NH-substituted, or N,N-substituted group, the length of R_1 chain can be from 4 to 20 atoms, the preferred length will be from 6 to 12 atoms.

Wherein R_2 and R_3 are alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, aromatic, arylalkyl, heterocyclyl or heteroaryl; or alternatively R_2 +R_3+ N can be an N-containing heterocyclic moiety.

[0035] One of skill in the art will appreciate that any sarmentine derivatives-containing materials for weed or phytopathogen management is included. Sarmentine derivatives in these materials can be natural and/or synthesized.

[0036] In certain embodiments, natural sarmentine derivatives may be obtained from plants, fungi, bacteria and soils. In a particular embodiment, sarmentine and its analogs used in the method of the present invention may be obtained from the fruits, leaves, stems and roots of any *Piper* species. In a more particular embodiment, non-limiting examples of *Piper* species that may contain sarmentine derivatives include but are not limited to the following species such as *Piper aborescens, P. acutisleginum, P. aduncum, P. amalago, P. argyrophylum, P. attenuatum, P. auranticaum, P. austrosinense* T., *P. arboricola* C. DC., *P. banksii, P. bartlingianum, P. betle* L., *P. boehmeriifolium* var. *tonkinense* C. DC., *P. brachystachyum, P. callosum, P. chaba, P. chiadoense, P. cubeba L., P. damiaoshaneense, P. demeraranum, P. falconeri, P. futokadsura, P. guayranum, P. guineense, P. hainanense* Hemsl. in F.B. Forbes and Hemsl., *P. hamiltonii, P. hancei* Maxim., *P. khasiana, P. kadsura* (Choisy) Ohwi, *P. laetispicum* C. DC., *P. longum* L., *P. longum* var.("round peepal"), *P. macropodum, P. manii, P. martinii* C. DC., *P. methysticum, P. nepalense, P. novae hollandiae, P. nigrum* L., *P. nudibaccatum* Y.C. Tseng, *P. officinarum, P. peepuloides, P. pedicellosum, P. ponesheense* C. DC., *P. puberulilimbum* C. DC., *P. puberulum* (Benth.) Maxim., *P. pubicatulum* C. DC., *P. ridleyi, P. rugosum, P. retrofractum* Vahl, *P. ribesioides, P. sanctum, P. sarmentosum* R., *P. schmidtii, P. semiimmersum* C. DC., *P. sintenense, P. spirei* C. DC., *P. syvaticum, P. thomsoni, P. verruscosum, P. trichostachyon, P. wallichii* (Miq.), *P. wightii* [Parma, V., Jain, S., Bisht, K., Jain, R., Poonam, T., Jha, A., Tyagi, O., Prasad, A., Wengel, J., Olsen, C. and Boll., P., Phytochemistry of the Genus Piper, Phytochem. 1997 (46) 597-673; Parma, V., Jain, S., Gupta, S., Talwar, S., Rajwanshi, V., Kumar, R., Azim, A., Malhotra, S., Kumar, N., Jain, R., Sharma, N., Tyagi, O., Lawrie, S., Errington, W., Howarth, O., Olsen, C., Singh, S. and Wengel, J. Polyphenols and Alkaloids from Piper Species Phytochem. 1998 (49) 1069-1078]. Sarmentine derivatives may also be obtained from microorganisms such as **Actinomycetes** [Cho, J., Williams, P., Kwon, H., Jensen, P., and Fenical, W., Lucentamycins A-D, Cytotoxic Peptides form the Marine-Derived Actinomycete Nocardiopsis lucentensis, J. Nat. Prod., 2007 (70) 1321-1328; Askolar, R., Jensen, P., Kauffman, C., and Fenical, W., Daryamides A-C, Weakly Cytotoxic Polyketides form a Marine-Derived Actinomycete of the Genus Streptomyces Strain CNQ-085, J. Nat. Prod., 2006 (69), 1756-1759].

[0037] Sarmentine derivatives can be extracted and purified in any physical and chemical means from *Piper longum* using procedures set forth in the Example, *infra,* or using procedures known in the art (see, for example, Likhitwitayawuid, K., Ruangrungsi, N, Lange, G and Decicco, C., Structural Elucidation and Synthesis of New Components isolated from Piper Samentosum Tetrahedron 1987 (43) 3689-3694 and Kiuchi, F., Nakamura, N., Tsuda, Y., Kondo, K and Yoshimura, H. Studies on Crude Drugs Effective on Visceral Larva Migrans. IV. Isolation and Identification of Larvicidal Principles in Pepper Chemical and Pharmaceutical Bulletin 1988(36):2452]. They can also be chemically synthesized using for example, the method set forth in [Bernabeu, M., Chinchilla, R. and Najera, C., (2E,4E)-5-Tosyl-2,4-pentadienamides: New Dienic Sulfones for the Stereoselective Synthesis of (2E,4E)-Dienamides, Tetrahedron Letter, 1995 (36)3901 -]].In a particular embodiment, a *Piper longum* sample is subject to extraction with an alkyl alcohol, preferably methanol. Sarmentine is subsequently isolated from the extract by for example, column chromatography, more particularly by HPLC and fractions containing the sarmentine are identified by, for example bioassay.

[0038] In a particular embodiment, the compound used may be sarmentine, also known as N-(2*E*, 4E- decadienoyl) pyrrolidine. Natural sarmentine can exist in either plant extracts or a purified form. The sarmentine analog may also be N-(Decanoyl)pyrrolidine, N-(Decenoyl)pyrrolidine, N-(Decanoyl)piperidine, N-(*trans*-Cinnamoyl)pyrrolidine, (2E,4Z-Decadienoyl)pyrrolidine, N-(Decenoyl)piperidine, (2E,4Z-Decadienoyl)piperidine, (2E,4Z-Decadienoyl)hexamethyleneimine, N-

(Decenoyl)hexamethyleneimine, or N-(Decanoyl)hexamethyleneimine.

Formulations

[0039] Sarmentine and/or sarmentine analog-containing herbicidal compositions (also alternatively referred to as "formulations") can be formulated in any form. Non-limiting formulation examples include emulsifiable concentrates (EC), wettable powders (WP), soluble liquids (SL), aerosols, ultra-low volume concentrate solutions (ULV), soluble powders (SP), microencapsulation, water dispersed granules, flowables (FL), microemulsions (ME), nano-emulsions (NE), etc. In any formulation described herein, percent of sarmentine and/or its analogs is within a range of 0.01% to 99.99%. In a particular embodiment, the formulations may be free of surfactants.

[0040] The compositions of the invention may further comprise a carrier and/or diluent. The term, 'carrier' as used herein means an inert, organic or inorganic material, with which the active ingredient is mixed or formulated to facilitate its application to the soil, seed, plant or other object to be treated, or its storage, transport and/or handling. Examples of carrier vehicles to be used when applying to growth substrates include, but are not limited to, active charcoal, corn gluten meal, soybean meal, vermiculite, bentonite, kaolinite, wheat germ, almond hulls, cottonseed meal, Fuller's earth, orange pulp, rice hulls, sawdust, Gum arabic, etc. If desired, plant essential oils such as cinnamon, clove, thyme (eugenol as active ingredient), wintergreen, soy methyl ester, citronella and pine oil, citrus oil (1-limonene as active ingredient) and the like, can be included in the granules. As noted above, the active ingredient alone or in the presence of the carrier vehicles, may be dissolved in for example, water, or organic solvent such as ethanol, formic acid or ethanol.

[0041] In further embodiments, sarmentine and its analogs themselves are easily oxidized because of two conjugated double bonds. This is proven by the fact that sarmentine can be an *in vivo* antioxidant for photoaged skin **11** [Cornacchione, S. ; Sadick, N. S. ; Neveu, M. ; Talbourdet, S. ; Lazou, K. ; Viron, C. ; Renimel, I.; de Queral, D.; Kurfurst, R.; Schnebert, S.; Heusele, C.; Andre, P.; Perrier, E., In vivo skin antioxidant effect of a new combination based on a specific Vitis vinifera shoot extract and a biotechnological extract , J. drugs in Dermatol. 2007 (6 suppl) S8-13]. Therefore, any antioxidant can be added into the sarmentine and /or its analogs-containing formulation to boost and/or elongate the phytotoxic activity. The non-limiting examples of antioxidants include alpha tocopherol, beta carotene, ascorbic acid, zinc oxide, titanium oxide, *Gynostemma pentaphyllum* extract, *Vaccinium angustifolium* (Blueberry) fruit extract, *Pinus strobus* bark extract, rhaponticin, plankton extract, *Monostroma* sp. extract, algae extract, venuceane, rosmarinic acid, and any other plant extracts or antioxidants.

[0042] Examples of phytopathogens controlled by sarmentine and/or its analogs include but are not limited to plant viruses, phytopathogenic fungi or bacteria, insects or nematodes. In a specific embodiment, the viruses include but are not limited to TMV, tobacco or cucumber mosaic virus, ringspot virus, necrosis virus, maize dwarf mosaic virus. Phytopathogenic fungi include but are not limited to *Fusarium* sp., *Botrytis* sp., *Monilinia* sp., *Colletotrichum sp, Verticillium sp.; Microphomina* sp., and *Phytophtora sp., Mucor sp., Rhizoctonia sp., Geotrichum sp., Phoma sp., and Penicillium sp.* Phytopathognic bacteria include but is not limited to *Bacillus* sp. or *Xanthomonas* sp.

[0043] Nematodes that may be controlled include but are not limited to parasitic nematodes such as root-knot, cyst, and lesion nematodes, including *Heterodera* and *Globodera* sp.; particularly *Globodera rostochiensis* and *G. pailida* (potato cyst nematodes); *Heterodera glycines* (soybean cyst nematode); *H. schachtii* (beet cyst nematode); and *H. avenae* (cereal cyst nematode).

[0044] Phytopathogenic insects controlled include but are not limited to insects from the order (a) Lepidoptera, for example, *Acleris* sp., *Adoxophyes* sp., *Aegeria* sp., *Agrotis* sp., *Alabama argillaceae, Amylois* sp., *Anticarsia gemmatalis, Archips* sp., *Argyrotaenia* sp., *Autographa* sp., *Busseola fusca, Cadre cautella, Carposina nipponensis, Chilo* sp., *Choristoneura* sp., *Clysia ambiguella, Cnaphalocrocis* sp., *Cnephasia* sp., *Cochylis* sp., *Coleophora* sp., *Crocidolomia binotalis, Cryptophlebia leucotreta, Cydia* sp., *Diatraea* sp., *Diparopsis castanea, Earias* sp., *Ephestia* sp., *Eucosma* sp., *Eupoecilia ambiguella, Euproctis* sp., *Euxoa* sp., *Grapholita* sp., *Hedya nubiferana, Heliothis* sp., *Hellula undalis, Hyphantria cunea, Keiferia lycopersicella, Leucoptera scitella, Lithocollethis* sp., *Lobesia botrana, Lymantria* sp., Lyonetia sp., *Malacosoma* sp., *Mamestra brassicae, Manduca sexta, Operophtera* sp., *Ostrinia nubilalis, Pammene* sp., *Pandemis* sp., *Panolis flammea, Pectinophora gossypiella, Phthorimaea operculella, Pieris rapae, Pieris* sp., *Plutella xylostella, Prays* sp., *Scirpophaga* sp., *Sesamia* sp., *Sparganothis* sp, *Spodoptera* sp, *Synanthedon* sp., *Thaumetopoea* sp., *Tortrix* sp., *Trichoplusia ni* and *Yponomeuta* sp.; (b) Coleoptera, for example, Agriotes sp., Anthonomus sp., Atomaria linearis, Chaetocnema tibialis, Cosmopolites sp., Curculio sp., Dermestes sp., Diabrotica sp., Epilachna sp., Eremnus sp., Leptinotarsa decemlineata, Lissorhoptrus sp., Melolontha sp., Orycaephilus sp., Otiorhynchus sp., Phlyctinus sp., Popillia sp., Psylliodes sp., Rhizopertha sp-, Scarabeidae, Sitophilus sp., Sitotroga sp., Tenebrio sp., Tribolium sp.

and Trogoderma sp.; (c) Orthoptera, for example, Blatta sp., Blattella sp., Gryllotalpa sp., Leucophaea maderae, Locusta sp., Periplaneta sp. and Schistocerca sp.; (d) Isoptera, for example, Reticulitermes sp.; (e) Psocoptera, for example, Liposcelis sp.; (f) Anoplura, for example, Haematopinus sp., Linognathus sp., Pediculus sp., Pemphigus sp. and Phylloxera sp.; (g) Mallophaga, for example, Damalinea sp. and Trichodectes sp.; (h) Thysanoptera, for example, Frankliniella sp., Hercinotnrips sp., Taeniothrips sp., Thrips palmi, Thrips tabaci and Scirtothrips aurantii; (i) Heteroptera, for example, Cimex sp., Distantiella theobroma, Dysdercus sp., Euchistus sp., Eurygaster sp., Leptocorisa sp., Nezara sp., Piesma sp., Rhodnius sp., Sahlbergella singularis, Scotinophara sp. and Tniatoma sp.; (j) Homoptera, for example, Aleurothrixus floccosus, Aleyrodes brassicae, Aonidiella sp., Aphididae, Aphis sp., Aspidiotus sp., Bemisia tabaci, Ceroplaster sp., Chrysomphalus aonidium, Chrysomphalus dictyospermi, Coccus hesperidum, Empoasca sp., Eriosoma larigerum, Erythroneura sp., Gascardia sp., Laodelphax sp., Lecanium corni, Lepidosaphes sp., Macrosiphus sp., Myzus sp., Nephotettix sp., Nilaparvata sp., Paratoria sp., Pemphigus sp., Planococcus sp., Pseudaulacaspis sp., Pseudococcus sp., Psylla sp., Pulvinaria aethiopica, Quadraspidiotus sp., Rhopalosiphum sp., Saissetia sp., Scaphoideus sp., Schizaphis sp., Sitobion sp., Trialeurodes vaporariorum, Trioza erytreae and Unaspis citri; (k) Hymenoptera, for example, Acromyrmex, Atta sp., Cephus sp., Diprion sp., Diprionidae, Gilpinia polytoma, Hoplocampa sp., Lasius sp., Monomorium pharaonis, Neodiprion sp., Solenopsis sp. and Vespa sp.; (1) Diptera, for example, Aedes sp., Antherigona soccata, Bibio hortulanus, Calliphora erythrocephala, Ceratitis sp., Chrysomyia sp., Culex sp., Cuterebra sp., Dacus sp., Drosophila melanogaster, Fannia sp., Gastrophilus sp., Glossina sp., Hypoderma sp., Hyppobosca sp., Liriomyza sp., Lucilia sp., Melanagromyza sp., Musca sp., Oestrus sp., Orseolia sp., Oscinella frit, Pegomyia hyoscyami, Phorbia sp., Rhagoletis pomonella, Sciara sp., Stomoxys sp., Tabanus sp., Tannia sp. and Tipula sp.; (m) Siphonaptera, for example, Ceratophyllus sp. und Xenopsylla cheopis and (n) from the order Thysanura, for example, Lepisma saccharina. The active ingredients disclosed herein may further be used for controlling crucifer flea beetles (Phyllotreta sp.), root maggots (Delia sp.), cabbage seedpod weevil (Ceutorhynchus sp.) and aphids in oil seed crops such as canola (rape), mustard seed, and hybrids thereof, and also rice and maize. Sarmentine and /or its analogs in these materials can be the only active ingredient(s) or a mixture with any other phytopathogenic and/or herbicidal compounds. In some embodiments, examples of natural herbicides that can used with sarmentine and its analogs include catechin, ellagic acid, sorgoleone, juglone, ceratiolin, usnic acid, 1,8-cineole, geranial, neral, cinmethylin, solstitiolide, ailanthone, chaparrine, ailanthinol B, hydroxamic acids, glucohirsutin, hirsutin, arabin, *meta*-tyrosine. Percent of sarmentine and/or its analogs in these compositions can be within a range of 0.01% to 99.99%.

[0045] In other embodiments, examples of synthetic herbicides that can used with sarmentine and/or its analog include aryloxyphenoxypropionic herbicides (e.g., chlorazifop, clodinafop, clofop, cyhalofop, diclofop, fenoxaprop, fenoxaprop-P, fenthiaprop, fluazifop, fluazifop-P, haloxyfop, haloxyfop-P, isoxapyrifop, metamifop, propaquizafop, quizalofop, quizalofop-P and trifop); benzoic acid herbicides (e.g., chloramben, dicamba, 2,3,6-TBA and tricamba); benzofuranyl alkylsulfonate herbicides (e.g., benfuresate and ethofumesate); benzoylcyclohexanedione herbicides (e.g., mesotrione, sulcotrione, tefuryltrione and tembotrione); carbamate herbicides (e.g., asulam, carboxazole chlorprocarb, dichlormate, fenasulam, karbutilate and terbucarb); carbanilate herbicides (e.g., barban, BCPC, carbasulam, carbetamide, CEPC, chlorbufam, chlorpropham, CPPC, desmedipham, phenisopham, phenmedipham, phenmedipham-ethyl, propham); cyclohexene oxime herbicides (e.g., alloxydim, butroxydim, clethodim, cloproxydim, cycloxydim, profoxydim, sethoxydim, tepraloxydim and tralkoxydim); cyclopropylisoxazole herbicides (e.g., isoxachlortole and isoxaflutole); dicarboximide herbicides (e.g., benzfendizone, cinidon-ethyl, flumezin, flumiclorac, flumioxazin and flumipropyn); dinitroaniline herbicides (e.g., benfluralin, butralin, dinitramine, ethalfluralin, fluchloralin, isopropalin, methalpropalin, nitralin, oryzalin, pendimethalin, prodiamine, profluralin and trifluralin); dinitrophenol herbicides (e.g., dinofenate, dinoprop, dinosam, dinoseb, dinoterb, DNOC, etinofen and medinoterb); dithiocarbamate herbicides (e.g., dazomet and metam; halogenated aliphatic herbicides such as alorac, chloropon, dalapon, flupropanate, hexachloroacetone, iodomethane, methyl bromide, monochloroacetic acid, SMA and TCA); imidazolinone herbicides (e.g., imazamethabenz, imazamox, imazapic, imazapyr, imazaquin and imazethapyr); inorganic herbicides (e.g., ammonium sulfamate, borax, calcium chlorate, copper sulfate, ferrous sulfate, potassium azide, potassium cyanate, sodium azide, sodium chlorate and sulfuric acid); nitrophenyl ether herbicides (e.g., acifluorfen, aclonifen, bifenox, chlomethoxyfen, chlornitrofen, etnipromid, fluorodifen, fluoroglycofen, fluoronitrofen, fomesafen, furyloxyfen, halosafen, lactofen, nitrofen, nitrofluorfen and oxyfluorfen); nitrile herbicides (e.g., bromobonil, bromoxynil, chloroxynil, dichlobenil, iodobonil, ioxynil and pyraclonil); organophosphorus herbicides (e.g., amiprofos-methyl, anilofos, bensulide, bilanafos, butamifos, 2,4-DEP, DMPA, EBEP, fosamine, glufosinate, glyphosate and piperophos); phenoxy herbicides (e.g., bromofenoxim, clomeprop, 2,4-DEB, 2,4-DEP, difenopenten, disul, erbon, etnipromid, fenteracol and trifopsime); phenoxyacetic herbicides (e.g., 4-CPA, 2,4-D, 3,4-DA, MCPA, MCPA-thioethyl and 2,4,5-T); phenoxybutyric herbicides (e.g., 4-CPB, 2,4-DB, 3,4-DB, MCPB and 2,4,5-TB); phenoxypropionic herbicides (e.g., cloprop, 4-CPP, dichlorprop, dichlorprop-P, 3,4-DP, fenoprop, mecoprop and mecoprop-P); phenylenediamine herbicides (e.g., dinitramine and prodiamine); picolinic acid herbicides (e.g., aminopyralid, clopyralid and picloram); pyrazolyl herbicides (e.g., benzofenap, pyrazolynate, pyrasulfotole, pyrazoxyfen, pyroxasulfone and topramezone); pyrazolylphenyl herbicides (e.g., fluazolate and pyraflufen; pyridazine herbicides such as credazine, pyridafol and pyridate); pyridazinone herbicides (e.g., brompyrazon, chloridazon, dimidazon, flufenpyr, metflurazon, norflurazon, oxapyrazon and pydanon); pyridine herbicides (e.g., cliodinate, dithiopyr, fluroxypyr, haloxydine, picolinafen, pyriclor, thiazopyr and triclopyr); pyrimidinediamine herbicides (e.g., iprymidam and tioclorim); quaternary ammonium herbicides (e.g., cyperquat, diethamquat, difenzoquat, diquat, morfamquat and paraquat); pyrimidinyloxybenzoic acid herbicides (e.g., bispyribac and pyriminobac); thiocarbamate herbicides (e.g., butylate, cycloate, di-allate, EPTC, esprocarb, ethiolate, isopolinate, methiobencarb, molinate, orbencarb, pebulate, prosulfocarb, pyributicarb, sulfallate, thiobencarb, tiocarbazil, triallate and vemolate); sulfonamide herbicides (e.g. asulam, carbasulam, fenasulam, oryzalin, penoxsulam, pyroxsulam); triazine herbicides (e.g., dipropetryn, triaziflam and trihydroxytriazine, atrazine, chlorazine, cyanazine, cyprazine, eglinazine, ipazine, mesoprazine, procyazine, proglinazine, propazine, sebuthylazine, simazine, terbuthylazine and trietazine, atraton, methometon, prometon, secbumeton, simeton and terbumeton; ametryn, aziprotryne, cyanatryn, desmetryn, dimethametryn, methoprotryne, prometryn, simetryn and terbutryn); triazinone herbicides (e.g., ametridione, amibuzin, hexazinone, isomethiozin, metamitron and metribuzin); triazolopyrimidine herbicides (chloransulam, diclosulam, florasulam, flumetsulam, metosulam); urea herbicides (e.g., benzthiazuron, cumyluron, cycluron, dichloralurea, diflufenzopyr, isonoruron, isouron, methabenzthiazuron, monisouron and noruron; anisuron, buturon, chlorbromuron, chloreturon, chlorotoluron, chloroxuron, daimuron, difenoxuron, dimefuron, diuron, fenuron, fluometuron, fluothiuron, isoproturon, linuron, methiuron, methyldymron, metobenzuron, metobromuron, metoxuron, monolinuron, monuron, neburon, parafluron, phenobenzuron, siduron, tetrafluron and thidiazuron; amidosulfuron, azimsulfuron, bensulfuron, chlorimuron, cyclosulfamuron, ethoxysulfuron, flazasulfuron, flucetosulfuron, flupyrsulfuron, foramsulfuron, halosulfuron, imazosulfuron, mesosulfuron, nicosulfuron, orthosulfamuron, oxasulfuron, primisulfuron, pyrazosulfuron, rimsulfuron, sulfometuron, sulfosulfuron and trifloxysulfuron; chlorsulfuron, cinosulfuron, ethametsulfuron, iodosulfuron, metsulfuron, prosulfuron, thifensulfuron, triasulfuron, tribenuron, triflusulfuron and tritosulfuron; buthiuron, ethidimuron, tebuthiuron, thiazafluron and thidiazuron), etc.

[0046] The composition may further comprise an additional fungicidal agent such as myclobutanil, and fenhexamide, azoxystrobin, azoxystrobin combination, boscalid, bacillus subtilis, copper sulfate, chlorothalonil, copper hydroxide, cymoxanil, dimethomorph, dechloropropene, fosetyl-aluminum, fludioxonil, fenamidone, iprodione, mefenoxam, mancozeb, metalaxyl, metam sodium, potassium bicarbonate, pyraclostrobin, propiconazole, propicocarb, thiram, thiabendazole, thiophanate-methyl, trifloxystrobin, vinclozolin, sulfur, ziram. They also may include the following antibacterial agents such as streptomycin and oxytetracycline.

[0047] The composition and method of the present invention will be further illustrated in the following examples. The examples are illustrative of various embodiments.

EXAMPLE

[0048] In the instant Example, results are disclosed showing that the methanol extract of dry long pepper (*Piper longum* L.) fruits are phytotoxic against bib lettuce (*Lactuca sativa*, L.) seedlings. The extract was subjected to bioassay-guided isolation and yielded one active compound. The active compound was identified as a known compound, called sarmentine and is the first time it is isolated from *P. longum.* Phytotoxic activity of sarmentine was examined with a variety of seedlings from crops, sedge and weeds. Results indicated that sarmentine is a contact herbicide and possesses broad-spectrum herbicidal activity. Sarmentine in the different dried *P. longum* fruits was quantified by liquid chromatography-mass spectrometry and found to vary dramatically, ranging from almost zero to 0.57%. In addition, a series of sarmentine analogs were then synthesized to study the structure-activity relationship (SAR). Results from SAR study suggested that either the long unsaturated fatty acid (i.e., 2*E*, 4*E*-decandienoic acid) or the amine (i.e., pyrrolidine) was crucial for activity, but the amide bond with a secondary amine seemed to be necessary for the phytotoxic activity of sarmentine.

MATERIALS AND METHODS

[0049] Chemical: Sepra C18-E (50 µM and 60 Å) and Silica gel sorbent (70-230 mesh size) were purchased from Phenomenex® (Torrance, CA, USA) and Fisher Scientific (Fair Lawn, NJ, USA), respectively. Polyoxyethylene (20) Sorbitan Monolaurate (i.e., Glycosperse O-20 KFG) and sodium lauryl sulfate (i.e., SLS) were obtained as free samples from Lonza Inc. (Allendale, NJ, USA) and Spectrum Chemical Mfg. Corp. (New Brunswick, NJ, USA), respectively. Cyclopentylamine, *trans*-cinnamic acid, ethyl *trans*-2-*cis*-4-decadienoate, hexamethyleneimine, *trans*-2-decenoic acid, decanoic acid, 4-dimethylaminopyridine are purchased from ACROS Organics (Morris Plains, New Jersey, USA). All other chemicals were of reagent grades.

[0050] Fruits of *P. longum* and pre-treatment: Four samples of dried *P. longum* fruits were purchased from Chinese medicinal herb stores. The fruits were completely ground with a coffee grinder (Toastmaster Inc., Boonville, MI, USA). The freshly ground powder of fruits was extracted with appropriate solvents.

[0051] Weed, sedge and crop seedlings: All weed, sedge and crop seedlings were planted in 8 cm X 8 cm X 7.2 cm or 10 cm

X 10 cm X 9 cm plastic pots. Seedlings including pigweed (*Amaranthus retroflexus*, L.), barnyard grass (*Echinochloa crusgalli* L.), bindweed (*Convolvulus arvensis* L.), crabgrass (*Digitaria sanguinalis* L.), dandelion (*Taraxacum officinale* F.), lambsquarters (*Chenopodium album* L.), bluegrass (*Poa annua* L.), wild mustard (*Brassica kaber* L.), black nightshade (*Solanum nigrum* L.), curly dock (*Rumex crispus* L.), horseweed (*Conyza Canadensis* L.), sweet corn (*Zea may* S.) and wheat PR 1404 (*Triticum aestivum* L.) were planted in Super Soil potting soil. Seedlings including rice M-104 (*Oryza saliva* L.), sedge (*Cyperus difformis* L.) and sprangletop (*Leptochloa fascicularis* Lam) were planted in mud which was collected from rice field (Woodland, CA, USA). When treated, all seedlings were 15 days old except for rice (10 days), wheat (20 days), corn (20 days) sprangletop (20 days old), sedge (20 days old) and horse weed (70 days old).

[0052] Bioassay-guided extraction and isolation: The active compound was isolated by four major steps described as follows: 1) the methanol extract of freshly ground *P. longum* fruit powder was screened in a 96-well plate bioassay with bib lettuce (*Lactuca sativa*) seedlings; 2) the methanol extract (0.5 gram) was subjected to a reverse C-18 column and was eluted with 20%, 40%, 60%, 80% and 100% methanol in water; Fractions were dried under vacuum and efficacy was re-evaluated by 96-well plate bioassay with bib lettuce (*Lactuca sativa*) seedlings. The active fraction was used to guide next step for separation; 3) Ethyl acetate extract (17.6 g) was loaded into a flash column. The column was sequentially eluted with hexane (1 L), hexane/ethyl acetate (3:1, 1L), hexane/ethyl acetate (1: 1, 1L), ethyl acetate (1L) and acetone (1L). Based on thin layer chromatography (TLC), nine fractions were collected. The efficacy of each fraction was evaluated by foliar spraying of barnyard grass (*Echinochloa crusgalli*). The concentration of each fraction was 5 mg/mL with a carrier solution consisting of 4% ethanol and 0.2% glycosperse O-20 KFG. The active fractions (3.4 g) were combined together and subjected to the next step; 4) A secondary silica column was performed with a combination of hexane and ethyl acetate (3:1) as an elution solvent. The active ingredient (0.96 g) was re-crystallized at - 20 °C in a mixture of hexane and ethyl acetate and yielded a pure active compound. Purity was examined by liquid chromatography and mass spectrometry (LC/MS). Detailed conditions for LC/MS was described later in Materials and Methods.

[0053] Structural elucidation: Structural identification of the active compound was based on data from both Nuclear Magnetic Resonance (NMR) spectra and high resolution mass spectrometry. NMR spectra including ^1H, ^{13}C, DEPT, COSY, HMQC and HMBC were acquired from a Bruker Avance 600 spectrometer (Bruker BioSpin Corporation, Billerica, MA, USA). Chemical shift values are given in ppm downfield from an internal standard (trimethylsilane). Signal multiplicities are represented as singlet (s), doublet (d), double doublet (dd), triplet (t), quartet (q), quintet (quint) and multiplet (m). Exact mass of the active compound was determined by high-performance liquid chromatography - tandem mass spectroscopy

[0054] Comparison of the active compound from different fruit samples: Ground fruit powder (10 g) of different samples was soaked in ethyl acetate (50 mL) for 20 h at room temperature. The solution was filtered by a Whatman® qualitative filter paper (NO 1, Ø 155 mm). The residue and filter paper was washed by ethyl acetate (25 mL). The combined organic phase was dried under vacuum. The weight of each extract was recorded. The active compound in the extracts was quantified by LC/MS.

[0055] Quantification of the active compound in the ethyl acetate extract of dried fruits by (LC/MS): Chromatographic separation was performed at 25°C on a Thermo high performance liquid chromatography (HPLC) instrument equipped with Finnigan Surveyor PDA plus detector, autosampler plus, MS pump and a 4.6 mm x 100 mm Luna C18 5 µm column (Thermo Electron Corp., San Jose, CA). The solvent system consisted of water (solvent A) and acetonitrile (solvent B). The mobile phase began at 10% solvent B and was linearly increased to 100% solvent B over 20 min and then kept for 4 min, and finally returned to 10% solvent B over 3 min and kept for 3 min. The flow rate was 0.5 mL/min. The injection volume was 10 µL and the samples were kept at room temperature in an auto sampler. The active compound was detected by a positive electrospray ionization mode in a full scan mode (m/z 100-1500 Da) on a LCQ DECA XP^{plus} Mass Spectrometer (Thermo Electron Corp., San Jose, CA). The flow rate of the nitrogen gas was fixed at 30 and 15 arb for the sheath and aux/sweep gas flow rate, respectively. Electrospray ionization (ESI) was performed with a spray voltage set at 5000 V and a capillary voltage at 35.0 V. The capillary temperature was set at 400°C.

[0056] The standard of the active compound was obtained by repeated crystallization in laboratory. A series of standard concentrations (125, 62.5, 31.25, 15.6, 7.8, 3.9, 1.95 and 0.976 ng/ml) was made in ethanol. Three independent samples (2.5µg/mL in ethanol) for each extract were made. Mass spectra were run in a SIM mode with a mass range of 221.0-224.0 and retention time (16.94 min). The limits of detection (LOD) of the active compound were determined by running decreasing amounts of standard solution until the ratio of the signal of the active compound over the background was greater or equal to 3. The concentration of fruit samples was presented by an average of three independent samples with a standard deviation.

[0057] Synthesis of sarmentine analogs: To the ice-cooled carboxylic acid (3 mmole) solution in dichloromethane (20 ml) was sequentially added 1-ethyl-3-(3'-dimethylaminopropyl) carbodiimide (3.3 mmole) and 4-dimethylaminopyridine (3 mmole). After 5 min, amine (3.3 mmole) was added in the reaction solution. The reaction was slowly warmed to the room temperature and lasted overnight. The reaction was extracted with ethyl acetate (200 mL). The organic phase was dried with anhydrous sodium sulfate. After evaporation under vacuum, the residue was run through a silica gel column with an appropriate ratio of ethyl acetate in hexane. The yield of the final products ranged from 85% to 90%. The final products were characterized with proton NMR.

[0058] ***N*-Cyclopentylcinnamamide** (7): ^{1}H NMR (CDCl$_3$): δ (ppm) 7.62 (d, *J*=15.6 Hz, 1H), 7.50 (d, *J*=7.0 Hz, 2H), 7.35 (m, 3H), 6.37 (d, *J*=15.6, 1H), 5.61 (d, *J*= 5.0, Hz, 1H, NH), 4.35 (sextet, *J*=7.0, 1H), 2.06 (m, 2H), 1.71 (m, 2H), 1.64 (m, 2H), 1.46 (m, 2H).

[0059] ***N*-(*trans*-Cinnamoyl)pyrrolidine** (11): ^{1}H NMR (CDCl$_3$): δ (ppm) 7.70 (d, *J*=15.5 Hz, 1H), 7.53 (d, *J*=7.0 Hz, 2H), 7.36 (m, 3H), 6.74 (d, *J*=15.5, 1H), 3.63 (t, *J*=7.0, 2H), 3.60 (t, *J*=7.0, 2H), 2.01 (quintet, *J*=7.0, 2H), 1.91 (quintet, *J*=7.0, 2H).

[0060] ***N*-(*trans*-Cinnamoyl)piperidine(15):** ^{1}H NMR (CDCl$_3$): δ (ppm) 7.64 (d, *J*=15.5 Hz, 1H), 7.52 (d, *J*=7.2 Hz, 2H), 7.36 (m, 3H), 6.90 (d, *J*=15.5, 1H), 3.67 (s, 2H), 3.59 (s, 2H), 1.68 (m, 2H), 1.62 (m, 4H).

[0061] ***N*-(*trans*-Cinnamoyl) hexamethleneimine (19):** ^{1}H NMR (CDCl$_3$): δ (ppm) 7.70 (d, *J*=15.4 Hz, 1H), 7.52 (d, *J*=7.6 Hz, 2H), 7.36 (m, 3H), 6.88 (d, *J*=15.4, 1H), 3.63 (t, *J*=6.0, 2H), 3.61 (t, *J*=6.0, 2H), 1.76 (m, 4H), 1.59 (m, 4H).

[0062] ***N*-Cyclopentyldecanamide (4):** ^{1}H NMR (CDCl$_3$): δ (ppm) 5.35 (br, 1H), 4.22 (sextet, *J*=7.00, 1H), 2.12 (t, *J*=7.20, 2H), 1.98(m, 2H), 1.59-1.67 (m, 6H), 1.26-1.36 (m, 14H), 0.88 (t, *J*=7.00, 3H).

[0063] ***N*-(Decanoyl)pyrrolidine** (8): ^{1}H NMR (CDCl$_3$): δ (ppm) 3.45(t, *J*=6.80, 2H), 3.40 (t, *J*=6.80, 2H), 2.24 (t, *J*=7.20, 2H), 1.94(quintet, *J*=6.80, 2H), 1.84(quintet, *J*=6.80, 2H), 1.62 (quintet, *J*=7.20, 2H), 1.25-1.30 (m, 12H), 0.87 (t, *J*=7.20, 3H).

[0064] ***N*-(Decanoyl)piperidine(12):** ^{1}H NMR (CDCl$_3$): δ (ppm) 3.55(t, *J*=5.20, 2H), 3.39 (t, *J*=5.20, 2H), 2.31(t, *J*=7.60, 2H), 1.58-1.65 (m, 4H), 1.52-1.57(m, 4H), 1.20-1.30 (m, 12H), 0.87 (t, *J*=7.20, 3H).

[0065] ***N*-(Decanoyl)hexamethyleneimine (16):** ^{1}H NMR (CDCl$_3$): δ (ppm) 3.52(t, *J*=6.00, 2H), 3.42 (t, *J*=6.00, 2H), 2.30(t, *J*=7.80, 2H), 1.66-1.74 (m, 4H), 1.60-1.66 (m, 2H), 1.50-1.6.0 (m, 4H), 1.20-1.30 (m, 12H), 0.87 (t, *J*=7.20, 3H).

[0066] ***N*-Cyclopentyldecanamide (5):** ^{1}H NMR (CDCl$_3$): δ (ppm) 6.82 (dt, J_1=15.20, J_2=7.20, 1H), 5.71 (d, *J*=15.20, 1H), 5.33 (br, 1H), 4.27 (sextet, *J*=7.00, 1H), 2.15 (m, 2H), 2.10(m, 2H), 1.67 (m, 2H), 1.60 (m, 2H), 1.40 (m, 4H), 1.28 (m, 8H), 0.88 (t, *J*=7.00, 3H).

[0067] ***N*-(Decenoyl)pyrrolidine (9):** ^{1}H NMR (CDCl$_3$): δ (ppm) 6.90 (dt, J_1=15.20, J_2=7.00, 1H), 6.07 (d, *J*=15.20, 1H), 3.52 (t, *J*=6.30, 2H), 3.50 (t, *J*=6.30, 2H), 2.19 (m, 2H), 1.96 (quintet, *J*=7.00, 2H), 1.85 (quintet, *J*=7.00, 2H), 1.44 (m, 2H), 1.28 (m, 8H), 0.88 (t, *J*=7.00, 3H).

[0068] ***N*-(Decenoyl)piperidine (13):** ^{1}H NMR (CDCl$_3$): δ (ppm) 6.82 (dt, J_1=15.20, J_2=7.00, 1H), 6.23(d, *J*=15.20, 1H), 3.59 (t, *J*=6.30, 2H), 3.47(t, *J*=6.30, 2H), 2.17 (m, 2H), 1.64 (quintet, *J*=5.60, 2H), 1.56 (quintet, *J*=5.60, 4H), 1.44 (quintet, *J*=7.00, 2H), 1.28 (m, 8H), 0.88 (t, *J*=7.00, 3H).

[0069] ***N*-(Decenoyl)hexamethyleneimine (17):** ^{1}H NMR (CDCl$_3$): δ (ppm) 6.91 (dt, J_1=15.20, J_2=7.00, 1H), 6.21(d, *J*=15.20, 1H), 3.57 (t, *J*=6.00, 2H), 3.49(t, *J*=6.00, 2H), 2.17 (m, 2H), 1.73 (m, 4H), 1.56 (m, 4H), 1.45 (m, 2H), 1.28 (m, 8H), 0.88 (t, *J*=7.00, 3H).

[0070] ***N*-Cyclopentyl 2*E*, 4*Z*-decadienamide(6):** ^{1}H NMR (CDCl$_3$): δ (ppm) 7.55(dd, J_1=14.80, J_2=11.70, 1H), 6.06 (t, *J*=11.70, 1H), 5.79 (d, J_1=14.80, 1H), 5.75 (m, 1H), 5.50 (br, 1H), 4.30 (sextet, *J*=7.00, 1H), 2.29 (quartet, *J*=8.20, 2H), 2.01 (m, 2H), 1.68 (m, 2H), 1.61(m, 2H), 1.40 (m, 2H), 1.28 (m, 6H), 0.88 (t, *J*=7.00, 3H).

[0071] **(2*E*, 4*Z*-Decadienoyl)pyrrolidine (10):** ^{1}H NMR (CDCl$_3$): δ (ppm) 7.62 (dd, J_1=14.60, J_2=11.70, 1H), 6.17 (d, *J*=14.60, 1H), 6.13 (t, *J*=11.70, 1H), 5.78 (m, 1H), 3.55 (t, *J*=7.00, 2H), 3.52 (t, *J*=7.00, 2H), 2.30 (quartet, *J*=7.40, 2H), 1.97 (quintet, *J*=7.40, 2H), 1.87 (quintet, *J*=7.40, 2H), 1.40 (quintet, *J*=7.40, 2H), 1.29 (m, 4H), 0.88 (t, *J*=7.00, 3H).

[0072] (2*E*,4*Z*-Decadienoyl)piperidine (14): ^{1}H NMR ($CDCl_3$): δ (ppm) 7.59(dd, J_1=14.60, J_2=11.70, 1H), 6.34 (d, *J*=14.60, 1H), 6.13 (t, *J*=11.70, 1H), 5.78 (m, 1H), 3.62 (t, *J*=7.00,2H), 3.45 (t, *J*=7.00, 2H), 2.31 (quartet, *J*=7.40, 2H), 1.67 (quintet, *J*=7.40, 4H), 1.57 (quintet, *J*=7.40, 2H), 1.40 (m, 2H), 1.27 (m, 4H), 0.88 (t, *J*=7.00, 3H).

[0073] (2*E*,4*Z*-Decadienoyl)hexamethleneimine (18): ^{1}H NMR ($CDCl_3$): δ (ppm) 7.64(dd, J_1=14.60, J_2=11.70, 1H), 6.30 (d, *J*=14.60, 1H), 6.16 (t, *J*=11.70, 1H), 5.78 (m, 1H), 3.60 (t, *J*=7.00, 2H), 3.51 (t, *J*=7.00, 2H), 2.31 (quartet, *J*=7.40, 2H), 1.76 (m, 4H), 1.57 (m, 4H), 1.40 (m, 2H), 1.30(m, 4H), 0.88 (t, *J*=7.00, 3H).

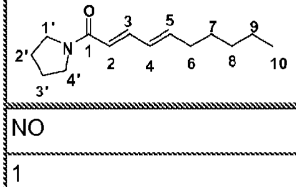
[0074] Evaluation of herbicidal activity: Herbicidal activity of the active compound and synthesized compounds was evaluated by foliar spraying. Spraying carrier solution contained 2% ethanol, 0.2% glycosperse O-20 and 0.1% sodium lauryl sulfate. Freshly made solution with the evaluated compound at a concentration of 5 mg/mL was used. In the spectrum study, spraying volume was dependent on the foliar surface area, ranging from approximately 1 to 3 mL/pot plants. One or two pots of plants were treated for each. Number of pots was dependent on both foliar area and availability. In the structure-activity relationship study, one pot of barnyard grass was used and the spraying volume of each compound was 3 mL of 5 mg/mL. Phytotoxic activity was evaluated at least 3 days after spraying. Efficacy of phytotoxic activity was graded as I (no effect), II (<20%), III (20-40%), IV (40-60%), V (60-80%) and VI (80-100%).

RESULTS

[0075] Bio-assay guided purification: The active compound was obtained by the following procedures. Initial experiment indicated phytotoxic activity in the methanol extract of *P. longum* dried fruits. The active ingredient(s) existed in the fraction with 100% methanol elution when a reversed C18 column was used, and no phytotoxic activity was shown from other fractions at 5 mg/mL (not shown). In our next experiment, ethyl acetate extract was run though a flash silica column. The elution was collected as 9 fractions (based on TLC indication). The weight of each fraction from 1 to 9 was 3.0, 1.0, 1.7, 3.6, 0.9, 2.5, 1.2, 0.2 and 2.3 gram, respectively. Two out of nine fractions were active against barnyard grass (Fig. 1). The combined two active fractions (i.e., Fr 5 & Fr 6, 3.4 g) were re-run through a silica column and yielded slightly yellowish oil as the active compound. This oil was re-crystallized in a mixture of hexane and ethyl acetate at -20 °C and obtained as colorless oil (0.83) at room temperature.

[0076] Structure elucidation: The active compound was identified based on the following evidence: High resolution mass data (TOF MS ESI$^+$) is 222.5386, indicating that the molecular formula of the active compound is most possibly $C_{14}H_{23}NO$. The data from ^{1}H and ^{13}C NMR listed in the Table 1 further supported this molecular formula. Data in the proton NMR indicate that there are a total of 23 protons including 4-olefenic protons (4CH), 1CH_3 and 8CH_2. Data from ^{13}C NMR and DEPT-135 (not shown) confirmed that there are 14 carbons including 1 amide carbonyl (N-CO-), 4CH, 8CH_2 and 1CH_3. Data from COSY (not shown) indicated that 2 spin systems are present in the molecule. One contains 4 consecutive CH_2. And another contains 4 conjugated olefin protons which are further connected to $CH_2CH_2CH_2CH_3$. Moreover, data from HMBC (not shown) indicated that the above-mentioned 2-spin systems are connected through an amide carbonyl to give the plane structure. Finally, geometric conformation is *trans* for both double bonds based on coupling constants (*J*=14.4 Hz). This active compound (Table 1) is a known compound called sarmentine, which was first purified from dried *P. sarmentosum* fruit powder (Likhitwitayawuid, K., Ruangrungsi, N, Lange, G and Decicco, C., Structural Elucidation and Synthesis of New Components isolated from Piper Samentosum, Tetrahedron 1987 (43) 3689-3694) and also from *P. nigrum* (Kiuchi, F.; Nakamura, N.; Tsuda, Y.; Kondo, K.; Yoshimura, H. Studies on crude drugs effective on visceral larva migrans, IV isolation and identification of larvicidal principles in Pepper, Chem Pharm. Bull, 1988, 36, 2452-2465). However, it is the first time that it was isolated from *P. longum* and found to be a phytotoxic compound.

Table 1 ^{1}H and ^{13}C NMR ($CDCl_3$) data of sarmentine



NO	^{13}C NMR data	^{1}H NMR data
1	165.4	-
2	120.0	6.08 1H d (*J*=14.4 Hz)

NO	^{13}C NMR data	^{1}H NMR data
3	142.4	7.26 1H dd (J_1=14.4, J_2=10.8 Hz)
4	128.8	6.16 1H dd (J_1=10.8, J_2=9.6 Hz)
5	143.4	6.07 1H dt (J_1=14.4, J_2=7.2 Hz)
6	33.1	2.13 2H quartet (J=7.2 Hz)
7	26.3	1.39 2H quintet (J=7.2 Hz)
8	24.5	1.27 2H m
9	22.7	1.27 2H m
10	14.2	0.87 3H t (J=7.2 Hz)
1'	46.6	3.50 2H t (J=7.2 Hz)
2'	31.5	1.95 2H quintet (J=7.2 Hz)
3'	28.6	1.85 2H quintet (J=7.2 Hz)
4'	46.0	3.52 2H t (J=7.2 Hz)

[0077] **Herbicidal spectrum of sarmentine:** Phytotoxic activity of sarmentine depended on the concentration. The optimal concentration of sarmentine was 5 mg/mL for excellent control of barnyard grass. Therefore, such a concentration was subjected to herbicidal spectrum study. Due to the hydrophobic property of sarmentine, a carrier solution containing 0.2% glycosperse O-20, 2% ethanol and 0.1% sodium lauryl sulfate was used. Although this solution contains a high concentration of surfactants, sarmentine can stay suspended in this solution no more than 15 min. Therefore, sarmentine was made freshly just before spraying. In addition, this solution did not show any phytotoxic activity toward tested plants when results were recorded.

[0078] Sarmentine displayed phytotoxic activity against a variety of plants including sedge, crops and weeds (Table 2).

Table 2 Phytoxtoxic activity of sarmentine toward different plants

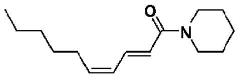
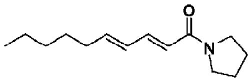
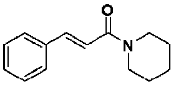
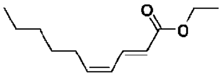
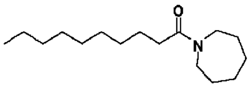
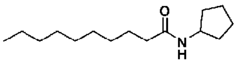
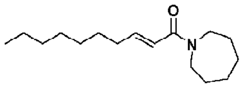
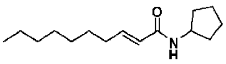
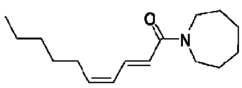
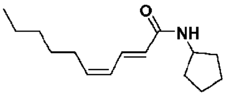
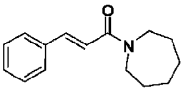
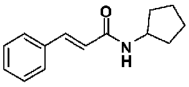
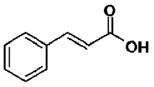
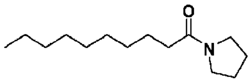
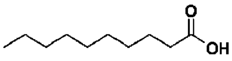
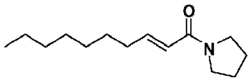
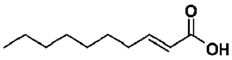
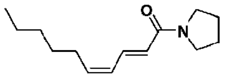
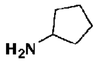
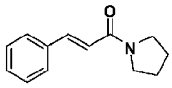
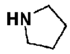
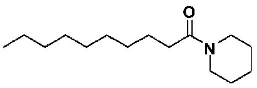
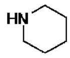
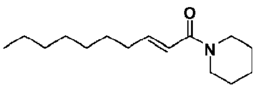
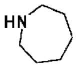
No	Plant name	Efficacy*	No	Plant name	Efficacy*
1	Pigweed (A*maranthus retroflexus*, L.)	VI	9	Lambsquarters (*Chenopodium album* L.)	VI
2	Barnyard grass (*Echinochloa crusgalli* L.)	VI	10	Bluegrass (*Poa annua* L.)	VI
3	Bindweed (*Convolvulus arvensis,* L.)	VI	11	Wild mustard (*Brassica kaber* L.)	VI
4	Crabgrass (*Digitaria sanguinalis* L.)	VI	12	Black nightshade (*Solanum nigrum* L.)	VI
5	Horse weed (*Conyza Canadensis* L.)	II	13	Curly dock (*Rumex crispus* L.)	VI
6	Sedge (*Cyperus difformis* L.)	III	14	Sweet corn (*Zea mays* S.)	VI
7	Sprangletop (*Leptochloa fascicularis* Lam.)	VI	15	Wheat (PR 1404) (*Triticum aestivum* L.)	VI
8	Dandelion (*Taraxacum officinale* F.)	VI	16	Rice (M 104) (*Oryza saliva* L)	I
*Efficacy of phytotoxic activity was graded as I (no effect), II (<20%), III (20-40%), IV (40-60%), V (60-80%) and VI (80-100%).					

[0079] Phytotoxic activity of sarmentine was dependent on the plants, ranging from zero to 100% killing. No visible phytotoxic activity (after 10 days) was shown on rice plants toward sarmentine. Slightly phytotoxic activity of sarmentine toward sedge and horseweed was shown. However, highly phytotoxic activity of sarmentine was displayed toward pigweed, barnyard grass, bindweed, crabgrass, sprangletop, dandelion, lambsquarters, blue grass, wild mustard, black nightshade, curly dock, sweet corn and wheat. The phytotoxic activity may be related to age of plants. For example, horseweed (70-day-old) was much older than other weeds, but less phytotoxic activity was shown.

[0080] **Structure-Activity Relationship (SAR):** The SAR study suggested that either the long unsaturated fatty acid or pyrrolidine of sarmentine is crucial for phytotoxic activity, but the amide bond with a secondary amine seemed to be necessary.

This conclusion was supported by the following experimental results which are summarized below in Table 3.

Table 3 Phytotoxic activity of sarmentine and its analogs toward barnyard grass

No	Structures	Efficacy *	No	Structures	Efficacy *
1 †	vector	I	14		VI
2		VI	15		IV
	(sarmentine)				
3 †		II	16		VI
4 †		II	17		VI
5 †		II	18		VI
6 †		II	19 †		II
7 †		II	20 †		V
8		VI	21 †		VI
9		VI	22 †		VI
10		VI	23 †		I
11		VI	24 †		I
12		VI	25 †		I
13		VI	26 †		I

*Efficacy of phytotoxic activity was graded as I (no effect), II (<20%), III (20-40%), IV (40-60%), V (60-80%) and VI (80-100%). † for reference, not according to the invention

[0081] Phytotoxic activity remained the same as the acid moiety of sarmentine was replaced by structurally similar fatty acids such as 2*E*, 4*Z*-decandienoic acid (i.e., geometric isomer of 2*E*, 4*E*-decandienoic acid) with two double bonds **(10),** 2 *E*-decenoic acid with one double bond **(9)** and decanoic acid without any double bond **(8),** and even structurally different acid such as *trans*-cinnamic acid **(11).** This suggested that the acid moiety of sarmentine can be various acids when the amine is pyrrolidine. Similarly, when the acid moiety remained the same, the amine can be various. For example, phytotoxic activity remained the same in terms of decanoic acid when the amine was changed from a five member ring **(8)** to a six or seven member ring **(12** & **16,** respectively). However, phytotoxic activity dropped dramatically when the amide bond with a secondary amine was changed into an ester bond (e.g., **3)** and an amide bond with a primary amine (e.g., **4-7).** In addition, results from SAR study (Table 3) also indicated that the amine moiety of sarmentine, pyrrolidine **(24),** and its analogs such as cyclopentylamine **(23),** hexamethyleneimine **(26)** and piperidine **(25)** were non toxic to barnyard grass; but the analogs of the acid moiety of sarmentine such as decanoic acid **(21),** 2*E*-decenoic acid and **(22)** and *trans*-cinnamic acid **(20)** were very active. To obtain a better SAR, the length of carbon chain in the acid moiety and disubstituted amines (non ring system) should be further investigated.

[0082] Symptom of phytotoxic activity: Sarmentine is a contact phytotoxic compound. When plants were treated with sarmentine solution, slightly black tiny spots would first show on the leaves and then became bigger and bigger until they covered the whole leaves, especially obvious on the barnyard grass. This symptom could be observed within half an hour to 2 hours after spraying. Predominant phytotoxic activity happened within 48 h after spraying. This symptom was observed very similarly to that of middle-chain fatty acids such as decanoic acid **(21,** Table 4) and 2*E*-decenoic acid **(22,** Table 3) during the SAR study.

[0083] Quantification of sarmentine in different *P. longum* fruit samples: The standard curve of sarmentine (Y=83324X-30784, R^2 =0.9998; X and Y stand for the concentration of sarmentine and peak area, respectively) was obtained. The limit of detection for sarmentine was 12 pg per injection (or 1.2 ng/mL). Based on this external standard curve, the concentration of sarmentine in the extracts of four different *P. longum* fruit samples varied from 0.0005% to 0.57%. These results are shown in Table 4.

Table 4. The concentration of sarmentine in different samples of dry *P. lungum* fruits

Sample	Percent of sarmentine in the ethyl acetate extract	Extract weight (g) from 10 gram of ground dried fruit powder	Percent content of sarmentine in the dry fruit
1	12.66 ± 0.45	0.45 ± 0.03	0.5697 ±.0380
2	1.83 ± 0.10	0.51 ± 0.03	0.0933 ± 0.0055
3	0.01 ± 0.001	0.55 ± 0.02	0.00055 ± 0.00002
4	0.008 ±0.001	0.66 ± 0.03	0.00053 ± 0.00002

[0084] This difference in amounts of sarmentine present in each of the samples may result from the age and/or origin of the dried fruits. The quantity of sarmentine in the ground powder of dried *P. longum* fruits can be viewed by naked eyes because the higher the concentration of sarmentine is, the more oily the ground powder is. For example, no oil was visible for the ground powder of samples 3 and 4, but oily powder was seen in the ground powder from samples 1 and 2.

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Patentkrav

1. Fremgangsmåde til bekæmpelse af et enkimbladet ukrudt, ukrudt af halvgræsfamilien eller tokimbladet ukrudt, hvilken fremgangsmåde omfatter påføring på ukrudtet af en mængde af et sarmentin eller en sarmentinanalog, som er effektiv til bekæmpelse af ukrudtet, hvor sarmentinanalogen er valgt blandt N-(decanoyl)pyrrolidin, N-(decenoyl)pyrrolidin, N-(decanoyl)piperidin, N-(trans-cinnamoyl)pyrrolidin, N-(trans-cinnamoyl)piperidin, (2E,4Z-decadienoyl)pyrrolidin, N-(decenoyl)piperidin, (2E,4Z-decadienoyl)piperidin, (2E,4Z-decadienoyl)hexamethylenimin, N-(decenoyl)hexamethylenimin og N-(decanoyl)hexamethylenimin, hvor sarmentinet eller sarmentinanalogen påføres ved bladpåføring.

2. Fremgangsmåde ifølge krav 1, hvor ukrudtet er et bredbladet ukrudt eller græsukrudt.

3. Fremgangsmåde ifølge krav 1, hvor ukrudtet er et risukrudt.

4. Fremgangsmåde ifølge et hvilket som helst af kravene 1-3, hvor sarmentinet eller sarmentinanalogen påføres på ukrudtet.

5. Fremgangsmåde ifølge et hvilket som helst af kravene 1-4, hvor ukrudtet er valgt blandt amarant, hanespore, snerle, fingeraks, canadisk bakkestjerne, sprangletop, løvetand, hvidmelet gåsefod, rapgræs, agersennep, sort natskygge og kruset skræppe.

6. Fremgangsmåde ifølge krav 1, hvor ukrudtet er valgt blandt *Amaranthus retroflexus,* L., *Echinochloa crusgalli* L., *Convolvulus arvensis,* L., *Digitaria sanguinalis* L., *Conyza canadensis* L., *Cyperus difformis* L., *Leptochloa fascicularis* Lam., *Taraxacum officinale* F., *Chenopodium album* L., Poa *annua* L., *Brassica kaber* L., *Solanum nigrum* L. og *Rumex crispus* L.

7. Herbicid sammensætning, der omfatter (a) sarmentin eller en sarmentinanalog, hvor sarmentinanalogen er valgt blandt N-(decanoyl)pyrrolidin, N-(decenoyl)pyrrolidin, N-(decanoyl)piperidin, N-(trans-cinnamoyl)pyrrolidin, N-(trans-cinnamoyl)piperidin, (2E,4Z-decadienoyl)pyrrolidin, N-(decenoyl)piperidin, (2E,4Z-decadienoyl)piperidin, (2E,4Z-decadienoyl)hexamethylenimin, N-(decenoyl)hexamethylenimin og N-(decanoyl)hexamethylenimin; og (b) ét eller flere andre herbicide midler til anvendelse ved modulering af fremkomsten af ukrudt.