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Herbicidal Activity of Glucosinolate Degradation Products in Fermented Meadowfoam (*Limnanthes alba*) Seed Meal

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Meadowfoam (*Limnanthes alba*) is an oilseed crop grown in western Oregon. After extraction of the oil from the seeds, the remaining seed meal contains 2−4% of the glucosinolate glucolimnanthin. This study investigated the effect of fermentation of seed meal on its chemical composition and the effect of the altered composition on downy brome (*Bromus tectorum*) coleoptile emergence. Incubation of enzyme-inactive seed meal with enzyme-active seeds (1% by weight) resulted in complete degradation of glucolimnanthin and formation of 3-methoxybenzyl isothiocyanate in 28% yield. Fermentation in the presence of an aqueous solution of $FeSO_4$ (10 mM) resulted in the formation of 3-methoxyphenylacetonitrile and 2-(3-methoxyphenyl)ethanethioamide, a novel natural product. The formation of the isothiocyanate, the nitrile, and the thioamide, as a total, correlated with an increase of herbicidal potency of the seed meal ($r^2 = 0.96$). The results of this study open new possibilities for the refinement of glucosinolate-containing seed meals for use as bioherbicides.

KEYWORDS: Meadowfoam; seed meal; *Limnanthes alba*; glucosinolate; glucolimnanthin; herbicide; isothiocyanate; nitrile; thioamide

INTRODUCTION

The continuing growth of organic farming practices calls for increased use of pesticides derived from naturally occurring materials. Many plants produce toxic phytochemicals when attacked by herbivores (phytoalexins) or deposit protoxic glycosides in leaves that prevent seed germination of other, neighboring plants when the aglycones are released from the shed leaves (allelochemicals). Glucosinolates form a group of allelochemicals produced by many species of the Brassicales, including *Brassica* and *Sinapis* spp. (mustards), *Lepidium* and *Nasturtium* spp. (cresses), and *Limnanthes* spp. (meadowfoams) (*1*). The interest in *Brassica* glucosinolates is primarily due to their presence in oilseeds because they are retained in the marc after oil extraction (meal). Glucosinolate-containing seed meals are intensively investigated as biofumigants for weed control (*2*, *3*).

White meadowfoam (*Limnanthes alba* Hartw. ex Benth., Limnanthaceae) is native to southern Oregon and northern California (*4*, *5*). Several cultivars have emerged from a meadowfoam breeding program at Oregon State University (*6*). The species is cultivated in the Willamette valley of western Oregon for the seed oil, which is rich in unusual 20:1 and 22:1 fatty acids (*7*). The oil has commercial value as an ingredient of skin care products. The spent seed material (meal) can be used as a bioherbicide due to the presence of allelochemicals. The meal contains the glucosinolate glucolimnanthin **1** (*8*) and 3-methoxyphenylacetonitrile (also referred to as 3-methoxybenzyl cyanide, **2**), a known allelochemical (*9*) formed by heat-induced degradation of **1** (**Figure 1**) during the oil extraction process. Because water is added at an early stage of the industrial oil extraction process to facilitate seed crushing, conversion of **1** into 3-methoxybenzyl isothiocyanate **3**, catalyzed by myrosinase in the seed, would occur if the enzyme were not inactivated by application of heat. Early heat treatment is necessary to inactivate myrosinase and prevent contamination of the oil with nonpolar breakdown products of **1**, whereas late-stage heat treatment follows extraction of seed oil with an organic solvent with the purpose of removing residual solvent.

When seed meal is applied to soil for weed control, a disadvantage of the lack of myrosinase activity in seed meal is that breakdown of **1** depends on the soil microenvironment, which may lead to variable results regarding degradation kinetics, profile of degradation products, and weed suppression. In this study, the conversion of **1** into the allelochemicals **2**, **3** (*9*) and 2-(3-methoxyphenyl)ethanethioamide (**4**) in enzyme-inactive meal was investigated by making use of active enzymes present in meadowfoam seeds and a cofactor, $FeSO_4$. We

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