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Volatile Constituents of *Amaranthus retroflexus* L.

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The volatile organic compound mixture released by aqueous *Amaranthus retroflexus* L. plant tissue suspensions was examined by combined headspace trapping/gas chromatography/mass spectrometry. The headspace profile was found to change significantly with time; large quantities of hexanal were released immediately after preparation of the blended suspension, along with lesser amouts of other five- and six-carbon oxygenated compounds. With time, the hexanal content dropped considerably, leaving *trans*-2-hexenal as the major released volatile. Headspace examination of a vacuum steam distillate prepared from a freshly prepared tissue suspension revealed no significant composition changes with time, but major quantitative differences were noted on comparison with the tissue suspension headspace profile. The common alcohols *cis*-3-hexen-1-ol, 1-hexanol, and *trans*-2-hexen-1-ol predominated in the steam distillate profile.

Parasitoids of certain crop pests often find a diverse plant environment preferable to the more typical monocultures in commercial agriculture. Presumably, complex crop mixtures are more chemically diverse than monocultures, and therefore they offer a more complex mosaic of local search areas, arousing parasitic wasps (Altieri et al., 1981). Structural plant diversity in crop fields can be increased by intercropping or by permitting selected weed growth in a monoculture. Chemical diversity, however, can be enhanced by applying blended aqueous suspensions of plants that are directly attractive to parasitoids (Monteith, 1960; Read et al., 1970) to the growing crop (Altieri et al., 1981). For example, spray application of *Amaranthus* suspensions to soybean plots resulted in increased parasitization of *Heliothis zea* (Boddie) eggs by the parasitic wasp *Trichogramma* spp. (Altieri et al., 1982). Similar parasitic enhancements have been observed by utilizing tomato extracts (Nordlund, 1983). Since the effectiveness of treatment with these suspensions is thought to be due to certain of their volatile constituents, the evolved volatiles mixtures from the most effective weed tested (*Amaranthus retroflexus* L., pigweed) was examined in some detail.

EXPERIMENTAL SECTION

Materials. Fresh *Amaranthus retroflexus* L. plants were collected from the grounds of the University of California's Gill Tract (Albany, CA) as needed. Tenax-GC (60–80 mesh) was obtained from Applied Science Laboratories, Inc. (State College, PA).

Equipment. Tenax sampling traps were constructed from 7.6-cm lengths of 0.635 cm o.d. Type 304 stainless steel tubing. Fine stainless steel mesh screens held the granular polymer in place (approximately 120 mg; 2.5-cm bed length). Sampling chambers consisted of 2-L glass canning jars fitted with machined aluminum top plates. An inlet tube for charcoal-filtered air and a Swagelok outlet fitting for attachment of the Tenax traps were mounted on the top plates.

A small battery-powered sampling pump was used to draw air from the sample chamber through the polymer trap at a constant rate (20, 50, or 100 cm^3/min) determined by an in-line flow restrictor. Details of the trap, sample chamber, and sampling procedure have been reported previously (Flath and Ohinata, 1982).

Fresh *A. retroflexus* Sample Examination. *A. retroflexus* L. volatiles were first collected from the headspace above intact fresh leaves and stems. Fresh leaves and stems were then blended with distilled water and the resulting headspace volatiles were collected in a second Tenax trap.

Vacuum Steam Distillation. In a typical preparation, *A. retroflexus* (3.9 kg of leaves, stems, and immature seed heads) was blended with distilled water (7 L), and the mixture was distilled at 30 mm. Because of excessive foaming, a quantity of silicone antifoam agent (preboiled with distilled water) was added. The distillate receiver was suspended in a solid carbon dioxide–2-propanol bath. After 5 h, 1.1 kg of distillate had collected. The pot contents were held at room temperature under vacuum overnight, and then two additional fractions were collected

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Table I. Identified Headspace Components

component	Kovats index GC/MS	Kovats index ref	aq susp	vac co-dist
acetaldehyde	410	413		+
methanol	450	456		+
ethanol	480	484		+
propanal	500	501		+
dimethyl sulfide	512	510	+	+
methyl acetate	519	519		+
2-methylpropanal	541	539		+
butanal	575	575	+	+
2-butanone	580	582		+
1-propanol	581	583		+
ethyl acetate	603	600		+
2-butanol	613	613		+
3-methylbutanal	637	635	+	+
2-methylbutanal	646	644	+	+
1-penten-3-one	676	671	+	+
3-pentanone	685	680	+	+
1-penten-3-ol	703	703	+	+
3-pentanol	710	708		+
trans-2-pentenal	741	740	+	
3-methylbutan-1-ol	749	750		+
hexanal	781	783	+	+
trans-2-hexenal	838	838	+	+
cis-3-hexen-1-ol	877	875	+	+
1-hexanol	885	885		+
trans-2-hexen-1-ol	893	890		+
2-heptanol	906	908		+
3-butenyl isothiocyanate	965	965		+
2,3-octanedione	971	971		+
myrcene	988	985		+
cis-3-hexenyl acetate	995	995		+
1-hexyl acetate	1000	1000		+
trans-2-hexenyl acetate	1003	1003		+
p-cymene	1017	1014		+
limonene	1027	1022		+
ocimene	1044	1040		+
cis-3-hexenyl propionate	1087	1087		+
nonanal	1094	1087		+
linalool	1105	1105		+
cis-3-hexenyl butyrate	1178	1175		+

(0.9 kg after 2 h; 0.8 kg after an additional 2 h). These three distillates were used for field testing without further treatment. In addition, headspace samples of the various fractions were collected with the appartus described above.

Trapped Volatile Desorption and Examination. Trapped volatiles were desorbed from the Tenax by reversing the gas flow (purified helium) and heating the trap. The desorbed material was retrapped in a liquid nitrogen cooled stainless steel spiral trap. The trapped volatiles were then transferred to the gas chromatographic (GC) column in a tight plug by rapidly heating the chilled spiral trap with a hot air blower. Details of the procedure and valving arrangements have been previously described (Noble et al., 1980; Flath and Ohinata, 1982).

Gas chromatographic separations were made with 152 m × 0.76 mm i.d. stainless steel capillary columns coated with methyl silicone oil containing a surfactant [SF 96(50) plus 5% Igepal CO-880]. A Hewlett-Packard 5830A gas chromatograph was used for flame ionization detector (FID) runs, and a quadruple mass spectrometer (EAI mass filter; Finnigan 3000 electronics) coupled with a lab-constructed gas chromatograph was employed for GC/MS work (Noble et al., 1980). During analytical FID runs, the column was temperature programmed as follows: 25 °C for 1 min; 25 to 50 °C at 5 °C/min; 50 °C for 4 min; then 50 to 180 °C at 1.25 °C/min. Mass spectral identifications were verified by retention index checks, using authentic samples of the components in question. Both the HP 5830A and the GC/MS unit were fitted with valving/spiral trap units for sample desorption and transfer.

RESULTS AND DISCUSSION

Table I lists the compounds identified in headspace examinations of the various *A. retroflexus* samples.

The headspace profile of fresh *Amaranthus* leaves and stems is strongly afffected by the treatment received by the plant tissue. Very little volatile organic material could be detected in the headspace above undamaged leaves and stems freshly collected from the *Amaranthus* plant. When a fresh leaf and stem sample was blended with distilled water, large quantities of hexanal were released, accompanied by lesser amounts of *trans*-2-hexenal, and small quantities of *cis*-3-hexen-1-ol, 1-penten-3-one, 3-pentanone, 1-penten-3-ol, and numerous minor components. When the blended material was allowed to stand for several hours, the hexanal headspace concentration was found to have decreased by a factor of 2.5, while *trans*-2-hexenal, *cis*-3-hexen-1-ol, and the other components remained fairly constant. The hexanal concentration continued to decrease with time; after overnight storage, the blended *A. retroflexus* tissue yielded a headspace profile containing hexanal as only a minor component. *trans*-2-Hexenal was now the major constituent, and the *cis*-3-hexen-1-ol concentration had increased slightly. No other major quantitative changes were observed. The factor(s) responsible for the selective reduction in hexanal concentration was (were) not determined. These appreciable changes in the blended *Amaranthus* tissue headspace profile with time are of interest because such blended material was used by Altieri et al. (1981) to increase *Trichogramma* predatory activity. The pattern of volatiles released by such blended material after application to a test plot is a function of the time interval between blending and application.

One of the practical difficulties in using an aqueous suspension of freshly blended plant tissue for test plot treatments is the instability of the material. After several days of storage, even at reduced temperature, the suspension is completely inactive, changing in the process from a bright green opaque suspension to a relatively clear aqueous phase above a dull green precipitate. In greenhouse studies, Altieri et al. (1982) found that parasitization rates progressively increased in a 24-h period with no observable decline. In soybean fields, however, the attractive effect of *Amaranthus* spp. application was lost after 72 h (Altieri et al., 1981). The vacuum steam distillate samples were prepared from blended plant tissue in an attempt to produce a more stable test solution for bioassay experiments. Headspace examination of the steam distillates revealed much higher concentrations of the common C-6 alcohols *cis*-3-hexen-1-ol, 1-hexanol, and *trans*-2-hexen-1-ol, relative to those of hexanal and *trans*-2-hexenal, than was found in the headspace of the blended plant tissue itself; the vacuum steam distillation process distorts the original plant tissue pattern. Although the distillate is much more stable than the plant tissue suspension, such compositional differences are undesirable, if the steam distillate is to be used as a more stable substitute for the unstable tissue suspension itself in bioassay efforts.

Testing of vacuum steam distillates and synthetic solutions for enhancing *Trichogramma* parasitization of lepidopterous spp. is under study; details of the test procedures and results will be published elsewhere.

Registry No. Acetaldehyde, 75-07-0; methanol, 67-56-1; ethanol, 64-17-5; propanal, 123-38-6; dimethyl sulfide, 75-18-3; methyl acetate, 79-20-9; 2-methylpropanal, 78-84-2; butanal, 123-72-8; 2-butanone, 78-93-3; 1-propanol, 71-23-8; ethyl acetate, 141-78-6; 2-butanol, 78-92-2; 3-methylbutanal, 590-86-3; 2-methylbutanal, 96-17-3; 1-penten-3-one, 1629-58-9; 3-pentanone, 96-22-0; 1-penten-3-ol, 616-25-1; 3-pentanol, 584-02-1; *trans*-2-pentenal, 1576-87-0; 3-methylbutan-1-ol, 123-51-3; hexanal, 66-25-1; *trans*-2-

hexenal, 6728-26-3; *cis*-3-hexen-1-ol, 928-96-1; 1-hexanol, 111-27-3; *trans*-2-hexen-1-ol, 928-95-0; 2-heptanol, 543-49-7; 3-butenyl isothiocyanate, 3386-97-8; 2,3-octanedione, 585-25-1; myrcene, 123-35-3; *cis*-3-hexenyl acetate, 3681-71-8; 1-hexyl acetate, 142-92-7; *trans*-2-hexenyl acetate, 2497-18-9; *p*-cymene, 99-87-6; limonene, 138-86-3; ocimene, 29714-87-2; *cis*-3-hexenyl propionate, 33467-74-2; nonanal, 124-19-6; linalool, 78-70-6; *cis*-3-hexenyl butyrate, 16491-36-4.

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Fate of Avermectin B_1a in Soil and Plants

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Laboratory studies of the fate of ^{3}H-labeled avermectin B_1a (AVM) in Lufkin fine sandy loam, Houston clay, and coarse sand demonstrated that under aerobic conditions the compound was degraded at a fairly rapid rate (respective half-lives of AVM in the three soils at a 1-ppm treatment rate were ca. 14–28, 28–56, and 56 days) to at least 13 radioactive products. The major soil degradation product was an equilibrium mixture (ratio of 1:2.5) of the 8α-hydroxy derivative and the corresponding ring-opened aldehyde derivative of AVM. AVM did not leach in any of the three soil types. In cotton seedlings grown either in aged or unaged samples of Lufkin fine sandy loam treated with [^{3}H]AVM (10 ppm) little ($\leq$0.1 ppm) radioactive material was absorbed by roots and translocated to the aerial portions of the plant. Surface residues of [^{3}H]AVM applied to individual cotton leaves in the field were rapidly depleted (half-life < 1 day) and little radioactive material (maximum of ca. 8%) was absorbed by treated leaves. Field tests of a fire ant bait formulation of [^{14}C]AVM applied to the soil furface at rates of 50, 100, and 500 mg of AI/acre indicated that little if any radioactive material (<0.01 ppm) was taken up by Bermuda grass grown in the treated areas.

The insecticide/acaricide avermectin B_1a (AVM, Figure 1) is one of several macrocyclic lactones formed during microbial fermentation reactions involving the actinomycete *Streptomyces avermitilis* (Burg et al., 1979). AVM is a neurotoxin that is thought to manifest its action by disrupting the normal function of γ-aminobutyric acid (GABA), an important neurotransmitter in the central nervous system of vertebrates and in the peripheral nervous system of invertebrates. In vitro studies with preparations of rat brain have shown that AVM stimulates presynaptic release of GABA (Pong et al., 1980) and enhances postsynaptic binding of GABA (Pong and Wang, 1982); the action of AVM is antagonized by bicuculline and picrotoxin. AVM is quite toxic to mammals; the acute oral LD_{20} (mice and rats) is 10–30 mg/kg and the acute dermal LD_{50} (rats and rabbits) is <400 mg/kg. However, the exceptionally high toxicity of this compound to certain arthropods is such that use patterns can probably be developed so that acute hazards to mammals and other nontarget organisms will be greatly minimized (Putter et al., 1981).

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AVM is being investigated for possible use in controlling different phytophagous pests of field crops and citrus (Ku, 1983) and fire ants (Lofgren and Williams, 1982). Our report contains the results of studies of the fate of AVM after application to laboratory and field soils and to cotton plants. Specific tests reported on here include (1) laboratory studies with three types of soil to characterize the leaching of radiolabeled AVM and its degradation over time following application at different concentrations, (2) greenhouse studies to determine if [^{3}H]AVM or its radioactive degradation products are taken up by cotton seedlings grown in treated soil, (3) field studies of the absorption and degradation of [^{3}H]AVM after foliar application to cotton, and (4) field studies to determine the fate of [^{14}C]AVM after its application in a fire ant bait formulation to the soil surface and to evaluate the possible uptake of AVM or its radioactive degradation products by grass grown in treated areas.

MATERIALS AND METHODS

Chemicals. Samples of technical (>95% pure) AVM, unlabeled or radiolabeled with ^{3}H at the 5-position (specific activity 1.74 mCi/mg) or with ^{14}C at the 3-, 7-, 11-, 13-, and 23-positions (specific activity 16.4 μCi/mg), were provided by Merck & Co., Inc., Rahway, NJ. Also provided was a bait formulation (vide infra) of [^{14}C]AVM comparable to one that is being tested for efficacy against fire ants. Unlabeled samples of two potential degradation products, the 5-ketone and monosaccharide derivatives of AVM, were made available for use as an analytical standards.

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