Short Communication

Arrestants to *Oryzaephilus surinamensis* L. from Wheat Flour Infested by the Same Weevil

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From a hexane extract of wheat flour infested by the sawtoothed grain beetle [*Oryzaephilus surinamensis* (L.); Coleoptera; Silvanidae], two compounds having arrestive activity were isolated and identified as 13-oxo-cis-9-octadecenoic acid and 15-oxo-cis-11-icosenoic acid.

Key words: Oryzaephilus surinamensis L.; infested wheat flour; arrestants; 13-oxo-cis-9-octadecenoic acid; 15-oxo-cis-11-icosenoic acid.

Prevention of grain beetle infestation in stored foods is requisite to preserve and improve food quality as well as ensuring ample foods on the Earth in our future. *Oryzaephilus surinamensis* L. is a famous weevil (noxious insect), which is globally distributed and is known to infest fresh wheat grain in particular. To seize the ecological aspects, we have studied the behavior of the insect in the infestation on the basis of pheromone chemistry. It was disclosed by us that in wheat flour infested by *Oryzaephilus surinamensis*, some substances existed which were not contained in the fresh wheat flour but had arrestive activity on the same pest. This phenomenon has been noted since some insects use chemicals to avoid intra- and interspecific competition, as recently reported by Byers for spruce bark beetles, *Ips typographus* and *Pityogenes chalcographus*. This communication describes the first isolation and structural identification of chemical components showing arrestive activity from infested wheat flour.

The weevils were reared on wheat flour containing 5% (w/w) brewer’s yeast at 26–28°C in the dark and were preconditioned without food five days before bioassay. The assay for arrestive activity was done in a Petri dish (4 cm dia.) with two paper disks (0.5 cm dia.) one of which was treated with sample solution and the other, blank. Here, the arrestive activity is defined as the number of insects arrested on a paper disk that is impregnated with the sample solution to be tested. Percent (%) response was calculated by a formula 100 (T − B)/N, where T and B were the number of beetles on the treated and blank disks, respectively after 10 min at 26–28°C in the dark, and N was the total number of beetles used.

The wheat flour (200 g) infested with newly emerging adults (about 200) of both sexes of *O. surinamensis* for 3 months was passed through a sieve for removing all life stages of mixed age and sex and was extracted with hexane (800 ml). After evaporation of the solvent, the residue (1.6 g) was chromatographed repeatedly on silica gel eluted with hexane/ethyl acetate, stepwise. Further purification was done on silylized precoated prep. TLC (MeOH/H2O, 7:3). Two components, compound 1 (Rf, 0.65, 2 mg) and compound 2 (Rf, 0.61, 1 mg) were isolated. Their biological activities are shown in the Figure. Their Rf values of 0.25 (compound 1) and 0.29 (compound 2) on silica gel 60 TLC (Merck 5554, hexane/EtOAc, 3:1) were increased greatly by treatment with diazomethane (Rf, 0.81 for compound 1 and 0.82 for compound 2), suggesting they have carboxyl groups. Here, we abbreviate methyl ester of the compounds 1 and 2 as 1-Me and 2-Me, respectively.

In the 1H-NMR spectrum of 1-Me, two olefin proton signals having =11 Hz were observed, suggesting the existence of one cis-double bond. The spectrum also showed that the component had a long chain normal hydrocarbon. Absorption at 1745 cm⁻¹ and 1717 cm⁻¹ on FT-IR as well as coloration with 2,4-dinitrophenylhydrazine suggested the presence of ester and carbonyl groups. The molecular weight was 310 by EI-MS. The prominent peak of fragment ion at m/z 99 (γ-scission), together with the peak at m/z 71 (loss of CO from the fragment ion at m/z 99) were observed, suggesting the presence of the ketone group at 13-position of the long chain fatty acid ester. Ozonolysis of 1-Me afforded methyl 9-oxononanoate. Based on all of the above data, we presumed the structure of the compound 1 as 13-oxo-cis-9-octadecenoic acid shown in Scheme.

![Figure](image)

**Fig.** Response of *O. surinamensis* to Compounds 1 and 2. (*) is significant at p < 0.05 based on t-test.

![Scheme](image)

Scheme Structures of Compounds 1 and 2.
Likewise, the structure of the compound 2 was assigned as 15-oxo-cis-11-icosenoic acid.  

The chemical syntheses of the two compounds in a large amount will hopefully contribute to the elucidation of their ecological meanings in the life of *O. surinamensis*. Their possible applicability to the prevention of grain weevils is also an interesting subject.

References and Notes


4) $^1$H-NMR (500 MHz, CDCl₃) δ: 0.86 (3H, t, $J = 7$ Hz, $\text{CH}_3$), 1.20-1.35 (12H, br., $\text{CH}_2$-), 1.58 (4H, m, $\text{CH}_2$-CH₂-), 2.27 (4H, m, COCH₂CH₂CH=CH₂-OOC-), 2.37 (2H, t, $J = 7.5$ Hz, CH₂(CH₃)₂CO-), 2.41 (2H, t, $J = 7.5$ Hz, COCH₂CH₂=CH₂-), 3.64 (3H, s, $\text{CH}_3$-O-), 5.28 (1H, dt, $J = 11, 7, 1.5$ Hz, =CH-CH₂-), and 5.36 (1H, dt, $J = 11, 7, 1.5$ Hz, COCH₂CH₂=CH₂-).

5) $^1$H-NMR (CDCl₃, 500 MHz) δ: 0.88 (3H, t, $J = 7$ Hz, $\text{CH}_3$), 1.20-1.35 (16H, br., $\text{CH}_2$-), 1.58 (4H, m, $\text{CH}_2$-CH₂-), 2.26 (4H, m, COCH₂CH₂CH=CH₂-OOC-), 2.37 (2H, t, $J = 7.5$ Hz, CH₂(CH₃)₂CO-), 2.42 (2H, t, $J = 7.5$ Hz, COCH₂CH₂=CH₂-), 3.65 (3H, s, $\text{CH}_3$-O-), 5.27 (1H, dt, $J = 11, 7, 1.5$ Hz, =CH-CH₂-), and 5.36 (1H, dt, $J = 11, 7, 1.5$ Hz, COCH₂CH₂=CH₂-).