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Effects of 2-Tridecanone and Analogues on the Reproduction and Mortality of Stored Product Insects[1]

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ABSTRACT: The effects of 2-tridecanone and 31 analogues on the reproduction and mortality of stored product insects were determined. The parent compound suppressed progeny development of the granary weevil, *Sitophilus granarius* L., maize weevil, *Sitophilus zeamais* Motschulsky and rice weevil *Sitophilus oryzae* L. with ED_{50} values of 167–497 ppm on wheat. No effects on the confused flour beetle, *Tribolium confusum* Jacquelin du Val, red flour beetle, *Tribolium castaneum* Herbst, lesser grain borer, *Rhyzopertha dominica* Fabricius, sawtoothed grain beetle, *Oryzaephilus surinamenis* L., Indianmeal moth, *Plodia interpunctella* Hubner and almond moth, *Ephestia cautella* Walker, were observed. 2-Tridecanone was repellent to the granary weevil at concentrations of 100 and 500 ppm on wheat. Of the 31 structural analogues or derivatives tested, only 2-tridecanyl acetate surpassed 2-tridecanone in insecticidal activity. This ester exhibited an acute toxicity toward the stored product beetles when impregnated into filter paper and when mixed with wheat based diets. 2-Tridecanyl acetate or a more active derivative may have potential as a protectant of stored commodities against insects.

2-Tridecanone is a natural product found in the foliage of wild and cultivated tomato plants (Soost et al., 1968; Williams et al., 1980; Dimock and Kennedy, 1983). This simple ketone occurs at high enough levels in the wild variety of tomatoes included in the plant genus *Lycopersicon* to produce a unique nonalkaloid chemical defense against certain phytophagous insects. The 5- and 6-homologues are feeding inhibitors for the adult striped cucumber beetle, *Acalymma vittata* (Fabricius) at 0.5% concentration on plants (Reed et al., 1981) while the 10-methyl derivative is a pheromone of the southern corn rootworm (Senda and Mori, 1983). Because these compounds have little or no mammalian toxicity (Lewis and Tatken, 1979), they may have potential as protectants of stored commodities. New protectants are needed because resistance to currently approved chemical insecticides is becoming acute and widespread (Beeman et al., 1982; Haliscak and Beeman, 1983). We therefore applied the tridecanones and several analogues to stored wheat and evaluated the growth-inhibiting activity of these compounds against eight species of insects that infest stored products.

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Materials and Methods

CHEMICALS AND INSECTS: 2-Tridecanone was obtained from Pfaltz and Bauer Inc. (Stanford, Connecticut) and the Organic Chemical Synthesis Laboratory (Beltsville, Maryland). Other chemicals were supplied by the Organic Chemical Synthesis Laboratory or BASF Aktiengesellschaft, Limburgerhof, West Germany and were >95% pure. Insects were from the U.S. Grain Marketing Research Laboratory cultures and had no prior exposure to insecticides. They were the maize weevil, *Sitophilus zeamais* Motschulsky; granary weevil, *Sitophilus granarius* L.; rice weevil, *Sitophilus oryzae* L.; confused flour beetle, *Tribolium confusum* (Jacquelin du Val); red flour beetle, *Tribolium castaneum* (Herbst); lesser grain borer, *Rhyzopertha dominica* F.; sawtoothed grain beetle, *Oryzaephilus surinamenis* L.; Indianmeal moth, *Plodia interpunctella* Hubner; and almond moth, *Ephestia cautella* Walker. Weevil species were reared on whole grain wheat. The lesser grain borer was reared on whole wheat containing a small amount of flour. The sawtoothed grain beetle was reared on a mixture of rolled oats, flour and corn meal (2:1:1 by volume), and flour beetle species on whole wheat flour containing 5% (wt/wt) brewer's yeast. Moth species were reared on a diet containing ground wheat (1 kg), wheat shorts (1.1 kg), wheat germ (24 g), brewer's yeast (25 g), sorbic acid (5 g), methyl *p*-hydroxybenzoate (5 g), honey (106 ml), glycerin (106 ml) and water (53 ml) (Kinsinger, 1975). Lancato wheat was used after the moisture was adjusted to 12%.

DOSE-RESPONSE DETERMINATION: For bioassay twenty coleopteran adults or lepidopteran eggs were added to 20 or 100 g diet that had been treated with 10 to 1000 ppm of 2-tridecanone by pipeting 5 ml chloroform solution onto the diet and mixing thoroughly (Kramer et al., 1979). The diet was allowed to equilibrate for 24–48 hr at room temperature to permit evaporation of the solvent. The 2-tridecanone analogues were initially screened for activity at 200 ppm on wheat using the granary weevil. Bioassays were conducted at 27 ± 1°C and 60 ± 10% RH with two to four replications with each insect species for each dose. The percentage mortality of moths was calculated from the difference between the number of eggs initially added and the number of adults that emerged after six weeks. For beetles the parent insects were removed from the tested substrate after three weeks and the total dead and live progeny counted after nine weeks. Values corrected for mortality in untreated samples were used to estimate LD_{50} or ED_{50} for adult mortality and progeny suppression, respectively (Finney, 1971).

To determine if progeny suppression was caused by adult sterilization, adult granary weevils were exposed for one week to wheat treated with 1000 ppm 2-tridecanone and fertility was determined after transfer to untreated wheat by counting progeny after twelve weeks. To measure the ovicidal-embryocidal action of 2-tridecanone, 50 granary weevils were allowed to oviposit in duplicate jars containing 50 g of untreated wheat. Adult insects were removed after seven days and the wheat (with deposited eggs) was gently mixed with an equal weight of wheat pretreated with 2000 ppm of 2-tridecanone, giving a final overall concentration of 1000 ppm. Progeny were determined after twelve weeks and compared to solvent only treated controls.

Bioassays of 2-tridecanone and 2-tridecanyl acetate with some of the insects were also conducted on filter paper treated with compound in an oil carrier consisting of a mixture of hexanes (b.p. 68–70°C), acetone and sunflower oil (3:1:1 by volume) at 50 to 500 μg/cm². Whatman #1 filter paper (7 cm diameter) was treated with 0.5 ml of each solution and the solvents were allowed to evaporate overnight at room temperature. The paper disc was laid on a glass plate and adult beetles or moth larvae (fifth instar) were introduced (20 per disc) and confined on the disc by a glass ring 5 cm in diameter and 2.5 cm high. Rings were coated with mineral oil (weevils) or liquid teflon (sawtoothed grain beetle) to prevent escape by climbing and were covered with fine mesh screen to prevent escape by flight. Mortality was assessed at 3, 6, 12, 24, 48, 96, and 200 hours. Mortality in the controls was less than 5% in all cases.

REPELLENCY TEST: To determine repellency to weevils, 2-tridecanone in methanol was added to pastry wheat at the rate of 100 and 500 ppm. An equivalent amount of methanol was added to the control. Two kg of wheat of each treatment were mixed in large glass jars by rolling for 30 minutes and then allowed to equilibrate for 16 hr before the addition of the test insects. Twelve glass test chambers similar to those utilized by Qi and Burkholder (1981) for evaluating repellency of oils to weevils were used in this experiment. A modification consisted of perforated plastic-tube traps 2.5 cm in diameter with 2.7 mm holes, instead of a metal trap. Each chamber held 450 g of pastry wheat adjusted to 12% moisture. One hundred granary weevil adults, 1–4 weeks old, were added to the top of each chamber (four replicates). The numbers of trapped weevils were recorded after 1, 3, 6, 12 and 24 hr and these values were used to estimate the time (RT_{50}) when 50% of the weevils were repelled from the grain (Finney, 1971).

Results and Discussion

2-TRIDECANONE ACTIVITY: Although 2-tridecanone was toxic to larvae of *Manduca sexta* (Johannson), *Heliothis zea* (Boddie) and *Aphis gossypii* (Glover) when applied to filter paper at a concentration of approximately 50 μg/cm² (Williams et al., 1980; Dimock et al., 1982), it was nontoxic to the species of stored product insects tested here, even at concentrations as high as 100 μg/cm². When the ketone was applied to wheat at 1000 ppm, it was slightly toxic to *Sitophilus* species with about 35% of the adult weevils killed after one week of exposure. There was a more dramatic effect on progeny development of the weevils, with ED_{50} values ranging from 167 to 497 ppm (Table 1). When the weevil-infested grain was examined by X-ray photography, we observed that eggs had been deposited in the kernels treated with 1000 ppm 2-tridecanone but that little or no larval development had occurred. There was no effect on the progeny of the other species tested (confused flour beetle, lesser grain borer, sawtoothed grain beetle, Indianmeal moth and almond moth).

Since suppression of weevil progeny by 2-tridecanone occurred at doses relatively nontoxic to adults, we determined whether this effect was caused by adult sterilization or by prevention of embryonic or neonatal larval development. Adult granary weevils were exposed to 2-tridecanone-treated wheat (1000 ppm) and then transferred to untreated wheat in order to measure fertility. Exposure to the ketone resulted in an acute mortality of 34% and also caused a slight reduction in the fertility of survivors during three subsequent sequential transfers to untreated wheat (Table 2). Only adults in the original jar of treated wheat failed to produce progeny. The reduction in progeny (31–57%) after transferring adults

Table 1. Activity of 2-tridecanone against development of insects exposed at the egg stage in wheat or in coarsely ground wheat medium.

Species	Number of F_1 insects in carrier-treated sample[a]	ED_{50} (ppm)[b]
Maize weevil	438	167 (153–180)
Granary weevil	169	183 (26–329)
Rice weevil	449	497 (407–621)
Confused flour beetle	127	>1000
Lesser grain borer	130	>1000
Sawtoothed grain beetle	268	>1000
Indianmeal moth	48	>1000
Almond moth	43	>1000

[a] Carrier solvent was chloroform.
[b] 95% confidence limits in parentheses.

from treated wheat primarily reflected the adult mortality which occurred in the first test. These results demonstrate that only a small degree of adult sterilization occurs with 2-tridecanone. To determine whether 2-tridecanone exerted an ovicidal-embryocidal action after oviposition, untreated wheat that had been previously deposited with granary weevil eggs was mixed with an equal weight of wheat treated with 2-tridecanone (2000 ppm). After twelve weeks an average of only 2 weevil progeny per jar developed in wheat treated with 2-tridecanone as compared with an average of 357 weevils per jar in solvent-treated control wheat. X-ray photography showed that although oviposition did occur, there was little or no larval development in the wheat treated with 2-tridecanone. Thus, 2-tridecanone exhibited an ovicidal or embryocidal action toward the granary weevil.

2-Tridecanone also exhibited a repellent action against the granary weevil on wheat at 100 and 500 ppm levels (Table 3). In untreated wheat, 50% of the population was trapped after 183 hours, but only 18 hours was required in the samples treated at 500 ppm. When exposed to filter paper impregnated with 2-tridecanone, weevils became more active than in controls and overtly attempted to move away from the treated paper.

The biochemical basis for the ovicidal-embryocidal-repellent action of 2-tridecanone toward *Sitophilus* species which lay eggs and develop inside grain kernels

Table 2. Progeny production from adult granary weevils preexposed to 2-tridecanone, then sequentially transferred to jars of untreated wheat for oviposition.[a]

Treatment	Number of progeny			
	Test number			
	1	2	3	4
Control ($CHCl_3$)	210 ± 5	176 ± 18	254 ± 3	282 ± 37
2-tridecanone	0	122 ± 4	156 ± 71	121 ± 21
Percent reduction	100	31	39	57

[a] Grain was treated with 2-tridecanone (1000 ppm) or carrier solvent ($CHCl_3$). After 72 hr, 50 adult weevils were added. After 1 wk, all living adults (50 from the control and 33 from the 2-tridecanone treatment) were sequentially transferred to jars of untreated wheat (test nos. 2–4) at 2 day intervals. Data are expressed as average number of progeny per jar ± SD.

Table 3. Repellency of 2-tridecanone towards the granary weevil.

Treatment[a]	RT_{50}[b]
Control	183 (118–326)
100 ppm	67 (50–97)
500 ppm	18 (15–21)

[a] Carrier solvent was methanol. Four replicates using 100 insects each were performed for each treatment.

[b] RT_{50} = time in hours when half of the weevil population had migrated from the grain into the trap. 95% confidence limits in parentheses.

is unknown and further studies on the mode of action of 2-tridecanone are needed to understand these effects. The insect species which were unaffected oviposit externally. Perhaps the ketone is translocated into the grain kernel, especially the endosperm, and therefore is more effective against internally developing species. The lack of biocidal activity of the ketone towards five of the eight stored product insect species was not unexpected. A related compound, 4,8-dimethyldecanal, is the aggregation pheromone of the red and confused flour beetles (Suzuki and Mori, 1983).

ACTIVITY OF 2-TRIDECANONE ANALOGS: Dimock et al. (1982) reported a significant influence of chain length on the toxicity to *Heliothis zea* of methyl ketones related to 2-tridecanone. We next screened for more active structural analogs of 2-tridecanone that affected the granary weevil. Wheat samples were treated at 200 ppm with 31 compounds related to 2-tridecanone and their ovicidal effect on the granary weevil was determined. That level of 2-tridecanone reduced granary weevil progeny by approximately 50%. In the present study alkyl ketones were tested which differed in carbon chain length, branch chain carbons, degree of unsaturation and/or position of the ketone moiety including 2-heptanone, 2-octanone, 2-decanone, 2-undecanone, 2-dodecanone, 4-dodecanone, 5-dodecanone, 2-tetradecanone, 6-methyl-5-octen-2-one, 6-methyl-5-hepten-2-one, 6,10-dimethyl-5,9-undecadiene-2-one, 6,10-dimethyl-3,5,9-undecatrien-2-one, 6,10-dimethyl-5,9-dodecadien-2-one, 3-tridecanone, 4-tridecanone, 5-tridecanone, 6-tridecanone, 7-tridecanone, 3-tetradecanone, 4-tetradecanone, 5-tetradecanone, 6-tetradecanone, 5-methyl-3-heptanone, 2-methyl-2-penten-4-one, 2-methyl-2-hexan-4-one, 2,4-dimethyl-4-nonen-8-one and 4-methylacetophenone. These compounds exhibited a moderate suppression of weevil progeny, but none surpassed 2-tridecanone in effectiveness. N-tridecane, 1-tridecanol and 2-tridecanol were also tested and the two alcohols were found to be similar in activity to 2-tridecanone. None of the compounds except 2-tridecanyl acetate were acutely toxic. All adult granary weevils were dead after 7 days of exposure to the ester at 200 ppm on wheat and no progeny were produced. There was no activity exhibited at either 2 or 20 ppm.

Other insects were also screened at 200 ppm 2-tridecanyl acetate on wheat. The rice weevil, maize weevil and sawtoothed grain beetle were killed after less than one week of exposure to the ester on whole kernels. LT_{50} values for the latter two species were 30 hr and 10 hr, respectively. Thirty percent of the lesser grain borer population died after three weeks of exposure. The red flour beetle and Indianmeal moth were unaffected at 200 ppm 2-tridecanyl acetate on ground wheat media after three weeks and their progeny developed normally. The latter two species may have been more tolerant of the compound or the physical nature of the ground wheat diet (finer particle size with increased surface area relative to whole wheat) may have diminished the ester's effectiveness. Regarding the latter possibility, malathion, the standard grain insecticide, must be applied at higher doses to flour than whole wheat for comparable insect control (Minett and Williams, 1976). When 2-tridecanyl acetate was applied to filter paper at 500 μg per cm^2, the LT_{50}'s for the red flour beetle and lesser grain borer were 3 hr and 100 hr, respectively, a relative susceptibility that is opposite to that expected considering the results of the treated diet bioassays.

2-Tridecanyl acetate therefore is an acutely toxic compound for several species of stored product insects. Insecticidal activity of C_{10}–C_{12} fatty acid esters towards other insects have been reported previously (Binder et al., 1979), but to our knowledge there has been no previous report of such an activity for the (short chain acid) type of ester tested here. The physiological basis for the toxic action is unknown. Because 2-tridecanyl acetate has no reported toxicity to higher animals (Lewis and Tatken, 1979), it or a more active analogue may be safe enough to use on human and animal food products for the control of certain insects.

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