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(E, Z)-2,6-NONADIEN-1-AL AND (E)-2-NONEN-1-AL PRESENT IN CRUSHED CUCUMBERS ARE NATURAL REPELLENTS FOR THE AMERICAN COCKROACH (*PERIPLANETA AMERICANA*)[1]

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ABSTRACT. The compounds (E, Z)-2,6-nonadien-1-al and (E)-2-nonen-1-al that are present in crushed cucumbers were found to repel 98% of American cockroaches, *Periplaneta americana* L., when present at concentrations of 50 ppm in a test chamber.

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INTRODUCTION

Our goal is to examine the chemical communication mechanism between plants and insects to determine if a new approach to analytical chemistry can be developed. To do this it is necessary to find plant compounds that give specific insect responses. To narrow the range of choices old wives' tales have been followed.

There is an old wives' tale that, "cucumber slices placed in a cupboard will keep roaches away." This was tested by a choice test bioassay with unsexed American cockroaches, *Periplaneta americana,* Linneus.

Kemp et al. (1974A) listed 15 compounds C_9 and higher found in the steam distillate of cucumbers. Forss et al. (1962) listed several of these plus a few of lower chain length. Previous work by Verma and Meloan (1981) and by Bodenstein and Fales (1976) led us to believe that a group such as $-HC=CH-C=O$ or $-HC=C-C\equiv N$ was necessary for cockroach repellency. The observation by Fleming et al. (1968) that carbonyl compounds were initially at low concentrations in whole cucumbers but increased in concentration with crushing served to narrow the choice of compounds to be tested.

Combining these observations, it was decided to test 5 compounds for repellency: (E, Z)-2,6-nonadien-1-al, (E)-2-nonen-1-al, (E)-2-hexen-1-al, 1-nonanal, and 1-nonanol. It was expected that the first 3 would be active and the other 2 much less active or inactive.

This paper reports on the tests used, the compounds that were found to be effective and a possible explanation as to why the cucumber must be sliced or crushed.

METHODS AND MATERIALS

CHEMICALS. All chemicals are reagent grade and were freshly distilled before use. Their purity was then verified by gas chromatographic methods.

(E, Z)-2,6-nonadien-1-al — Alfa products, 152 Andover St., Danvers, MA 01923
(E)-2-nonen-1-al — ICN Pharmaceuticals, Plainview, NY 11803
(E)-2-hexen-1-al — Aldrich Chemical Co. Milwaukee WI, 53201
1-nonanal — Alfa Products, 152 Andover St., Danvers, MA 01923
1-nonanol — J. T. Baker Chemical Co., Phillipsburg, NJ 08865

APPARATUS. Gas Chromatograph — Tracor Model 560 with FID. Steam distillation apparatus — Typical laboratory all-glass steam distillation apparatus, blanks were obtained on the steam.

COCKROACHES. The cockroaches were from a colony of *P. americana* maintained by the Department of Entomology at Kansas State University. The cockroaches used were adults 3-4 weeks old and were well fed and watered before each test, as well as during each test.

CUCUMBERS. *(Cucumis sativus).* Purchased at local grocery store.

BIOASSAY. The bioassay was a choice test. It consisted of 2 crystallizing dishes, 9 cm × 17 cm (volume ~2,000 cm^3), each having 2 half circles of 2-cm diameter cut in the outer rim. These dishes were then covered with cardboard (with 2 half circles 2 cm in diameter to match the holes in the dish)

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around the sides and a removable cardboard cover was made for each one. This was to make the chamber darker than any surrounding area and more attractive to the cockroaches. A small piece of glass wool was placed in the bottom (top when overturned for the test) and held in place by a piece of metal screen wire. The test compounds or the control solvents then were added to the glass wool and allowed to evaporate in the chamber. Cucumber slices were handled in the same manner and the whole cucmber was placed in the test chamber. The crystallizing dishes were placed in a water bath jar 25 cm × 40 cm.

To begin the test, the test compound was added to one dish and the solvent (if necessary) to the other chamber to serve as a control. Ten to 25 cockroaches (depending on availability) were added and a fluorescent lamp was turned on. The cockroaches would try to leave the lighted area and go into the darkened chambers. If the repellent was effective, they either would not go into the test chamber or stay only a short time. The test was continued for 48 h, with counts in each chamber being taken every 2 h for 12 h, then every 12 h. The dishes were interchanged and the test repeated. This was done several times for each compound and at various concentrations.

Attractancy-repellency effects were measured by the following formula (Leonard and Ehrman 1977):

$$A = \frac{N_c - N_b}{N_t}$$

where: A = attractancy (+) or repellency (−); N_c = number of insects in the test dish; N_b = number of insects in the control dish; N_t = total number of insects in both dishes.

The value A can be used further if desired to calculate χ^2.

$$\chi^2 = A^2 N_t$$

The significance level of the χ^2 test can be obtained from any statistics manual.

Negative values for A indicate that the insects are repelled by the test compound and the greater the deviation from zero toward the minimum −1 the greater the repellency. The reverse is true for attractiveness. In this type of bioassay more than 50% of the insects have to be repelled for the test compound to be considered effective as a repellent.

RESULTS AND DISCUSSION

Table 1 shows the results of the initial studies testing the effectiveness of whole cucumbers to cucumber slices.

It was found that whole cucumbers had little repellent effect but that well-crushed cucumbers would repel 90% of the cockroaches under the test conditions. Fleming et al. (1968) had observed that 2 of the compounds found in cucumbers, the nonenals previously mentioned, increased in concentration in the steam distillate if the cucumbers were crushed. This observation combined with the results in table 1 and the fact that the 2 compounds each contained the —CH=CH—C=O group was the deciding factor in narrowing the choice of compounds to test.

1-Nonanal was present in the cucumbers and was chosen because it was a 9 carbon compound and contained only the aldehyde group. If this compound was less active than the previous 2 compounds then evidence for the necessity of the double bond in the 2 position would be obtained.

1-Nonanol was present in the cucumbers but is an alcohol rather than an aldehyde and was chosen for the same reason as well as not containing a double bond between the O and the C.

(E)-2-hexen-1-al had not been reported to be in the cucumbers, but it had the desired functional groups with 3 fewer carbons on the chain. This was used as a test for the necessity of the —C=C—C=O

TABLE 1

Overall effects of whole and crushed cucumbers as a repellent on cockroaches.

Material	No. of cockroaches* In sample dish	In control dish	Repellency factor (A)
Whole cucumber	63	72	−0.05
Cucumber slices	32	146	−0.64
Whole cucumber crushed in a blender	20	280	−0.87

*Cockroaches that did not enter either dish were not counted as being repelled.

TABLE 2

Repellent effects of selected compounds from cucumbers on cockroaches.

Compound (b.p.°C)	Concentration† (500ppm) NS*	NC**	R(A)***	(50ppm) NS	NC	R(A)	(5ppm) NS	NC	R(A)	(0.8ppm) NS	NC	R(A)
(E) − 2−nonen-1-al (215)	1	219	(−0.99)	2	208	(−0.98)	43	162	(−0.58)	44	140	(−0.52)
(E,Z)-2,6-nonadien-1-al (230)	0	248	(−1.00)	3	271	(−0.98)	18	239	(−0.86)	41	292	(−0.75)
(E)-2-hexen-1-al (150)	32	501	(−0.88)	29	235	(−0.78)	27	108	(−0.60)			
1-nonanal (200)	41	301	(−0.76)	53	188	(−0.56)	38	65	(−0.26)			
1-nonanol (215)	26	109	(−0.61)	44	110	(−0.43)	88	13	(+0.74)			

*NS = Number in sample dish
**NC = Number in control dish
***R(A) = Repellency factor
†Cockroaches that did not enter either dish were not counted as being repelled.

group as being the effective smallest group in the molecule.

Each test was done at least 3 times with 10-25 cockroaches depending upon their availability. The compounds were placed in either water or ethanol to obtain the desired dilutions (5, 50, 500 ppm). Previous work by Verma and Meloan (1981) had shown that these solvents had little repellent effect on cockroaches. The highest response was obtained on the third and fourth counts. The results are shown in table 2.

The results clearly show that the first 2 compounds are excellent repellents even at quite low concentrations. The removal of 3 carbons from the chain tends to reduce the effectiveness but not as much as the removal of a C═C in the 2 position. The removal of one pair of non-bonding electrons from the C═O group by reducing it from an aldehyde to an alcohol has a small but measureable effect.

The nonenals both were effective so one was compared directly to the other in a choice test at a concentration of 0.8 ppm. The results are shown in table 3. Clearly the diene compound is the better repellent of the two.

An explanation for the observation that crushing the cucumber provides more

TABLE 3

Choice tests between dishes containing (E,Z)-2,6-nonadien-1-al and (E)-2-nonen-1-al.

	Number of cockroaches in each dish* (E)-2-nonen-1-al	(E,Z)-2,6-nonadien-1-al
Trial 1	51	7
Trial 2	86	3

*Cockroaches that did not enter either dish were not counted as being repelled.

repellency is based on a combination of proposals by Fleming et al. (1968), Kemp et al. (1974B), and Grosch and Schwarz (1971). They have shown that the C_{18} unsaturated fatty acids in cucumbers are enzymatically cleaved to produce C_9 compounds. Grosch and Schwarz (1971) used C-14 labeling to show that the (E, Z)-2,6-nonadien-1-al and (E)-2-nonen-1-al came from the linolenic and linoleic acids, respectively. This is similar to the formation of garlic (Stoll and Seebeck 1951) and onion odors (Schwimmer and Weston 1961) in that crushing the cucumber cells causes an enzymatic reaction to take place and produce the repellent compounds.

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