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Aversion of European Starlings (*Sturnus vulgaris*) to Garlic Oil Treated Granules: Garlic Oil as an Avian Repellent. Garlic Oil Analysis by Nuclear Magnetic Resonance Spectroscopy

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European starlings significantly reduced their consumption of a food mixture that was 50% food-grade garlic oil (GO)-impregnated granules, even after overnight food deprivation, as demonstrated by "one-choice" ("no-choice") tests. Food consumption during 3 h following overnight food deprivation was reduced by 61−65% compared to controls. By testing the same subjects with 25, 10, and 1% mixtures of granules in feed, it was shown that commercial GO granules were repellent to birds in lower concentrations, with more than a 50% decrease in feeding for birds presented with a 10% mixture of commercial GO granules in food and a 17% decrease for the 1% treatment. Products containing GO show considerable promise as inexpensive, environmentally benign, nonlethal bird repellents. In comparing various GO preparations used in this work, nuclear magnetic resonance (NMR) spectroscopic methods prove to be particularly useful for rapid quantitation of major and minor components without requiring fractionation or isolation procedures, which could adversely effect the less stable components.

KEYWORDS: Garlic oil; *Allium sativum*; European starlings; *Sturnus vulgaris*; avian repellents; NMR methods

INTRODUCTION

While various chemical repellents, such as methiocarb, methyl anthranilate, anthraquinone (*1*, *2*), neem extract (*3*), and elemental sulfur (*4*), for crop damaging birds have been evaluated, none of these is completely satisfactory for the purpose intended. In searching for an environmentally benign, nonlethal bird repellent (e.g., for agricultural, urban, and airport applications), we examined the utility of garlic oil (GO)-based products (mixed diallyl, dimethyl, and allyl-methyl polysulfides). Garlic (*Allium sativum*)-derived preparations possess insect-repellent activity (*5*−*7*); there are also a few claims of repellent activity toward small animals, including starlings (*8*−*11*). Previous experiments with starlings, however, were conducted using 2-choice testing, which is useful for marginal repellents but less effective at detecting strong repellents (*12*). The reports that topical application of garlic reduced northern fowl mite infestation in laying hens (*13*) and that garlic paste in the diets of laying hens reduced serum and yolk cholesterol concentrations while at the same time had no adverse effects on layer performance (*14*) suggests that garlic preparations show low toxicity toward hens and presumably other birds as well. We report herein our studies of the feeding responses of European starlings (*Sturnus vulgaris*) when their food is mixed with various proportions of GO-impregnated granules. Our results bode well for the development of GO-based bird repellents. In connection with these studies, we needed a method to rapidly establish the purity of commercial GO and GO-like products. In particular, there was a need to determine the composition and identify additives that might compromise interpretation of results, for example, by possessing repellent or attractive activity different from that of "standard" GO. We find that NMR spectroscopy is ideal for this purpose.

MATERIALS AND METHODS

Subjects. The subjects for this experiment were European starlings drawn from a colony of birds that had been trapped as wild adults and housed at Monell Chemical Senses Center. Birds were maintained in group housing conditions and held under a 14:10 h light/dark photoperiod in a room equipped with broad-spectrum fluorescent lighting. Birds were provided with a mixture of commercial passerine feed and fresh tap water ad libitum; their meals were supplemented weekly with mealworms (*Tenebrio* larvae) and apples. Two weeks prior to the onset of the first experiment, 24 birds were removed from the group flight cage, placed into individual cages, and allowed to habituate to the individual housing environment. While singly caged, for environmental enrichment, birds were provided with cat toys, which were changed weekly. Individually housed birds could see and hear other birds in the same room. Food was provided in partially covered bowls that were

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attached to the cage doors, both features designed to minimize food spillage. Throughout the course of the experiments, birds were weighed and examined weekly, and any bill or nail overgrowth was trimmed.

Pretesting and Group Assignment. Birds were assigned into treatment groups according to pre-experimental consumption level. The day before the pretest, food but not water was removed from the cage of each subject at 1600 h. The following morning, at 0900 h, each bird was presented with a 50.0-g portion of standard passerine feed. Three hours later (1200 h), the food was removed from each bird's cage and reweighed. On the basis of the amount of food eaten, birds were then divided into low, medium, or high consumption groups (eight birds per group). Finally, two individuals from each of the consumption groups were assigned into one of four experimental treatment groups. We chose a "no-choice" (one cup) with deprivation testing paradigm because it yields a conservative measure of a repellent's effectiveness (*12*).

Materials and Analysis. Commercial food-grade GO ("Chinese"; 700 mg; R. C. Treatt & Company, Ltd.) was added to reagent grade ether (500 mL). To the homogeneous solution, 175.00 g of wood-based granules (ca. 1 mm in diameter) was added. Ether was removed using a rotary evaporator until the GO-impregnated granules weighed 175.70 g, corresponding to 4 mg of GO per gram of granules. In a similar manner, diallyl polysulfides-impregnated granules were prepared containing 4 mg of diallyl polysulfides per gram of granules. The diallyl polysulfide sample was obtained by heating commercial diallyl disulfide; NMR analysis indicated it to be a mixture of diallyl disulfide through pentasulfide. Similarly compounded, granular, garlic-derived materials, "Product A" (uncoated granules) and "Product B" (granules with inert coating), were obtained from a commercial source in the UK. The chemical composition of the food-grade GO and the commercial garlic juice-derived Products A and B was determined by analysis of ^{1}H and ^{13}C data obtained on 500 MHz NMR spectrometers, using known standards for calibration, and by parallel GC-MS and HPLC methods. The GO was dissolved in $CDCl_3$ for NMR analysis; Products A and B were repeatedly extracted with diethyl ether, and the solvent was carefully removed at or below room temperature prior to dissolving the residue in $CDCl_3$.

Experiment One. This experiment tested the hypothesis that garlic is an avian repellent and that the commercial Product A granules were as effective as food-grade GO-impregnated granules. Birds were assigned into one test group or one of three control groups. The treatments for each bird (6 birds per treatment) were: 25 g of Product A granules mixed with 25 g of feed (test group), 25 g of food-grade GO-treated granules mixed with 25 g of feed (garlic control group), 25 g of untreated wood granules ("blank" control group) mixed with 25 g of feed, and 50 g of feed (standard control group). Testing proceeded in a manner similar to the pretesting procedure. The night before testing, food was removed from each bird's cage at 1600 h. The next morning, at 0900 h, each bird was presented with a partially covered food container holding one of the four possible food treatments. The food was removed and reweighed 3 h later. Cage floors were inspected to rule out food spillage.

Experiment Two. The goal of this experiment was to generate a dose−response curve for the Product A granules and to observe the behavior of a bird exposed to food treated with the Product A granules. The same 24 subjects served in experiment two as in experiment one; subjects were divided into the same four groups as during the earlier experiment. The treatments were a series of three different mixtures of Product A granules/feed (12.5 g granules/37.5 g feed, 5 g granules/45 g feed, or 0.5 g granules/49.5 g feed, which correspond to a 25, 10, and 1% mixture of granules in feed, respectively) and a fourth control (feed only) group. The experimental paradigm with respect to the timing of food deprivation and experimental presentation of treatments was the same as during the first experiment.

Experiment Three. This experiment consisted of three parts and was designed to generate dose−response curves at lower concentrations and using different products than we had used while conducting the second experiment. Birds were presented with treatments corresponding to a 0, 2.5, 5, and 10% mixture of granules in feed with a total mass of 50 g. The experiment was repeated three times on different days, with one rest day between each bout of experimentation. During the first bout, the product used was the food-grade GO treated granules ("homemade"). Product B was tested during the second bout of the experiment. On the last day, granules infused with diallyl polysulfides were used. The same 24 subjects were used for the experiment but were rotated with respect to treatment so that no group was presented with the same percentage treatment more than once. Other procedures of the experiment were similar to those described above.

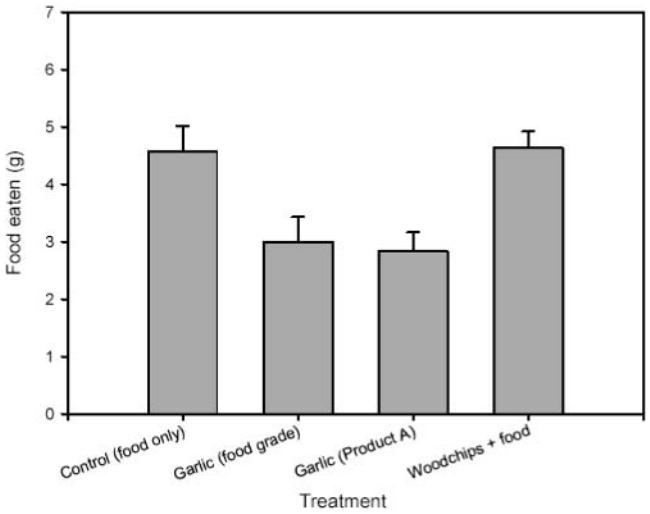

Figure 1. Comparison of food consumption for feed with no additive (control), food with GO impregnated granules (garlic, food grade), food with Product A granules (garlic, Product A) and food with blank granules (woodchips + food).

Experiment Four. The final experiment was intended to determine whether the mechanism of repellency was primary or secondary. Primary repellency is achieved when a repellent causes an immediate withdrawal response due to its irritating or distasteful properties. Secondary repellency is a mechanism by which animals experience malaise following consumption of a repellent, and as a result consumption decreases over time. Following overnight deprivation, birds were presented with a 50% mixture of Product B in feed, while a second group received feed alone. Bowls and feed were weighed together before initially being placed into the cages. For the next 4 h, the bowls were removed hourly, weighed, and then replaced in the cages. Other procedures remained the same as those of the previous experiments.

Statistical Analysis. Data were analyzed using the Statistica 6.0 software package. One-way ANOVA (analysis of variance) was employed for experiments one through three, and repeated measures ANOVA was necessary for the analysis of experiment four data. Fisher's LSD test was chosen for the post-hoc analysis when ANOVA indicated significant effects. Descriptive data are reported as means and standard error of means.

RESULTS AND DISCUSSION

Experiment One. Both the GO-treated and the Product A granules mixed 50:50 with the standard feed were significantly repellent to the birds. Birds in the feed-only control group and in the "blank" control group ate 4.57 ± 0.45 g and 4.63 ± 0.29 g of food during the trial, respectively. Birds in the Product A and food-grade GO treatment groups ate significantly less ($F_{3,20} = 6.57$, $P = 0.0029$) than did the birds in the control groups, consuming only 2.83 ± 0.29 g and 3.00 ± 0.43 g of food, respectively. Post-hoc analysis revealed that the two control groups ate significantly more than did the two garlic groups. There was no difference between the "blank" and the feed only controls, nor between the two garlic groups (**Figure 1**). The group that ate the least amount of food was the Product A group, although there was not a significant difference between this group and the food-grade GO group.

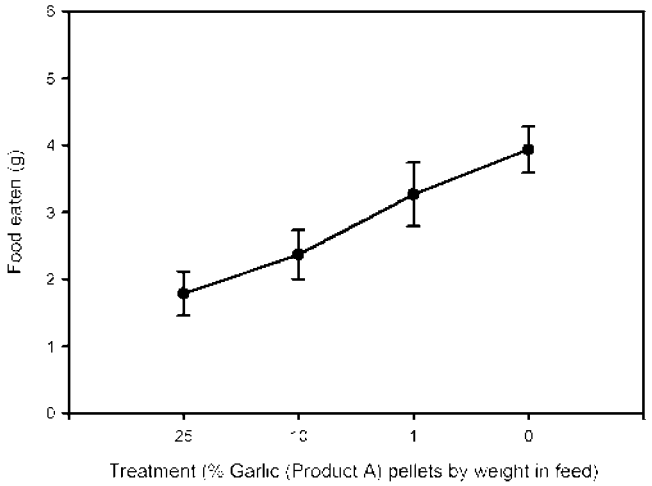

Figure 2. Comparison of food consumption for Product A granules mixed with food in 1:4, 1:10, and 1:100 ratios by weight versus control (no Product A).

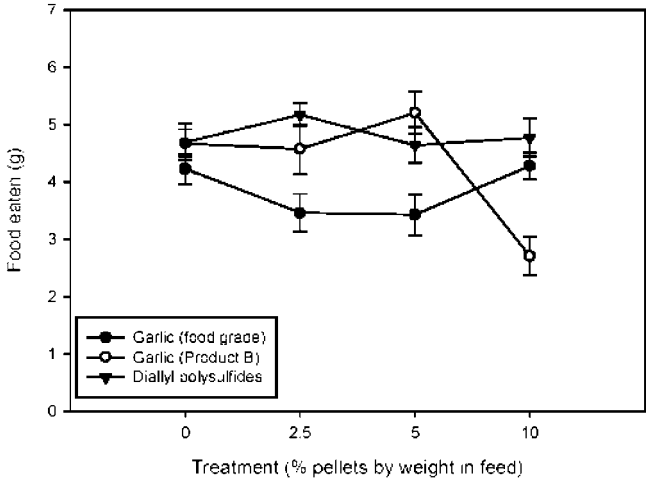

Figure 3. Dose–response curves generated by treatments of three different concentrations of three different products, garlic oil (food grade), Product B garlic granules, mixed diallyl polysulfides, and control.

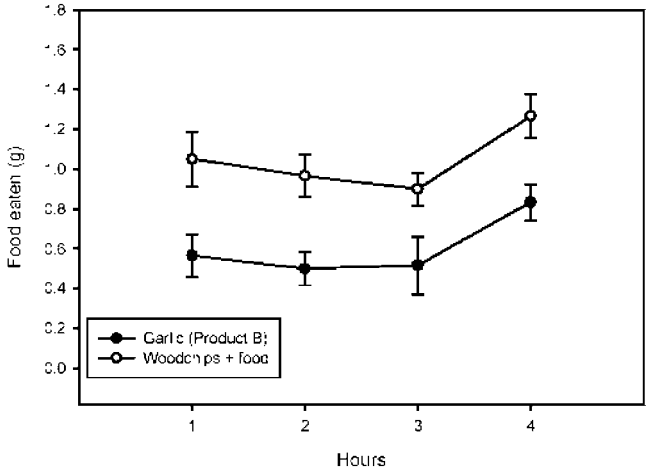

Figure 4. Hourly responses of birds to 50% concentration of Product B garlic granules or the control wood pellets in feed.

Experiment Two. This experiment revealed that birds significantly decreased their feeding behavior when their food was treated with low concentrations of Product A granules. In the first experiment, birds ate significantly less of the 50% granules in food mixture than the control. During the second experiment, birds ate significantly less of the 25 and 10 mixtures as compared to controls (ANOVA: $F_{3,20} = 5.47$, $P = 0.0038$, Fisher's LSD post-hoc analysis; see **Figure 2**). The reduction in food consumed compared to controls ranged from more than 50% for the birds presented with a 10% mixture of Product A granules in food, to about 17% decrease in feeding for the birds experiencing the 1% Product A treatment. Despite the statistical nonsignificance of the 1% treatment, a 17% decrease in feeding would be economically important and deserves further investigation.

Experiment Three. Product B was effective as a repellent at the 10% concentration, but granules containing homemade GO or diallyl polysulfides did not induce any repellency compared to controls at the tested levels. Because the diallyl polysulfide sample contains no methyl-group containing polysulfides, it is possible that the latter compounds that are present in both GO and Product B are more distasteful than the allyl group-only polysulfides. Differences in repellency between Product B and the homemade GO granules may reflect small variations in levels of the methyl-group containing polysulfides in the two materials. There was a significant overall effect on feeding for product B only ($F_{3,20} = 9.70$, $P = 0.00037$), and post-hoc analysis (Fisher's LSD) revealed that there was significantly less consumption of the 10% concentration of product B in feed than there was for the other concentrations or the control treatment (**Figure 3**).

Experiment Four. The behavioral response over 4 h was inconsistent with a secondary repellency mechanism. This suggests that the product acts as a primary repellent, with either a distasteful (flavor) or painful (trigeminal irritation) result of exposure to the animals. Overall, subjects consumed significantly less of Product B than the control ($F_{2,15} = 13.105$, $P = 0.00051$). When each treatment group was examined separately across time, a time effect was found for Product B ($F_{3,15} = 44.6$, $P = 0.001$) and for the control ($F_{3,15} = 44.6$, $P = 0.004$). In both cases, post-hoc analysis (Fisher's LSD) revealed an increase in consumption during the fourth time period (**Figure 4**).

Garlic Oil Analysis. Commercial food-grade GO typically consists of a mixture of more than 17 polysulfides of formulas $CH_2{=}CHCH_2S_nR$, where R = allyl, with lesser amounts of R = methyl and (*E/Z*)-1-propenyl, as well as MeS_nMe, $n = 1-6$, together with trace amounts of other organosulfur compounds (*15*, *16*). While GO has been characterized by GC-MS (*17*) and HPLC (*18*, *19*), there are difficulties associated with each of these procedures (*20*). Thermal instability of some of the heavier components of GO leads to underestimation by GC methods of the concentrations of these compounds, while peak overlap, the need for standards, and the absence of directly obtained structural information limit specificity and sensitivity by both methods. At the outset, it was not known whether the avian repellent activity of GO was due primarily to a few compounds in the mixture or was more general. Furthermore, since distilled food grade GO is too expensive for the intended use, we evaluated the repellent activity of a less costly commercial garlic juice-derived formulation similar in composition to GO. It was therefore important to determine the components present in samples of GO from different sources being tested. We find that NMR spectroscopy is uniquely useful for this purpose, directly providing % molar composition.

For a complex mixture of naturally derived products, GO has a surprisingly simple ^{1}H NMR spectrum (**Figure 5**, **Table 1**). It consists of a nicely separated series of doublets ($J = 7.3$) from 3.1 to 3.7 ppm for the thioallylic protons ($CH_2{=}CHC\boldsymbol{H}_2S$), a similarly well separated series of singlets from 2.0 to 2.7

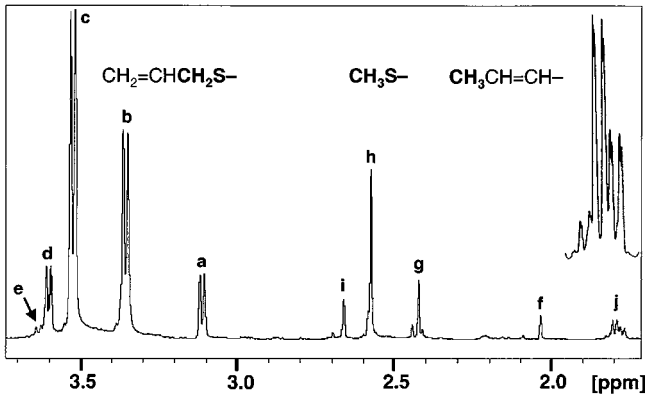

Figure 5. The 1.8–3.7 ppm region of the ^{1}H NMR spectrum (500 MHz; $CDCl_3$) of a representative commercial sample of distilled oil of garlic. Peaks a–e correspond to the allylic CH_2S protons (doublets) of All_2S, All_2S_2, All_2S_3, All_2S_4, and All_2S_5, respectively; peaks f–i correspond to the CH_3S protons (singlets) of MeSAll, MeS_2All, MeS_3All, and MeS_4All, respectively; multiplet j (also shown in enlarged form; two doublets of doublets) corresponds to the CH_3 protons of the (*E*,*Z*)-CH_3CH═CHS– group.

Table 1. 500 MHz ^{1}H and ^{13}C NMR Data for Garlic Oil

δ^1H (δ^{13}C)[e]	multiplicity (*J*), group	mole (wt) %[m]	compound
3.67	d (ca. 7), CH_2S	tr	All_2S_6
3.63 (42.5)[a]	d (7.3), CH_2S	1 (1)	All_2S_5
3.60 (42.0)[a,l]	d (7.3), CH_2S	6 (8)	All_2S_4
3.52 (41.6)[a,h,l]	d (7.3), CH_2S	33 (37)	All_2S_3
3.36 (42.3)[a]	d (7.3), CH_2S	26 (23)	All_2S_2
3.11 (33.3)[a]	d (7.1), CH_2S	7 (5)	All_2S
2.70 (- -)	s, CH_3	tr	MeS_5All
2.67 (23.2)[f,j]	s, CH_3	tr	Me_2S_4
2.66 (23.2)	s, CH_3	2 (3)	MeS_4All
2.59 (22.6)[f,j]	s, CH_3	1 (1)	Me_2S_3
2.58 (22.8)[d,j]	s, CH_3	11 (10)	MeS_3All
2.44 (22.0)[f,j]	s, CH_3	0.4 (0.2)	Me_2S_2
2.42 (23.4)	s, CH_3	5 (4)	MeS_2All
2.04 (14.2)[g,j]	s, CH_3	2 (1)	MeSAll
1.80 (18.1)[b,i]	dd (6.5, 0.9), CH_3	4 (5)	(*E*)-MeCH═CHS_nAll
1.77 (14.3)[c,i]	dd, (6.9, 1.1), CH_3	2 (2)	(*Z*)-MeCH═CHS_nAll

[a] ^{13}C Olefinic absorption for allyl ═CH, allyl ═CH_2: All_2S_5, 132.2, 119.9; All_2S_4 132.5, 119.6; All_2S_3 132.7, 119.1; All_2S_2 133.5, 118.4; All_2S 134.2, 117.2 ppm. [b] ^{13}C Olefinic absorption for ═CHMe, ═CHS: 130.4, 125.3 ppm. [c] ^{13}C Olefinic absorption for ═CHMe, ═CHS: 129.5, 127.5 ppm. [d] Allylthio CH_2, 41.5 ppm. [e] Assignments confirmed by proton DQF–COSY and carbon APT methods. [f] Values are for synthetic samples; Me_2S and Me_2S_5 have ^{1}H (^{13}C) NMR δ 2.09 (18.2) and 2.68 (23.9), respectively. [g] Additional data: ^{1}H NMR δ 3.09 (d, CH_2S); ^{13}C NMR δ ═CH 133.9, ═CH_2 116.9, CH_2S 38.8 ppm. [h] Also see ref 22. [i] Also see ref 21. [j] Also see ref 23. [k] Also see ref 24. [l] Also see ref 25. [m] By NMR.

ppm for the CH_3S groups, a weak but characteristic set of doublet of doublets centered at 1.8 ppm (J = ca. 7 and 1) for the (*E*)- and (*Z*)-1-propenyl groups (2:1 E:Z ratio)(*21*), along with 5−6 ppm olefinic multiplets. There is virtually no absorption in the 0−1.8 ppm region nor in the 2.7−3.1 and 3.7−5.0 ppm regions. It is notable that in **Figure 5** the pattern of the four major singlets (peaks f, g, h, i) almost exactly parallels the pattern of the four major doublets (peaks a, b, c, d), which is consistent with the view that these sequences of peaks reflect the corresponding RS_nAll, (n is 1, 2, 3, and 4, R = Me or All). Further scrutiny of the spectrum reveals a similar peak pattern for the three major dimethyl polysulfides (e.g., MeSSMe (intermediate intensity), MeSSSMe (highest intensity) and MeSSSSMe (lowest intensity)) appearing as downfield shoulders on the MeSSAll, MeSSSAll, and MeSSSSAll peaks, respectively.

The ^{13}C NMR spectrum is equally simple and informative with methyl peaks at ca. 14, 18 ppm (***C***H_3CH═CH-), and 22−23 (CH_3S_n−), allylic methylene peaks at 33/42−43 (CH_2═CH***C***H_2S-), and allyl group olefinic peaks at 116−119 (CH═) and 132−134 (CH_2═). Some samples also showed weak signals at ca. 125, 127, and 130 ppm corresponding to Me***C***H═***C***HS− (*21*). Regions of the ^{13}C spectrum not mentioned above showed no peaks. The ^{1}H NMR spectra showed a monotonic increase in shielding with increase in n for the methyl shifts of CH_3S_n-CH_3 and C***H***$_3S_nCH_2CH$═CH_2 and the methylene shifts of CH_2═CHC***H***$_2S_n$− ($CH_3S_nCH_3$, δ 2.09, 2.44, 2.59, 2.67, 2.70, 2.71 for n = 1−6, respectively; C***H***$_3S_nCH_2CH$═CH_2, δ 2.04, 2.42, 2.58, 2.66, 2.70 for n = 1−5, respectively, and −CH_2S_n−, δ 3.11, 3.36, 3.52, 3.60, 3.63, 3.67 for n = 1−6, respectively).

The corresponding ^{13}C NMR shifts changed in a more erratic manner ($CH_3S_nCH_3$, δ 18.2, 22.0, 22.6, 23.2, 23.9, 23.8 for n = 1−6, respectively; C***H***$_3S_nCH_2CH$═CH_2, δ 14.2, 23.4, 22.8. 23.2 for n = 1−4, respectively; −CH_2S_n−, δ 33.3, 42.3, 41.6, 42.0, 42.5 for n = 1−5, respectively), as determined using authentic samples, proton DQF-COSY, carbon APT, and published NMR data (*22*−*24*). Our assignment of ^{1}H and ^{13}C NMR chemical shifts to GO components is consistent with published NMR data for Me_2S_n (*23*), MeSAll (*24*), All_2S_n (*22*, *25*) and our own earlier work on MeCH═CHSSR (*21*).

The % molar composition of GO samples can be estimated as follows: (1) On the basis of the simplicity of the 3.1−3.7 ppm region of the ^{1}H NMR spectrum, we assume that the CH_2S chemical shifts for CH_2═$CHCH_2S_n$R vary with n but, for each value of n, not with R (e.g., allyl, methyl, 1-propenyl). (2) On the basis of GC-MS and HPLC analysis (*17*−*19*), we assume that the major methyl-containing components of GO are allyl methyl sulfide, disulfide, trisulfide, and tetrasulfide. The integrated areas of the four largest methyl signals are multiplied by 0.67 to provide the areas corresponding to the SCH_2 portion of the allyl groups of these four compounds. These calculated values are then subtracted from the respective integrated areas of the SCH_2 portion of the Sallyl, SSallyl, SSSallyl, and SSSSallyl groups. (3) On the basis of GC-MS and HPLC analysis (*17*−*19*), we assume that the remaining small methyl groups belong to dimethyl disulfide, trisulfide, and tetrasulfide. (4) In what we assume is a 1.5:1 mixture of allyl 1-propenyl trisulfide (major) and disulfide (minor; based on the 1.5:1 ratio of All_2S_3/All_2S_2), the respective integrated areas of the methyl signals of the (*E*)- and (*Z*)-1-propenyl groups are multiplied by 0.67 to provide the areas of the SCH_2 portion of the allyl groups of these two compounds. These calculated values are then also subtracted from the integrated areas of the SCH_2 portion of the SSSallyl and SSallyl groups. (5) To normalize each integrated signal to correspond to a single proton per compound, the thus corrected areas for each individual CH_2 group were then divided by 4 (diallyl compounds), while the integrated areas for each individual CH_3 group were divided by 3 (monomethyl compounds) or 6 (dimethyl compounds). The fractional molar composition of the mixture was then calculated based on the ratio of each normalized value to the sum of all normalized values. The weight percent composition of the GO was also calculated (**Table 1**).

The relative peak areas determined by ^{1}H NMR can be *qualitatively* compared to the intensities of the various ^{13}C peaks which are well separated in *both* the olefinic and aliphatic regions for each compound CH_2═$CHCH_2S_n$R (the olefinic region in the ^{1}H spectrum of GO is too complex to be of any

use analytically, apart from the total integration). The allyl group carbon shifts appear not to be significantly affected by the nature of the R group. There was reasonable correspondence between the percent compositions estimated from NMR and by GC-MS for the more volatile and thermally stable constituents ($n \leq 3$).

In the sample of food-grade GO used in this study, the major components (>80%) were found to be diallyl disulfide, trisulfide, and tetrasulfide as well as allyl methyl disulfide and trisulfide, in accord with published data (*14*). Analysis of extracts of Products A and B by ^{1}H and ^{13}C NMR methods showed them to be quite similar in composition to the food-grade GO. A mixture of diallyl polysulfides (mainly diallyl disulfide, trisulfide, and tetrasulfide, devoid of methyl or 1-propenyl components, as verified by NMR methods) was also used for impregnating granules.

Conclusions. We conclude from these results that GO is an effective avian repellent. Particularly interesting is the repellency of GO at low concentrations even under the extreme conditions of one-choice testing following overnight (17 h) food deprivation. It is unlikely that our results are due to neophobia, as the same group of animals was used repeatedly, and repellency was consistent across experiments. It is also unlikely that differences in the caloric values of the treated and control foods is an important factor, because there was no difference in consumption between GO-impregnated and plain wood chips. If the nutritional value of the GO had an effect, we might have expected the birds to consume some of the GO-treated wood chips, which did not occur.

At the present time, it is not known if any of the components of GO are significantly more aversive than others, if there is a synergistic effect involving several components, and if the aversive effect is associated principally with the avian senses of smell or taste. It also remains to be established if similar repellent effects are seen with other bird species. Answers to these questions should come from work currently underway.

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NOTE ADDED AFTER ASAP

Author Zhang was omitted from original posting of March 26, 2004; corrected posting made April 2, 2004.

Supporting Information Available: Full ^{1}H NMR spectrum of garlic oil (2 pages) is available free of charge via the Internet at http://pubs.acs.org.

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