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Volatile Sulfides of the Amazonian Garlic Bush

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The essential oil from *Adenocalymma alliaceum* leaves (ca. 0.04%) was investigated with GC and GC-MS. Of the 13 compounds tentatively identified, 9 are likely to be part of a homologous series. The most abundant components were diallyl disulfide and diallyl trisulfide, which comprise 62% of the oil.

The garlic bush (Portuguese, cipó d'algo) is a widespread plant in Brazil, particularly in the north where the principal species is *Adenocalymma alliaceum* Miers. Upon the sample handling of the large leaves, a strong odor exudes, similar to that of garlic (*Allium sativum*). Although infusions of the leaves are used in treating colds and fevers (Pio Correa, 1931; Figueiredo, 1979), its principal use is in the substitution of garlic, especially in the interior regions of difficult access.

The ethereal extracts of steam distillates from fresh leaves of the garlic bush were first studied by Apparao et al. (1978), using packed column gas chromatography-mass spectrometry (GC-MS). The principal components of the extracts to be the diallyl di-, tri-, and tetrasulfides.

Not surprisingly, these are also among the major constituents in garlic (Oaks et al., 1964; Brodnitz et al., 1971). As part of an ongoing study of the essential oil of amazonian plants, we have characterized the volatiles of garlic bush, using capillary column gas chromatography-mass spectrometry, and we now report the presence of additional alkenyl sulfides.

EXPERIMENTAL SECTION

Plant material of *A. alliaceum* was collected in Aurá, near Belém, state of Pará, and an exsiccate (no. 69734) has been placed in the herbarium at the Emilio Goeldi Museum, in Belém. The air-dried leaves were subjected to steam distillation, and the volatile oil obtained was dried in the presence of sodium sulfate. The yield was 0.04%.

The volatile oil was analyzed with a Carlo Erba 4160 gas chromatography (FID), with a 30 m × 0.25 mm fused silica capillary column containing a 0.25 μm film of SE-54. Hydrogen was used as the carrier gas, adjusted to a linear velocity of 33 cm/s (measured at 150 °C); the split flow was adjusted to give a 20:1 ratio, and the septum sweep was a constant 10 cm³/min. Splitless injection of 2 μL, on a 1:1000 *n*-hexane solution, was followed by a delay of 30 s before beginning the purge. Injection was done with the oven at 50 °C. After a 3-min initial wait, the temperature was programmed at 6 °C/min to 230 °C.

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Table I. Constituents of *A. alliaceum*

peak no.	compound ^a	Kovats indices	% of oil ^b
1	diallyl sulfide	850	trace
2	allyl methyl disulfide	910	trace
3	dithiacyclopentene	945	2.18
4	allyl propyl disulfide	1048	trace
5	diallyl disulfide	1065	31.38
6	allyl methyl trisulfide	1123	0.96
7	3-vinyl-1,2-dithi-5-ene	1160	2.60
8	trithiacyclohexene (tent.)	1168	6.67
9	3-vinyl-1,2-dithi-4-ene	1205	4.71
10	allyl propyl trisulfide	1262	0.75
11	diallyl trisulfide	1296	30.55
12	allyl methyl tetrasulfide	1535	2.51
13	diallyl tetrasulfide	1690	1.23

^a All of the compounds were identified by comparison of their mass spectra with those in the data system library or from the literature and are considered tentative. ^b Relative to the quantitation report of the Incos data system.

Gas chromatography-mass spectrometry was performed on a Finnigan 4021 GC-MS system, which includes on Incos data system. An identical 30-m SE-54 silica capillary column was installed in the GC, in a Grob-type injector, and directly coupled to the ion source of the MS. Helium was used as carrier gas, and injection and oven-programming temperatures were the same as above except a 4 °C/min gradient was used. The mass spectrometer was in EI mode at 70 eV. The quadrupole filter was scanned from 34 to 434 daltons once every second, and resulting spectra were stored on computer discs for later recall.

Identifications were based on mass spectra by comparison with those in the data system library and confirmed by retention data (Kovats, 1958).

RESULTS AND DISCUSSION

A gas chromatogram of the essential oil of the garlic bush is presented in Figure 1. From this GC trace one can see the simplicity of the mixture and the prominence of two components, peaks 6 and 13. These were tentatively confirmed to be the diallyl di- and trisulfides, as reported by Apparao et al. (1978). Diallyl tetrasulfide (peak 15) was also found to be present, although not as abundant as reported. For each of these sulfides, the MS matched almost perfectly with that given by Apparao et al. (1978). Several other major peaks were present, most of which

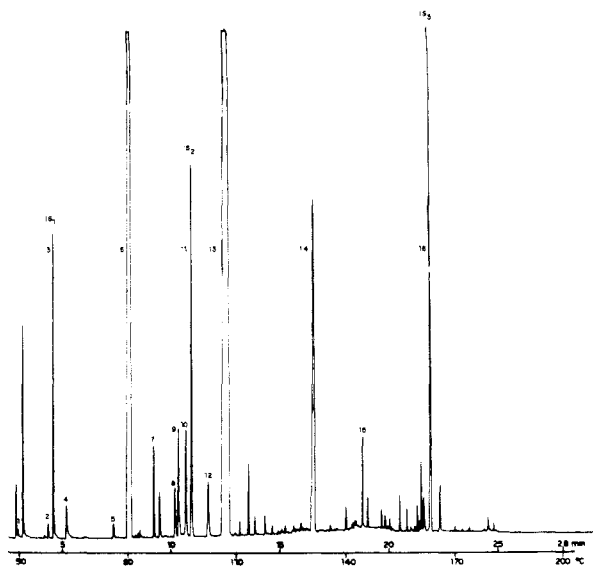


Figure 1. Gas chromatogram of the essential oil of the garlic bush.

produced fairly unambiguous mass spectra. For example, peaks 5 and 12 each had molecular weights 2 units higher than their neighboring peaks, the diallyl di- and trisulfides, respectively. On the basis of their MS fragmentation, these were determined to be either allyl propyl or propenyl propyl di- and trisulfides. From a discussion of the relative stabilities of the 1-propenylthio and allylthio cations (Nishimura et al., 1971), it was apparent that the two compounds were, in fact, allyl propyl sulfides. Similarly, peak 7 presented a mass spectrum that appeared to be a allyl methyl trisulfide. The components tentatively identified are listed in Table I.

All of the sulfides mentioned above with the exception of diallyl tetrasulfide have been determined in garlic and onion (Oaks et al., 1964; Brodnitz et al. 1971; Boelens et al., 1971). Oaks et al. (1964) showed by means of a log plot of the relative retention time (RRT) vs. the number of sulfur atoms that each additional sulfur atom is additive in its effect on the retention time. By using a similar strategy, making a normal plot (instead of log, because we used temperature programming) of RRT and the number of sulfur atoms (Figure 2), we were able to locate minor peaks in the chromatogram likely to be part of a homologous series. Thus, peak 1 was identified as the diallyl sulfide and peaks 2 and 14 were identified as allyl methyl di- and tetrasulfides.

Peaks 4 and 8–10 did not produce mass spectra that were easily interpreted. Brodnitz et al. (1971), in analyzing garlic extracts, found the principal components to be the vinylthiophenes (peaks 8 and 10) shown in Table I. Dithiacyclopentene (peak 4) was detected in the flavor of cooked asparagus (Tressl et al., 1977), and the mass spectrum given compares very well with that for our peak. Peak 9 is the only peak for which we had no confirmatory mass spectrum. By calculation of isotope ratios, its molecular formula, based on the apparent molecular ion at 136 daltons, appeared to be $C_3H_4S_3$. We propose this compound is trithiacyclohexane, based on the MS fragmentation and the presence of dithiacyclopentene, but this has not yet been confirmed.

The somewhat unpleasant, although characteristic, aromas of all the plants mentioned are due in large part to the presence of a combination of these alkenyl sulfides and the thiosulfonates, coproducts formed from the

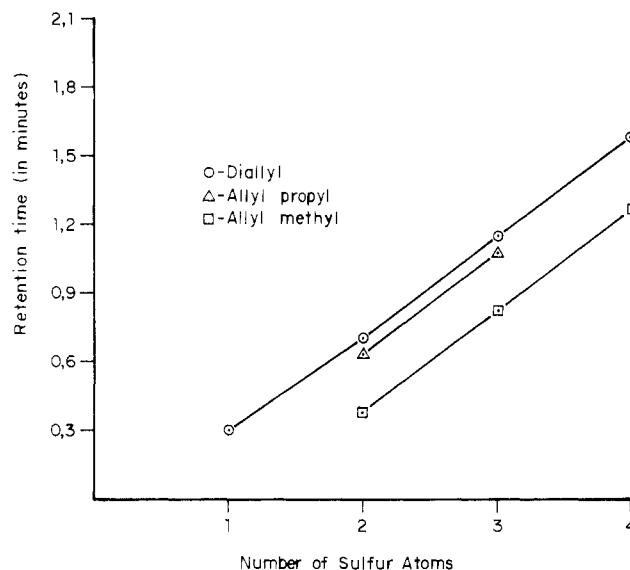


Figure 2. Normal plot of retention time vs. number of sulfur atoms.

alkylcysteine sulfoxides, precursors in the intact plant material (Whitaker, 1976). Although the leaves of the garlic bush quickly produce the pungent, garlicky odor upon handling, the aroma disappears after several days of drying. As shown by Boelens et al. (1971), the quality (i.e., the mixture of alkenyl sulfides) of cut onion is considerably modified over time. Further studies must be done to determine the viability of the garlic bush as a large-scale substitute of garlic, in particular, with respect to harvesting and storage.

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Registry No. Diallyl sulfide, 592-88-1; allyl methyl disulfide, 2179-58-0; dithiacyclopentene, 288-26-6; allyl propyl disulfide, 2179-59-1; diallyl disulfide, 2179-57-9; allyl methyl trisulfide, 34135-85-8; 3-vinyl-1,2-dithi-5-ene, 62488-53-3; 3-vinyl-1,2-dithi-4-ene, 62488-52-2; allyl propyl trisulfide, 33922-73-5; diallyl trisulfide, 2050-87-5; allyl methyl tetrasulfide, 90195-83-8; diallyl tetrasulfide, 2444-49-7.

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