

Volatile Flavor Components and Antithrombotic Agents: Vinylthiins from *Allium victorialis* L.

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Volatile sulfur compounds enzymatically produced from caucas (*Allium victorialis* L.) were identified. The occurrence of 1-propenyl-containing disulfides and 2-methyl-2-pentenal, one of the breakdown products of propanethial *S*-oxide in caucas, which is one of the garliclike *Allium* species, is chemotaxonomically interesting. 3,4-Dihydro-3-vinyl-1,2-dithiin (1) and 2-vinyl-4*H*-1,3-dithiin (2), which have antithrombotic activity, were isolated from caucas and identified by IR, NMR (2D ^1H - ^1H COSY), and mass spectrometry. Furthermore, the mass spectral fragmentation of vinylthiins was proposed for the first time.

Caucas (*Allium victorialis* L.) is one of the *Allium* species that grows well wild in Hokkaido, the northern part of Japan. The Ainu, the native people of Hokkaido, have eaten the leaves and stalks of caucas as a vegetable for a long time. Although it has not been as well-known as other *Allium* species such as onion and garlic, it seems to have potential in terms of the utilization of nutritious vegetables.

Yurugi et al. (1954) gave the first report about the ingredients of caucas in studies on the reaction between thiamine (vitamin B₁) and thiosulfinates of the *Allium* species. The present authors (Nishimura et al., 1971; Akashi et al., 1975) have investigated the identification of volatile components responsible for caucas flavor and the enzymatic development of the *Allium* volatiles. The significant flavor components of caucas were presumed to be 1-propenyl-containing disulfides and 2-methyl-2-pentenal, one of the breakdown products of propanethial *S*-oxide in addition to methyl allyl disulfide, diallyl disulfide, and so on (Nishimura et al., 1971).

Garlic is reputed to offer protection against strokes, coronary thrombosis, atherosclerosis, and platelet aggregation (Adamu et al., 1982; Samson, 1982; Qureshi et al., 1983). Ariga et al. (1981) have isolated a platelet aggregation inhibitor identified as methyl allyl trisulfide from garlic. Recently, it was reported that garlic had potent antithrombotic agents identified as 2-vinyl-4*H*-1,3-dithiin, 3,4-dihydro-3-vinyl-1,2-dithiin, diallyl trisulfide, and a compound named ajoene; these compounds were nonenzymatically derived from alliin ($\text{CH}_2=\text{CHCH}_2\text{S}(\text{O})\text{SCH}_2\text{CH}=\text{CH}_2$, allyl 2-propenethiosulfinate) (Apitz-Castro et al., 1983, 1986; Block et al., 1984, 1986).

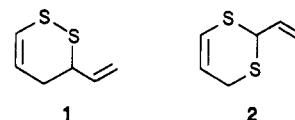
The discovery of vinylthiins in caucas volatiles, which have antithrombotic activity, is also of great interest in terms of the search for more useful vegetables. This paper deals with the isolation and identification of vinylthiins in caucas extracts as well as flavor components.

EXPERIMENTAL SECTION

Sample Preparation. Young caucas were collected from several places in Hokkaido, Japan. Both leaves and stalks were cut into small pieces. One part was placed in a three-necked flask, and volatile flavor components were distilled off by passing through nitrogen gas as a carrier at approximately 40 °C and absorbing into an isopentane trap cooled with dry ice-ethanol. This process is called headspace gas distillation extraction. Extraction from the other part was made by placing it in methylene chloride

for 2 weeks at room temperature and is called direct solvent extraction. The sample obtained by headspace gas distillation extraction was concentrated and directly used for analysis. However, the directly extracted one had to be separated from chlorophyll and some other pigments by column chromatography (Florisol column; 0-5% ether/hexane, v/v) before further analysis.

Isolation of Vinylthiins. The vinylthiins were isolated from the direct-extraction sample. The total concentrate was chromatographed over a SiO₂ column using ether and hexane as gradient eluants to give several fractions (each 5 mL). The fractions suspected to contain vinylthiins 1 and 2 (*R_f* 0.24 and 0.12 on TLC in *n*-pentane; also detected by GC and GC-MS) were gathered. Purification by HPLC (hexane) gave rise to two fractions each containing pure vinylthiin. The structures were confirmed by spectral data as mentioned later.



Authentic Vinylthiins: 3,4-Dihydro-3-vinyl-1,2-dithiin (1) and 2-Vinyl-4*H*-1,3-dithiin (2). Both vinylthiins were derived from alliin by modification of the method of Block et al. (1984). In this experiment, alliin was prepared by the oxidation of diallyl disulfide with *m*-chloroperbenzoic acid in chloroform.

The decomposition of alliin in methanol at room temperature for 7 days gave vinylthiins as well as diallyl disulfide and diallyl trisulfide. The synthesized vinylthiins were isolated by SiO₂ column chromatography and preparative HPLC (hexane). Physicochemical data are as follows.

3,4-Dihydro-3-vinyl-1,2-dithiin (1): IR (film) 1630 (C=C), 985 and 915 cm⁻¹ (vinyl double bond); ^1H NMR (270 MHz, CDCl₃) δ 2.41-2.68 (m, 2 H allylic methylene), 3.68-3.76 (m, 1 H, methine proton), 5.23-5.32 (m, 2 H, CH₂=C), 5.94 (dd, 1 H, exo olefinic =CH), 6.04 (m, 1 H, endo olefinic SC=CH), 6.37 (dt, 1 H, *J* = 9 and 2 Hz, endo olefinic SCH=C); ^{13}C NMR (67.5 MHz, CDCl₃) δ 30.3 (C₄), 44.1 (C₃), 117.5 (C₈), 120.6 (C₇), 126.0 (C₅), 136.4 (C₆); MS *m/z* (relative intensity, %) 144 (M⁺, 78), 111 (100), 103 (51), 97 (70), 85 (17), 79 (43), 77 (48), 72 (57), 71 (55), 45 (59), 39 (40).

2-Vinyl-4*H*-1,3-dithiin (2): IR (film) 1630 (C=C), 982 and 918 cm⁻¹ (vinyl double bond); ^1H NMR (270 MHz, CDCl₃) δ 3.23 and 3.40 (two ddd, 2 H, *J* = 17, 5, and 2 Hz, allylic methylene), 4.73 (d, 1 H, *J* = 7 Hz, methine proton), 5.30 and 5.40 (two d, 2 H, *J* = 17 and 10 Hz, CH₂=C), 5.92-6.05 (m, 2 H, exo olefinic =CH and endo olefinic

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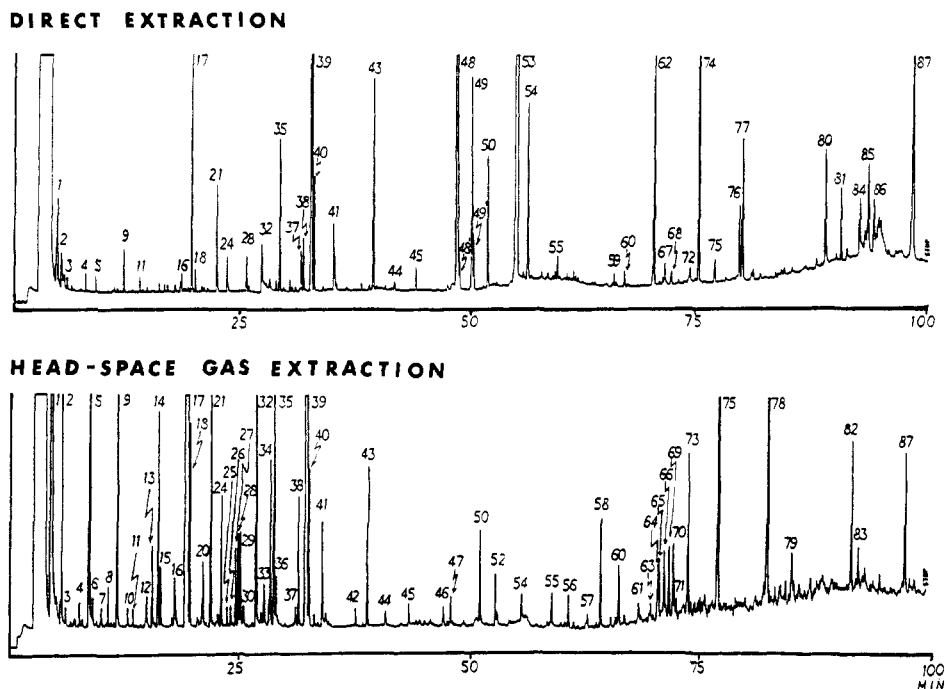


Figure 1. Gas chromatogram of the volatile components of fresh caucas (*A. victorialis* L.). Conditions: column, PEG-20M bonded, 0.35 mm (i.d.) \times 50 m, silica; column temperature, 40–220 °C; program rate, 2 °C/min; flow rate, 1.2 mL/min (He); detectors, fid.

SC=CH), 6.31 (dt, 1 H, endo olefinic SCH=C); ^{13}C NMR (67.5 MHz, CDCl_3) δ 25.1 (C_4), 45.1 (C_2), 117.2 (C_3), 118.3 (C_7), 122.2 (C_5), 134.3 (C_6); MS m/z (relative intensity, %) 144 (M^+ , 45), 111 (35), 103 (10), 97 (16), 85 (7), 79 (11), 72 (100), 71 (78), 45 (41), 39 (23).

Other Authentic Compounds. Methyl allyl sulfide, diallyl sulfide, dimethyl disulfide, methyl allyl disulfide, diallyl disulfide, methyl propyl disulfide, allyl propyl disulfide, dimethyl trisulfide, methyl allyl trisulfide, and diallyl trisulfide were prepared by the method of Kirner and Richter (1929), and methyl 1-propenyl disulfides (cis and trans), propyl 1-propenyl disulfides (cis and trans) and di-1-propenyl disulfide (cis,cis and cis,trans), by the methods of Wijers et al. (1969). 2-Methyl-2-pentenal was prepared by the method of Paquin (1949).

These compounds were purified by using a Varian aerograph Model 90-P (TCD) gas chromatograph on a 3 m \times $\frac{1}{4}$ in. (i.d.) stainless steel column packed with 15% PEG-20M on 60–80-mesh Uniport HP at a helium flow rate of 28 mL/min and were confirmed by mass spectral fragmentation (Nishimura et al., 1973) and elemental analysis.

Instrumental Analysis. Gas chromatography (GC) was carried out on a Hitachi 263-30 instrument equipped with a flame ionization detector and a 50 m \times 0.35 mm (i.d.) PEG-20M-bonded capillary column at a helium flow rate of 1.2 mL/min; the column temperature was programmed linearly from 40 to 220 °C at 2 °C/min; the injection port temperature was 250 °C. Mass spectrometry (MS) using electron impact (EI; JEOL JMS-DX 300) and field ionization (FI; JEOL JMS-01SG-2) was performed to identify the purified components. In the case of EI-MS, the operating parameters were as follows: inlet temperature, 30–70 °C; ion source pressure, 10^{-6} Torr; ion source temperature, 250 °C; acceleration voltage, 3 kV; chamber voltage, 70 eV. In FI-MS, the operating parameters were as follows: inlet temperature, 25 °C; ion source pressure, 0.2×10^{-6} Torr; acceleration voltage, 9 kV; cathode high voltage, 4 kV. The method of GC-MS combination (JMS-DX 300 GC-MS) was preferred for obtaining the mass spectral data of a mixture and/or trace amounts of components. The operating parameters were as follows.

Gas chromatograph: column, a 30 m \times 0.28 mm (i.d.) PEG-HT SCOT capillary column; flow rate, helium carrier gas at 1.2 mL/min; temperature, 40–220 °C at 4 °C/min; injection port temperature, 230 °C. Mass spectrometer: inlet temperature, 30–70 °C; ion source pressure, 10^{-6} Torr; ionization current, 300 μA ; total emission, 160 μA , chamber voltage, 70 eV. Proton nuclear magnetic resonance (^1H NMR) spectra were recorded on a JEOL JNM-GX FT (270-MHz) spectrometer: solvent, CDCl_3 ; internal standard, Me_4Si . Infrared (IR) and ultraviolet (UV) absorption spectrometry was performed on a Hitachi 285 infrared spectrometer and Hitachi EPS-3T UV spectrometer, respectively. High-performance liquid chromatography (HPLC) was carried out on a Jasco PG-350 D with a Shodex RI SE-31 refractometer and a Unisil Q 100-5 (30 cm \times 16.7 mm (i.d.)) or Lichrospher SI 60/II super 250-4 column (24 cm \times 4 mm (i.d.)).




RESULTS AND DISCUSSION

Flavor Components. The gas chromatographic separation of volatile flavor components of caucas (*A. victorialis* L.) has been improved as shown in Figure 1. Identification was accomplished by comparing their gas chromatographic retention times and mass spectra with those of authentic compounds and published data. The components identified are summarized in Table I. The peak numbers correspond to those of Figure 1.

The major components responsible for the caucas flavor have been reported (Nishimura et al., 1971): methyl allyl disulfide (peak 17, chinese chivelike odor), diallyl disulfide (peak 39, garliclike odor), and dimethyl disulfide and methyl allyl trisulfide (peaks 5 and 43, picklelike odor). These disulfides have also been thought to be produced via thiyl radicals (anisotropic signals of ESR, $g = 2.00$ – 2.05) formed in the first stage of the enzymatic reaction of *S*-alk(en)yl-L-cysteine sulfoxides with alliinase (Akashi et al., 1975).

Interestingly, a considerable number of 1-propenyl-containing disulfides and 2-methyl-2-pentenal, one of the breakdown products of propanethial *S*-oxide (a lachrymatory substance), were found in the caucas volatiles as shown in Table I, although caucas belongs to the garliclike

Table I. Identification of Volatile Components Found in Caucas

peak no.	compound (M^+ , m/z)	identification ^a	extract ^b
1	$CH_2=CHCH_2SH$ (74)	MS, Rt, A	H, D
2	$CH_3SCH_2CH=CH_2$ (88)	MS, Rt, A	H, D
3	$CH_3COCH=CHCH_3$ (84)	MS, R, T	D, H
5	CH_3SSCH_3 (94)	MS, Rt, A	H, D
7	$CH_2=CHCH_2SCH_2CH_2CH_3$ (116)	MS, Rt, A	H
8	 (106)	MS, T	H
9	$CH_2=CHCH_2SCH_2CH=CH_2$ (114)	MS, Rt, A	D, H
12	$CH_3CH=CHCH(OH)CH_3$ (86)	MS, R, T	H
13	(106)	MS, T	H
14	$CH_3CH_2CH=C(CH_3)CHO$ (98)	MS, Rt, A	H
15	$CH_3SSCH_2CH_2CH_3$ (122)	MS, Rt, A	H
16	<i>cis</i> - $CH_3SSCH=CHCH_3$ (120)	MS, Rt, A	D, H
17	$CH_3SSCH_2CH=CH_2$ (120)	MS, Rt, A	D, H
18	<i>trans</i> - $CH_3SSCH=CHCH_3$ (120)	MS, Rt, A	D, H
20	(108)	MS, T	H
21	CH_3SSSCH_3 (126)	MS, Rt, A	D, H
24	(134)	MS, Rt, A	D, H
28	$CH_3CH_2CH_2SSCH_2CH_2CH_3$ (150)	MS, Rt, A	D, H
32	$CH_3SSO_2CH_3$ (126)	MS, Rt, A	D, H
34	<i>cis</i> - $CH_3CH_2CH_2SSCH=CHCH_3$ (148)	MS, Rt, A	H
35	$CH_3CH_2CH_2SSCH_2CH=CH_2$ (148)	MS, Rt, A	D, H
38	$CH_3CH=CHSSCH=CHCH_3$ (146)	MS, Rt, A	H, H
39	$CH_2=CHCH_2SSCH_2CH=CH_2$ (146)	MS, Rt, A	D, H
40	<i>trans,trans</i> - $CH_3CH=CHSSCH=CHCH_3$ (146)	MS, Rt, A	D, H
41	$CH_3SSSCH_2CH_2CH_3$ (154)	MS, Rt, A	D, H
42	<i>cis</i> - $CH_3SSSCH=CHCH_3$ (152)	MS, Rt, A	D, H
43	$CH_3SSSCH_2CH=CH_2$ (152)	MS, Rt, A	D, H
44	<i>trans</i> - $CH_3SSSCH=CHCH_3$ (152)	MS, Rt, A	D, H
45	$CH_3SCH_2SSCH_3$ (140)	MS, T	D, H
48	 (144)	MS, Rt, A	D
49	(146)	MS, Rt, A	D
50	$CH_2=CHCH_2SSSCH_2CH=CH_2$ (178)	MS, Rt, A	D, H
52	(167)	MS, T	H
53	 (144)	MS, Rt, A	D
54	(166)	MS, T	D, H
62-87	polymeric hydrocarbons		

^aKey: MS = mass spectrometry; Rt = gas chromatographic retention time; T = tentative; R = reference data; A = authentic compound.

^bKey: H = headspace; D = direct. ^cCis, cis or cis, trans.

Allium species and those volatiles have never been found so far in garlic-type plants. The occurrence of those compounds in caucas is of interest in terms of chemotaxonomy.

Isolation and Identification of the Vinylthiols. When the two chromatograms shown in Figure 1 are compared, the significant difference is the appearance of the relatively big peaks 48 and 53 around 50 min on the GC trace. Those peaks were found in the direct extracted sample but not in the headspace gas extracted one. The two peaks were suspected to represent vinylthiols 1 and 2 detected by GC-MS. To confirm the structure of the peaks, isolation and identification were carried out. Both were obtained as pale yellow oils with a characteristic sulfur odor.

A high-resolution MS (M^+ 144.0056) of the earlier eluted product (compound I) suggested $C_6H_8S_2$. The 1H NMR spectral datum of compound I agreed well with the known 3,4-dihydro-3-vinyl-1,2-dithiin structure (Brodnitz et al., 1971; Beslin, 1983). A 2D-COSY experiment was performed in an effort to establish proton connectivities through J coupling. The 2D 1H - 1H NMR spectrum of compound I is shown in Figure 2. The spectrum revealed the existence of the following spin-spin interactions: A coupled to B, G, and H; B coupled to A, G, and H; C coupled to D-H; D coupled to C, E, and F; E coupled to C, D, and F; F coupled to C-E, G, and H; G coupled to

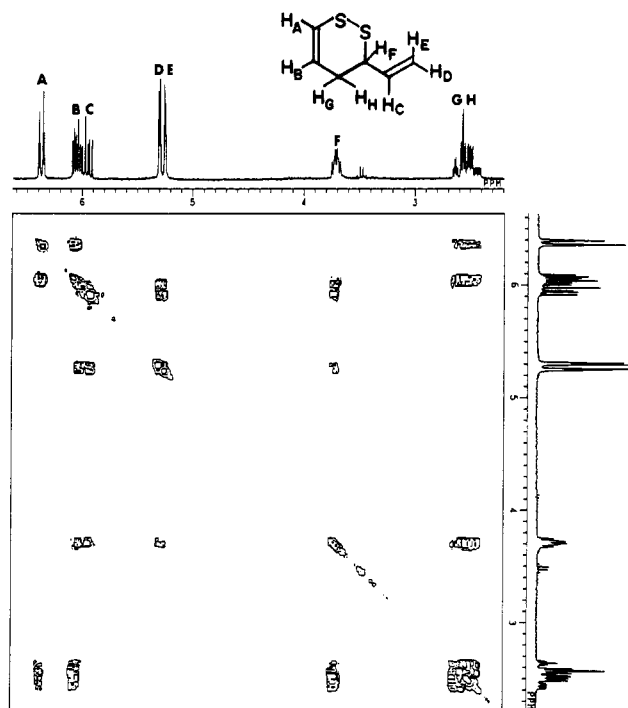


Figure 2. 1H - 1H chemical shift correlation map (COSY 45) of 3,4-dihydro-3-vinyl-1,2-dithiin (1).

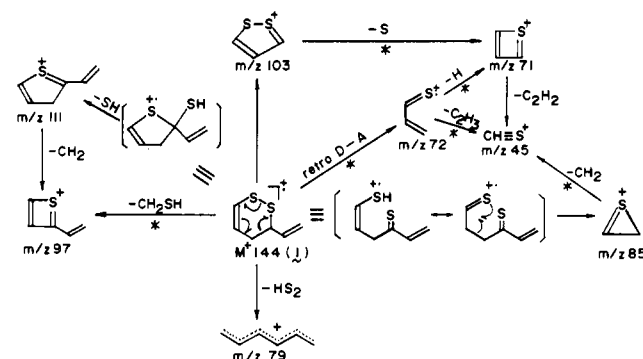


Figure 3. Mass spectral fragmentation of 3,4-dihydro-3-vinyl-1,2-dithiin (1). * indicates observed metastable ion.

A-C, F, and H; H coupled to A-C, F, and G. From these data, there is no doubt that the isolated compound I is 3,4-dihydro-3-vinyl-1,2-dithiin (1). Compound I was confirmed by comparing with mass and NMR spectra of the synthetic compound (see the Experimental Section). The mass spectral fragmentation of 3,4-dihydro-3-vinyl-1,2-dithiin is proposed as shown in Figure 3. The evidence of the fragmentation mechanism was obtained by the observation of metastable ion peaks.

On the other hand, a high-resolution MS (M^+ 144.0071) of the later eluted product (compound II) also suggested $C_6H_8S_2$. Compound II has a vinyl double bond, i.e. IR ν_{max} 982 and 918 cm^{-1} . The decoupling data of 1H NMR are as follows: Irradiation at δ 4.73 changes δ 5.92-6.05, a complex multiplet, to simply a multiplet. Irradiation at δ 5.96 changes δ 3.23-3.40, two double doublets, to two double doublets; δ 4.73, a doublet, to a singlet; and δ 6.31, a double triplet, to a singlet. Furthermore, the 2D 1H - 1H NMR spectrum of compound II is shown in Figure 4. The spectrum revealed the existence of the following spin-spin interactions: A coupled to C, G, and H; B coupled to D-F; C coupled to A, G, and H; D coupled to B, E, and F; E coupled to B, D, and F; F coupled to B, D, and E; G coupled to A, C, and H; H coupled to A, C, and G. As a result, compound II was identified as 2-vinyl-4H-

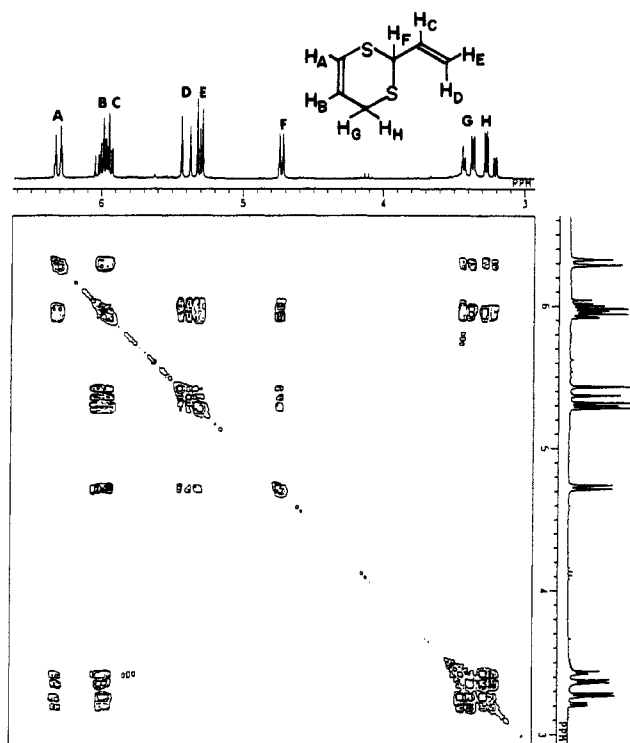


Figure 4. ^1H - ^1H chemical shift correlation map (COSY 45) of 2-vinyl-4H-1,3-dithiin (2).

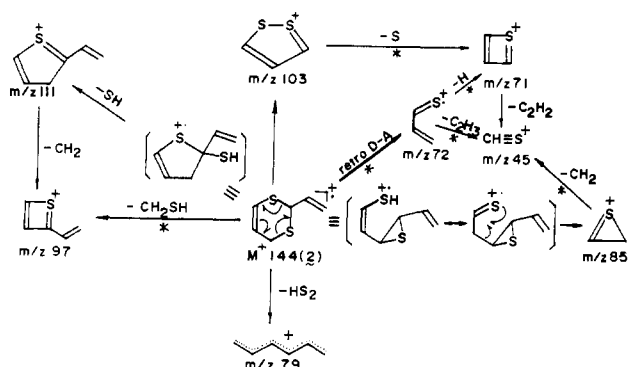


Figure 5. Mass spectral fragmentation of 2-vinyl-4H-1,3-dithiin (2).

1,3-dithiin (2). The NMR and mass spectra of compound II were in accordance with reported data (Bock, 1982; Beslin, 1983). The mass spectral fragmentation of 2-vinyl-4H-1,3-dithiin was elucidated by the observation of metastable ion peaks as shown in Figure 5.

Neither of the vinyl dithiins was detected in the headspace gas of caucas (see Table I). However, those compounds were found in the ether extract of residue after removal of the volatile components.

ACKNOWLEDGMENT

We acknowledge the technical assistance of Kenji Watanabe for performing the metastable ion analyses. We also thank Yoshiko Atsuta and Yumiko Misu for measurements of the mass spectra and ^1H NMR, respectively. We are grateful to Robert Barker, the director of Hokkaido Christian Center, for revising the manuscript.

Registry No. 1, 62488-53-3; 2, 80028-57-5; $\text{CH}_2=\text{CHCH}_2\text{SH}$, 870-23-5; $\text{CH}_3\text{SCH}_2\text{CH}=\text{CH}_2$, 10152-76-8; $\text{CH}_3\text{COCH}=\text{CHCH}_3$, 625-33-2; CH_3SSCH_3 , 624-92-0; $\text{CH}_2=\text{CHCH}_2\text{S}(\text{CH}_2)_2\text{CH}_3$, 27817-67-0; $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_3$, 100-41-4; $\text{CH}_2=\text{CHCH}_2\text{SCH}_2\text{CH}=\text{CH}_2$,

592-88-1; $\text{CH}_3\text{CH}=\text{CHCH}(\text{OH})\text{CH}_3$, 1569-50-2; $\text{CH}_3\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CHO}$, 623-36-9; $\text{CH}_3\text{SS}(\text{CH}_2)_2\text{CH}_3$, 2179-60-4; *cis*- $\text{CH}_2\text{SSCH}=\text{CHCH}_3$, 23838-18-8; $\text{CH}_3\text{SSCH}_2\text{CH}=\text{CH}_2$, 2179-58-0; *trans*- $\text{CH}_3\text{SSCH}=\text{CHCH}_3$, 23838-19-9; $\text{CH}_3\text{SSSCH}_3$, 3658-80-8; $\text{CH}_3(\text{CH}_2)_2\text{SS}(\text{CH}_2)_2\text{CH}_3$, 629-19-6; $\text{CH}_3\text{SSO}_2\text{CH}_3$, 2949-92-0; *cis*- $\text{CH}_3(\text{CH}_2)_3\text{SSCH}=\text{CHCH}_3$, 23838-20-2; $\text{CH}_3(\text{CH}_2)_2\text{SSCH}_2\text{CH}=\text{CH}_2$, 2179-59-1; $\text{CH}_3\text{CH}=\text{CHSSCH}=\text{CHCH}_3$, 53925-82-9; $\text{CH}_2=\text{CHCH}_2\text{SSCH}_2\text{CH}=\text{CH}_2$, 2179-57-9; *trans,trans*- $\text{CH}_3\text{CH}=\text{CHSSCH}=\text{CHCH}_3$, 23838-23-5; $\text{CH}_3\text{SS}(\text{CH}_2)_2\text{CH}_3$, 17619-36-2; *cis*- $\text{CH}_3\text{SSSCH}=\text{CHCH}_3$, 23838-24-6; $\text{CH}_3\text{SSSCH}_2\text{CH}=\text{CH}_2$, 34135-85-8; *trans*- $\text{CH}_3\text{SSSCH}=\text{CHCH}_3$, 23838-25-7; $\text{CH}_3\text{SCH}_2\text{SSCH}_3$, 42474-44-2; $\text{CH}_2=\text{CHCH}_2\text{SSSCH}_2\text{CH}=\text{CH}_2$, 2050-87-5; allicin, 539-86-6.

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