excited singlet state of **1**. However, recent experiments have led us to conclude that, although the reactive species produced when **1** is illuminated in its $S_2 \leftarrow S_0$ absorption band in cyclohexane may indeed have a lifetime of ca. 250 ps, that species is not the second excited singlet state of adamantanethione.

1 was prepared by the method of Greidanus[8] and was purified by low-temperature crystallization from *n*-pentane followed by HPLC. Adamantanone (**2**), a common impurity readily identified by its fluorescence, could only be removed by excluding oxygen at every stage of the purification of **1**. A pure sample of **2** was obtained by repeated sublimation of a commercial product (Aldrich). Pentane (BDH, LC grade) and perfluoro-*n*-hexane (PCR, redistilled) were free from measurable fluorescence when excited in the $\lambda_{ex} > 230$ nm range. Fluorescence spectra and quantum yields were obtained on a Spex, Model 222, Fluorolog instrument, which employs single photon counting detection and digital spectral correction. Fluorescence quantum yields were measured relative to quinine bisulfate in 1.0 N H_2SO_4 ($\phi_f = 0.54$).[9] Fluorescence lifetimes were measured with a frequency-doubled, cavity-dumped, synchronously pumped dye laser system described previously.[10]

No measurable emission in the 300 nm $< \lambda_{em} <$ 550 nm range could be observed when degassed pentane or perfluoro-*n*-hexane solutions of **1** at room temperature were illuminated in the $S_2 \leftarrow S_0$ absorption band. The quantum yield of adamantanethione's $S_2 \rightarrow S_0$ fluorescence, ϕ_f, must therefore be less than 5×10^{-5} on the basis of the known sensitivity of the emission spectrometers. By contrast, both dilute pentane and perfluoro-*n*-hexane solutions of **2**, illuminated in its $S_1 \leftarrow S_0$ ($n \rightarrow \pi^*$) absorption band at $\lambda_{ex} = 290$ nm, gave readily measurable emission with $\phi_f = 6 \times 10^{-3}$, in moderate agreement with a previous value of ca. 15×10^{-3} in acetonitrile.[11] The fluorescence lifetime of **2** (2×10^{-3} M in pentane), excited at 297 nm, was 9.1 ± 0.1 ns, in excellent agreement with a previous report of 9.12 ns in hexane.[12]

Adamantanethione is a rigid molecule and its $S_2 \leftarrow S_0$ radiative transitions are electric dipole allowed. It should therefore be possible to estimate accurately the intrinsic radiative lifetime of the S_2 state of **1**, $\tau_{S_2}{}^0$, by the integrated absorption method of Strickler and Berg.[13] There is some uncertainty in this estimate because of the difficulty in separating the $S_2 \leftarrow S_0$ absorption from an overlapping, higher energy (likely Rydberg) transition of lower intensity with λ_{max} near 223 nm. Nevertheless, a reasonably secure value of $\tau_{S_2}{}^0 = 1.6 \times 10^{-9}$ is (leading to $k_r = 1/\tau_{S_2}{}^0 = 6.3 \times 10^8$ s^{-1}) can be obtained. The difference between this calculated should be no more than a factor of 2, considering the success achieved in calculating $\tau_{S_2}{}^0$ for the S_2 states of several rigid, fluorescent aromatic thiones by the same method.[14,15] The actual lifetime of the second excited singlet state of **1** is given by $\tau_{S_2} = \tau_{S_2}{}^0\phi_f$. Since $\phi_f < 5 \times 10^{-5}$, τ_{S_2} should be less than ca. 10^{-13} s. Even if errors in estimating the lower limit of ϕ_f and in calculating $\tau_{S_2}{}^0$ are much larger than anticipated, the S_2 lifetime of **1** must still be considerably less than a picosecond. Such an estimate of τ_{S_2} is consonant with the complete absence of vibronic structure in the $S_2 \leftarrow S_0$ absorption system of **1** in any solvent. Thus, the reactive species observed by de Mayo and co-workers[4-6] having a lifetime of ca. 250 ps cannot be the second excited singlet state of **1**.

There are several possible alternate identities for the 250-ps intermediate. The broad, unstructured nature of the $S_2 \leftarrow S_0$ absorption band suggests that S_2 may undergo a prompt intramolecular reaction. However, neither of the most likely photoprocesses, excited-state isomerization to form either strained enethiol or cyclopropanethiol and α C–C bond cleavage to form a biradical, would likely lead to the final products that are observed when **1** is illuminated in alkane solution and in the presence of olefins.[4] The involvement of a higher triplet can be excluded on the basis of sensitization experiments.[4] By this process of elimination, reactive intermediates derived from intermolecular interactions between S_2 and the cycloalkane solvent must be considered.

We have shown recently[16,17] that alkanes (and many other addends) quench the second excited singlet states of several aromatic thiones at diffusion-controlled rates. The branching ratio between "physical" and net "chemical" quenching paths is of the order of 100:1 for 2,2,3,3-tetramethylindanethione in alkane solvents.[17] The second excited singlet state of **1** is likely much more chemically reactive than that of any aromatic thione because its excitation energy is considerably higher and its orbitally unpaired electrons are highly localized on the C–S moiety. Thus, highly indiscriminate H abstraction (as observed[5,6]) by the excited thione within the solvent cage on a subpicosecond time scale is entirely reasonable. Alternatively, a dark exciplex of 250-ps duration could be formed from S_2–solvent interaction. Such an exciplex might be expected to radiationlessly decay, in part, to adamantanethione S_1, which is known to intersystem cross quantitatively to the phosphorescent T_1 state;[18] weak phosphorescence is observed in our experiments when **1** is illuminated in its $S_2 \leftarrow S_0$ absorption band in both alkane and perfluoroalkane solutions. Picosecond transient absorption spectroscopy should prove to be very useful in identifying the reactive transient unambigously.

Acknowledgment. We are grateful for the continuing support of the Natural Sciences and Engineering Research Council of Canada.

Registry No. Adamantanethione, 23695-65-0.

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(8) Greidanus, J. W. *Can. J. Chem.* **1970**, *48*, 3530-3536.

(9) Meech, S. R.; Phillips, D. *J. Photochem.* **1983**, *23*, 193-217.

(10) James, D. R.; Demmer, D. R. M.; Verrall, R. E.; Steer, R. P. *Rev. Sci. Instrum.* **1983**, *54*, 1121-1130.

(11) Hara, K.; Schuster, G. B.; Drickamer, H. G. *Chem. Phys. Lett.* **1977**, *47*, 462-465.

(12) Charney, D. R.; Dalton, J. C.; Hautala, R. R.; Synder, J. J.; Turro, N. J. *J. Am. Chem. Soc.* **1974**, *96*, 1407-1410.

(13) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 438-448.

(14) Maciejewski, A.; Steer, R. P. *J. Am. Chem. Soc.* **1983**, *105*, 6738-6740.

(15) Maciejewski, A.; Safarzadeh-Amiri, A.; Verrall, R. E.; Steer, R. P. *Chem. Phys.* **1984**, *87*, 295-303.

(16) Maciejewski, A.; Steer, R. P. *J. Photochem.* **1984**, *24*, 303-307.

(17) Maciejewski, A.; Demmer, D. R.; James, D. R.; Safarzadeh-Amiri, A.; Verrall, R. E.; Steer, R. P. *J. Am. Chem. Soc.* **1984**, submitted.

(18) Lawrence, A. H.; Liao, C. C.; de Mayo, P.; Ramamurthy, V. *J. Am. Chem. Soc.* **1976**, *98*, 2219-2226.

Novel Oxidative Dehydrogenation Reaction of α-Amino Acids Chelated to Cobalt(III) Ion: Synthesis of (2-Iminocarboxylato)cobalt(III) Complexes

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Coordinated amine compounds such as diamines or macrocyclic tetraamines are known to be dehydrogenated to imine compounds.[1] The oxidative dehydrogenation of 1,2-diamines of Fe(II),[2] Ru(II),[3] Os(II),[4] and Pt(IV)[5] complexes by chemical and/or electro-

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(1) Hipp, C. J.; Busch, D. H. "Coordination Chemistry" American Chemical Society: Washington, DC, 1978; Vol. 2, pp 435-444.

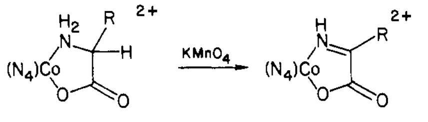
(2) (a) Goedken, V. L. *J. Chem. Soc., Chem. Commun.* **1972**, 207-208. (b) Christoph, G. G.; Goedken, V. L. *J. Am.* Chem. *Soc.* **1973**, *95*, 3869-3875. (c) Goto, M.; Takeshita, M.; Sakai, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2491-2495.

(3) (a) Lane, B. C.; Lester, J. E.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1971**, 1618-1619. (b) Mahoney, D. F.; Beattie, J. K. *Inorg. Chem.* **1973**, *12*, 2561-2565. (c) Brown, G. M.; Weaver, T. R.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 190-196.

chemical oxidation has been reported. In these systems, generally unstable imine compounds are stabilized by coordination to metal ion.

The oxidative deamination of α-amino acids occurs with various oxidizing reagents including metal ions.[6] To the best of our knowledge, however, the oxidative dehydrogenation of α-amino acids coordinated to metal ions has not been reported.[7,8] We now wish to report the formation of the (2-iminocarboxylato)cobalt(III) complexes $[Co(NH{=}C(R)COO)(tetraamine)]^{2+}$ (where R = C_6H_5, CH_3, and $CH(CH_3)_2$), from the oxidation of α-amino acidato complexes. This appears to be the first report of the isolation of 2-iminocarboxylates derived from α-amino acidates with the oxidative dehydrogenation.[9]

During the study of synthesis of the Co(III) complex with phenylglycinate (pgly), a 2-iminocarboxylato complex, $[Co(NH{=}C(C_6H_5)COO)(tetraamine)]^{2+}$, was detected as a byproduct.[10] It was presumed that the oxidative dehydrogenation of the coordinated amine group occurred.[11] The fact that the oxidation of the phenylglycinato complex with $KMnO_4$ yielded the same iminocarboxylato complex confirmed this presumption.



1, **3**, R = C_6H_5
4, R = CH_3
2, **5**, R = $CH(CH_3)_2$

To a solution of the phenylglycinato complexes Λ(or Δ)-β_2-$[Co((R)\text{-pgly})(N_4)](ClO_4)_2$[12,13] was added 2% $KMnO_4$ aqueous solution (50% excess) dropwise, and the mixture stirred for 3 min. On chromatographic separation (SP-Sephadex C25, eluted with 0.1 N $NaClO_4$), a single noncharged band (trace), two 1+ bands (minor), and a single 2+ band (major) were developed. After evaporation of the 2+ band, the diperchlorate salt precipitated as organge needles in moderate yield (55%). Further, the oxidative dehydrogenation of the alaninato and valinato complexes was successfully achieved with the same procedure[14] to give the corresponding iminocarboxylato complexes in low yields (12%, ala; 28–33%, val).[15,16]

The solution of (2-iminocarboxylato)cobalt(III) complexes, which is orange at neutral pH, showed spontaneous dramatic color change to intense dark red upon basifying with alkali.[15] This is attributed to the deprotonation of the imine group coordinated

$$[Co(NH{=}C(R)COO)(N_4)]^{2+} \rightleftharpoons [Co(N{=}C(R)COO)(N_4)]^{+}$$

to a Co(III) ion.[9,17] The ultraviolet–visible spectra in both neutral and basic solution and its pK_a values are similar to those reported for the tetraammine(iminocarboxylato)cobalt(III) complexes.[9] Similarly, a characteristic change was observed in the circular dichroism (CD) spectra. The positive Cotton effect in neutral solution, consistent with the Λ configuration,[13] turned negative in basic solution.[15] The CD spectra of the oxidation product derived from (*S*)-amino acidato complexes were identical with those derived from (*R*)-amino acidato complexes, which indicates the loss of chirality at the α-carbon of the amino acidate moiety. The ^{13}C NMR spectra of the iminocarboxylato complexes exhibit a signal in the vicinity of that of the carboxylate carbon, which is assigned to the imine carbon.[15] The ^1H NMR spectrum of the alaninato complex after oxidation shows no doublet attributable to the methyl proton of the alaninate, while a new singlet appeared at 2.35 ppm with ~0.9 ppm downfield shift. Similar downfield shifts (0.2–0.3 ppm) were observed for the two methyl groups of the valinate moiety after oxidation (1.25 (d), 1.35 ppm (d) for **2**).[18] A resonance at ~12 ppm (in Me_2SO-d_6) was assigned to the imine proton.[9,15] Further, the fact that the iminocarboxylato complexes can be reduced with $NaBH_4$ to yield the corresponding amino acidato complexes supports the structure proposed.

Although the mechanistic study has not been done yet, the mechanism of the oxidative dehydrogenation of chelated α-amino acidates to 2-iminocarboxylate appears to be different from that of macrocyclic or bidentate amine complexes of M(II)[2-4,19-22] to imines. In these oxidations it is widely accepted that the higher oxidation state of the metal ions is present as intermediates: the reaction involves prior oxidation of the metal ions followed by oxidation of the ligand and reduction of the metal ion. On the other hand, the Co(III) ion is resistant to further oxidation under

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[4] Lay, P. A.; Sargeson, A. M.; Skelton, B. W.; White, A. H. *J. Am. Chem. Soc.* **1982**, *104*, 6161-6164.

[5] Kukushkin, Yu. N.; Varshavskii, Yu. S. *Zh. Neorg. Khim.* **1966**, *11*, 356-362.

[6] See, for example: (a) Denis, W. *J. Biol. Chem.* **1911**, *9*, 365-374. (b) Nyilasi, J. *Mag. Kem. Foly.* **1958**, *64*, 474-480. (c) Sheikh, R. A.; Waters, W. A. *J. Chem. Soc. B* **1970**, 988-991. (d) Chandra, G.; Srivastava, S. N. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 3000-3003. (e) Beileryan, N. M.; Chshmarityan, D. G. *Kinet. Katal.* **1974**, *15*, 1400-1404. (f) Kumar, A.; Neta, P. *J. Am. Chem. Soc.* **1980**, *102*, 7284-7289.

[7] The oxidation of the coordinated sulfur atom on cysteinato complexes has been studied. See: (a) Schubert, M. P. *J. Am. Chem. Soc.* **1933**, *55*, 3336-3342. (b) Sloan, C. P.; Krueger, J. H. *Inorg. Chem.* **1975**, *14*, 1481-1485. (c) Jackson, W. G.; Sargeson, A. M.; Whimp, P. O. *J. Chem. Soc., Chem. Commun.* **1976**, 934-935. (d) Herting, D. L.; Sloan, C. P.; Cabral, A. W.; Krueger, J. H. *Inorg. Chem.* **1978**, *17*, 1649-1653.

[8] The oxidative dehydrogenation of peptide at the amino or amide nitrogen has been postulated in the oxidative rearrangement of the oxygen complexes of the cobalt(II)-peptide complexes[8a] and the oxidative fragmentation of the copper(II)-peptide complex with $IrCl_6^{2-}$ ion:[8b] (a) Harris, W. R.; Bess, R. C.; Martell, A. E.; Ridgway, T. H. *J. Am. Chem. Soc.* **1977**, *99*, 2958-2963. (b) Levitzki, A.; Anbar, M.; Berger, A. *Biochemistry* **1967**, *6*, 3757-3765.

[9] Several 2-iminocarboxylato complexes derived from the intramolecular condensation reaction of (2-ketocarboxylato)pentaamminecobalt(III) complexes have been reported: (a) Harrowfield, J. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1974**, *96*, 2634-2635. (b) Harrowfield, J. M.; Sargeson, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 1514-1520.

[10] Yamaguchi, M.; Oikawa, H.; Saburi, M.; Yoshikawa, S., unpublished results.

[11] The oxidizing reagent was presumably oxygen, since this dehydrogenation reaction did not occur under nitrogen.

[12] The ligands, 3,7-diazanonane-1,9-diamine (2,3,2-tet) and 2*S*,10*S*-4,8-diazaundecane-2,10-diamine (2(*S*), 10(*S*)-Me_2-2,3,2-tet) were employed as tetraamine (N_4).

[13] Yamaguchi, M.; Yamamatsu, S.; Furusawa, T.; Yano, S.; Saburi, M.; Yoshikawa, S. *Inorg. Chem.* **1980**, *19*, 2010-2016.

[14] In the case of the alaninato and valinato complexes, the starting amino acidato complexes were recovered (ca. 25%) from the 2+ red band, moving slower than that of the iminocarboxylato complexes.

[15] Λ-β_2-$[Co(NH{=}C(C_6H_5)CO_2)(2,3,2\text{-tet})](ClO_4)_2$ (**1**), Δ-β_2-$[Co(NH{=}C(CH(CH_3)_2)CO_2(2,3,2\text{-tet})](ClO_4)_2$ (**2**), Λ-β_2-$[Co(NH{=}C(C_6H_5)CO_2)(2(S),10(S)\text{-}Me_2\text{-}2,3,2\text{-tet})](ClO_4)_2\cdot H_2O$ (**3**), Λ-β_2-$[Co(NH{=}C(CH_3)CO_2)(2(S),10(S)\text{-}Me_2\text{-}2,3,2\text{-tet})](ClO_4)_2$ (**4**), and Λ-β_2-$[Co(NH{=}C(CH(CH_3)_2)CO_2)(2(S),10(S)\text{-}Me_2\text{-}2,3,2\text{-tet})](ClO_4)_2$ (**5**) were obtained.[16] **Caution**: Although these perchlorate salts are moderately stable, they are potential hazards and should therefore be handled with care and in small quantities. All compounds reported (**1–5**) gave satisfactory elemental analyses and ^1H NMR (90 or 400 MHz) and ^{13}C NMR (25 or 100 MHz) spectra in accord with the structure given. NMR spectral and spectrophotometrical data are exemplified by those of **3** as follows: ^1H NMR (D_2O) δ 1.37, 1.41 (d, 6 H, CH_3) 1.55–3.50 (br, 12 H, tetraamine), 7.35–8.20 (m, 5 H, phenyl); ^1H NMR (Me_2SO-d_6 with a drop of D_2SO_4) δ 12.20 (br, 1 H, C=NH); ^{13}C NMR (D_2O) δ 18.0*, 23.3, 46.5, 49.8, 52.7, 54.3, 55.7, 61.9 (tetraamine, overlapping peaks are indicated with asterisk), 130.0*, 130.7*, 132.3, 135.1 (phenyl), 173.1 (C=NH), 181.1 (C=O); vis/UV (H_2O) $\epsilon_{474}{}^{max}$ 177 $M^{-1}\,cm^{-1}$, $\epsilon_{317}{}^{sh}$ 5200, $\epsilon_{268}{}^{max}$ 11 800, $\epsilon_{222}{}^{max}$ 22 900, $\epsilon_{213}{}^{max}$ 22 900; vis/UV (N/100 NaOH) $\epsilon_{513}{}^{max}$ 270, $\epsilon_{398}{}^{sh}$ 734, $\epsilon_{337}{}^{sh}$ 3150, $\epsilon_{284}{}^{max}$ 18 200, $\epsilon_{220}{}^{sh}$ 21 800, $\epsilon_{204}{}^{max}$ 36 000; Circular dichroism (CD) (H_2O) $\Delta\epsilon_{501}{}^{max}$ 2.04, $\Delta\epsilon_{461}{}^{max}$ 2.18; CD (N/100 NaOH) $\Delta\epsilon_{568}{}^{max}$ 1.23, $\Delta\epsilon_{500}{}^{max}$ –3.76, $\Delta\epsilon_{429}{}^{max}$ 0.19. Although these complexes are somewhat unstable in basic solution, vis/UV and CD spectra showed no change over at least 15 min.

[16] To our surprise, some attempts to obtain the 2-iminocarboxylato complex from the oxidation of Λ(or Δ)-β_2-$[Co(ala)(2,3,2\text{-tet})](ClO_4)_2$ failed, contrary to the alaninato complex with 2(*S*),10(*S*)-Me_2-2,3,2-tet.

[17] This deprotonation is fully reversible, although the deprotonated complexes decompose slowly in basic solution.[15]

[18] In the case of **5**, the peaks of the methyl groups of iminocarboxylate overlap with those of tetraamine and are not assignable.

[19] Goedken, V. L.; Busch, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 7355-7363.

[20] (a) Black, D. St. C.; Hartshorn, A. J. *Tetrahedron Lett.* **1974**, 2157-2160. (b) Tang, S. C.; Holm, R. H. *J. Am. Chem. Soc.* **1975**, *97*, 3359-3366. (c) Raleigh, C.; Martell, A. E. *J. Chem. Soc., Chem. Commun.* **1984**, 335-336.

[21] (a) Curtis, N. F. *J. Chem. Soc., Chem. Commun.* **1966**, 881-883. (b) Curtis, N. F. *J. Chem. Soc. A* **1971**, 2834-2838.

[22] (a) Ridd, M. J.; Keene, F. R. *J. Am. Chem. Soc.* **1981**, *103*, 5733-5740. (b) Keene, F. R.; Ridd, M. J.; Snow, M. R. *J. Am. Chem. Soc.* **1983**, *105*, 7075-7081.

these conditions.[23] It is noteworthy that the tetraamine ligand was intact during the oxidation of chelated α-amino acids.[24] This suggests that the carboxylate group of amino acids enhances the susceptibility of α-amino group of amino acids to oxidation.

Nucleophilic addition of hydride (as BH_4^-) to the imine carbon center of the $NH{=}C(CH_3)CO_2$ chelate complex has been reported.[9] Since the complexes employed here have a chiral metal center, it will provide a new synthetic pathway to chiral α-amino acids.[25] It indicates a possibility of a kind of asymmetric transformation[13] of DL-amino acids to chiral amino acids via iminocarboxylates wtih chiral (tetraamine)cobalt(III) complexes. The study in this line is in progress.

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(23) It has been reported that some attempts to achieve amine oxidation of Co(III) complexes failed.[2a,19]

(24) With [Co(oxalato)(2,3,2-tet)]ClO$_4$ complex, no reaction was observed under the same conditions.

(25) Preliminary results of the reduction of the 2-iminocarboxylato complexes with NaBH$_4$ showed stereoselectivity on hydride addition. The *R*/*S* values of the reduced product for **3** was 75/25.

(*E*,*Z*)-Ajoene: A Potent Antithrombotic Agent from Garlic[1]

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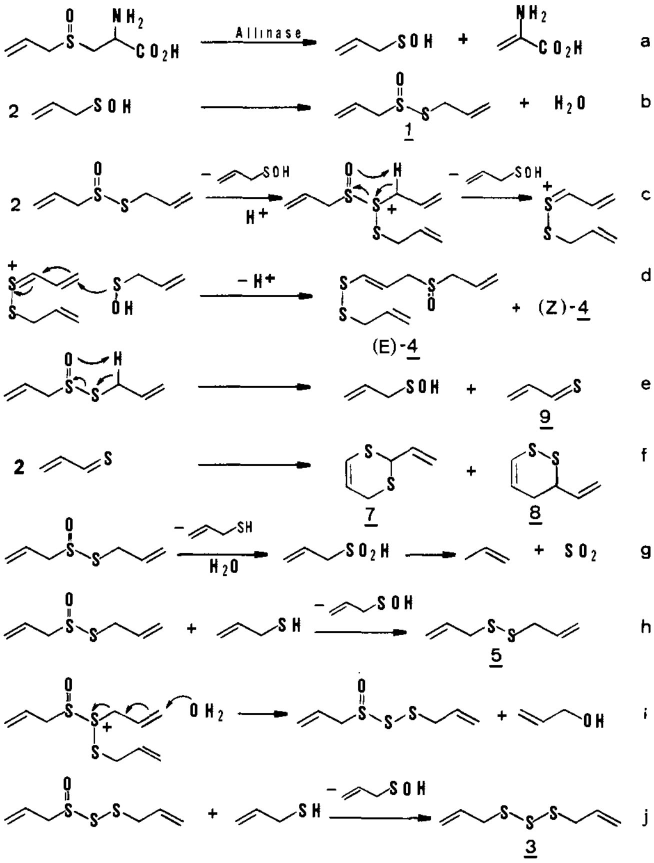
Garlic (*Allium sativum*) is reputed to offer protection against stroke, coronary thrombosis, and atherosclerosis.[2,3a] These beneficial effects of garlic have been attributed to its ability to inhibit platelet aggregation.[3b] This effect, in turn, has been ascribed to allicin ($CH_2{=}CHCH_2S(O)SCH_2CH{=}CH_2$, *S*-allyl 2-propenethiosulfinate (**1**)), allyl methyl trisulfide (**2**), and diallyl trisulfide (**3**), all of which are found in garlic extracts.[3c] Recently Apitz-Castro et al.[4a] reported that 2-vinyl-4*H*-1,3-dithiin (**7**) and an unknown compound, now named ajoene,[4b] are potent antithrombotic agents derived from garlic extract. Unlike several other inhibitors of platelet aggregation, these components have been found to inhibit aggregation induced by all known inductors.[4a] We report herein the structural characterization and a simple synthesis of (*E*,*Z*)-ajoene (**4**) as well as **7** from allicin (**1**).

Scheme I



Extraction and separation of the garlic-derived components was monitored with bioassay for inhibition of platelet aggregation.[4a] Chopped garlic pieces were soaked in methanol at 25 °C for 48 h; the concentrate was suspended in water and was extracted with diethyl ether. The extract was concentrated, and the residue was stored at 25 °C for 4 days as a 10% solution in methanol, filtered, and concentrated giving a yellow oil (1.6 g/5 kg of garlic bulbs). Chromatography (silica gel; hexane to benzene to chloroform) gave 18 components, of which three fractions inhibited platelet aggregation. Preparative TLC (silica gel) led to the isolation of pure samples of the nonpolar components. TLC fractions with R_f 0.5 and 0.25 in hexane were identified as diallyl trisulfide (**3**) and 2-vinyl-4*H*-1,3-dithiin (**7**),[4a,5] respectively. Allicin (**1**), allyl methyl trisulfide (**2**), diallyl disulfide (**5**), diallyl tetrasulfide (**6**), and 3-vinyl-4*H*-1,2-dithiin (**8**)[5,9] were also isolated and identified

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[†] Fellow of the John Simon Guggenheim Memorial Foundation, 1984–1985.

(1) (a) The material covered in this communication is the subject of U.S. Patent Applications filed by the Research Foundation of the State University of New York. (b) Presented at the 1984 International Chemical Congress of Pacific Basin Societies, Honolulu, December 16, 1984. (c) The Chemistry of Alkyl Thiosulfinate Esters. 8. (d) Part 7: Block, E.; O'Connor, J. *J. Am. Chem. Soc.* **1974**, *96*, 3929–3944.

(2) Lau, B. H. S.; Adetumbi, M. A.; Sachez, A. *Nutr. Res.* (*N.Y.*) **1983**, *3*, 119–128. Bolton, S.; Null, G.; Troetel, W. M. *Am. Pharm.* **1982**, *NS22*, 40–43. Singer, M. "The Fanatic's Ecstatic Aromatic Guide to Onions, Garlic, Shallots and Leeks"; Prentice Hall: Englewood Cliffs, NJ, 1981. Pros, J. S. "Virtudes Curativas del Ajo"; Editorial Sintes: Barcelona, 1975. Harris, L. J. "The Book of Garlic"; Holt, Rinehart and Winston: New York, 1974. Watanabe, T. "Garlic Therapy"; Japan Publications: Tokyo, 1974. Binding, G. J. "About Garlic"; Thorsons Publishers: London, 1970; and references therein.

(3) (a) Garlic also displays antibacterial, antifungal, and anticandidal activity, attributed to allicin (**1**): Cavallito, C. J.; Bailey, J. H. *J. Am. Chem. Soc.* **1944**, *66*, 1950–1951. Cavallito, C. J.; Buck, J. S.; Suter, C. M. *J. Am. Chem. Soc.* **1944**, *66*, 1952–1954. Barone, F. E. *Mycologia* **1977**, *69*, 793–825. (b) Bordia, A. *Atherosclerosis* (*Shannon, Irel.*) **1978**, *30*, 355–360. Samson, R. R. *Atherosclerosis* (*Shannon, Irel.*) **1982**, *44*, 119–120. (c) Augusti, K. T.; Mathew, P. T. *Experientia* **1974**, *30*, 468–470. Ariga, T.; Oshiba, S.; Tamada, T. *Lancet* **1981**, *1*, 150–151.

(4) (a) Apitz-Castro, R.; Cabrera, S.; Cruz, M. R.; Ledezma, E.; Jain, M. K. *Thromb. Res.* **1983**, *32*, 155–169 (4 was misassigned here). (b) "Ajo" (pronounced "aho") is garlic in Spanish.

(5) Bock, H.; Mohmand, S.; Hirabayashi, T.; Semkow, A. *Chem. Ber.* **1982**, *115*, 1339–1348. Vedejs, E.; Eberlein, T. H.; Varie, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1445–1447.

(6) Structures such as $CH_2{=}CHCH_2SCH_2CH{=}CHS(O)SCH_2CH{=}CH_2$ possessing a –S(O)S– group instead of a C–S(O)–C group are ruled out by the IR spectrum since the former group shows strong absorption[1c] at 1100 cm^{-1}. Since allyl 1-alkenyl sulfoxides undergo facile thio-Claisen rearrangement at or below room temperature[7] the isomeric structure $CH_2{=}CHCH_2S(O)CH{=}CHCH_2SSCH_2CH{=}CH_2$ can also be ruled out.

(7) (a) Ahmad, S.; Block, E., unpublished results. (b) Bell, R.; Cottam, P. D.; Davies, J.; Jones, D. N.; Meanwell, N. A. *Tetrahedron Lett.* **1980**, *21*, 4379–4382.

(8) It has been previously noted[3a] that allicin decomposes to a water-insoluble nondistillable liquid of undefined structure. Compound 4 can be purified by Kugelrohr distillation at 0.05 mm (air temperature 150–200 °C).

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