extract was recrystallized from hexane to give α-chloriminophenylacetonitrile (1.6 g), mp 40–42°.

Preparation of α-Fluorimino-4-chlorophenylacetonitrile.—A solution of the crude adduct from tetrafluorohydrazine and 10 g of 4-chlorostyrene (72.3 mmoles) in 120 ml of methylene chloride was stirred at ambient temperature while a solution of 17 ml (220 mmoles) of pyridine in 100 ml of methylene chloride was added dropwise. The temperature of the solution increased slowly, and the rate of pyridine addition was regulated so as to maintain a slow reflux of the solvent. The mixture was then stirred overnight. The methylene chloride solution was washed with water and dilute, aqueous hydrochloric acid, dried (magnesium sulfate), and stripped. One recrystallization from hexane gave α-fluorimino-4-chlorophenylacetonitrile (8.9 g), mp 39–41°. The sample was purified by chromatography on silica gel; elution was accomplished with pentane–methylene chloride (5:1), mp 41–42°.

The F^{19} nmr spectrum had a strong peak at ϕ −56.5 and a very weak peak at −41.6. In fractions eluted from the silica gel column just after the center cut the ϕ −41.6 peak was stronger.

α-Fluoriminiphenylacetonitrile.—The styrene–tetrafluorohydrazine adduct in methylene chloride was dehydrofluorinated as described above. The methylene chloride solution was washed with water, 10% aqueous hydrochloric acid, and water; the solution was dried and stripped. Distillation of the residue gave α-fluoriminophenylacetonitrile, bp 82° (4.5 mm). The F^{19} nmr had peaks at ϕ −52.8 (very strong) and −40.0 (very weak). A sample recrystallized from hexane had mp 31–32° and exhibited only the ϕ −52.8 fluorine resonance.

Reaction of α-Fluorimino-4-chlorophenylacetonitrile and Sulfuric Acid.—There was no sign of solution or interaction when 0.91 g (5 mmoles) of the fluorimine and 3 ml of concentrated sulfuric acid were mixed at room temperature. Warming to 60° produced a homogeneous solution, but white crystals separated upon cooling the mixture to 20°. The mixture was then maintained at 85° for 20 min, cooled, and poured into water. An insoluble solid was removed by filtration. Recrystallization of the solid from chloroform–ethanol gave N-4-chlorophenyloxamide (0.79 g, 80%), mp 238–240°, lit[24] 241°.

(20) F. D. Chattaway and W. H. Lewis, *J. Chem. Soc.*, **89**, 158 (1906).

Reaction of α-Fluorimino-4-chlorophenylacetonitrile and Sodium Ethoxide.—A solution of 0.91 g of the fluorimine in 10 ml of absolute ethanol was treated with 12 ml of 0.94 *N* sodium ethoxide in ethanol at ambient temperature. The mixture was stirred for 2 hr and was then poured into water. The organic products, isolated by extraction with methylene chloride, were chromatographed on silica gel. Pentane–methylene chloride mixtures eluted 4-chlorobenzonitrile (0.225 g, mp 92–93°, 33%) from the column. The next fraction eluted (methylene chloride–ethyl acetate, 9:1) was methyl N-(4-chlorophenyl)carbamate (0.428 g, 53%), having an infrared spectrum identical with that of an authentic sample. The last fraction eluted from the column (0.064 g, 8%) was 4-chlorobenzamide containing a little 4-chlorobenzoic acid (infrared spectrum).

Reaction of α-Fluorimino-4-chlorophenylacetonitrile and Sodium Methoxide.—A solution of 0.91 g of the fluorimine in 10 ml of methanol was treated with 20 ml of 0.54 *N* sodium methoxide in methanol. After 2 hr at ambient temperature the reaction mixture was processed as described above. The fractions isolated from the chromatographic column were 4-chlorobenzonitrile (0.313 g, 45.5%), methyl N-(4-chlorophenyl)carbamate (0.130 g, 14%, mp 116–117°; lit.[21] mp 115–116°), and 4-chlorobenzamide (0.205 g, 26.3%, mp 179–180°).

Reaction of Sodium Methoxide and α-Chlorimino-4-chlorophenylacetonitrile.—A solution of 0.51 g of the chlorimine, mp 82–84°, was treated with 10 ml of 0.54 *N* sodium methoxide in methanol at ambient temperature. After 1 hr at ambient temperature the mixture was poured into water. The organic product was isolated and chromatographed as usual. The products obtained from the column were 4-chlorobenzonitrile (0.205 g, 58.3%), methyl N-(4-chlorophenyl)carbamate (0.022 g, 4.7%), and 4-chlorobenzamide (0.107 g, 26.9%).

Registry No.—IIIa (*anti*), 7541-02-8; IIIa (*syn*), 7541-03-9; IIIb (*anti*), 7541-06-2; IIIb (*syn*), 7541-07-3; Va, 7541-10-8; IVa (*anti*), 7541-11-9; Vb, 7541-12-0; IVb (*anti*), 7541-13-1; VIa, 7541-14-2; VIb, 7541-15-3.

(21) M. J. Kolbezen, R. L. Metcalf, and T. R. Fukuto, *J. Agr. Food Chem.*, **2**, 864 (1954); *Chem. Abstr.*, **49**, 4224 (1955).

The Synthesis of (+)- and (−)-*cis*-S-(β-Styryl)-L-cysteine S-Oxides

JOHN F. CARSON AND LOIS E. BOGGS

Western Regional Research Laboratory,[1] *Albany, California 94710*

Received September 7, 1966

L-cysteine in the presence of sodium in ethanol and dimethylformamide has been treated with phenylacetylene to yield *cis*-S-(β-styryl)-L-cysteine. *cis,cis*-β,β′-Distyryl sulfide is a by-product. Oxidation of the styrylcysteine with hydrogen peroxide in acetic acid–trifluoroacetic acid yielded the crystalline trifluoroacetic acid salts of the diastereomeric sulfoxides from which the pure (+)- and (−)-*cis*-S-(β-styryl)-L-cysteine S-oxides were isolated.

The S-(1-propenyl)-L-cysteine S-oxides have unusual properties in that they are attacked by an enzyme present in onion or garlic to yield a lachrymator[2] and in the presence of base, undergo internal addition to produce cyclic sulfoxide amino acids.[3] The (+)-*trans* isomer[4] and its γ-glutamyl peptide[5] are important consituents of *Allium cepa*. Däbritz and Virtanen[6] have synthesized the analog, S-vinyl-L-cysteine S-oxide and we have recently prepared the (+)- and (−)-*cis*-S-(1-propenyl)-L-cysteine S-oxides[7] which are isomers of the naturally occurring sulfoxide found in onions. For further investigations of the chemistry of this class of compounds, *cis*-S-(β-styryl)-L-cysteine (I) has been prepared and converted into the (+)- (VI) and (−)-sulfoxides (V). (See Scheme I.)

In particular, it was of interest to determine whether the styrylcysteine sulfoxides would cyclize in base in a manner similar to the propenylcysteine sulfoxides.[3] Virtanen[2] has proposed propenylsulfenic acid ($CH_3CH{=}CHS(H)O$) as the structure of the highly unstable lachrymator produced on enzymic decomposition of propenylcysteine sulfoxide. It was hoped that the new sulfoxide amino acids might produce a more stable analog of the lachrymator.

L-cysteine and phenylacetylene in the presence of sodium in ethanol and dimethylformamide reacted to

(1) A laboratory of the Western Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) A. I. Virtanen and C. G. Spåre, *Suomen Kemistilehti*, **B34**, 72 (1961); **B35**, 28 (1962).

(3) A. I. Virtanen and E. J. Matikkala, *Acta Chem. Scand.*, **13**, 623 (1959); A. I. Virtanen and C. G. Spåre, *Suomen Kemistilehti*, **B34**, 81 (1961).

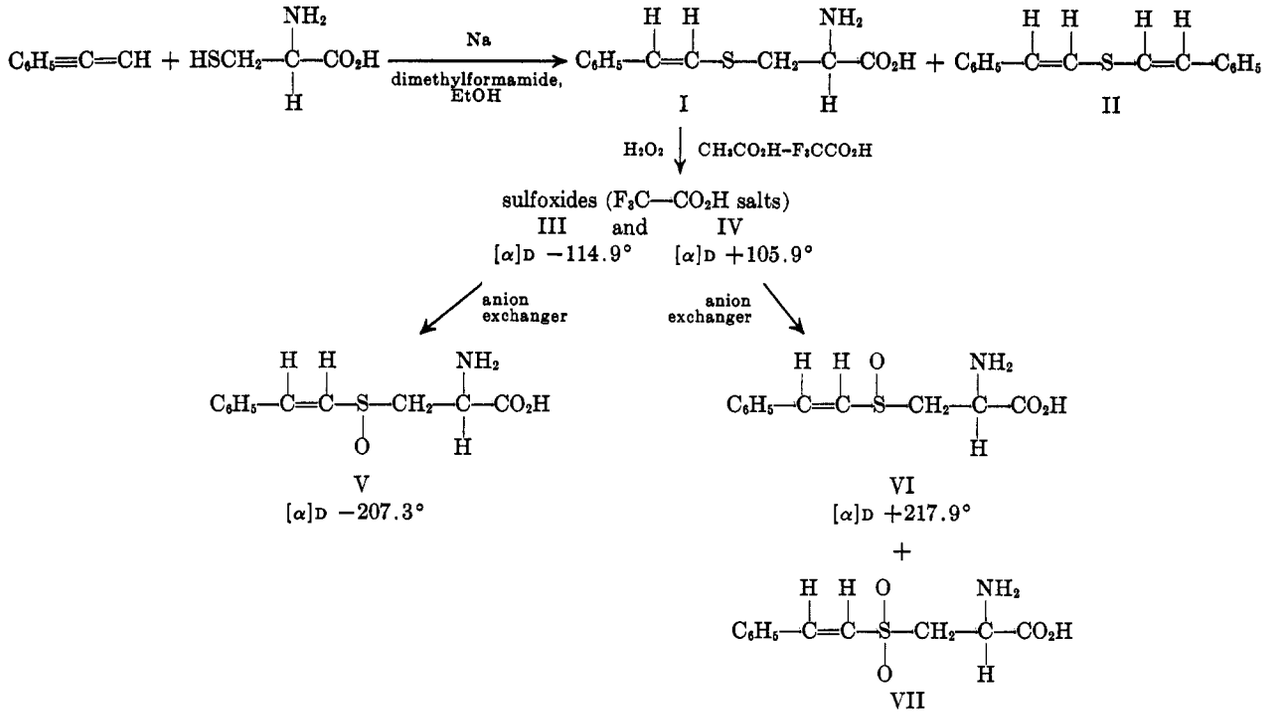
(4) C. G. Spåre and A. I. Virtanen, *Acta Chem. Scand.*, **15**, 1280 (1961); J. F. Carson, R. E. Lundin, and T. M. Lukes, *J. Org. Chem.*, **31**, 1634 (1966).

(5) A. I. Virtanen and E. J. Matikkala, *Suomen Kemistilehti*, **B34**, 84, 114 (1961).

(6) E. Däbritz and A. I. Virtanen, *Acta Chem. Scand.*, **18**, 837 (1964).

(7) J. F. Carson and L. E. Boggs, *J. Org. Chem.*, **31**, 2862 (1966).

SCHEME I



give *cis*-S-(β-styryl)-L-cysteine (I 71%). The new amino acid was characterized by the preparation of crystalline N-acetyl and N-*p*-toluenesulfonyl derivatives. The pmr spectrum of the latter confirmed the structure and established the *cis* configuration of the vinylic protons (spin–spin coupling constant, J_{HH} = 9 cps). This is consistent with the findings of Truce[8] and co-workers who established that in the nucleophilic addition of sodium mercaptides to acetylenes, addition is in a *trans* manner so that a terminal acetylene will yield a *cis* product.

Oxidation of I in acetic acid–trifluoroacetic acid (6:1) with hydrogen peroxide at 10° yielded a mixture of diastereomeric sulfoxides which were partially separated by fractional crystallization as the trifluoroacetic acid salts. Crystallization from water yielded the less soluble pure levorotatory trifluoroacetate (III), $[\alpha]^{26}D$ −114.9° (water), and the more soluble dextrorotatory salt (IV), $[\alpha]^{26}D$ +105.9°. Attempted oxidation of styrylcysteine in acetic acid without addition of trifluoroacetic acid failed probably owing to insolubility of the amino acid.

Removal of trifluoroacetic acid from III with a weak anion exchanger yielded (−)-*cis*-S-(β-styryl)-L-cysteine S-oxide (V) which after several recrystallizations from aqueous acetone had $[\alpha]^{25}D$ −207.3° (water). In a similar manner, the dextrorotatory salt (IV) yielded (+)-*cis*-S-(β-styryl)-L-cysteine S-oxide (VI), $[\alpha]^{26}D$ +217.9°, and small quantities of sulfone VII.

Like other acyclic sulfoxide amino acids, the rotation at the D line appears to be dominated by the configuration of the sulfoxide group. The (+)- and (−)-sulfoxides show positive and negative Cotton effects, respectively. Although the absolute configurations of these new sulfoxides are not known, by analogy with the D-line rotations and Cotton effects of other sulfoxide amino acids,[9] one would predict that the dextrorotatory sulfoxide (VI) would have the same configuration at sulfur as (+)-S-methyl-L-cysteine S-oxide for which the absolute configuration is known by X-ray analysis.[10] The (−)-sulfoxide (V) would then have an opposite configuration at sulfur and would correlate with (−)-S-methyl-L-cysteine S-oxide.

In the infrared (KBr pellet), the (−)-sulfoxide showed three closely spaced approximately equal absorptions at 1000, 1010, and 1015 cm^{-1} in the region usually assigned to sulfoxide absorption, and the (+)-sulfoxide showed three strong maxima at 1017, 1035, and 1040 cm^{-1}. These absorptions were absent in the spectra of styrylcysteine (I) and of the sulfone (VII).

Other vinyl-type cysteine sulfoxides have been shown to cyclize in aqueous base at room temperature. (+)-*trans*-S-(1-Propenyl)-L-cysteine sulfoxide cyclizes in high yield to cycloalliin (L-3-carboxy-5-methyl-1,4-thiazane S-oxide).[3] The corresponding (+)- and (−)-*cis*-sulfoxides yield cycloalliin and a stereoisomer[7] in dilute ammonium hydroxide and under similar conditions S-vinyl-L-cysteine sulfoxide yields L-3-carboxy-1,4-thiazane S-oxide.[6] However, both styrylcysteine sulfoxides are inert to dilute ammonium hydroxide at room temperature. Neither cyclization nor epimerization of the sulfoxide occurred and starting material was recovered of unimpaired optical purity. Unlike vinyl-[6] and propenylcysteine sulfoxides[2,7] which produce lachrymators when treated with onion alliinase or with the C–S lyase of *Albizzia lophanta*,[11] the new

(8) W. E. Truce and J. A. Simms, *J. Am. Chem. Soc.*, **78**, 2756 (1956); W. E. Truce in "Organic Sulfur Compounds," Vol. I, N. Karasch, Ed., Pergammon Press, Ltd., London, 1961.

(9) W. Gaffield, F. F. Wong, and J. F. Carson, *J. Org. Chem.*, **30**, 951 (1965).

(10) R. Hine, *Acta Cryst.*, **15**, 635 (1962).

(11) S. Schwimmer and A. Kjaer, *Biochim. Biophys. Acta*, **42**, 316 (1960).

sulfoxide amino acids under the same conditions yield no lachrymatory compounds. Enzymic reaction occurs with the production of pyruvate and a product insoluble in water but soluble in organic solvents.

In the reaction between phenylacetylene and L-cysteine, in addition to styrylcysteine (I), *cis,cis*-β,β′-distyryl sulfide (II) is formed as a by-product. The sulfide may be formed as a result of loss of hydrogen sulfide from cysteine followed by reaction of the former with phenylacetylene. The structure of II was established by pmr spectra (J_{HH} = 10.8 cps, indicative of all *cis* configuration). Previously, *cis,trans*- and *trans,trans*-distyryl sulfides have been prepared by a Wittig reaction of benzaldehyde on dimethyl ether-α,α′-bistriphenylphosphonium bromide.[12] The *cis,trans* isomer has also been obtained by the radiation-induced addition of hydrogen sulfide to phenylacetylene.[13] A sample of II on standing for 3 years in a vial on the laboratory shelf, spontaneously changed, in part, to the *cis,trans* isomer identical with the compound obtained by Dimroth, *et al.*,[12] on the basis of elemental analysis, melting point, and ultraviolet and pmr spectra. A sample of II stored for the same length of time protected from light at +3° showed no change.

Experimental Section

The pmr spectra were obtained with Varian A-60[14] and HR-100 spectrophotometers. Infrared spectra were obtained with a Perkin-Elmer Model 237 instrument and ORD measurements with a Cary Model 60 spectropolarimeter.

***cis*-S-(β-Styryl)-L-cysteine (I).**—To a suspension of 19.3 g (0.110 mole) of L-cysteine hydrochloride hydrate in 500 ml of absolute ethanol, there was added 6.9 g (0.30 g-atom) of sodium in small quantities under nitrogen. When the reaction had subsided, the suspension was heated to 60° and 500 ml of dimethylformamide was added which produced a more fluid suspension. Freshly distilled phenylacetylene (25.5 g, 0.25 mole) was added and the reaction mixture was stirred under nitrogen for 48 hr at 58–62°. The mixture originally white became successively yellow, olive green, and finally a grey-brown. At the conclusion of the reaction, a solution of 40 ml of acetic acid in 150 ml of water was added and the suspension was concentrated *in vacuo* to a pasty, yellow solid. The solid was stirred with 300 ml of 10% aqueous acetic acid, filtered, and washed successively with 300 ml of water and 400 ml of acetone to give 17.6 g (71.8% yield) of styrylcysteine. The acetone extraction removes distyryl sulfide. The amino acid was recrystallized by dissolving 5.1 g of solid in 800 ml of boiling water containing 35 ml of reagent ammonium hydroxide followed by filtration and acidification of the cooled filtrate with 45 ml of acetic acid to yield 4.8 g of pure *cis*-S-(β-styryl)-L-cysteine (I): decomposes at 183.5–184° (gas evolution), $[\alpha]^{26}D$ +44.27° (l = 2; c 1.1, 1 N NaOH); ultraviolet (0.1 N NaOH) λ_{max} 222 mμ (ε 8930), λ_{max} 284 mμ (ε 14,600).

Anal. Calcd for $C_{11}H_{13}NO_2S$: C, 59.17; H, 5.87; S, 14.36. Found: C, 59.3; H, 5.80; S, 14.5.

The compound is insoluble in water, acetic acid, dimethyl sulfoxide, and dimethylformamide. It is very soluble in trifluoroacetic acid with gradual decomposition, moderately soluble in aqueous sodium hydroxide, and slightly soluble in hot ammoniacal solution.

Maximum yields of the amino acid were obtained when sodium was used in the ratio of 2.4 to 2.8 g-atoms per mole of cysteine hydrochloride with a 100–150% molar excess of phenylacetylene. The acetone extract of the crude amino acid in this experiment yielded 1.5 g (5.7% yield) of *cis,cis*-β,β′-distyryl sulfide. When a smaller excess of phenylacetylene was used, larger quantities of distyryl sulfide and only low yields of the amino acid were obtained.

***cis,cis*-β,β′-Distyryl Sulfide.**—Reaction of 11 g (0.070 mole) of cysteine hydrochloride, 4.58 g (0.20 g-atom) of sodium, and 11 g (0.108 mole) of phenylacetylene in 300 ml of dimethylformamide and 300 ml of absolute ethanol with reaction conditions as previously described yielded 12.5 g of yellow, semicrystalline product. Extraction with acetone yielded 3.45 g (22%) of S-β-styryl-L-cysteine (I) as the insoluble portion. The acetone extract on evaporation yielded a brown oil which crystallized on stirring with 40 ml of methanol to give 6.5 g of brown, greasy crystals. Recrystallization from ethanol (decolorization with carbon) gave 5.2 g of *cis,cis*-β,β′-distyryl sulfide (31% yield based on cysteine) as colorless needles: mp 39–39.5°, ultraviolet (ethanol) λ_{max} 314 mμ (ϵ_M 25,800).[15]

Anal. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92; S, 13.45. Found: C, 80.5; H, 5.98; S, 13.8.

In carbon tetrachloride solution, in the pmr spectrum, the vinylic protons had a spin–spin coupling constant of 10.8 cps indicating an all-*cis* configuration. In the infrared (KBr disk) no absorption occurred in the region for a *trans* double bond (940–1000 cm^{-1}).

Spontaneous Isomerization of II.—A 1-g sample of *cis,cis*-β,β′-distyryl sulfide after storage for 3 years in a bottle at room temperature had partially liquefied and had become amber in color. Crystallization from 50 ml of ethanol (decolorization with carbon) yielded 469 mg of plates, mp 94–96°. Recrystallization from ethanol yielded 300 mg of *cis,trans*-β,β′-distyryl sulfide as micaceous plates: mp 98°, ultraviolet (ethanol) λ_{max} 319 mμ (ϵ_M 33,200), infrared (KBr) strong absorption at 955 cm^{-1} (region for *trans* double bond). The pmr spectrum in carbon tetrachloride (100-Mc spectrometer) showed two vinylic protons with J_{AB} = 10.8 cps (*cis*) and two vinylic protons with J_{AB} = 15.6 cps (*trans*).

Anal. Calcd for $C_{16}H_{14}S$: C, 80.63; H, 5.92; S, 13.45. Found: C, 80.8; H, 5.97; S, 13.5.

N-Acetyl-*cis*-S-(β-styryl)-L-cysteine.—The derivative was prepared in an 83% yield by reaction of I with acetic anhydride and 1 N sodium hydroxide at +5°. It was crystallized from acetone as long needles: mp 168.5–169°, $[\alpha^{26}]D$ +87.4° (l = 2; c 1.2, ethanol).

Anal. Calcd for $C_{13}H_{15}NO_3S$: C, 58.85; H, 5.70; N, 5.28. Found: C, 58.9; H, 5.66; N, 5.17.

N-*p*-Toluenesulfonyl-*cis*-S-(β-styryl)-L-cysteine.—To a solution of 1.5 g (0.0067 mole) of I in 50 ml of 1 N sodium hydroxide, 4 g (0.021 mole) of *p*-toluenesulfonyl chloride and 25 ml 1 N sodium hydroxide were added alternately in small portions with stirring over a 7-hr period. Stirring was continued for 18 hr and the product was isolated by acidification and extraction into ethyl acetate. Evaporation of solvent and crystallization from 50% aqueous ethanol yielded 1.58 g (62%) of the pure compound as needles: mp 145–146°, $[\alpha]^{26}D$ +41.3° (l = 2; c 1.2, ethanol). The pmr spectrum in deuterioacetone confirmed the structure by integration of protons and established the *cis* configuration (J_{HH} = 9 cps).

Anal. Calcd for $C_{18}H_{19}NO_4S_2$: C, 57.27; H, 5.07; S, 16.99. Found: C, 57.4; H, 5.19; S, 17.0.

(+)- and (−)-Trifluoroacetic Acid Salts of *cis*-S-(β-Styryl)-L-cysteine S-Oxides (III, IV).—To a solution of 420 ml of acetic acid and 70 ml of trifluoroacetic acid at 10°, 7.20 g (0.0323 mole) of I was added and 4.20 ml (0.0370 equiv) of 32% hydrogen peroxide was added at a rate of 0.5 ml/hr with stirring while the temperature was maintained at 7–10°. After addition of hydrogen peroxide was complete, the solution was stirred for an additional 2 hr at 10°. The solution was then concentrated *in vacuo* to 50 ml, 250 ml of water was added, and the resulting solution was concentrated *in vacuo* to 125 ml. The resulting crystalline mixture, after refrigerating for several hours, was filtered and washed with 25 ml of ice–water to yield 5.90 g of white solid, $[\alpha]^{25}D$ −68° (water). The mother liquor on concentration to 25 ml yielded a second crop, 2.7 g, $[\alpha]^{25}D$ +105.9°, and a third crop, 1.1 g, $[\alpha]D$ +81°.

The levorotatory fraction was recrystallized from 60 ml of cold water to yield 3 g of III: 26% yield, decomposes at 100–101°, $[\alpha]^{26}D$ −114.9° (l = 1; c 2.0, water). The rotation was unchanged on recrystallization. In the infrared (KBr disk),

(12) K. Dimroth, H. Follmann, and G. Pohl, *Chem. Ber.*, **99**, 642 (1966).

(13) F. W. Stacey and J. F. Harris, Jr., *J. Am. Chem. Soc.*, **85**, 963 (1963).

(14) Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

(15) K. Dimroth, *et al.*,[12] reported λ_{max} 319 mμ (ϵ_M 32,000) for the *cis,trans* and *trans,trans* isomers.

the compound showed maxima at 1725 (un-ionized carboxyl) and at 1675 cm^{-1} (ionized carboxyl). Sulfoxide absorption appeared at 1000 cm^{-1}. The dextrorotatory salt could not be obtained analytically pure.

Anal. Calcd for $C_{13}H_{14}F_3NO_5S$: C, 44.19; H, 3.99. Found: C, 44.1; H, 4.07.

(−)-*cis*-S-(β-Styryl)-L-cysteine S-Oxide (V).—A solution of 3.0 g of III ($[\alpha]^{25}D$ −107.8°) in 400 ml of water was stirred with 80 ml of Duolite A-4 (NH_2)[14] to pH 6.0. The solution was filtered from the ion exchanger and concentrated *in vacuo* to a white solid. Crystallization from 40 ml of acetone–H_2O (3:1) gave 1.00 g $[\alpha]^{25}D$ −202.5°. Two recrystallizations from aqueous acetone yielded 790 mg of the (−)-sulfoxide (V) as long needles which decomposed sharply at 144° (gas); $[\alpha]^{25}D$ −207.3° (l = 1; c 2, water); infrared (KBr pellet) showed strong absorption at 1650 cm^{-1} (ionized carboxyl) and three closely spaced peaks 1001, 1010, and 1015 cm^{-1} (sulfoxide region); ultraviolet (water solution) gave λ_{max} 203 mμ (ε 17,000) and λ_{max} 256 mμ (ε 10,700). On paper chromatography with butanol–acetic acid–water (63:10:27), the compound moved with a relative R_f with respect to alanine of 2.26. With collidine–lutidine (1:3) saturated with water, the relative R_f was 1.91.

Anal. Calcd for $C_{11}H_{13}NO_3S$: C, 55.21; H, 5.48. Found: C, 55.3; H, 5.49.

(+)-*cis*-S-(β-Styryl)-L-cysteine S-Oxide (VI) and Sulfone (VII).—These compounds were isolated in the same manner as the (−)-sulfoxide. From 2.65 g of IV ($[\alpha]^{26}D$ +104°) on treatment with ion exchanger and concentration of the aqueous solution *in vacuo* to 25 ml, 189 mg of white solid was obtained. Recrystallization from 15 ml of water yielded 98 mg of ***cis*-S-(β-styryl)-L-cysteine S-dioxide (VII)** which decomposed at 147°; infrared showed strong absorption at 1132 cm^{-1} (sulfone), no absorption 1000–1050 cm^{-1} (sulfoxide).

Anal. Calcd for $C_{11}H_{13}NO_4S$: C, 51.75; H, 5.13. Found: C, 51.9; H, 5.15.

The aqueous mother liquor after removal of sulfone was taken to dryness. Crystallization from 30 ml acetone–water (5:1) gave 952 mg of product, $[\alpha]^{25}D$ +182°. Three recrystallizations from aqueous acetone yielded 498 mg of pure (+)-*cis*-S-(β-styryl)-L-cysteine S-oxide (VI) as small needles which decomposed sharply at 130° (gas), $[\alpha]^{26}D$ +217.9 (l = 1; c 2, water).

Anal. Calcd for $C_{11}H_{13}NO_3S$: C, 55.21; H, 5.48; N, 5.85. Found: C, 55.1; H, 5.48; N, 5.87.

Additional (+)-sulfoxide could be obtained from the mother liquor by fractional crystallization from aqueous ethanol. Thus 1.00 g, with $[\alpha]^{25}D$ +123° from 35 ml of ethanol–water (7:1) yielded 459 mg, $[\alpha]^{25}D$ +65.8°, while the mother liquor of this when taken to dryness and recrystallized from aqueous acetone gave 400 mg of VI, $[\alpha]^{25}D$ +214.2°; infrared (KBr disk) showed strong absorption at 1612 (ionized carboxyl), and three maxima at 1017, 1035, and 1040 cm^{-1} (general range of sulfoxide absorption). Ultraviolet (water) showed λ_{max} 203 mμ (ε 17,900) and λ_{max} 257 mμ (ε 11,400). On paper chromatography, the (+)- and (−)-sulfoxides were inseparable with the solvent systems, butanol–acetic acid–water (63:10:27) and collidine–lutidine (1:3) saturated with water. For ORD data, see Table I.

TABLE I

OPTICAL ROTATORY DISPERSION OF STYRYLCYSTEINE SULFOXIDES IN WATER

Sulfoxide	Absorption, λ_{max} (mμ)	Amplitude, $[\phi] \times 10^{-4}$	Estimated midpoint, mμ	Cotton effect
(+)	257	+4.56	260	+
(−)	256	−7.05	260	−

Attempted Cyclization of (+)- and (−)-*cis*-S-β-Styryl-L-cysteine S-Oxides.—A solution of 285 mg of the (+)-sulfoxide (IV) ($[\alpha]D$ +201°) in 200 ml of 1.5 *N* ammonium hydroxide was allowed to stand for 6 days under nitrogen in the dark. Concentration *in vacuo* to dryness and recrystallization from acetone–water yielded 212 mg of product $[\alpha]^{25}D$ +221° (water)] with infrared identical with that of the starting material.

Treatment of 275 mg of the (−)-sulfoxide (III) ($[\alpha]^{26}D$ −203.9°) with ammonium hydroxide yielded 206 mg of starting material ($[\alpha]^{25}D$ −204.4°). In both experiments, the isolated products and mother liquors from crystallization were chromatographically homogeneous (paper) and no evidence for cyclic sulfoxides could be obtained.

Reaction of (+)- and (−)-*cis*-S-(β-Styryl)-L-cysteine S-Oxides with Enzyme.—A solution of 100 mg of V ($[\alpha]^{25}D$ −201°), in 15 ml of water containing 100 mg of sodium bicarbonate was mixed with 15 ml of filtered, aqueous solution containing 60 mg of enzyme from *Albizzia lophanta*.[11] The mixed solution, originally clear, rapidly became turbid and finally milky after 6 hr at 25°. Only a slight odor was developed. Centrifugation gave *ca.* 40 mg of solid precipitate which was insoluble in water but almost completely soluble in acetone or ethyl acetate. That enzymic reaction had occurred was demonstrated by the formation of pyruvic acid which was precipitated as the 2,4-dinitrophenylhydrazone. The (+)-sulfoxide (VI) exhibited a similar behavior. Under similar conditions, (+)-*trans*-S-(1-propenyl)- and (+)- and (−)-*cis*-S-(1-propenyl)-L-cysteine S-oxides generated strong lachrymatory products.

Registry No.—I, 7732-23-2; *cis,cis*-β,β′-distyryl sulfide, 7732-24-3; *cis,trans*-β,β′-distyryl sulfide, 7732-25-4; N-acetyl-*cis*-S-(β′-styryl)-L-cysteine, 7732-26-5; N-*p*-toluenesulfonyl-*cis*-S-(β-styryl)-L-cysteine, 7732-27-6; III, 7732-28-7; V, 7732-29-8; VII, 7732-30-1; VI, 7732-31-2.

Acknowledgment.—The authors are indebted to William Gaffield for ORD measurements, to Robert Lundin and Nancy Henderson for pmr spectra, and to L. M. White and Geraldine Secor for elemental analyses.