

much as 30 mg of epinephrine to human beings via the oral route (14). However, physiological changes were observed at this level.

Of immediate clinical significance is the fact that ingestion of bananas may lead to erroneous chemical diagnoses of carcinoid tumors (2) and pheochromocytoma by producing an increased urinary excretion of serotonin and norepinephrine and their metabolites. Also, bananas should be eliminated from the diets of patients whose urinary indoles and catecholamines are being measured for other purposes—for example, in mental disease. It remains to be determined whether other edible plants contain these agents.

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2-Thiazolidinethione-4-Carboxylic Acid from the Reaction of Captan with Cysteine

In studies of the mechanism of fungitoxic action of captan [N-(trichloromethylthio)-4-cyclohexene-1,2-dicarboximide] (1), it was found that certain

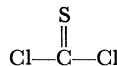
sulfhydryl compounds react with this fungicide to form ultraviolet absorbing products. A compound with an absorption maximum at 272 mμ is formed when cysteine is reacted with captan or trichloromethylsulfenyl chloride (ClSCCl₃). The evidence presented in this paper demonstrates that the ultraviolet absorbing compound formed in the reaction between captan and cysteine is 2-thiazolidinethione-4-carboxylic acid.

This compound was made by reacting captan and L-cysteine in aqueous solutions. Tetrahydrophthalimide formed in this reaction was removed by extraction at pH 6.0 with ethyl acetate, and 2-thiazolidinethione-4-carboxylic acid was then removed at pH 1.5 with the same extractant. The latter was further purified by passing it through ethyl acetate and sodium carbonate solutions in the manner described for purifying the hydrazones of keto acids (2). The purified compound was converted to the sodium salt and recrystallized from ethanol by addition of excess ethyl ether. The sodium salt was dissolved in water and converted to the acid form, which was then extracted with ethyl acetate. White to pale yellow crystals formed upon evaporation of the ethyl acetate.

The following evidence was obtained for the identity of the compound. The equivalent weight was determined by base titration. Ninhydrin and nitroprusside tests were negative but were positive when cysteine was reformed upon base hydrolysis or partial reduction of the compound. Values obtained by analyses for carbon, hydrogen, nitrogen, and sulfur were comparable to the theoretical values (3). The ultraviolet absorption of the compound is similar to that for 2-thiazolidinethione (Fig. 1). Infrared analysis suggested the presence of a secondary amine, a thioureide, and a carboxyl structure in the molecule.

The melting point of the compound was 180 to 181°C. Chatterjee *et al.* (4) and Behringer and Zillikens (5) have reported different syntheses of the compound or its isomers in which the reported melting point or decomposition temperature was 161°C and 190° to 194°C, respectively.

Thiophosgene



is apparently an intermediate in the reaction of captan or ClSCCl₃ with cysteine, since a compound with the same ultraviolet absorption spectrum and the

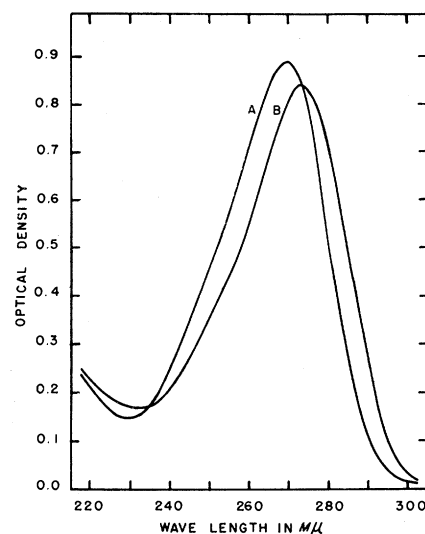


Fig. 1. Comparison of the ultraviolet absorption spectrum of 2-thiazolidinethione with that of 2-thiazolidinethione-4-carboxylic acid. Curve A, 2-thiazolidinethione, $6.1 \times 10^{-5} M$; curve B, 2-thiazolidinethione-4-carboxylic acid, $6.1 \times 10^{-6} M$.

same chromatographic R_f value as 2-thiazolidinethione-4-carboxylic acid is formed when thiophosgene is reacted with cysteine. Barron (6) reported that cysteine reacts with phosgene to form 2-thiazolidone-4-carboxylic acid. Apparently thiophosgene behaves the same as phosgene in its reactivity with cysteine.

A description of other products of the reaction of captan with cysteine and the significance of the reaction in the fungitoxic mechanism of captan is presented elsewhere (7).

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References and Notes

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