PRODUCTION OF DIMETHYLTELLURIDE BY THE SOIL FUNGUS,

PENICILLIUM SP.

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by

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THESIS

Presented to the Faculty of the Graduate School of

The University of Texas at El Paso

in Partial Fulfillment

of the Requirements

for the Degree of

MASTER OF SCIENCE

THE UNIVERSITY OF TEXAS AT EL PASO

May 1983

ACKNOWLEDGMENTS

I would like to dedicate this thesis to my family, and to Dr. Larry P. Jones whose help and assistance made this research possible. I would also like to thank Dr. Keith Pannell and Dr. Gordon Robertstad for their advice and cooperation in finishing this work.

This research was made possible by a grant from the Minority Biomedical Support Program (Grant No. 5S06RR08012).

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LITERATURE REVIEW

Toxic substances in the environment can be categorized as naturally occurring or industrially synthesized. The danger associated with naturally occurring toxic compounds depends on their distribution in the environment. Under natural conditions, their distribution remains relatively constant, largely because of natural biological processes that effect both their degradation and synthesis, and thus, they do not pose serious health problems. When used and produced as by-products in industrial processes, however, they may re-enter the environment and disrupt the natural action of organisms in such a way that the balance between degradation and synthesis can no longer be maintained.

Industrial effluents containing Arsenic (As), Tellurium (Te), and Selenium (Se) are converted by natural biological processes to their methyl-derivatives. Because these organometallic products are produced at a rate faster than other organisms can accomplish their degradation, they can accumulate in higher life forms and pose a threat to health.

The effect of metalloids on man and other organisms has been recognized since the latter part of the nineteenth century. As, Te, and Se can generally be recognized by

their characteristic garlic-like odors when metabolized to their methyl-derivatives by natural biological processes. Challenger (1945) reported on the deaths of two children playing in a room permeated with a garlic-like odor. In Germany, at that time, As was used in wallpapering rooms. The damp walls allowed molds to grow, metabolizing the As to the deadly product, trimethylarsine. Challenger (1945) also stated that it was Rosenheim who showed that when Scopulariopsis brevicaulis was grown in sterilized bread in the presence of Te and Se, the organism evolved powerful garlic-like odors. Challenger and North (1934) concluded that the powerful volatile compounds given off by S. brevicaulis were dimethyltelluride and dimethylselenide, respectively.

In 1945 Challenger postulated the mechanism by which arsenite, tellurite, and selenite could be methylated. He proposed that for the formation of the methyl-derivative, the negative ion of the metalloid must first undergo reduction and ionization with subsequent methylation to form the organometallic product.

The problem as to which methyl-containing compounds could serve as donors of methyl-groups to these elements remained unsolved for some time. Challenger reasoned that the methyl-donors might be compounds like betaine, choline, methionine and/or their derivatives. It was not until much later that he was able to show $^{14}[CH_3]$ S-adenosylmethionine

(SAM) capable of donating methyl-groups to As yielding the volatile compound trimethylarsine. More recently, Cox and Alexander (1973a) found a yeast capable of producing trimethylarsine. Its formation was stimulated by methionine. Fleming and Alexander (1972) found a strain of Penicillium capable of forming dimethylselenide and dimethyltelluride (the latter compound only being formed in the presence of both Se and Te ions). Again, methylation was stimulated by incorporation of methionine into the medium. In each of the above two reports, SAM was not used. Doran and Alexander (1977) showed that cell-free extracts of Corynebacterium sp. could produce dimethylselenide, and that the rate of production was stimulated by SAM. Recently, workers (Hada, M.S. thesis, U.T. El Paso; Vasquez, M.S. thesis, U.T. El Paso) have isolated several fungi capable of detoxifying their environment through the methylation of derivatives of As, Te, and Se. The rates of methylation were shown to be stimulated not only by SAM, but by N^5-methyltetrahydrofolic acid (MTHFA), another methyl-donor to these metalloids.

Other elements can be methylated. After the demonstration that mercury (Hg) in fish was present predominantly in the form of methylmercury (Westöö,1966), it was shown that unidentified microorganisms in natural organic lake sediments could methylate Hg. Hg is an example of an element that cannot be methylated by SAM or MTHFA.

These methyl-donors are incapable of donating their methyl-groups to Hg^{++} because they are not able to donate them as CH_3^- ions. Only methyl-corrinoid derivates are able to perform this function. A non-enzymatic methylation of Hg by cell-free extracts was shown in methanorganic bacterium with methyl-cobalamin (MCA) as the donor of methyl-groups in the presence of adenosine-5-triphosphate (ATP) and a mild reductant (Wood, et al., 1968).

Challenger (1945) postulated that As, Te, and Se had to be reduced, ionized, and then methylated in order for detoxification to occur. The necessity for the reduction of all metalloids in order for detoxification to occur can be illustrated using Hg^{++}. This ion is reduced enzymatically with reduced nicotinamide adenine dinucleotide ($NADH_2$) participating as the coenzyme for catalysis (Wood, 1974). The conversion of Hg^{++} to Hg^{o} is regarded as much of a detoxification process as the formation of methyl-derivatives discussed above.

Terai, et al. (1957), investigated a tellurite reductase in cell-free extracts of Mycobacterium avium. The presence of the enzyme was shown by following the development of a black precipitate in the reaction mixture, indicating the production of Te^{o}. They found that upon the addition of malate to the cell-free extracts containing excess malic acid dehydrogenase (MDH) enzyme and the tellurite reductase, a more intense black color developed.