Effect of Soil Applications of Molybdenum on the Biochemical Composition of Katahdin Potatoes: Nitrate Nitrogen and Total Glycoalkaloids

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The effect of molybdenum on nitrate nitrogen (NO_3-N) and total glycoalkaloid (TGA) content of Katahdin potatoes was investigated. Sodium molybdate was applied to the soil at rates of 0, 2.5, 6, and 9 lb/acre 1 day prior to planting. At all levels of molybdenum application, NO_3-N and TGA content decreased significantly ($p < 0.01$) from the controls. The greatest decrease occurred at the highest level of molybdenum application.

Molybdenum is the only period 5 transition element essential for normal metabolic activity in plants. Although molybdenum is a metal, it exhibits several properties of non-metals and other divalent inorganic anions (da Silva and Williams, 1976). Thus, although it usually occurs as Mo(IV) in aqueous solutions, it is oxidized to the molybdate oxyanion MoO_4^{2+} [Mo(VI)], which is the form available to plants. The requirement for molybdenum by higher plants is lower than that for any of the other mineral nutrients. The predominant functions of molybdenum as a plant nutrient are due to the valency changes it undergoes as a metal component of the enzymes (1) xanthine oxidase/dehydrogenase, (2) aldehyde oxidase, (3) sulfite oxidase, (4) nitrate reductase, and (5) nitrogenase. Only nitrate reductase and nitrogenase have been extensively studied in higher plants. Hence, molybdenum has been known to be indispensable for the fixation of nitrogen (Evans et al., 1950; Mulder, 1948) and the reduction of nitrate (Beevers and Hageman, 1980). The element has also been shown to be necessary for normal ascorbic acid levels in plant tissues (Agarwala, 1952) and conversion of inorganic phosphorus to organic phosphorus (Possingham, 1954).

Nitrates. Nitrates are precursors of nitrites, which oxidize ferrous hemoglobin to ferric hemoglobin, subsequently inhibiting oxygen transportation through the body causing methemoglobinemia (Phillips, 1971). Nitrites also react with secondary or tertiary amines to form carcinogenic and mutagenic *N*-nitroso compounds (Walters et al., 1979). According to White (1975) potatoes contribute approximately 14% of the per capita ingestion of nitrates in the United States. Formation of nitrates has been shown to vary with the cultivar, type and amount of nitrogen fertilizer, climate, moisture stress, and storage conditions (Augustin et al., 1977; McDole and McMaster, 1978a,b).

Glycoalkaloids. Glycoalkaloids are a class of naturally occurring toxicants present in potatoes and hence are important during the assessment of tuber quality. The most predominant glycoalkaloids in potato tubers are α-solanine and α-chaconine, glycosides of the steroidal alkaloid solanidine. These toxicants are known to possess anticholinesterase activity (Patil et al., 1972), and their intake by humans through consumption of potato tubers high in the alkaloids has resulted in severe illness and sometimes death (McMillan and Thompson, 1979). The presence of high levels of these compounds in potatoes also results in bitter flavor (Sinden et al., 1976). Several factors such as cultivar, environment, fertilization practices, and mechanical- and chemical-induced stress have been shown to affect glycoalkaloid biosynthesis in potato tubers (Sinden et al., 1984). Nair et al. (1981) found that enzymes involved in solanidine synthesis are present in the chloroplasts. Retardation of reducing sugar accumulation in potatoes by curing reduces glycoalkaloid synthesis, indicating that availability of reducing sugars may be a determining factor (Zitnak, 1981).

Since molybdenum, through its presence in nitrate reductase, is important for the channeling of nitrogen from nitrate to the carbon skeleton of amino acids such as leucine, arginine, alanine, and asparagine, which are required for synthesis of the aglycon solanidine, it is important to determine the interrelationships of molybdenum, nitrate nitrogen, and glycoalkaloid synthesis in potato tubers. This study was undertaken to determine the effect of soil application of molybdenum on the nitrate nitrogen and the glycoalkaloid content of potato tuber. Soil application of molybdenum was used in this experiment since earlier studies have shown that foliar applications decreased carbohydrate and dry matter content although they increased the nucleic acid content and the protein/nonprotein N ratio of the plant (Timashov, 1959).

MATERIALS AND METHODS

Katahdin potatoes grown at the Cornell Vegetable Research Farm, Freeville, NY, were used. The soil type was Howard gravely loam. Each plot, 30 × 11.3 ft, consisted of four rows, each with dimensions of 34 in. × 30 ft. The seed potatoes were planted mechanically. Sodium molybdate was sprayed using a hand sprayer (MAT-OSU Plot Sprayer, Mater International, Inc.) on the soil at rates of 0.0, 2.5, 6.0, and 9.0 lb/acre 1 day prior to planting. Each treatment was repeated twice. A hand sprayer was used, and the soil was tilled immediately after spraying was completed. The soil was adjusted to 6.7 by liming to facilitate maximum availability of molybdenum to plants (Mulder, 1954). The molybdenum content of the soil prior to treatment was 0.061 ppm Mo and following treatment was 0.069, 0.075, and 0.82 ppm for the 2.5, 6.0, and 9.0 lb Na_2MoO_4 applications, respectively. Tubers were harvested 21 weeks following planting and stored in 10-lb mesh bags at 5 °C and 95% relative humidity in the dark until analyzed. Tubers were analyzed immediately following harvest and after 5 months of storage.

Size C (medium size, about 3.5 in diameter) tubers were cut longitudinally into quarters from bud to stem end in order to obtain equal sampling of both ends and the slices separated into cortex and pith sections along the vascular ring. Cortex tissue (which was about 25–30% of the tuber) was used for determination of total glycoalkaloid and ni-

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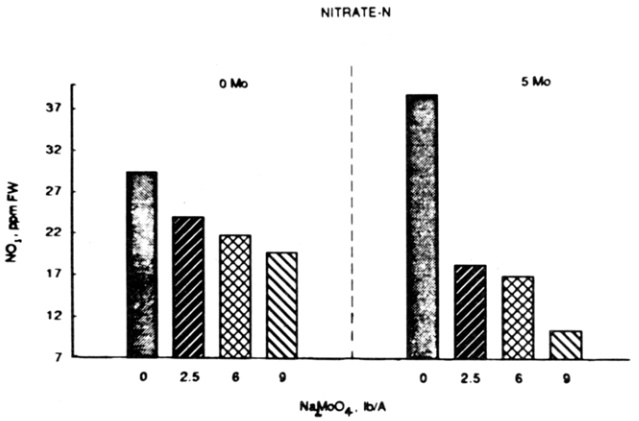

Figure 1. Effect of soil applications of sodium molybdate (Na_2MoO_4) on the NO_3-N content of Katahdin potato tubers after 0 month (0 Mo) and 5 months (5 Mo) of storage.

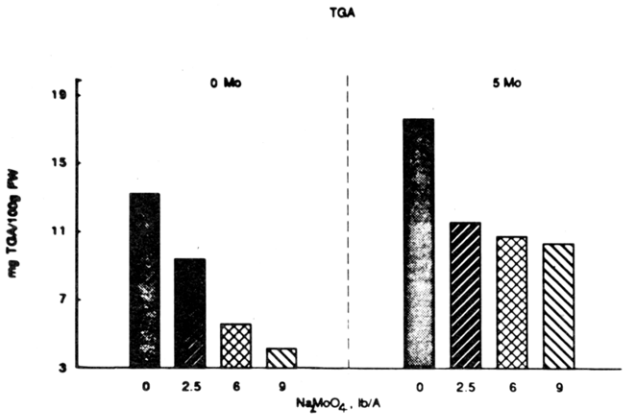

Figure 2. Effect of soil applications of sodium molybdate (Na_2MoO_4) on total glycoalkaloid (TGA) content of Katahdin potato tubers after 0 month (0 Mo) and 5 months (5 Mo) of storage.

trate content since it is the region of highest metabolic activity. Two samples, each consisting of eight tubers, were analyzed for each treatment. Duplicate determinations were made on each sample.

Determination of Nitrate Nitrogen (NO_3-N). The NO_3-N content was determined by the phenoldisulfonic acid method using an aqueous extraction of fresh tubers as described by Ulrich et al. (1959).

Determination of Total Glycoalkaloids (TGA). The TGA content was determined by the modified titration method of Bushway et al. (1980). The TGA values were calculated from a calibration curve using tomatine as the standard.

Statistical Analysis. Complete random design was employed, and statistical significance of the data was determined by analysis of variance with a protected LSD test (Steel and Torrie, 1980).

RESULTS AND DISCUSSION

Nitrate Nitrogen Content. Increasing the level of Na_2MoO_4 fertilization resulted in significantly lower ($p < 0.01$) NO_3-N levels in the tubers. Tubers receiving the highest rate of application (9 lb/acre) had the lowest NO_3-N content (Figure 1). After a storage period of 5 months, the NO_3-N content was higher in tubers receiving no molybdenum than at 0 months while the NO_3-N content was reduced in the molybdenum-treated tubers. The decrease in nitrates may have resulted from an increase in nitrate reductase activity since molybdenum, in addition to heme iron, is the metallic component of the enzyme (Beevers and Hageman, 1980). Nitrate reductase contains two atoms of molybdenum in addition to heme iron and catalyzes, by a reversible valency change, the reduction of nitrate to nitrite. Electrons for the reduction are known to be supplied to cytochrome *b*, which transfers electrons to the Mo protein for nitrate reduction.

Total Glycoalkaloid Content. At all levels of Na_2MoO_4 application the TGA content of tubers immediately following harvest and after 5-month storage was significantly ($p < 0.01$) lower than of the controls (Figure 2). After 5 months of storage, the TGA levels in all the molybdenum-treated tubers were similar, but higher than at 0 months and lower than in the control tubers. The lowest TGA level was observed when 9 lb/acre Na_2MoO_4 was applied. The incorporation of the amino acids arginine (Kaneko et al., 1976), alanine, leucine (Jadhav et al., 1973), and glycine and serine (Nair et al., 1981) into the aglycon solanidine has been reported. Possingham (1956) reported an increase in the free amino acids arginine and β-alanine due to molybdenum deficiency in tomato plants, and Steinberg (1956) reported an increase in arginine caused by molybdenum deficiency in tobacco plants. Molybdenum may have inhibited glycoalkaloid synthesis either by decreasing the synthesis of argine and β-alanine, and possibly leucine, glycine, and serine, or by stimulating the incorporation of these amino acids into other compounds such as proteins.

Na_2MoO_4 applications decreased NO_3-N and TGA contents of tubers as compared to controls. The addition of controlled amounts of molybdenum to fertilizers might be useful in improving potato quality by decreasing the levels of glycoalkaloids and nitrates in the tuber.

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Registry No. Mo, 7439-98-7; NO_3^-, 14797-55-8; Na_2MoO_4, 7631-95-0.

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Effect of Autofermentation on the Physicochemical Properties of Proteins of Sorghum–Groundnut Composite Flour

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The effect of autofermentation on the physicochemical properties of proteins of sorghum–groundnut (70:30 by weight) composite flour is studied by sedimentation velocity measurements, gel filtration on ACA-44, polyacrylamide gel electrophoresis at pH 9.2, spectral measurements, fluorescence spectra, and circular dichroism measurements. Sedimentation velocity measurements, gel filtration, and PAGE suggest a decrease in the molecular size of the proteins due to autofermentation. Both groundnut and sorghum proteins are equally susceptible to proteolysis during fermentation. The spectral measurements indicate increased polyphenol–protein interactions, conformational changes in the proteins resulting in an altered chromophoric environment of aromatic amino acids, and a decrease in the content of the limited ordered structure.

Fermented sorghum-based foods are prepared traditionally in Africa for human consumption (Vogel and Graham, 1979). Studies on Kisra bread, one of the traditional sorghum-based foods of Sudan, revealed that Kisra is nutritionally inadequate in terms of promoting growth or maintaining nitrogen balance (Eggum et al., 1983; Ahmed et al., 1987). An addition of 30% edible groundnut flour to sorghum meal was found to produce significant improvement in conventional Kisra bread (Ahmed et al., 1987). The proteins of the fermented composite flour differ from that of fermented sorghum flour in their functional characteristics (Ahmed and Ramanatham, 1987b) as well as their digestibility (Ahmed et al., 1987; Ahmed and Ramanatham, 1987c). In the present investigation the changes that occur in the physicochemical properties of the proteins during autofermentation of sorghum–groundnut composite flour were studied.

MATERIALS AND METHODS

Locally purchased sorghum grain was cleaned, dried, and milled to pass through 60-mesh sieve to obtain sorghum flour. The edible groundnut flour (EGF) was prepared by further defatting of the expeller-pressed groundnut cake (TGL, Adoni, A.P., India) with hexane and removing traces of solvent by hot air (48 ± 2 °C). The dried material was ground into fine powder.

Ultrogel ACA44 (ACA44) was a product of LKB Chemicals; acrylamide, amido black, and ammonium persulfate were from E. Merck; *N,N,N′,N′*-tetramethylethylenediamine (TEMED) was from Fluka; bisacrylamide was from Koch-Light Laboratories Ltd. All other chemicals and reagents were analytical grade (BDH; Sarabhai M. Chemicals).

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