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To my family

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CHEMICAL STUDIES ON SOME PLANTS THAT HYPERACCUMULATE NICKEL

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ABSTRACT

Following the discovery of the hyperaccumulation of nickel by the Philippine plants Dichapetalum gelonioides subsp. tuberculatum and Phyllanthus 'palawanensis', the nature of the nickel in aqueous extracts has been investigated by gel filtration chromatography, ion-exchange chromatography, high-voltage electrophoresis and GC-MS.

Nickel in D.gelonioides subsp. tuberculatum was shown to associate mainly with compounds of high polarity and low molar mass. In P.'palawanensis' only about 50 % of the nickel demonstrated this association, while 25 % of the metal appeared to be in the form of pectate or bound to proteins. In both plants, nickel was shown to exist in anionic and cationic forms. A discussion of the usefulness of assigning portions of nickel to these forms is presented in the light of changes in the relative amounts of cationic and anionic nickel observed during ion-exchange chromatography and high-voltage electrophoresis.

Nickel , citric acid and malic acid comprised 95 % of the purified extract from D. gelonioides subsp. tuberculatum. Only 25 % of the low molar mass, high polarity nickel-rich fraction from P.'palawanensis' was accounted for by these constituents. Small amounts of Ca, Mg, K and Na were detected in each extract. The nickel:citric acid:malic acid mole ratios were 1:0.4:1 and 1:0.4:0.4 for D.gelonioides subsp. tuberculatum and P.'palawanensis' respectively. These observations are discussed in terms of the stabilities of the nickel citrate and nickel malate complexes. Tartaric acid was identified in both extracts, while 4-oxopentanoic acid and 2-furylacetic acid were identified in the nickel-rich fraction from P.'palawanensis' only. The role of these acids in the plant is discussed in an attempt to explain their presence in the nickel-rich material.

By using X-ray crystallography, it was shown that crystals obtained from a nickel-citrate-malate solution simulating the extract from D. gelonioides subsp. tuberculatm, contained nickel exclusively in the form of an anionic Ni(II)-citrato complex. It was assumed that a crystal obtained from a nickel-citrate-malate solution of mole ratio 1:0.4:0.4, as in the nickel-rich fraction from P.'palawanensis',would have yielded similar results given the greater stability of the Ni-citrate complex over the Ni-malate complex.

Pot trials carried out on Alyssum troodii confirmed its hyperaccumulating status, and showed it to be a cobalt hyperaccumulator as well. The amount of cobalt taken up by the plant was an order of magnitude lower than that of nickel. It was observed that A.troodii survived soils with

available concentrations of nickel and cobalt at least five times higher than those commonly found in serpentine soils. Possible reasons for this behaviour are presented. Alyssum troodii also co-accumulated nickel and cobalt. However, while the cobalt concentration in plant organs showed little difference from that obtained when the plant was cultivated in soil enriched with cobalt only, the nickel levels were lower.

Aurinia saxatilis did not hyperaccumulate nickel and cobalt. The levels of the metals found in the plant were one-tenth of those observed in A.troodii. As in the Ni-hyperaccumulating plant, cobalt uptake appeared to suppress nickel uptake when the plant was cultivated in media containing added nickel and cobalt. A possible uptake mechanism giving rise to this differential uptake is discussed. Very little difference was discerned in the tolerance to, and uptake of, copper in the two plants. The levels of this metal in A.troodii were about one-tenth those of cobalt, while in Au.saxatilis the levels of copper and cobalt were comparable.

Low concentrations of nickel exerted a stimulatory effect on the germination of A.troodii seeds. Cobalt appeared to exert this effect on Au saxatilis seeds at higher concentrations. Copper was not observed to be stimulatory to either plant.

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