ABSTRACT

In-situ generation of a flavonol bound copper(II) complex from tetrakisacetonitrilecopper(I) anion, tris-1-ethyl-4-methylimidazolylphosphine (T1Et4MIP) and substituted 3-hydroxylflavone (flav) under atmosphere to produce complexes formulated as [Cu(T1Et4MIP)(flav)]X. The complexes are formed and characterized using standard techniques as well as X-ray crystallography. The complexes form square-based pyramidal complexes which are structurally similar to the active site of Quercetin 2,3-Dioxygenase (QDO). These complexes further undergo oxidative scission of the pyrone ring via a photolytically (300 nm) or a thermally (120 °C) induced reaction with molecular oxygen to produce the corresponding methylethylated degradation products methyleugenol, methyl salicylate and N,N-dimethylbenzamide. The synthesis of these complexes, structural information as well as their oxidative chemistry will be presented.

INTRODUCTION

Our focus on preparing “open face” copper metal complexes that are structural models for the protein 2,3-quercetin dioxygenase are reported. Quercetin 2,3-dioxygenase (QDO) is a widely occurring copper metalloenzyme found in plants. QDO catalyzes ring opening scission of quercetin with molecular oxygen to the corresponding depside.

The active site of QDO contains two structural motifs of interest, three histidine residues and a bound quercetin moiety. Our ligand system is designed to prepare a complex which is comprised of two very different regions based on reactivity. The tripod ligand provides a means by which to lock down one side of the metal complex with tris-imidazolyl complexation (histidine residue bimicron). The opposite face which allows for facile complexation of substituted 3-hydroxylflavone and the potential for chemical reaction on this face. The ligand preparation, characterization and the X-ray results of the reactions of these complexes will be presented.