# Chapter 1

Introduction

Some phenolic compounds in edible plants have received much attention as powerful antioxidants not only to protect against the oxidative deterioration of food but also to reduce oxidation-induced diseases by their ingestions. The main mechanism for a phenolic antioxidant in food is the trapping and stabilizing of radical species, such as the lipid peroxyl radical, which is generated from radical chain oxidation of food components. This property is also important in biological systems for scavenging harmful oxygen radicals. The antioxidation process is thought to be divided into two stages as shown in the following schemes:

1. Radical trapping stage

$$S-OO^{\bullet} \text{ (or } S^{\bullet}) + AH \rightarrow S-OOH \text{ (or SH)} + A^{\bullet}$$
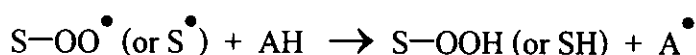
2. Radical termination stage

$$A^{\bullet} \rightarrow \text{nonradical materials}$$

S is the substance for oxidation, AH is the antioxidant and $A^{\bullet}$ is the antioxidant radical.

Recent mechanistic studies of a plant phenolic antioxidant have been focused on the trapping stage using a kinetic approach or a structure-activity relationship approach. The antioxidant radical, which forms in the trapping stage, should be converted to a nonradical material in the termination stage without any production of further radical species. Structural information about these nonradical products would afford important contributions to the antioxidant mechanism studies (Masuda, et al., 1999).

Curcumin [1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione] is the main yellow phenolic material of turmeric and has been widely used as a food coloring agent. Various curcumin-related phenols (curcuminoids) have also been

found in edible plants, especially Zingiberaceae plants in Asia. It derived from the rhizome of *Curcuma longa*, which has attracted considerable attention in recent years due to its wide spectrum of biological and pharmacological activities, including antioxidant, antitumor, anti-inflammatory, antibacterial, antifungal, antiviral and anticoagulant activities, *etc*. Recent studies suggest that curcumin is a multipotent agent to combat Alzheimer's disease with the activities of scavenging radicals, blocking amyloid-β($A\beta$) aggregation and chelating metal ions (Shen, et al .,2006).

Toxicologically, curcumin is relatively inert and does not show toxicity to either animal or humans even at high dose. It has been found to be non-toxic to humans up to the dose of 10 g per day. In addition, the pharmacological safety of curcumin, demonstrated by its consumption for centuries by people in certain countries, makes it a potential compound to be applied in various pharmacological areas (Shen, et al.,2006).

Despite much effort devoted on curcumin, there still exist some open questions concerning the fundamental physicochemical properties of this small molecule. For instance, curcumin is unique in structure for possessing two isomers, enol form and β-diketone form (Figure 1, **1** and **2**). To gain deeper insight into the mechanism of the wide spectrum of biological and pharmacological activities of curcumin, and correlate its activities with structural features (Shen, et al.,2006).
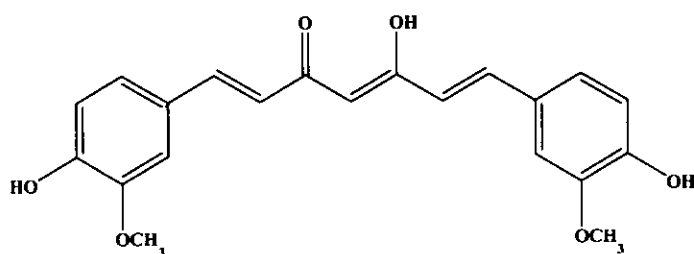
Enol form of curcumin (1)
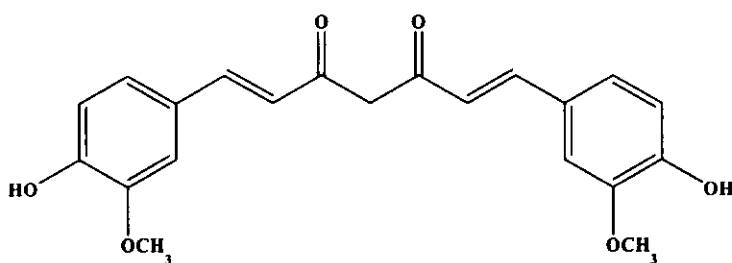
Keto form of curcumin(2)

Figure 1 Structures of enol form(1) and keto form (2) (Shen et al .,2006)

In addition, the enol form of curcumin has three ionizable protons (Figure 1, 1), corresponding to the enolic group and two phenolic groups. However, there has been much debate concerning which proton is the most easily dissociable one. The two experiments previously observed pKa values of 8.54 (8.38), 9.30 (9.88) and 10.69 (10.51) have been attributed by Saladini et al. and Alberto et al. (in parentheses) to the dissociation of the enolic proton and the two phenolic protons, respectively. Photochemical study estimated the lowest pKa of curcumin to be 8.55, which was assigned to the dissociation of the enolic group too. However, Zsila et al., Tang et al. and Dietze et al. have attributed the lowest pKa (8.10, 8.28 and 8.89) for curcumin to the dissociation of phenolic proton (Shen et al.,2006).

Chromium is a white, hard, lustrous, and brittle metal (m.p.1903°C $\pm 10^{\circ}$C). It is extremely resistant to ordinary corrosive agents, which accounts for its extensive use as an electroplated protective coating. The metal dissolves fairly readily in nonoxidizing mineral acids, for example, hydrochloric and sulfuric acids, but not in cold aqua regia or nitric acid, either concentrated or diluted. The chief ore is *chromite* ($FeCr_2O_4$), which is a spinel with Cr^{III} on octahedral sites and Fe^{II} on the tetrahedral ones.

Chromium (III) complexes are all hexacoordinate. The principle characteristic of these complexes in aqueous solutions is their relative kinetic inertness. The magnetic properties of octahedral Cr^{III} complexes are uncomplicated. All such

complexes must have three unpaired electrons irrespective of the strength of ligand field, and this has been confirmed for all known mononuclear complexes. The spectra of Cr^{III} complexes are also well understood in their main features. A partial energy level diagram indicates that three spin-allowed transitions are expected, and these have been observed in a considerable number of complexes (Cotton and Wilkinson, 1976: 721 and 727).

Manganese is relatively abundant, constituting about 0.085% of the earth's crust. Among the heavy metals, only iron is more abundant. Although widely distributed, it occurs in a number of substantial deposits, mainly oxides, hydrous oxides, or carbonate. It is roughly similar to iron in its physical properties, the chief difference being that it is harder and more brittle but less refractory (m.p. $1247^{o}C$). It is quite electropositive and readily dissolves in dilute, nonoxidizing acids. It is not particularly reactive toward nonmetals at room temperature.

Manganese (II) forms many complexes, but the equilibrium constants for their formation in aqueous solution are not high compared to those for the divalent cations of succeeding elements. The majority of Mn^{II} complexes are high spin. In octahedral fields this configuration gives spin-forbidden as well as parity-forbidden transitions. In tetrahedral environments, the transitions are still spin forbidden but no longer parity forbidden (Cotton and Wilkinson, 1976: 736 and 739).

Iron is the second most abundant metal, after aluminum, and the fourth most abundant element in earth's crust. The core of the earth is believed to consist mainly of iron and nickel, and the occurrence of many iron meteorites suggests that it is abundant throughout the solar system. The major iron ores are *hematite* (Fe_2O_3), *magnetite* (Fe_3O_4), *limonite* [FeO(OH)], and *siderite* ($FeCO_3$). Pure iron is white, lustrous metal (m.p. 1528 ^{o}C). It is not particularly hard, and it is quite reactive. The metal dissolves readily in diluted mineral acids. With nonoxidizing acids and in absence of air, Fe^{II} is

obtained. With air present or when warm dilute nitric acid is used, some of the iron goes to Fe^{III}.

Iron (III) complexes. The majority of iron complexes are octahedral, but tetrahedral and square pyramidal ones are also important. Iron (III) is isoelectronic with manganese (II), but much less is known of the details of Fe^{III} spectra because of the much greater tendency of the trivalent ion to have charge-transfer bands in the near ultraviolet region with strong low-energy wings in the visible that obscure the very weak, spin-forbidden d-d bands. Magnetically iron(III), like Mn(II), is high spin in nearly all its complexes, except those with the strong ligands, exemplified by $[Fe(CN)_6]^{3-}$, $[Fe(bipy)_3]^{3+}$, $[Fe(phen)_3]^{3+}$, and other tris complexes with imine nitrogen atoms as donors(Cotton and Wilkinson, 1976: 750-751 and 758-761).

Cobalt always occurs in nature in association with nickel and usually also with arsenic. It is a hard, bluish-white metal (m.p. $1493^{o}C$, b.p. $3100^{o}C$). It dissolves slowly in dilute mineral acids. It does not combine directly with hydrogen or nitrogen. The metal will combine with carbon, phosphorus, and sulfur on heating. It also is attacked by atmospheric oxygen and by water vapor at elevated temperatures, giving CoO. The most important cobolt minerals are *smaltite* ($CoAs_2$) and *coboltite* (CoAsS), but the chief technical sources of cobalt are residues called "speisses", which are obtained in . the smelting of arsenical ores of nickel, copper, and lead.

Cobalt (II) forms numerous complexes, mostly either octahedral or tetrahedral but five-coordinate and square species are also known. Cobalt (II) occurs in a great variety of structural environments; because of this the electronic structures, hence the spectral and magnetic properties of the ion, are extremely varied (Cotton and Wilkinson, 1976: 766-770).

Nickel is silver-white, with high electrical and thermal conductivities (both ~15% of those of silver) and m.p. $1452^{o}C$, and it can be drawn, rolled, forged, and polished. It is resistant to attack by air or water at ordinary temperatures when compact

and is therefore often electroplated as a protective coating. The metal dissolves readily in dilute mineral acids. Like iron, it does not dissolve in concentrated nitric acid because it is rendered passive by this reagent. Nickel occurs in nature mainly in combination with arsenic, antimony, and sulfur, for example, as *millerite* (NiS), NiAs, and in deposits consisting chiefly of NiSb, $NiAs_2$, NiAsS, or NiSbS. The most important deposits commercially are *garnierite*, a magnesium-nickel silicate of variable composition, and certain varieties of the iron mineral *pyrrhotite* (Fe_nS_{n+1}) which contain 3 to 5% Ni.

Nickel (II) forms a large number of complexes encompassing coordination numbers 4, 5, and 6, and all the main structural types (viz., octahedral, trigonal-bipyramidal, square-pyramidal, tetrahedral, and square). Moreover, it is characteristic of Ni^{II} complexes that complicated equilibria, which are generally temperature dependent and sometimes concentration dependent, often exist between these structural types (Cotton and Wilkinson, 1976: 783-786).

Copper is a tough, soft, and ductile reddish metal, second only to silver in its high thermal and electrical conductivities. It is widely distributed in nature as metal, in sulfides, arsenides, chlorides, carbonates, etc. It is extracted from ores usually by wet processes. It readily dissolves in nitric acid and sulfuric acid in the presence of oxygen. It is also soluble in ammonia, ammonium carbonate or potassium cyanide solutions in precence of oxygen. It is used in many alloys such as brasses and is completely miscible with gold. It is only superficially oxidized in air, sometimes acquiring a green coating of hydroxo carbonate and hydroxo sulfate (Cotton and Wilkinson, 1976: 800).

Cadmium is soft, bluish-white metal and is easily cut with a knife. It is similar in many respects to zinc. Interestingly, a characteristic cadmium *"scream"* is heard on bending a cadmium bar. Cadmium and its compounds are highly toxic. Silver solder, which contains cadmium, should be handled with care. Cadmium is used to small extent as coatings (often achieved by electroplating) to protect metals such as iron. Its

use is restricted because of environmental concerns. The metal is a component of some specialist alloys including solders and alloy with low coefficients of friction and good fatigue resistance. Cadmium is a component of Ni-Cd batteries. Cadmium is used in black and white television phosphors and in blue and green phosphors for color TV tubes. Some semiconductors contain cadmium. The sulphide (CdS) is used as a yellow pigment (http://www.webelements.com).

Mercury is the only common metal liquid at ordinary temperatures. It rarely occurs free in nature and is found mainly in cinnabar ore (sometimes called HgS). Mercury is a heavy, silver-white liquid metal. It is a rather poor conductor of heat as compared with other metals but is a fair conductor of electricity. It alloys easily with many metals, such as gold, silver, and tin. These alloys are called amalgams. Mercury is used in laboratories for making thermometers, barometers, diffusion pumps, and many other instruments. It is used for mercury switches and other electrical apparatus. It is used as an electrode in some types of electrolysis and for making batteries (mercury cells) (http://www.webelements.com).

Lanthanum is silvery white, malleable, ductile, and soft enough to be cut with a knife. It is one of the most reactive of the rare-earth metals. It oxidizes rapidly when exposed to air. Cold water attacks lanthanum slowly, and hot water attacks it much more rapidly. The metal reacts directly with elemental carbon, nitrogen, boron, selenium, silicon, phosphorus, sulphur, and with halogens. It is a component of misch metal (used for making lighter flints). Lanthanum is extensively used in carbon lighting applications, especially by the motion picture industry for studio lighting and projection. It is used making for lighter flints and alloys. Small amounts as an additive are used to produce nodular cast iron. ^{203}La improves the alkali resistance of glass, and is used in making special optical glasses (http://www.webelements.com).

Praseodymium is soft, malleable, and ductile. It was prepared in relatively pure form in 1931. It is somewhat more resistant to corrosion in air than europium, lanthanum, cerium, or neodymium, but it does develop a green oxide coating that *"spalls"* away when exposed to air. The metal should be stored under an inert atmosphere or under mineral oil or petroleum. The rare-earth oxides, including Pr_2O_3, are among the most refractory substances known. It is a component of misch metal, used for lighter flints, and of the glass in welders' goggles. Praseodymium is used as a core material for carbon arc lights used by the motion picture industry and making for alloy. Praseodymium salts used to colour glasses and enamels; when mixed with certain other materials, praseodymium produces an intense clean yellow color in glass. Components of didymium glass are a colourant for welder's goggles. Praseodymium metal contains about 5% in making cigarette lighters) (http://www.webelements.com).

Neodymium is present in misch metal to the extent of about 18%. The metal has a bright silver metallic luster. Neodymium is one of the more reactive rare-earth metals and quickly tarnishes in air, forming an oxide that spalls off and exposes the metal to further oxidation. It is one of the rare earth metals. Neodymium used making for alloy and lasers (to produce coherent light). It is used in very powerful permanent magnets - $Nd_2Fe_{14}B$. Neodymium used in astronomy to calibrate spectral lines. The metal is a component of didymium used for colouring glass to make welders' goggles. Neodymium salts are used as a colourant for enamels (http://www.webelements.com).

Samarium is a silvery-white metal belonging to the lanthanide group of the periodic table. It is relatively stable at room temperature in dry air, but it ignites when heated above 150 ^{O}C and forms an oxide coating in moist air. Like europium, samarium has a relatively stable oxidation state (II). Samarium is used as a catalyst in certain organic reactions: the samarium iodide (SmI_2) is used by organic research chemists to make synthetic versions of natural products. The oxide, samaria, is used for making special infrared adsorbing glass and cores of carbon arc-lamp electrodes

and as a catalyst for the dehydrogenation of ethanol. Its compound with cobalt ($SmCo_5$) is used in making a new permanent magnet material. Soluble samarium salts are mildly toxic by ingestion and there are health hazards associated with these because exposure to samarium causes skin and eye irritation (http://www.webelements.com).

Gadolinium is silvery white, has a metallic luster, and is malleable and ductile. It is ferromagnetic (strongly attracted by a magnet). The metal is relatively stable in dry air, but in moist air it tarnishes with the formation of a loosely adhering oxide film which "spalls" off and exposes more surfaces to oxidation. The metal reacts slowly with water and is soluble in dilute acid. Gadolinium has the highest thermal neutron capture cross-section of any known element. It is used for making gadolinium yttrium garnets which have microwave applications, making phosphors for colour TV tubes, making alloy and CD disks. Solutions of gadolinium compounds are used as intravenous contrasts to enhance images in patients undergoing magnetic resonance imaging (http://www.webelements.com).

Dysprosium has a metallic, bright silver luster. It is relatively stable in air at room temperature, but dissolves readily, with the evolution of hydrogen, in mineral acids. The metal is soft enough to be cut with a knife and can be machined without sparking if overheating is avoided. It is a rare earth metal found in minerals such as xenotime, monazite, and bastnaesite. It is possible used in improving the grain refinement, strength, and other mechanical properties of stainless steel. One isotope of the metal apparently used as a radiation source as a substitute for a portable X-ray machine where electricity is unavailable (http://www.webelements.com).

Pure erbium metal is soft and malleable and has a bright, silvery, metallic luster. As with other rare-earth metals, its properties depend to a certain extent on impurities present. The metal is fairly stable in air and does not oxidize as rapidly as some of the other rare-earth metals. It is used for nuclear industry, photographic filter

and metallurgical uses. Moreover erbium oxide is pink and is a colorant in glasses and porcelain enamel glazes (http://www.webelements.com).

Ytterbium has a bright silvery luster, is soft, malleable, and quite ductile. While the element is fairly stable, it should be kept in closed containers to protect it from air and moisture. Ytterbium is readily attacked and dissolved by mineral acids and reacts slowly with water. Ytterbium is possible used in improving the grain refinement, strength, and other mechanical properties of stainless steel. It is used making for lasers. One isotope apparently used as a radiation source as a substitute for a portable X-ray machine where electricity is unavailable (http://www.webelements.com).

Literature reviews

Tonnesen, et al. (1982) determined the crystal structure of curcumin by X-ray crystallographic methods. The result showed that the crystals are monoclinic, space group *P2/n* with unit cell dimensions a=20.028(3) Å, b=7.073(1) Å, c= 12.609(2) Å; β=94.94(1)$^{\circ}$; Z=4.
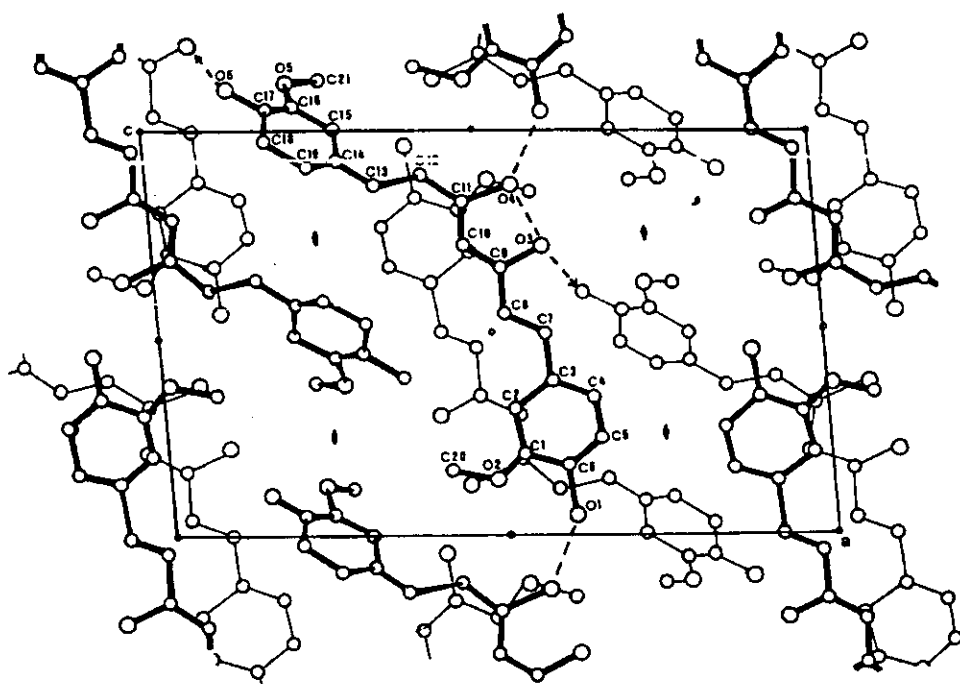

Figure 2 Numbering of the atoms and the molecular packing in crystals of curcumin (Tonnesen, et al.,1982)
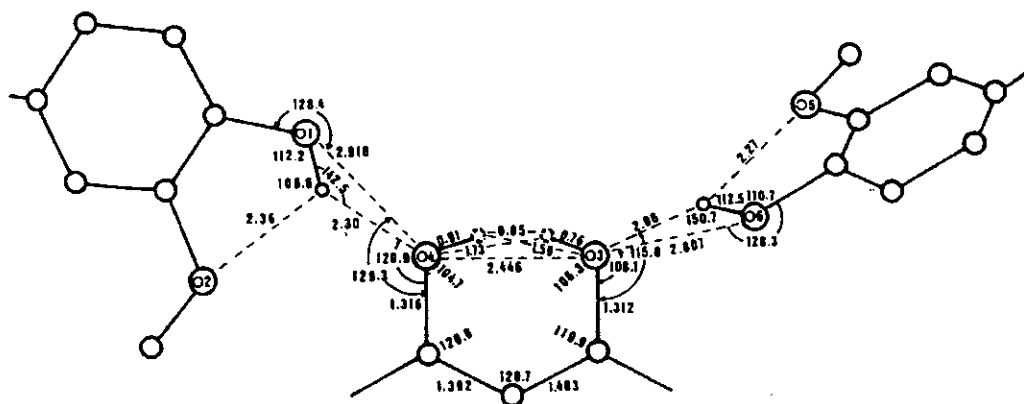

Figure 3 Geometry in the enol ring and the hydrogen bond system (Tonnesen, et al., 1982)

Sharma, et al. (1987) synthesized and characterized the gold (I) complex, $[AuL_2]Cl$ (L = diferuloylmethane or curcumin) by elemental analysis, magnetic moment, infrared spectroscopic and electronic spectral study. The complex was a d^{10} and diamagnetic. The result from infrared spectroscopic data showed that the ligand coordinates with the central metal ion through the C=O group. Moreover, the gold curcumin complex was used for anti-arthritic study.
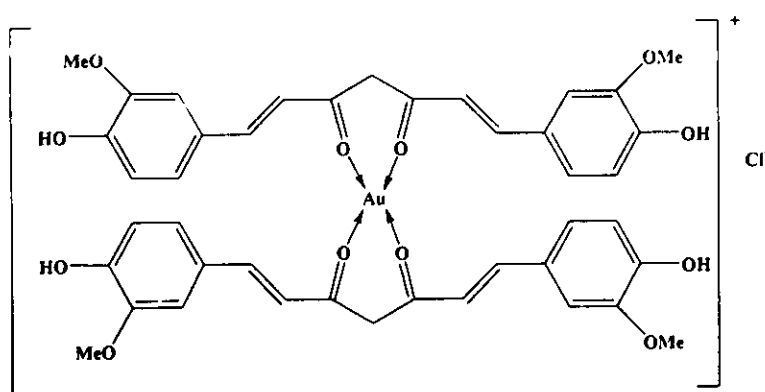

Figure 4 Structure of the gold(I) curcumin complex (Sharma, et al.,1987)

Rouseff (1988) studied the determination of the pigments in the food colorants, annatto and turmeric by high performance liquid chromatography (HPLC) and identified by visible and fluorescence spectra. The three major pigments in turmeric were curcumin, demethoxycurcumin, and bis-demethoxycurcumin.
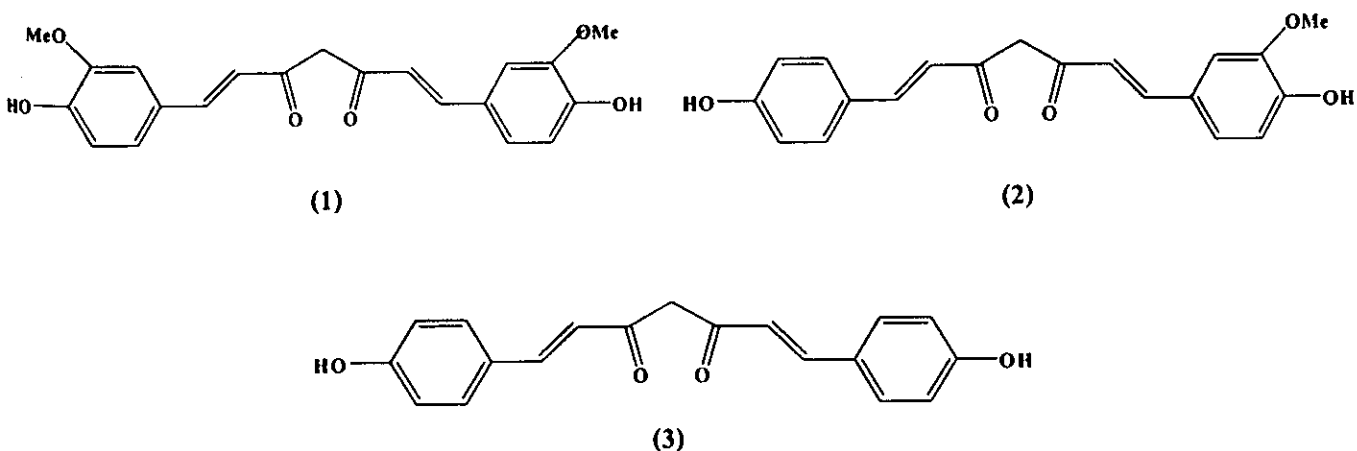

igure 5 Structures of curcumin (1), demethoxycurcumin (2) and bis-demethoxycurcumin (3) (Rouseff, 1988)

Taylor and McDowell (1992) studied the determination of the curcuminoid pigments in turmeric, which are curcumin, demethoxycurcumin, and bis-demethoxycurcumin, by reversed - phase high performance liquid chromatography. And a comparison was made between HPLC and spectrophotometric methods in the determination of total curcuminoid content of turmeric. The comparison result showed that the spectrophotometric method yielded higher results.

Masuda, et al. (1999) studied the antioxidant mechanism of radical reaction products from curcumin. The radical reaction gave several products, three of which were structurally identified to be vanillin, ferulic acid, and a dimer of curcumin. The dimer was a newly identified compound bearing a dihydrofuran moiety, its chemical structure was elucidated by 2D NMR techniques. A mechanism for the dimer product was studied by gel permeation chromatography (GPC) and high performance liquid chromatography (HPLC). The results of these indicated that the dimer was a radical-terminated product initial stage.
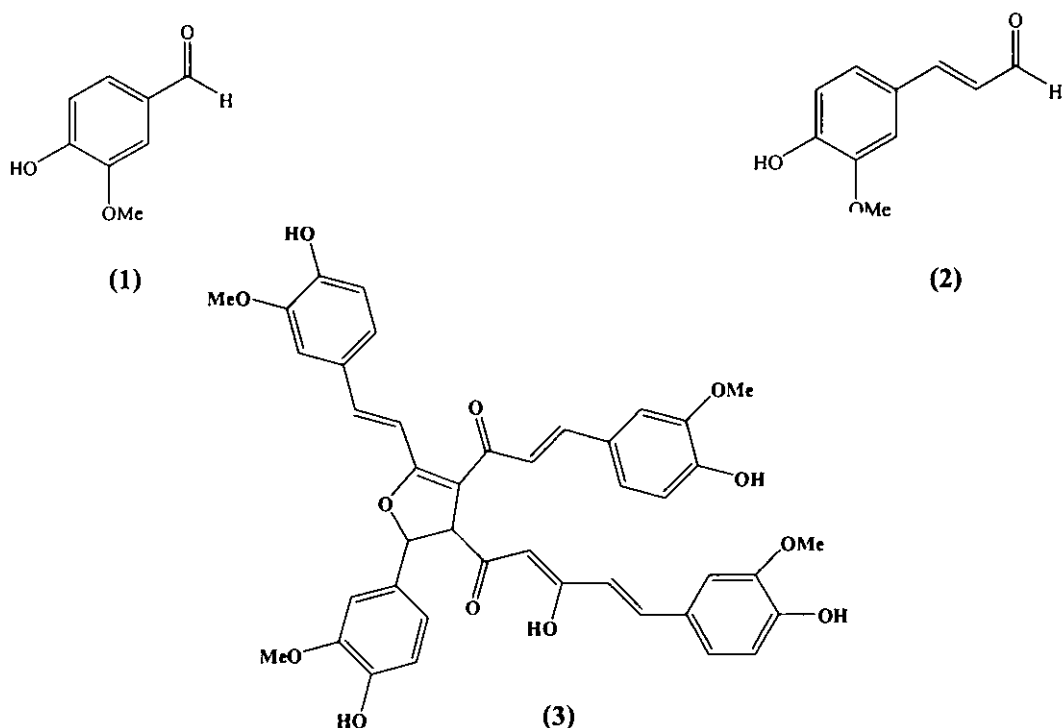
Figure 6 Structures of vanillin (1), ferulic acid (2), a dimer of curcumin (3) (Masuda et al., 1999)

Jovanovic, et al. (1999) studied antioxidant mechanisms of curcumin or bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione by laser flash photolysis and pulse radiolysis. The results showed that the keto-enol-enolate equilibrium of the heptadienone moiety of curcumin determines its physicochemical and antioxidant properties. In neutral and acidic aqueous solution (from pH 3 to 7), the keto form dominates, and curcumin acted as an extraordinarily potent H-atom donor but the reaction mechanism of curcumin changed dramatically above pH 8, where the enolate form of the heptadienone link predominated. As a consequence, the phenolic part of the molecule took over as the reaction site (electron donor).

Ishigami, et al. (1999) investigated the molecule and crystal structure of curcumin. Anhydrous curcumin was obtained from methanol. In this structure, the molecules were aggregated intermolecularly into infinite chains linked between the Ph-OH and the carbonyl O (or-OH). Such a network formation was attributed to intermolecular hydrogen bonds between terminal phenol moieties of curcumin assembling in a fibrous structure. The crystal was in monoclinic system with space group P2/n, a = 12.688(3), b = 7.2061(5), c = 19.897(5) Å; β = 95.28(1)$^{\circ}$; Z = 4.

Bong (2000) studied spectral and photophysical behaviors of curcumin and curcuminoids by the absorption and fluorescence spectra. The results indicated that the spectral and photophysical properties of both of curcumin and curcuminoids were strongly influenced by solvent, water, and pH.
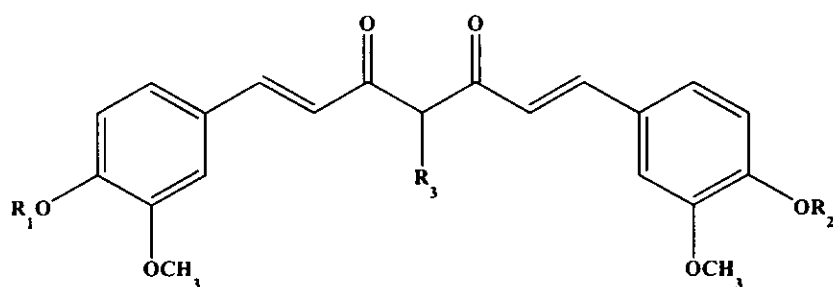
1: $R_1 = R_2 = R_3 = H$

2: $R_1 = CH_3$, $R_2 = R_3 = H$

3: $R_1 = R_2 = CH_3$, $R_3 = H$

4: $R_1 = R_2 = R_3 = CH_3$

5: $R_1 = R_2 = C_6H_5CH_2$, $R_3 = H$

6: $R_1 = R_2 = R_3 = C_6H_5CH_2$

7: $R_1 = R_2 = CH_3CO$, $R_3 = H$

8: $R_1 = R_2 = C_6H_5CO$, $R_3 = H$

9: $R_1 = R_2 = R_3 = C_6H_5CO$

Figure 7 Structures of curcumin (1) and curcuminoids (2-9) (Bong, 2000)

Borsari, et al. (2002) studied the interaction of Fe^{3+} with curcumin and diacetylcurcumin in water/methanol 1:1 solution which led to the formation of the complexes species $[FeH_2CU(OH)_2]$ and $[FeDCU(OH)_2]$ near pH 7. At more basic condition the prevailing species a were $[FeH_2CU(OH)_3]^-$ and $[FeDCU(OH)_3]^-$. The complexes were characterized by UV-Vis spectroscopy, ^1H NMR spectroscopy, potentiometry, and cyclic voltammetry. The result from ^1H NMR data showed that the dissociated β-diketo moiety of the ligands was involved in metal chelation. In addition, the properties of iron-chelating agent are interesting in clinical use.

Tonnesen, et al. (2002) studied the solubility, chemical, and photochemical stability of cyclodextrin complexes. Complexes between curcumin and cyclodextrins could be formed under slightly acidic conditions (pH 5) at room temperature. The

complex formation led to an increase in water solubility of curcumin, the hydrolytic stability of curcumin under alkaline conditions and a decrease in photostability was observed by complex formation with cyclodextrins compared to solutions of curcumin in organic solvent systems.

Sundaryono, et al. (2003) studied the synthesis and complexation properties of two new curcuminoid molecules bearing a diphenylmethane linkage by mass spectroscopy, NMR spectroscopy, and UV-visible absorption spectroscopy. The results from mass and NMR data indicated that the structures of two curcuminoids were bis-curcuminoids 3 and 4. The study of complexation properties with UV-visible data showed differences between curcumin and bis-curcuminoid 3.
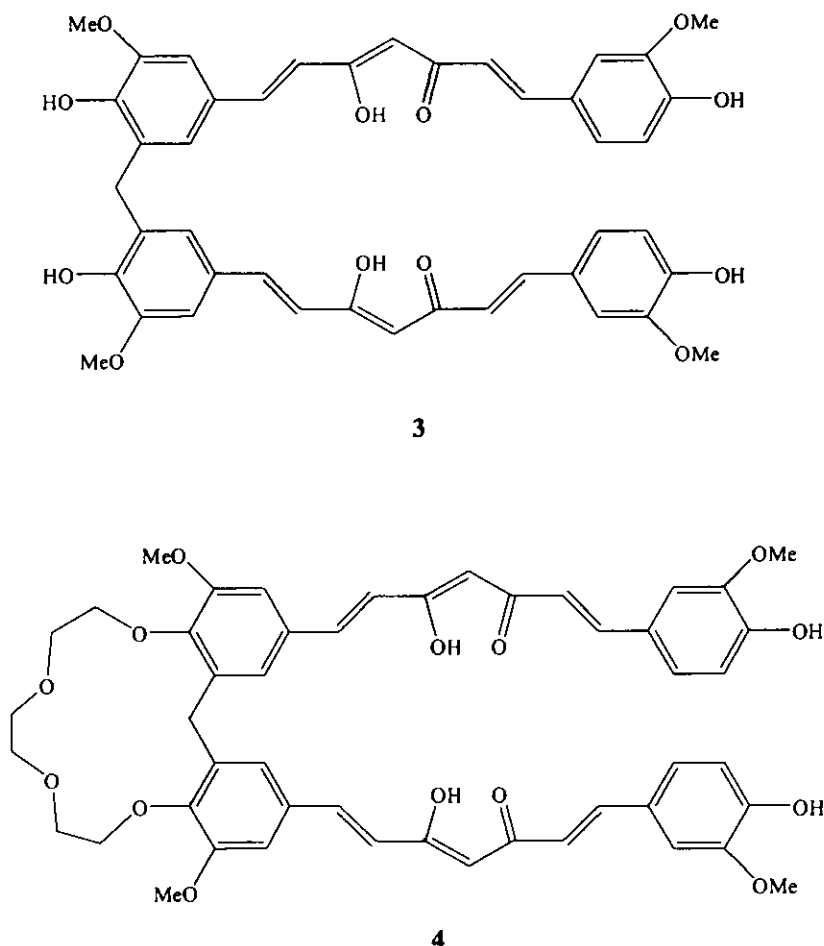

3

4

Figure 8 Structures of bis-curcuminoids 3 and 4 (Sundaryono et al., 2003)

Mohammadi, et al.,(2005) studied the syntheses and characterizations of dual function vanadyl, gallium, and indium curcumin complexes. Novel bis[4-hydroxy-3-methoxyphenyl]-1,6-heptadiene-3,5-dione complexes with the formula, ML_3, where M is Ga(III) or In(III), or of the formula, ML_2, where M is $[VO]^{2+}$ were synthesized and characterized by mass spectrometry, infrared and absorption spectroscopies, and elemental analysis. A series of novel oxovanadium(IV) curcuminoid complexes $(VO(DMC)_2, VO(BDC)_2, VO(DAC)_2)$ and $VO(DABC)_2$, as well as two new Ga(III) complexes, $Ga(cur)_3$ and $Ga(DAC)_3$, and their In(III) analogs, $In(cur)_3$ and $In(DAC)_3$ were reported. Spectroscopic characterzation of the ligands and their complexes confirmed the proposed structures (Figs 9 and 10). IR spectra of all ligands showed $V_{C=O}$ in the typical 1600-1630 cm^{-1} range, which shifted to lower energy in the vanadyl complexes of the same ligands. Vanadyl complexes also had no broad band in the 2600-3400 cm^{-1} range, related to the stretching of intramolecular H in the enol function. Vanadyl complexes did show a $V_{V=O}$ medium intensity band at $\sim$ 975-995 cm^{-1}. A prominent band at 960-975 cm^{-1}, due to the trans—CH=CH— group, also remained unchanged in the vanadyl complexes. The curcumin ligands showed two absorption bands in the UV/Vis region: an n$\rightarrow\pi$* transition at $\sim$360-430 nm and a $\pi\rightarrow\pi$*transition at $\sim$240-290 nm, which shifted to slightly higher energy in the vanadyl complexes, indicative of involvement of the carbonyl group in metal complexation. Further evidence of complexation comes from the mass spectra of all complexes, which showed intense peaks for $[VOL_2]^+$, $[VOL_2+H]^+$ and $[VOL_2 + Na]^+$, and confirmed a stoichiometry of 2:1 curcuminoid to oxovanadium(IV).
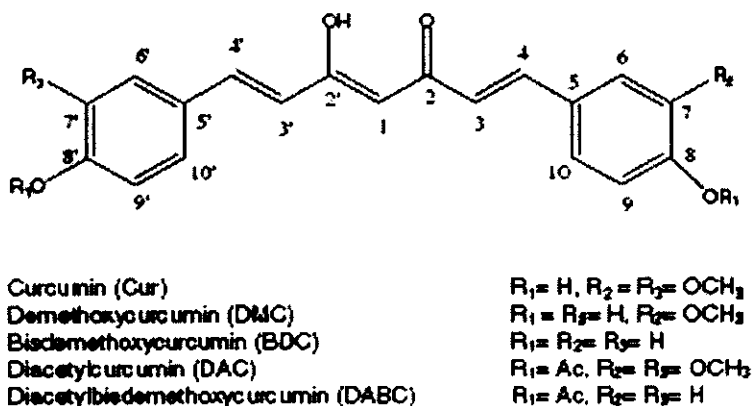
Figure 9 The structure of curcumin and curcumin derivatives (Mohammadi et al.,2005)
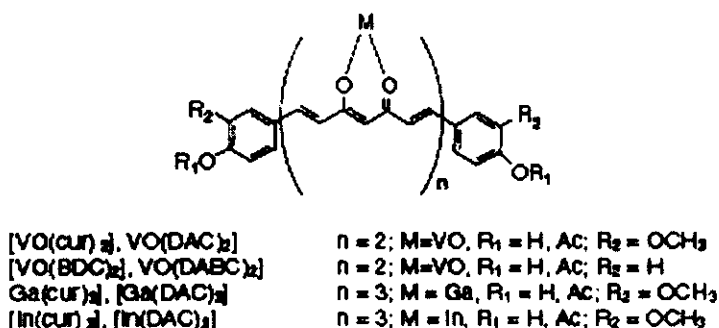

Figure 10 The structure of the metal complexes (Mohammadi et al.,2005)

Barik et al., (2006) synthesized and characterized a new copper(II)-curcumin complex as superoxide dismutase mimic by elemental analysis, IR, NMR, UV-VIS, EPR, mass spectroscopic methods and TG-DTA. Elemental analysis showed that the complex contains C 55.5%(54.3%), H 5.5%(4.7%), Cu 12.8%(12.5%). IR spectra showed that O-H appear ~3000 cm^{-1}; alkane C-H 1620 cm^{-1}; methoxy C-O 1020 cm^{-1}; phenolic C-O 1280 cm^{-1}; aromatic C-H 980 cm^{-1}. The difference between V_{asym} and V_{sym} bands for acetate in the complex appeared respectively at 1510 and 1400 cm^{-1} ; the difference of 110 cm^{-1} indicated acetate bound as a monodentate ligand. The C=O

frequency in curcumin appeared at 1630 cm^{-1} and shifted by 10 cm^{-1} on copper complexation, indicating its involvement in complexation. Supporting evidence for the structure was obtained by TG-DTA analysis. Initially a 54.05-mg sample was loaded and a weight loss of ~1.97 mg was observed at 100–110 $^{\circ}$C. This weight loss corresponded to the loss of one water molecule at the above temperature. This analysis confirmed the presence of one water molecule. Mass spectrometric analysis of the complex showed a molecular ion peak at 490 ±2 mass units. This mass number corresponds to a molecular ion which was formed by the loss of one water molecule from the parent molecule due to the high temperatures employed in the experimental setup. From all the above studies the molecular formula of the Cu(II)–curcumin complex was deduced as $C_{21}H_{19}O_6Cu-\cdot OCOCH_3 \cdot H_2O$. A UV–visible spectrum of the complex in DMSO showed absorption maximum at 426 nm and two shoulders at 410 and 450 nm. Another weak nonfeatured d–d transition was observed at 500–600 nm. Comparing this with that of curcumin , it was noted that the 432 nm peak due to curcumin in DMSO, attributed to the $\pi \rightarrow \pi^*$ band of curcumin, was blue-shifted by 6 nm, and the shoulders at 410 and 450 nm were attributed to a curcumin $\rightarrow$ Cu(II) charge transfer band while the other features were associated with the copper complex.
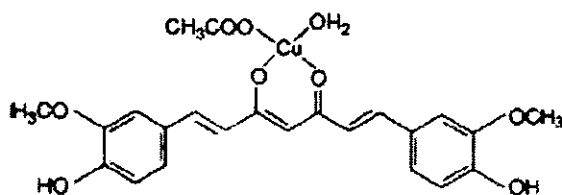

Figure 11 Structure of the Cu(II)-curcumin complex (Barik et al., 2006)

Objectives

The objectives of this work are as follows:

1. Study reactions of curcumin and some metal ions.

2. Isolate products and characterize them by using appropriate techniques.