Chapter 3

Results

3.1 Syntheses of complexes

The complex syntheses were attempted by various approaches from the reaction between curcumin and transition elements. The following results from these studies are given below.

3.1.1 Finding the suitable solvent for curcumin

Before carrying out the reaction, a suitable solvent must be selected. Solubility of curcumin was studied qualitatively in various solvents. The results are summarized in Table 1.

Table 1 Comparative solubility of curcumin in various solvents.

Solvents	**Curcumin**	
	Observed solubility	**Solution color**
Water	-	-
Hexane	-	-
Chloroform	-	-
Benzene	-	-
Ethanol	+	Orange
Dichloromethane	+	Yellow
Methanol	++	Orange
Ether	++	Yellow
Acetone	+++	Yellow
Acetyl acetate	+++	Yellow

The symbols of solubility test are: - represents insolubility, + represents partial solubility, ++ represents better solubility, and the +++ represents 68-70 mg of curcumin completely soluble in 10 ml of solvents.

3.1.2 Varying mole ratio of reactants

The results from these reactions are summarized in Table 2-6.

Table 2 The results of mixing metals in water with curcuin in methanol

Metal salts	**Mole ratio (curcumin in MeOH : metal salt in H_2O)**	**Results**
$NiCl_2.6H_2O$	1 : 1	No solid product
	2 : 1	No solid product
$CuSO_4.5H_2O$	1 : 1	No solid product
	2 : 1	No solid product
$FeSO_4.7H_2O$	1 : 1	Small amount of red brown precipitate
	2 : 1	Small amount of red brown precipitate
$FeCl_3.6H_2O$	1 : 1	Dark brown precipitate
	2 : 1	Dark brown precipitate

Table 3 The results of mixing metals in water with curcumin in acetone

Metal salts	**Mole ratio (curcumin in acetone : metal ion in H_2O)**	**Results**
$NiCl_2.6H_2O$	1 : 1	No solid product
	2 : 1	No solid product
$CuSO_4.5H_2O$	1 : 1	No solid product
	2 : 1	No solid product
$FeSO_4.7H_2O$	1 : 1	Small amount of red brown precipitate
	2 : 1	Small amount of red brown precipitate
$FeCl_3.6H_2O$	1 : 1	Red brown precipitate
	2 : 1	Red brown precipitate

Table 2 and 3 showed that the mixing of curcumin with ferric chloride in 1:1 or 1:2 mole ratio in water/methanol solution and mixing of curcumin with ferric chloride in 1:1 or 1:2 mole ratio in water/acetone solution, the dark brown (Fe-CU1) and red brown (Fe-CU2) precipitates were obtained, respectively. The products were characterized by XRF and IR techniques.

Table 4 Results from 2.3.2 (method 2.1)

Metal salts	**Mole ratio (mmol) (curcumin : metal salt)**	**Results**
$NiCl_2.6H_2O$	1.6 : 1.0	No solid product
	1.6 : 2.2	"
	1.6 : 4.4	"
$CuSO_4.5H_2O$	1.6 : 1.0	No solid product
	1.6 : 2.2	"
	1.6 : 4.4	"
$CrCl_3 6H_2O$	1.6 : 1.0	No solid product
	1.6 : 2.2	"
	1.6 : 4.4	"
$HgCl_2$	1.6 : 1.0	No solid product
	1.6 : 2.2	"
	1.6 : 4.4	"

Table 5 Results from 2.3.2 (method 2.2)

Metal salts	**Mole ratio (curcumin : metal salt)**	**Results**
$NiCl_2.6H_2O$	1.6 : 1.0	No solid product
	1.6 : 2.2	"
	1.6 : 4.4	"

Table 5 (continued)

Metal salts	**Mole ratio (curcumin : metal salt)**	**Results**
$CuSO_4.5H_2O$	1.6 : 1.0	No solid product
	1.6 : 2.2	"
	1.6 : 4.4	"
$CrCl_3 6H_2O$	1.6 : 1.0	No solid product
	1.6 : 2.2	"
	1.6 : 4.4	"
$HgCl_2$	1.6 : 1.0	No solid product
	1.6 : 2.2	"
	1.6 : 4.4	"

Table 6 Results from 2.3.2 (method 2.3)

Metal salts	**Mole ratio (curcumin : metal salt)**	**Results**
$NiCl_2.6H_2O$	1.6 : 1.0	No solid product
	1.6 : 2.2	"
	1.6 : 4.4	"
$CuSO_4.5H_2O$	1.6 : 1.0	No solid product
	1.6 : 2.2	"
	1.6 : 4.4	"
$CrCl_3 6H_2O$	1.6 : 1.0	No solid product
	1.6 : 2.2	"
	1.6 : 4.4	"
$HgCl_2$	1.6 : 1.0	No solid product
	1.6 : 2.2	"
	1.6 : 4.4	"

From Table 4-6, the complexes were prepared by three difference media. All these three methods did not yield any crystalline products.

3.1.3 Varying the reaction temperatures

Mixing curcumin with various metal salts ($NiCl_2.6H_2O$, $Ni(CH_3COO)_2.4H_2O$, $MnCl_2.4H_2O$, $Cd(NO_3)_2.4H_2O$, $CrCl_3.6H_2O$, $FeCl_3.6H_2O$, $LaCl_3.H_2O$, $Co(CH_3COO)_2.4H_2O$, $HgCl_2$) in the mole ratio 2:1 in ethanol. The mixtures were refluxed in one set and were not refluxed in another. The resulting complexes are summarized in Table 7.

Table 7 Physical appearance of complexes (prepared by mixing 2:1 mole of metal and curcumin).

Metal ions	**Physical appearance**	
	Refluex 8 hrs.	**No reflux**
Ni(II) ; Cl^-	Orange needle shape crystal	Orange square shape crystal
Ni(II) ; OAc^-	Dark orange powder	No solid product
Mn(II)	Yellowish-orange square shape crystal	Yellowish-orange square shape crystal
Cr(III)	Orange square shape crystal (single crystal; CUCr)	Orange square shape crystal
Cd(II)	Yellow needle shape crystal	No solid product
La(III)	Yellowish-orange square shape crystal (single crystal; CULa)	No solid product
Hg(II)	Dark orange needle shape crystal	No solid product
Fe(III)	Dark brown powder	Dark brown powder
Co(II)	Brownish-red powder	No solid product

Remark *Ni(II) ; Cl^- is $NiCl_2.6H_2O$ and Ni(II) ; OAc^- is $Ni(CH_3COO)_2.4H_2O$*

From Table 7, the single crystals of complexes (CUCr and CULa) were studied by X-ray diffraction technique.

3.1.4 Addition of NaOH to promote the reaction

A solution of NaOH at difference concentration (2.5, 5.0, 10, 20 and 50 mM) was added to solution of curcumin with metal salts. The results from these reactions are summarized in Table 8.

Table 8 Physical appearance of crystals at various concentration of NaOH.

Transition elements	**Physical appearance of crystals at various concentration of NaOH (mM)**				
	2.5	**5.0**	**10.0**	**20.0**	**50.0**
Mn(II)	Orange needle shape (A1)	Yellowish-orange needle shape (A2)	Yellowish-orange square shape (A3)	No solid product	No solid product
Cd(II)	Yellowish-orange square shape (B1)	Yellowish-orange square shape (B2)	Yellowish-orange needle shape (B3)	Yellowish-orange square shape (B4)	No solid product
Ni(II)	Yellowish-orange needle shape (C1)	Yellowish-orange needle shape (C2)	Yellowish-orange needle shape (C3)	Yellowish-orange square shape (C4)	No solid product

A1, B1 and B2 are single crystals. The single crystals can be characterized by X-ray diffraction technique.

3.1.5 Attempts to synthesize curcumin complex with lanthanide elements

A solution of metal oxide (Sm_2O_3, La_2O_3, Gd_2O_3, Nd_2O_3, Yb_2O_3, Dy_2O_3, Er_2O_3 and Pr_6O_{11} 0.10, 0.25, 0.50 and 1.00 ml was added to a solution of curcumin, stirred for 15 minutes at room temperature. The precipitates were filtered, collected to dryness, and allowed to crystallize. The results are shown in Tables 9-10.

Table 9 Products obtained from the reactions when adding lanthanide ions.

Amount of curcumin (mg)	Solution of metal oxide	Volume of solution metal oxide (ml)	Characteristic of mixture	
			Before adding metal oxide	After adding metal oxide
30	Sm_2O_3	0.10, 0.25, 0.50	Reddish brown solution	Orange precipitate in yellow solution
		1.00	Reddish brown solution	Yellow precipitate (like curcumin powder) in yellow solution
	La_2O_3	0.10, 0.25, 0.50, 1.00	Reddish brown solution	Orange precipitate in yellow solution
	Gd_2O_3	0.10, 0.25, 0.50, 1.00	Reddish brown solution	Orange precipitate in yellow solution
	Nd_2O_3	0.10, 0.25, 0.50, 1.00	Reddish brown solution	Orange precipitate in yellow solution
	Yb_2O_3	0.10, 0.25, 0.50, 1.00	Reddish brown solution	Orange precipitate in yellow solution
	Dy_2O_3	0.10	Reddish brown solution	Brownish orange solution
		0.25, 0.50, 1.00	Reddish brown solution	Orange precipitate in yellow solution
	Er_2O_3	0.10, 0.25, 0.50, 1.00	Reddish brown solution	Orange precipitate in yellow solution
	Pr_2O_3	0.10, 0.25, 0.50, 1.00	Reddish brown solution	Orange precipitate in yellow solution

Table 10 Products obtained from the reactions when adding diluted (5 folds) lanthanide ions.

Amount of curcumin (mg)	Solution of metal oxide	Volume of solution metal oxide (ml)	Characteristic of mixture	
			Before adding metal oxide	After adding metal oxide
30	Sm_2O_3	0.50 [Sm-CU(0.5)]	Reddish brown solution	Orange precipitate in yellow solution
		1.00 [Sm-CU]	"	Yellow precipitate (like curcumin powder) in yellow solution
	La_2O_3	0.50 [La-CU(0.5)]	"	Orange precipitate in yellow solution
		1.00 [La-CU]	"	"
	Gd_2O_3	0.50 [Gd-CU(0.5)]	"	"
		1.00 [Gd-CU]	"	"
	Nd_2O_3	0.50 [Nd-CU(0.5)]	"	"
		1.00 [Nd-CU]	"	"
	Yb_2O_3	0.50 [Yb-CU(0.5)]	"	"
		1.00 [Yb-CU]	"	"
	Dy_2O_3	0.50 [Dy-CU(0.5)]	"	"
		1.00 [Dy-CU]	"	"
	Er_2O_3	0.50 [Er-CU(0.5)]	"	"
		1.00 [Er-CU]	"	"
	Pr_2O_3	0.50 [Pr-CU(0.5)]	"	"
		1.00 [Pr-CU]	"	"

3.2 X-ray Fluorescence Spectrometry

The X-ray Fluorescence spectra of the compounds are illustrated in Figures 12-18.

3.3 Single crystal X-ray diffraction

The X-ray crystallographic data and the structure plots of the overall complexes are shown in Figures 19-20 and Tables 11-19.

3.4 Infrared Spectroscopy

The infrared spectra of curcumin, derivatives of curcumin and the complexes are shown in Figures 21-42.

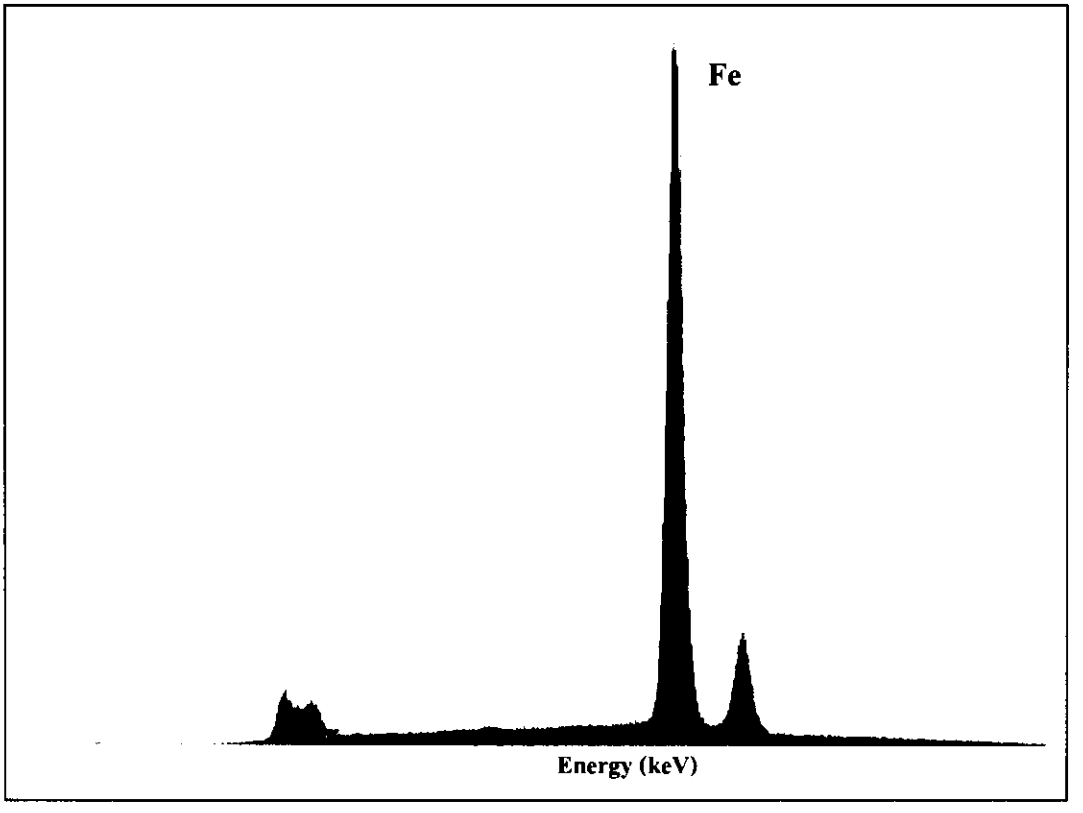

Figure 12 The XRF spectrum of Fe in Fe-CU1

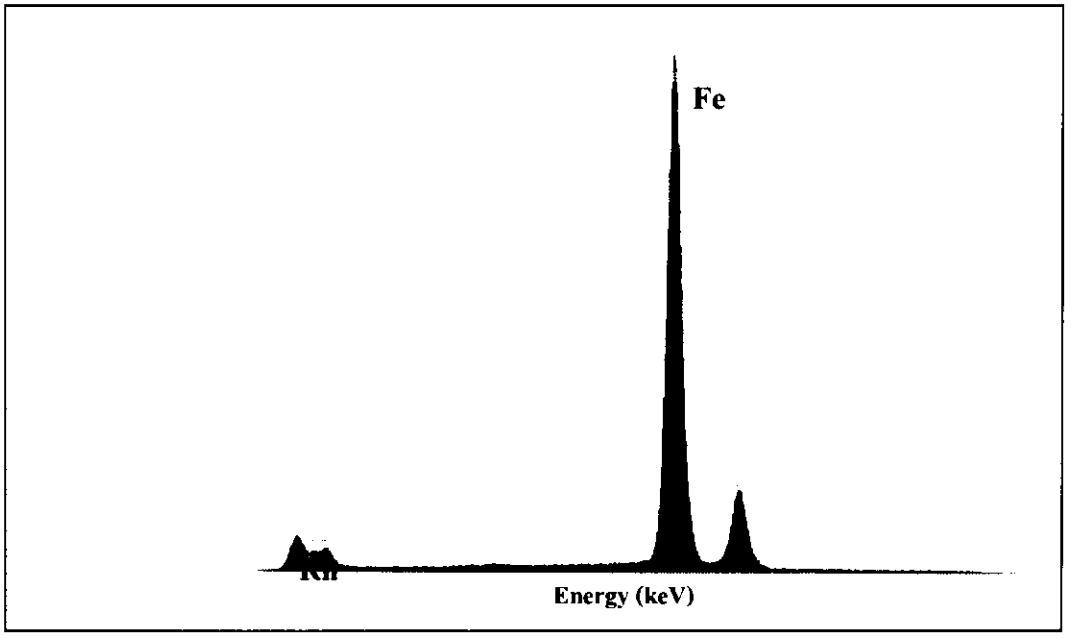

Figure 13 The XRF spectrum of Fe in Fe-CU2

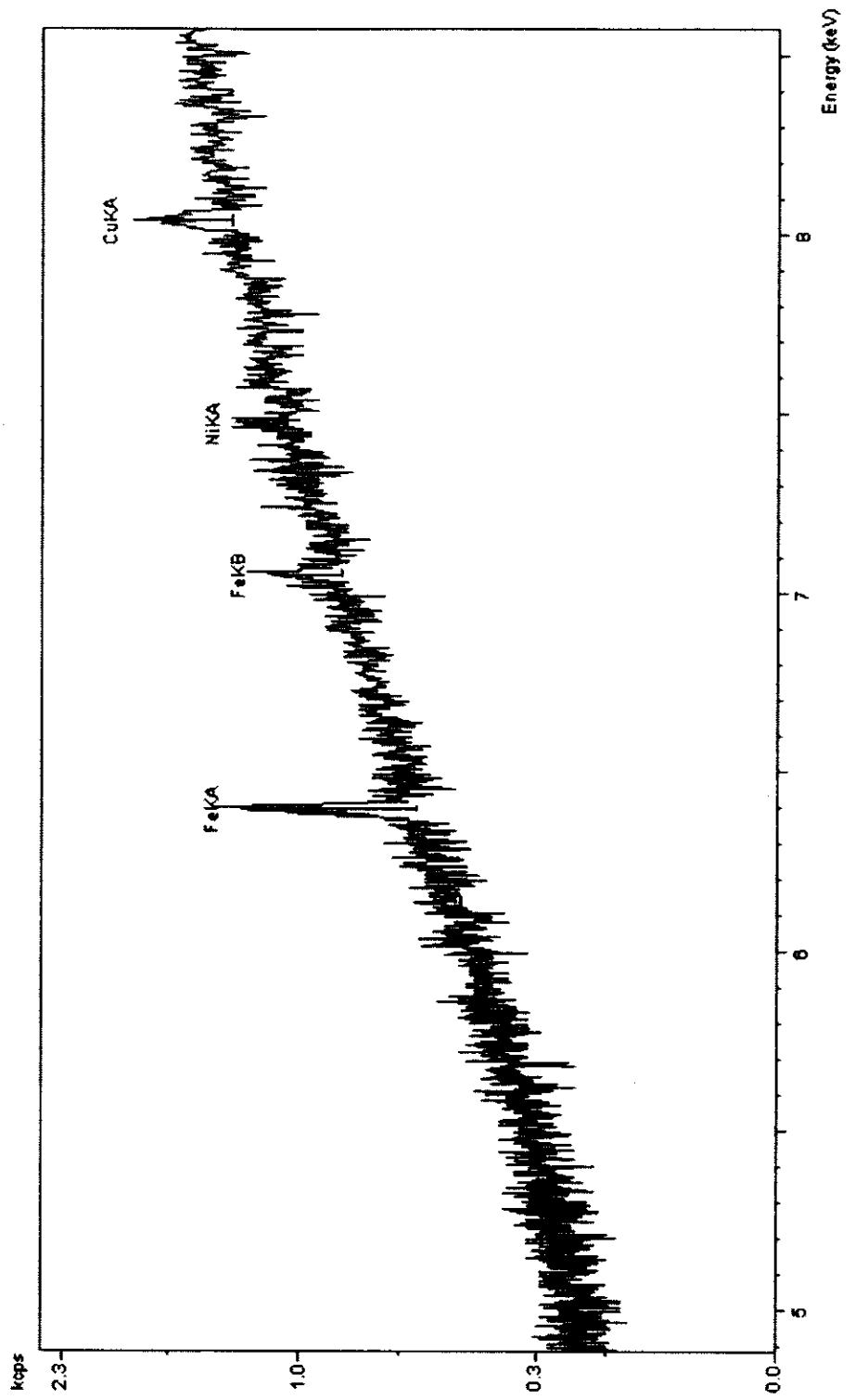

Figure 14 The XRF spectrum showing Fe, Ni and Cu as impurities in La-CU

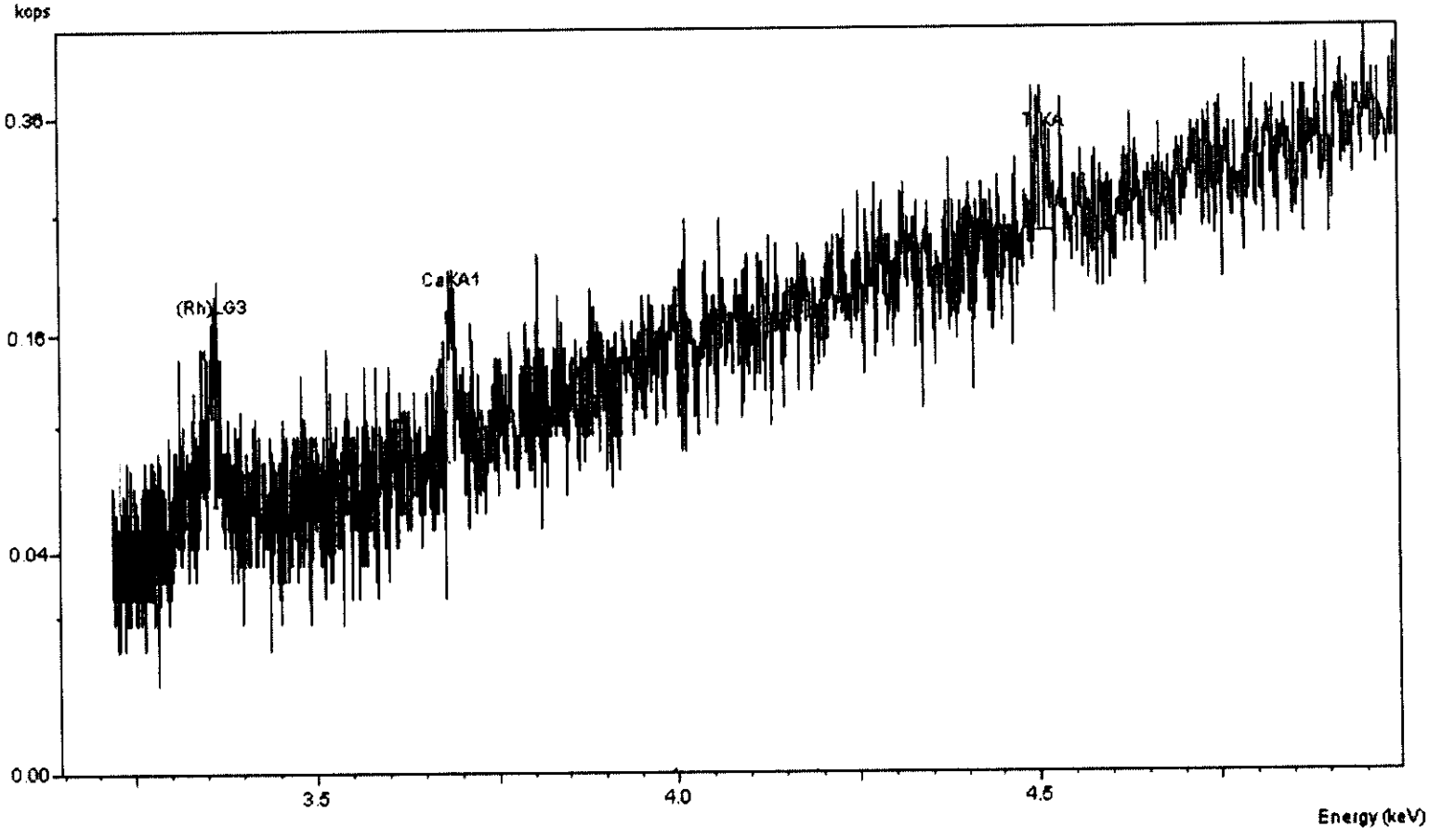

Figure 15 The XRF spectrum showing Ca and Ti as impurities in La-CU

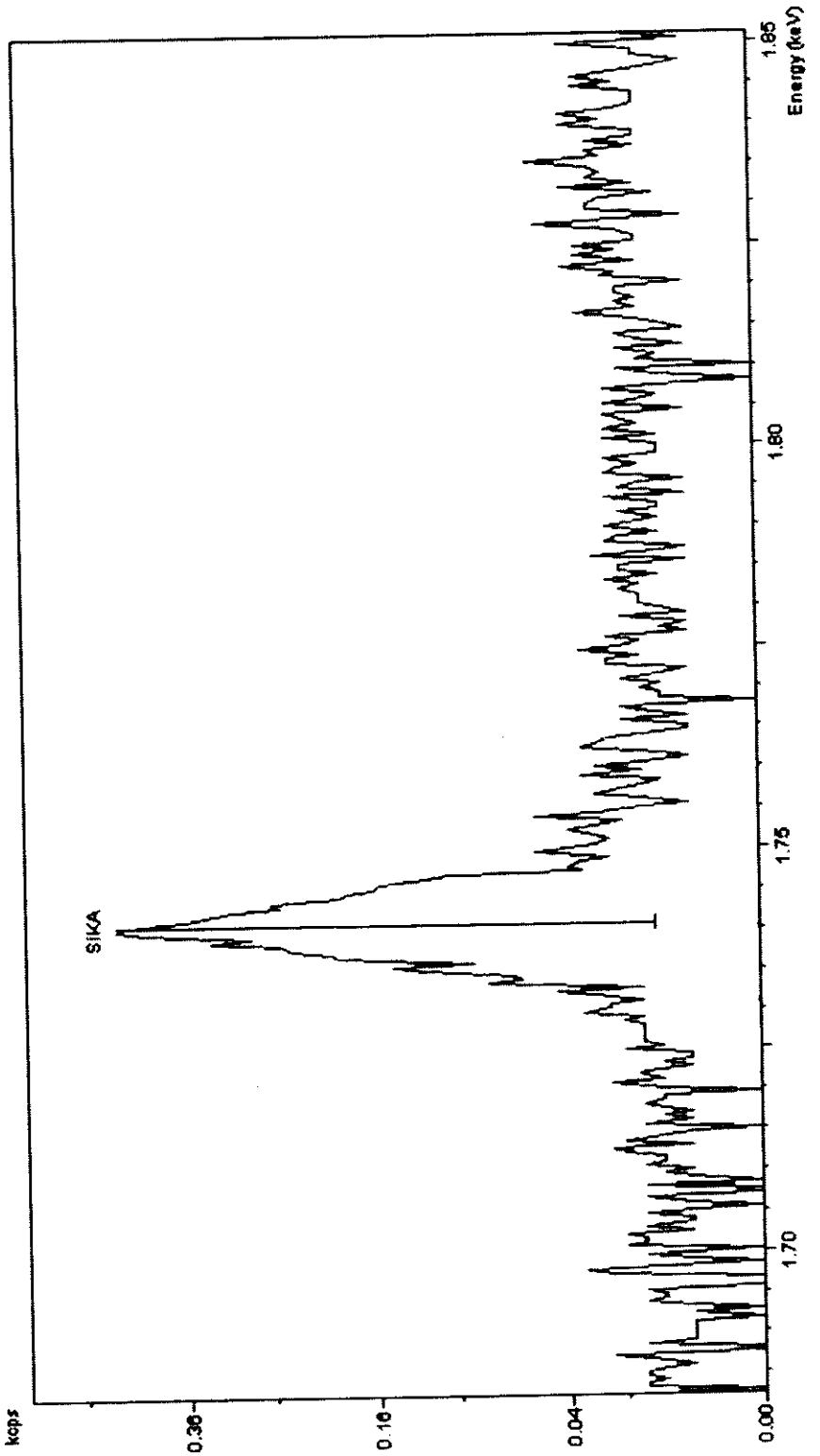

Figure 16 The XRF spectrum showing Si as impurity in La-CU

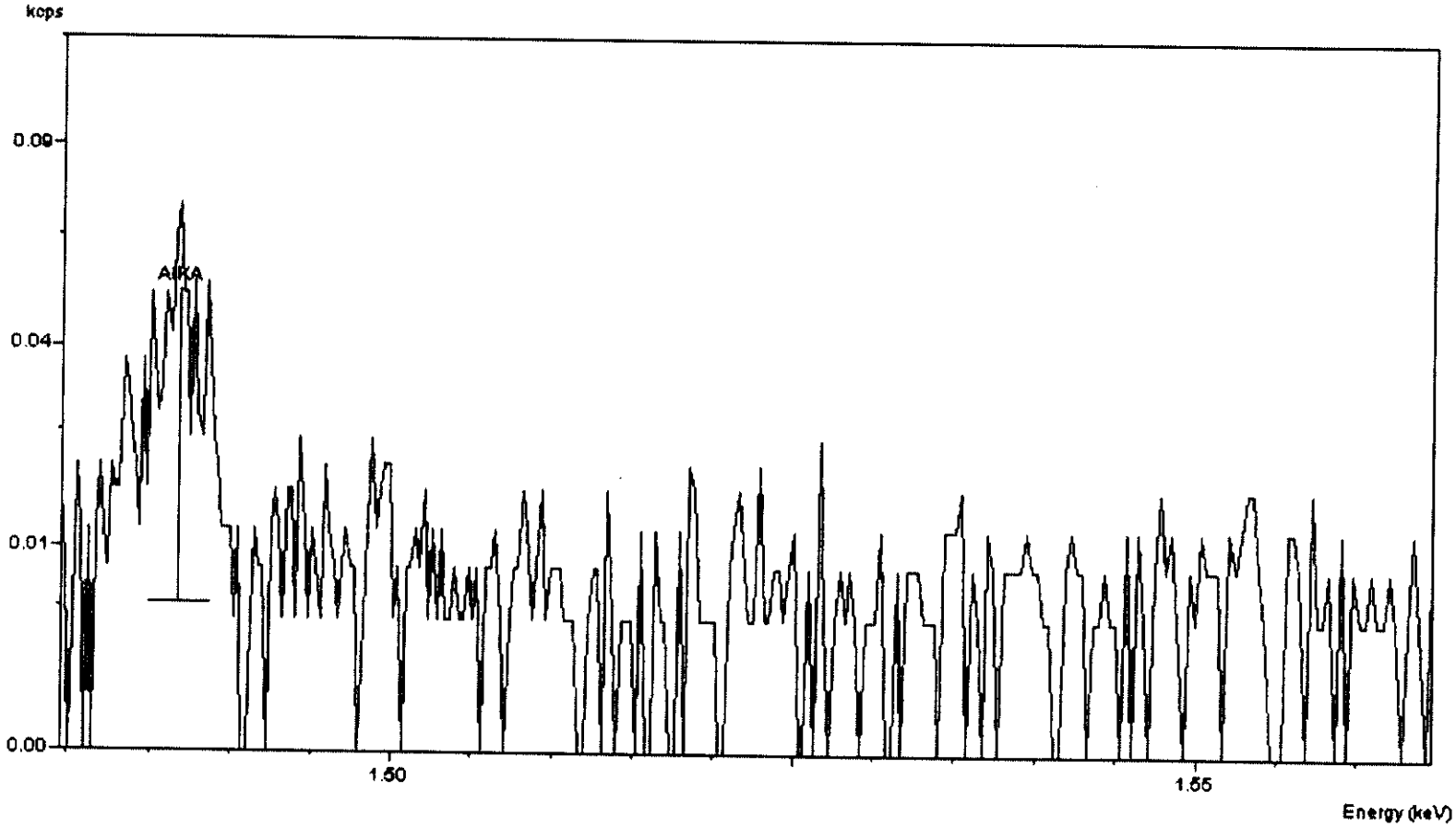

Figure 17 The XRF spectrum showing of Al as impurity in La-CU

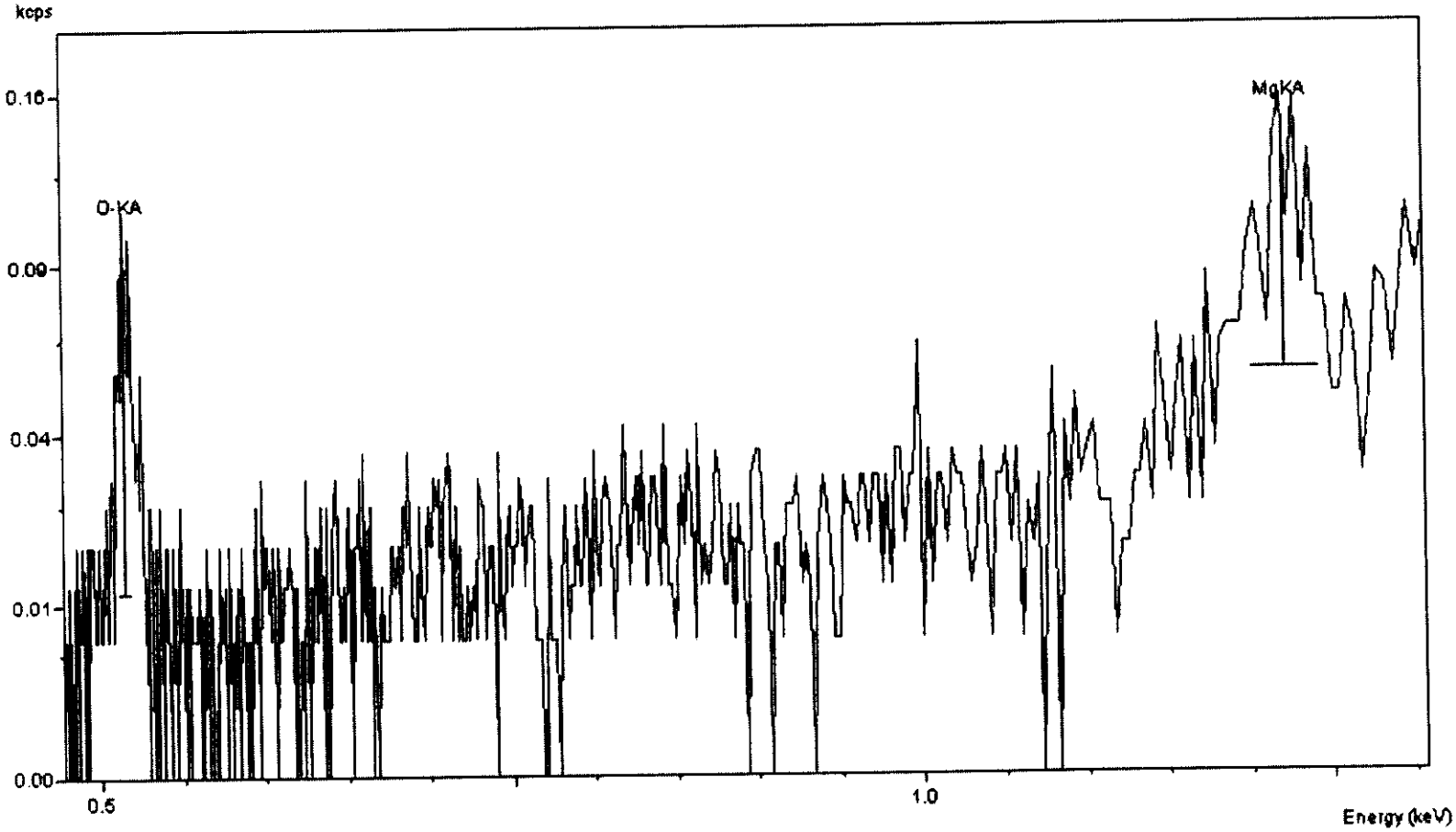

Figure 18 The XRF spectrum showing of Mg as impurity in La-CU

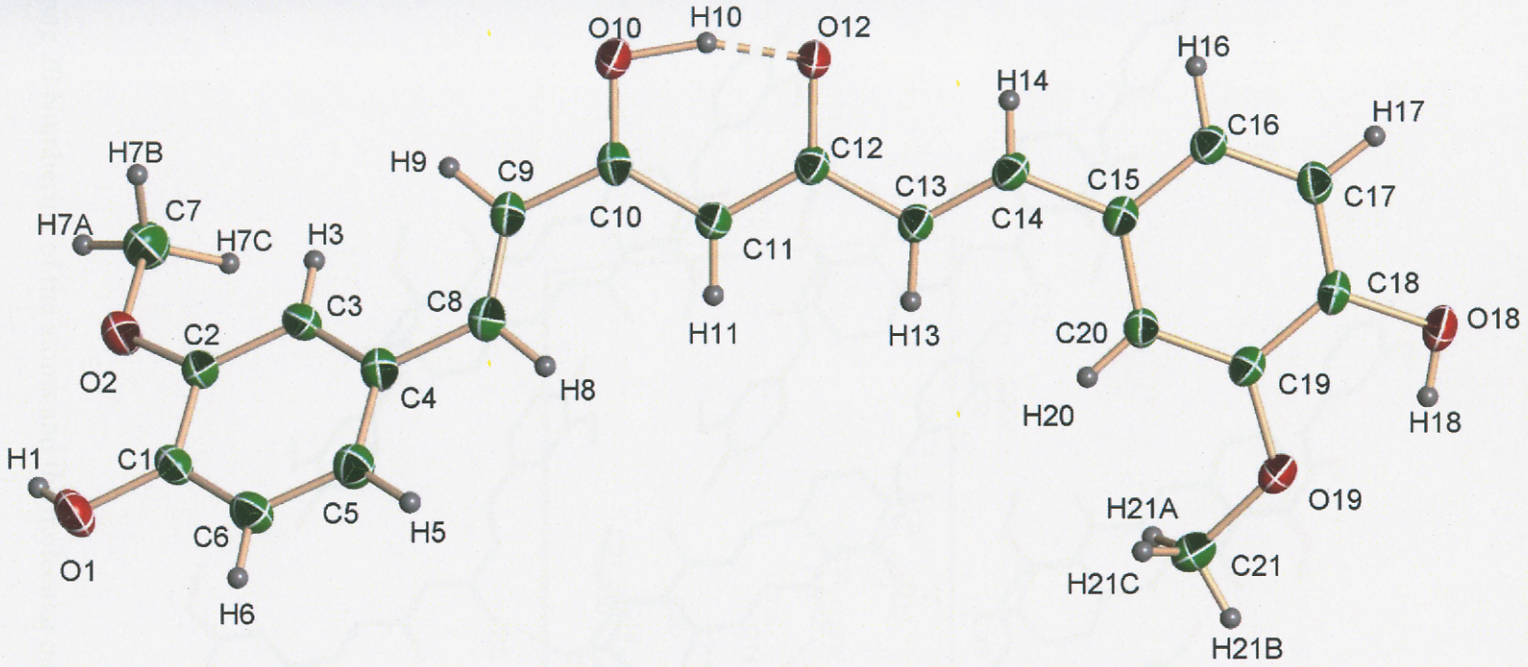

Figure 19 The molecular plot of CUCr, CULa, A1 and B2 (curcumin).

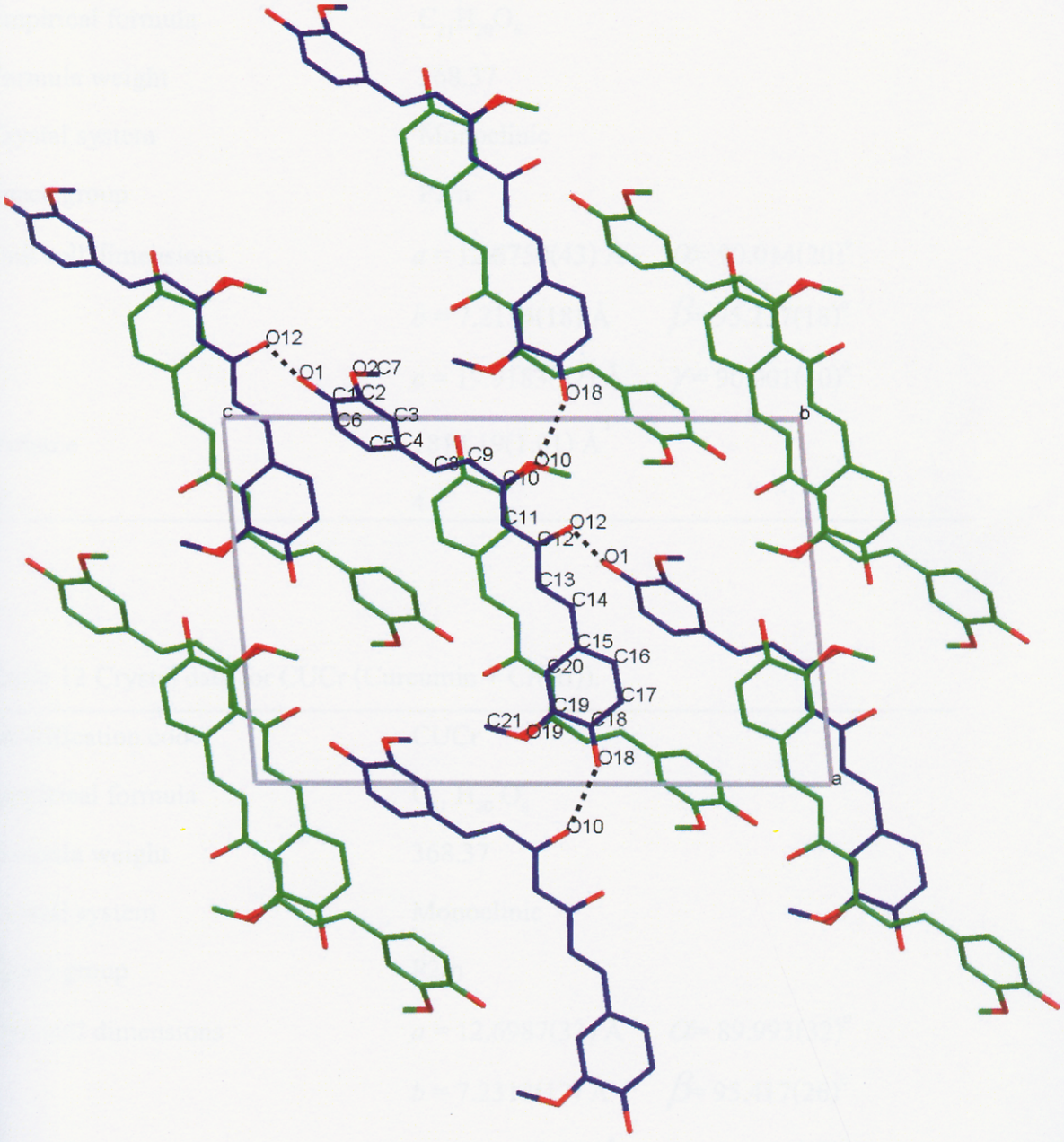

Figure 20 Numbering of the atoms and the molecular packing in crystals of A1 (curcumin).

Table 11 Crystal data for CULa (Curcumin + La(III)).

Identification code	CULa	
Empirical formula	$C_{21}H_{20}O_6$	
Formula weight	368.37	
Crystal system	Monoclinic	
Space group	P2/n	
Unit cell dimensions	a = 12.6750(43) Å	α= 90.014(20)°
	b = 7.2154(18) Å	β= 95.237(18)°
	c = 19.9183(57) Å	γ= 90.001(40)°
Volume	1814.19(1.01) Å^3	
Z	4	

Table 12 Crystal data for CUCr (Curcumin + Cr(III)).

Identification code	CUCr	
Empirical formula	$C_{21}H_{20}O_6$	
Formula weight	368.37	
Crystal system	Monoclinic	
Space group	P2/n	
Unit cell dimensions	a = 12.6987(33) Å	α= 89.993(32)°
	b = 7.2312(12) Å	β= 95.417(26)°
	c = 19.8682(76) Å	γ= 90.008(25)°
Volume	1816.24(76) Å^3	
Z	4	

Table 13 Crystal data for B2

Identification code	B2	
Empirical formula	$C_{21}H_{20}O_6$	
Formula weight	368.37	
Crystal system	Monoclinic	
Space group	P2/n	
Unit cell dimensions	a = 12.6934(43) Å	α= 90.051(51)°
	b = 7.2135(29) Å	β= 95.256(31)°
	c = 19.9120(66) Å	γ= 90.042(64)°
Volume	1815.29(1.21) Å^3	
Z	4	

Table 14 Crystal data and structure refinement for A1

Identification code	A1
Empirical formula	$C_{21}H_{20}O_6$
Formula weight	368.37
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2/n (no.13)
Unit cell dimensions	a = 12.7013(10) Å α= 90°
	b = 7.2174(6) Å β= 95.2520(10)°
	c = 19.9093(16) Å γ= 90°
Volume	1817.4(3) Å ^{3}
Z	4
Density (calculated)	1.346 Mg/m^3
Absorption coefficient	0.099 mm^{-1}
F(000)	776
Crystal size	0.325 x 0.279 x 0.153 mm^3
Theta range for data collection	1.83 to 26.02°
Index ranges	-15<=h<=15, -8<=k<=8, -24<=l<=23
Reflections collected	9903
Independent reflections	3555 [$R(int)$ = 0.0200]
Completeness to theta = 26.02°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.990 and 0.755
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3555 / 0 / 324

Table 14 (continued)

Goodness-of-fit on F^2	1.079
Final R indices [$I>2\ \sigma(I)$]	$R1 = 0.0584$, $wR2 = 0.1336$
R indices (all data)	$R1 = 0.0728$, $wR2 = 0.1424$
Largest diff. peak and hole	0.306 and -0.239 e. $Å^{-3}$

Table 15 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for A1.

	x	y	z	U(eq)
C(1)	-461(2)	1748(3)	8080(1)	51(1)
C(2)	-526(2)	382(3)	7581(1)	50(1)
C(3)	81(2)	521(4)	7041(1)	50(1)
C(4)	782(2)	1988(3)	6995(1)	51(1)
C(5)	864(2)	3293(4)	7504(1)	60(1)
C(6)	241(2)	3181(4)	8037(1)	59(1)
C(7)	-1186(3)	-2621(5)	7263(2)	76(1)
C(8)	1423(2)	2154(4)	6417(1)	53(1)
C(9)	1169(2)	1439(3)	5818(1)	51(1)
C(10)	1811(2)	1530(3)	5249(1)	47(1)
C(11)	2892(2)	1970(3)	5302(1)	46(1)
C(12)	3464(2)	1922(3)	4740(1)	44(1)
C(13)	4590(2)	2333(3)	4787(1)	46(1)
C(14)	5134(2)	2369(3)	4247(1)	47(1)
C(15)	6264(2)	2677(3)	4211(1)	44(1)
C(16)	6677(2)	2500(3)	3593(1)	49(1)
C(17)	7745(2)	2734(3)	3535(1)	51(1)
C(18)	8412(2)	3154(3)	4094(1)	47(1)
C(19)	8014(2)	3360(3)	4721(1)	46(1)
C(20)	6949(2)	3111(3)	4777(1)	45(1)
C(21)	8442(2)	3798(5)	5898(1)	67(1)
O(1)	-1055(2)	1687(3)	8613(1)	68(1)

Table 15 (continued)

O(2)	-1179(2)	-1053(3)	7696(1)	73(1)
O(10)	1322(1)	1127(3)	4672(1)	65(1)
O(12)	2995(1)	1487(3)	4153(1)	60(1)
O(18)	9466(1)	3358(3)	4027(1)	64(1)
O(19)	8758(1)	3803(3)	5234(1)	62(1)

Table 16 Anisotropic displacement parameters ($Å^2 \times 10^3$) for A1.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	52(1)	63(2)	41(1)	-2(1)	9(1)	9(1)
C(2)	46(1)	61(2)	43(1)	1(1)	6(1)	-5(1)
C(3)	52(1)	57(2)	41(1)	-6(1)	6(1)	1(1)
C(4)	48(1)	53(1)	52(1)	5(1)	9(1)	2(1)
C(5)	61(2)	58(2)	62(2)	-2(1)	11(1)	-6(1)
C(6)	68(2)	59(2)	52(1)	-9(1)	10(1)	1(1)
C(7)	79(2)	78(2)	74(2)	-9(2)	13(2)	-20(2)
C(8)	48(1)	52(1)	60(2)	4(1)	10(1)	-3(1)
C(9)	42(1)	56(1)	58(1)	7(1)	11(1)	-1(1)
C(10)	44(1)	47(1)	51(1)	9(1)	13(1)	4(1)
C(11)	41(1)	53(1)	43(1)	2(1)	4(1)	-1(1)
C(12)	37(1)	51(1)	44(1)	8(1)	3(1)	0(1)
C(13)	38(1)	57(1)	44(1)	5(1)	2(1)	-1(1)
C(14)	38(1)	54(1)	48(1)	7(1)	-2(1)	-4(1)
C(15)	36(1)	45(1)	49(1)	8(1)	3(1)	-1(1)
C(16)	40(1)	60(2)	46(1)	9(1)	1(1)	-3(1)
C(17)	44(1)	62(2)	48(1)	7(1)	11(1)	-2(1)
C(18)	32(1)	50(1)	58(1)	9(1)	9(1)	0(1)
C(19)	36(1)	48(1)	52(1)	4(1)	1(1)	0(1)
C(20)	40(1)	50(1)	45(1)	4(1)	7(1)	0(1)
C(21)	52(2)	87(2)	59(2)	-4(2)	-6(1)	-10(2)
O(1)	75(1)	79(1)	54(1)	-7(1)	28(1)	-2(1)
O(2)	72(1)	92(1)	56(1)	-12(1)	21(1)	-22(1)

Table 16 (continued)

O(10)	40(1)	105(2)	52(1)	4(1)	4(1)	-12(1)
O(12)	37(1)	102(1)	41(1)	0(1)	5(1)	-7(1)
O(18)	35(1)	92(1)	66(1)	4(1)	9(1)	-5(1)
O(19)	40(1)	88(1)	57(1)	-2(1)	-1(1)	-11(1)

Table 17 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for A1.

	x	y	z	U(eq)
H(1)	-1350(20)	670(40)	8642(14)	77(10)
H(3)	-3(18)	-330(30)	6728(11)	52(7)
H(5)	1378(19)	4350(40)	7479(12)	65(7)
H(6)	324(19)	4090(40)	8367(12)	61(7)
H(8)	2050(20)	2910(40)	6482(12)	65(7)
H(9)	510(20)	790(40)	5747(12)	68(7)
H(10)	2030(30)	1210(50)	4343(18)	124(12)
H(11)	3238(18)	2210(30)	5716(12)	50(6)
H(13)	4916(17)	2540(30)	5236(12)	47(6)
H(14)	4783(18)	2180(30)	3849(12)	50(6)
H(16)	6212(19)	2190(30)	3190(12)	56(7)
H(17)	8035(19)	2600(30)	3125(13)	61(7)
H(18)	9690(30)	3540(50)	4438(16)	89(11)
H(20)	6713(17)	3280(30)	5182(11)	43(6)
H(7A)	-1580(30)	-3710(50)	7515(16)	105(11)
H(21A)	8190(20)	2570(50)	6024(14)	84(9)
H(7B)	-1690(40)	-2170(70)	6830(30)	190(20)
H(21B)	9050(20)	4070(40)	6169(13)	71(8)
H(7C)	-320(30)	-3060(60)	7205(19)	135(13)
H(21C)	7870(20)	4680(40)	5937(13)	73(8)

Table 18 Bond lengths [Å] and angles [°] for A1.

C(1)-O(1)	1.358(3)
C(1)-C(6)	1.373(4)
C(1)-C(2)	1.396(3)
C(2)-O(2)	1.359(3)
C(2)-C(3)	1.383(3)
C(3)-C(4)	1.392(3)
C(3)-H(3)	0.87(2)
C(4)-C(5)	1.382(3)
C(4)-C(8)	1.473(3)
C(5)-C(6)	1.383(3)
C(5)-H(5)	1.01(3)
C(6)-H(6)	0.93(3)
C(7)-O(2)	1.423(4)
C(7)-H(7A)	1.08(3)
C(7)-H(7B)	1.08(5)
C(7)-H(7C)	1.15(4)
C(8)-C(9)	1.313(3)
C(8)-H(8)	0.97(3)
C(9)-C(10)	1.457(3)
C(9)-H(9)	0.95(3)
C(10)-O(10)	1.288(3)
C(10)-C(11)	1.405(3)
C(11)-C(12)	1.389(3)
C(11)-H(11)	0.91(2)
C(12)-O(12)	1.300(3)

Table 18 (continued)

C(12)-C(13)	1.455(3)
C(13)-C(14)	1.330(3)
C(13)-H(13)	0.96(2)
C(14)-C(15)	1.461(3)
C(14)-H(14)	0.88(2)
C(15)-C(16)	1.388(3)
C(15)-C(20)	1.395(3)
C(16)-C(17)	1.382(3)
C(16)-H(16)	0.98(2)
C(17)-C(18)	1.369(3)
C(17)-H(17)	0.93(3)
C(18)-O(18)	1.367(3)
C(18)-C(19)	1.397(3)
C(19)-O(19)	1.363(3)
C(19)-C(20)	1.380(3)
C(20)-H(20)	0.89(2)
C(21)-O(19)	1.416(3)
C(21)-H(21A)	0.98(3)
C(21)-H(21B)	0.93(3)
C(21)-H(21C)	0.97(3)
O(1)-H(1)	0.83(3)
O(10)-H(10)	1.16(4)
O(12)-H(10)	1.33(4)
O(18)-H(18)	0.85(3)
O(10)-O(18)	3.014(2)
O(12)-O(1)	2.998(3)

Table 18 (continued)

O(10)-H(18)	2.405(3)
O(12)-H(1)	2.251(2)
O(1)-C(1)	118.9(2)
O(1)-C(1)-C(2)	122.1(2)
C(6)-C(1)-C(2)	118.9(2)
O(2)-C(2)-C(3)	125.3(2)
O(2)-C(2)-C(1)	114.56(19)
C(3)-C(2)-C(1)	120.0(2)
C(2)-C(3)-C(4)	120.8(2)
C(2)-C(3)-H(3)	117.5(15)
C(4)-C(3)-H(3)	121.6(15)
C(5)-C(4)-C(3)	118.4(2)
C(5)-C(4)-C(8)	120.5(2)
C(3)-C(4)-C(8)	121.1(2)
C(4)-C(5)-C(6)	120.9(2)
C(4)-C(5)-H(5)	119.0(14)
C(6)-C(5)-H(5)	120.1(14)
C(1)-C(6)-C(5)	120.9(2)
C(1)-C(6)-H(6)	121.4(15)
C(5)-C(6)-H(6)	117.7(16)
O(2)-C(7)-H(7A)	106.1(18)
O(2)-C(7)-H(7B)	103(3)
H(7A)-C(7)-H(7B)	109(3)
O(2)-C(7)-H(7C)	109(2)
H(7A)-C(7)-H(7C)	109(3)
H(7B)-C(7)-H(7C)	120(3)

Table 18 (continued)

C(9)-C(8)-C(4)	124.8(2)
C(9)-C(8)-H(8)	118.3(15)
C(4)-C(8)-H(8)	116.8(15)
C(8)-C(9)-C(10)	125.5(2)
C(8)-C(9)-H(9)	117.8(15)
C(10)-C(9)-H(9)	116.7(15)
O(10)-C(10)-C(11)	120.40(19)
O(10)-C(10)-C(9)	115.2(2)
C(11)-C(10)-C(9)	124.4(2)
C(12)-C(11)-C(10)	120.9(2)
C(12)-C(11)-H(11)	119.1(14)
C(10)-C(11)-H(11)	119.8(14)
O(12)-C(12)-C(11)	119.93(19)
O(12)-C(12)-C(13)	118.32(18)
C(11)-C(12)-C(13)	121.8(2)
C(14)-C(13)-C(12)	122.1(2)
C(14)-C(13)-H(13)	122.5(13)
C(12)-C(13)-H(13)	115.4(13)
C(13)-C(14)-C(15)	128.9(2)
C(13)-C(14)-H(14)	117.8(15)
C(15)-C(14)-H(14)	113.3(15)
C(16)-C(15)-C(20)	118.63(19)
C(16)-C(15)-C(14)	118.8(2)
C(20)-C(15)-C(14)	122.53(19)
C(17)-C(16)-C(15)	121.0(2)
C(17)-C(16)-H(16)	118.9(13)

Table 18 (continued)

C(15)-C(16)-H(16)	120.0(13)
C(18)-C(17)-C(16)	119.9(2)
C(18)-C(17)-H(17)	118.0(15)
C(16)-C(17)-H(17)	122.0(15)
O(18)-C(18)-C(17)	118.9(2)
O(18)-C(18)-C(19)	120.9(2)
C(17)-C(18)-C(19)	120.19(19)
O(19)-C(19)-C(20)	125.9(2)
O(19)-C(19)-C(18)	114.35(18)
C(20)-C(19)-C(18)	119.7(2)
C(19)-C(20)-C(15)	120.5(2)
C(19)-C(20)-H(20)	117.9(14)
C(15)-C(20)-H(20)	121.5(14)
O(19)-C(21)-H(21A)	111.6(17)
O(19)-C(21)-H(21B)	104.4(16)
H(21A)-C(21)-H(21B)	109(2)
O(19)-C(21)-H(21C)	110.5(16)
H(21A)-C(21)-H(21C)	108(3)
H(21B)-C(21)-H(21C)	114(2)
C(1)-O(1)-H(1)	112(2)
C(2)-O(2)-C(7)	118.3(2)
C(10)-O(10)-H(10)	99.0(18)
C(12)-O(12)-H(10)	98.1(15)
C(18)-O(18)-H(18)	99(2)
C(19)-O(19)-C(21)	117.53(18)

Symmetry transformations used to generate equivalent atoms:

Table 19 Torsion angles [°] for A1.

O(1)-C(1)-C(2)-O(2)	-3.9(3)
C(6)-C(1)-C(2)-O(2)	175.0(2)
O(1)-C(1)-C(2)-C(3)	178.8(2)
C(6)-C(1)-C(2)-C(3)	-2.4(4)
O(2)-C(2)-C(3)-C(4)	-175.4(2)
C(1)-C(2)-C(3)-C(4)	1.7(4)
C(2)-C(3)-C(4)-C(5)	0.6(4)
C(2)-C(3)-C(4)-C(8)	-179.4(2)
C(3)-C(4)-C(5)-C(6)	-2.1(4)
C(8)-C(4)-C(5)-C(6)	177.9(2)
O(1)-C(1)-C(6)-C(5)	179.8(2)
C(2)-C(1)-C(6)-C(5)	0.9(4)
C(4)-C(5)-C(6)-C(1)	1.4(4)
C(5)-C(4)-C(8)-C(9)	-155.1(3)
C(3)-C(4)-C(8)-C(9)	24.9(4)
C(4)-C(8)-C(9)-C(10)	-177.6(2)
C(8)-C(9)-C(10)-O(10)	-164.7(2)
C(8)-C(9)-C(10)-C(11)	17.0(4)
O(10)-C(10)-C(11)-C(12)	-2.0(3)
C(9)-C(10)-C(11)-C(12)	176.2(2)
C(10)-C(11)-C(12)-O(12)	0.8(3)
C(10)-C(11)-C(12)-C(13)	-178.6(2)
O(12)-C(12)-C(13)-C(14)	3.5(3)
C(11)-C(12)-C(13)-C(14)	-177.0(2)
C(12)-C(13)-C(14)-C(15)	-177.1(2)

Table 19 (continued)

C(13)-C(14)-C(15)-C(16)	174.6(2)
C(13)-C(14)-C(15)-C(20)	-4.2(4)
C(20)-C(15)-C(16)-C(17)	0.4(3)
C(14)-C(15)-C(16)-C(17)	-178.5(2)
C(15)-C(16)-C(17)-C(18)	-0.2(4)
C(16)-C(17)-C(18)-O(18)	179.2(2)
C(16)-C(17)-C(18)-C(19)	-0.5(4)
O(18)-C(18)-C(19)-O(19)	1.2(3)
C(17)-C(18)-C(19)-O(19)	-179.1(2)
O(18)-C(18)-C(19)-C(20)	-178.8(2)
C(17)-C(18)-C(19)-C(20)	0.9(3)
O(19)-C(19)-C(20)-C(15)	179.3(2)
C(18)-C(19)-C(20)-C(15)	-0.7(3)
C(16)-C(15)-C(20)-C(19)	0.1(3)
C(14)-C(15)-C(20)-C(19)	178.9(2)
C(3)-C(2)-O(2)-C(7)	5.5(4)
C(1)-C(2)-O(2)-C(7)	-171.8(2)
C(20)-C(19)-O(19)-C(21)	8.0(4)
C(18)-C(19)-O(19)-C(21)	-172.0(2)

Symmetry transformations used to generate equivalent atoms:

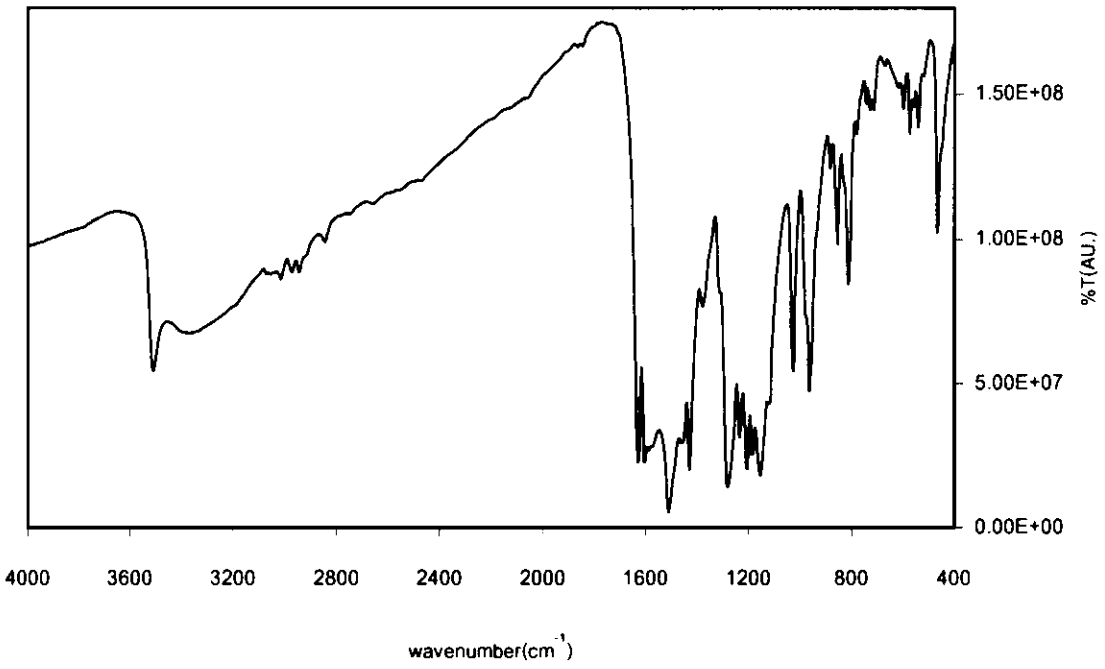

Figure 21 IR spectrum of curcumin (in-house separation).

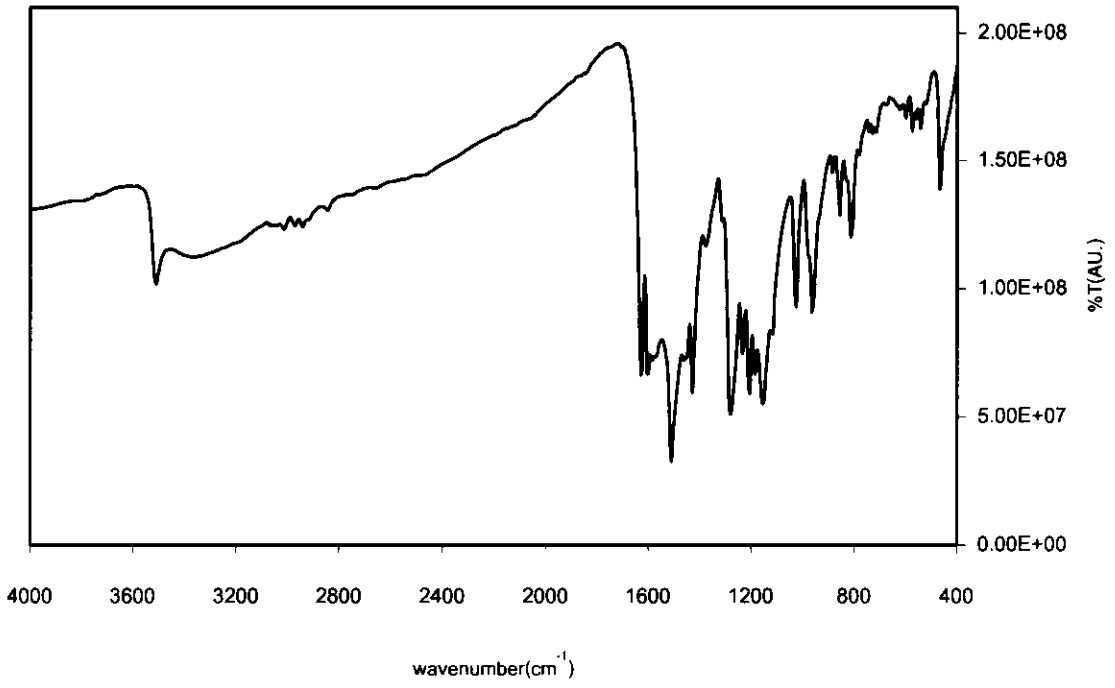

Figure 22 IR spectrum of curcumin (commercial).

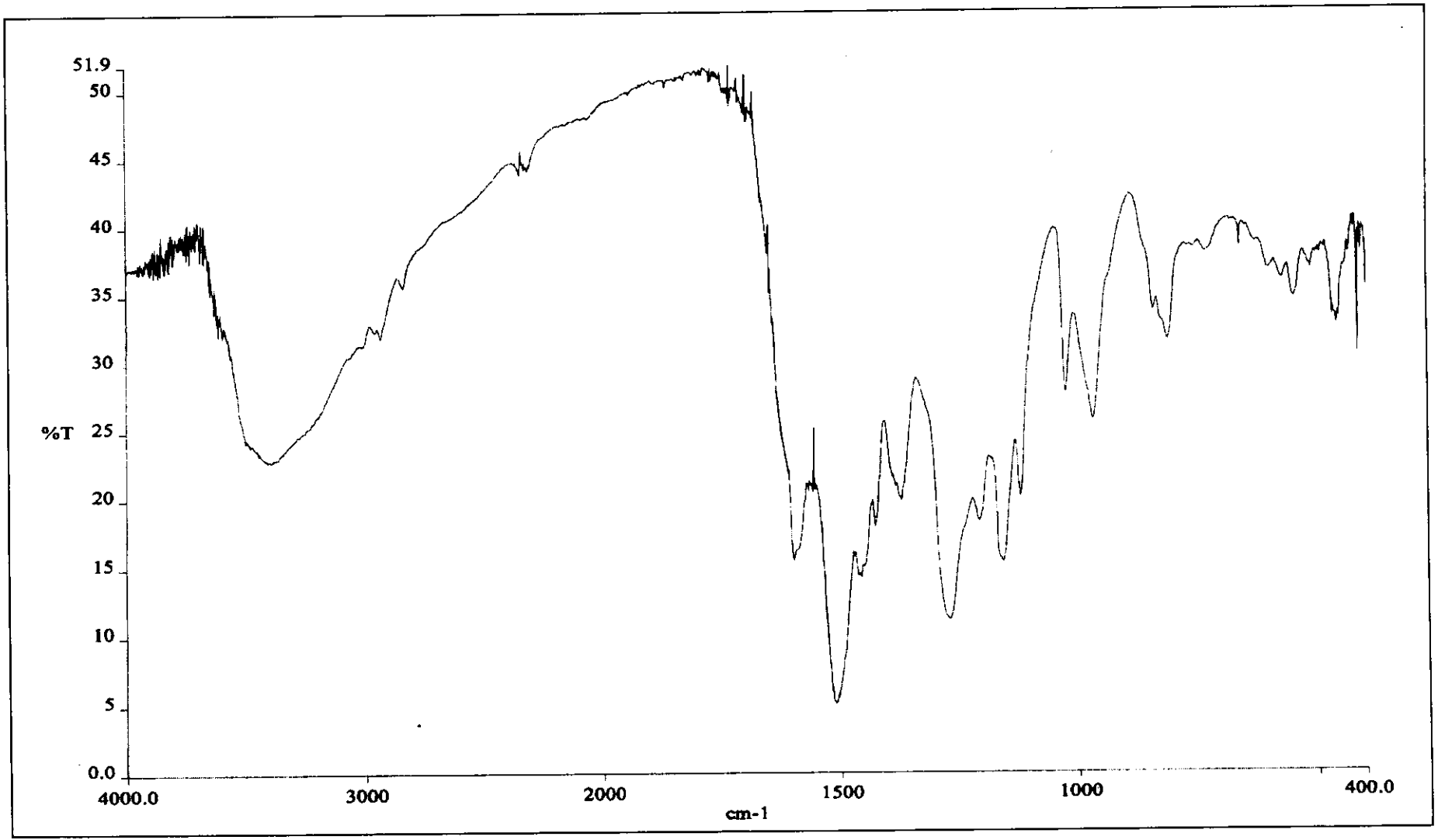

Figure 23 IR spectrum of Fe-CU1

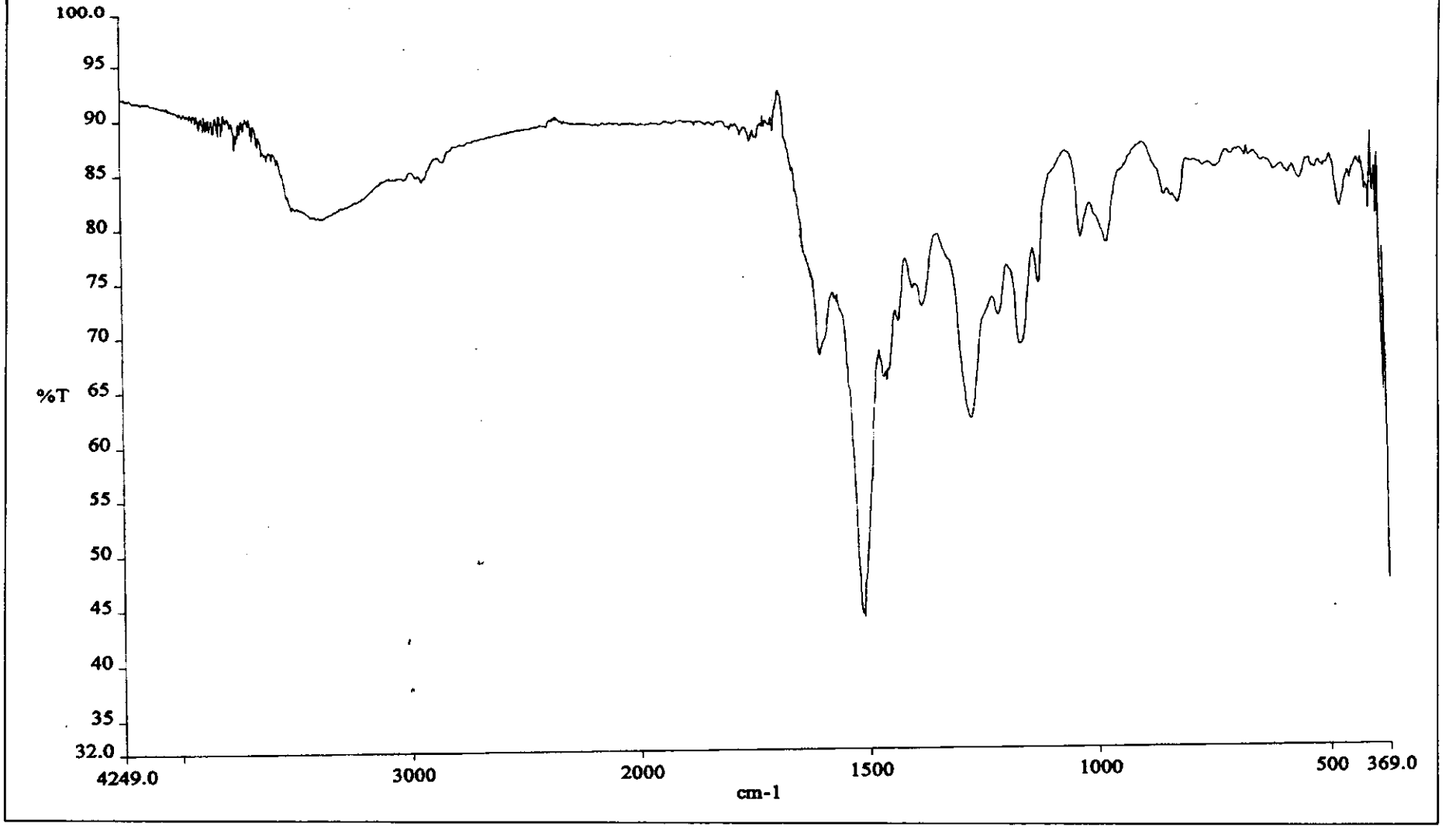

Figure 24 IR spectrum of Fe-CU2

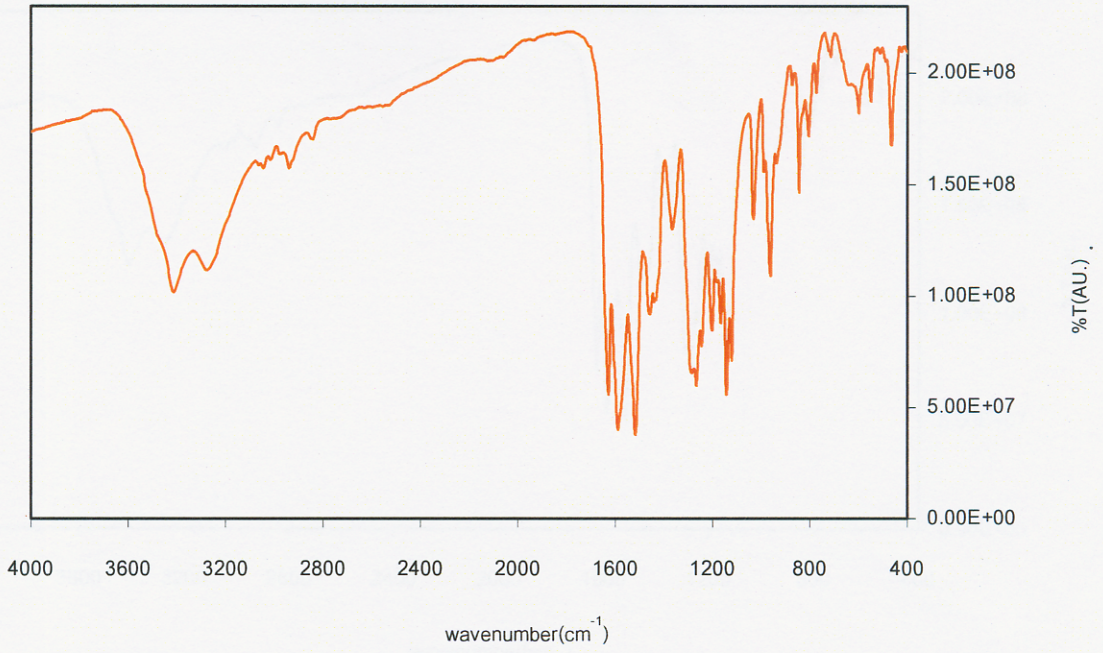

Figure 25 IR spectrum of Dy-CU

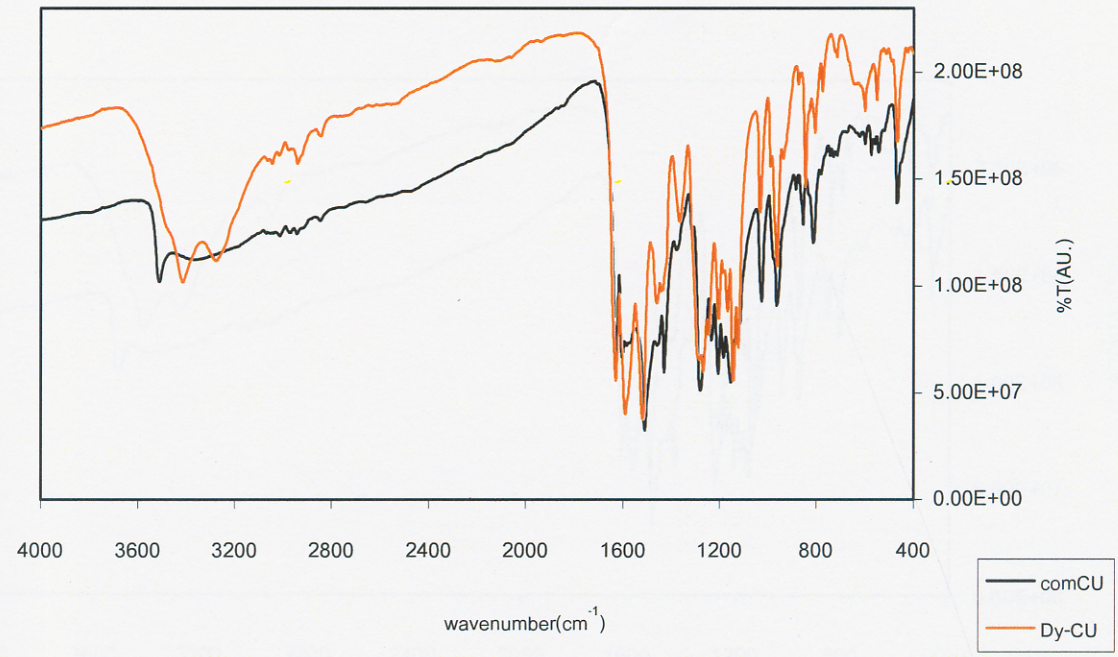

Figure 26 IR spectra of Dy-CU and commercial curcumin.

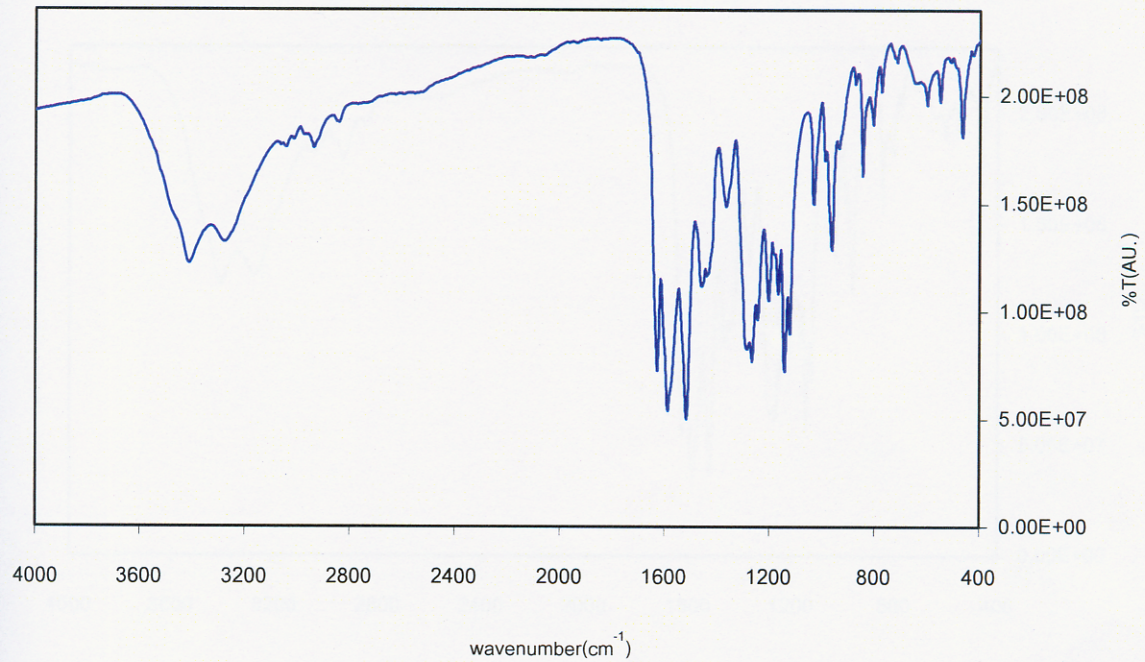

Figure 27 IR spectrum of Gd-CU

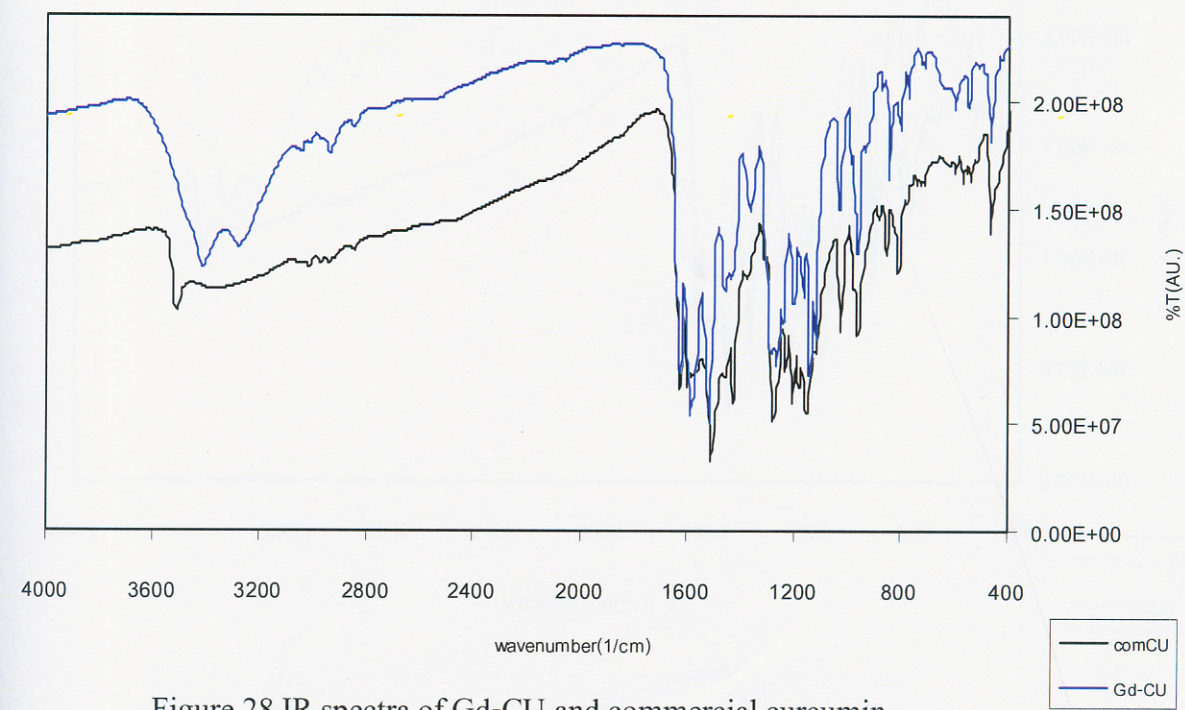

Figure 28 IR spectra of Gd-CU and commercial curcumin.

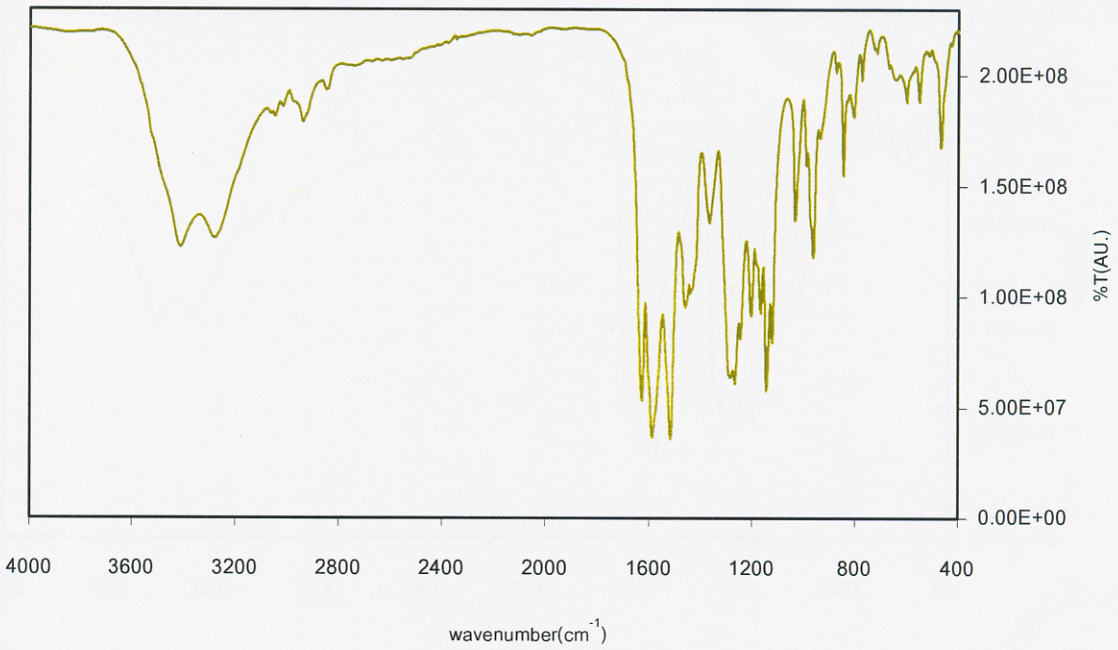

Figure 29 IR spectrum of Er-CU

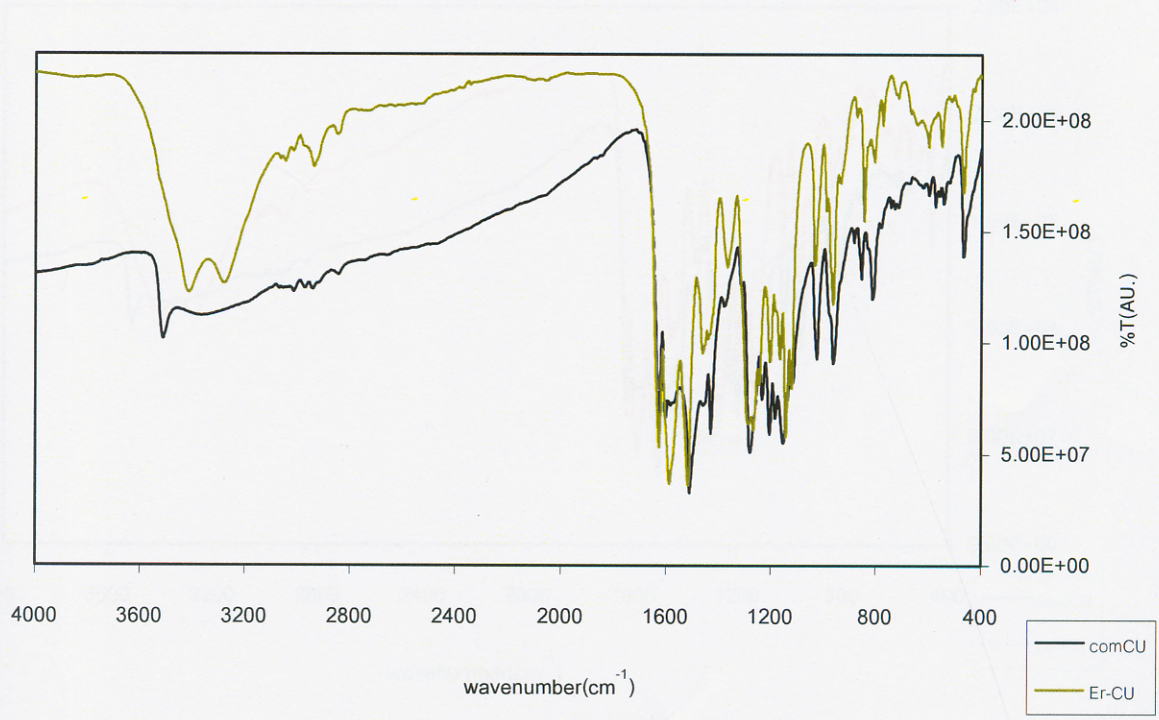

Figure 30 IR spectra of Er-CU and commercial curcumin.

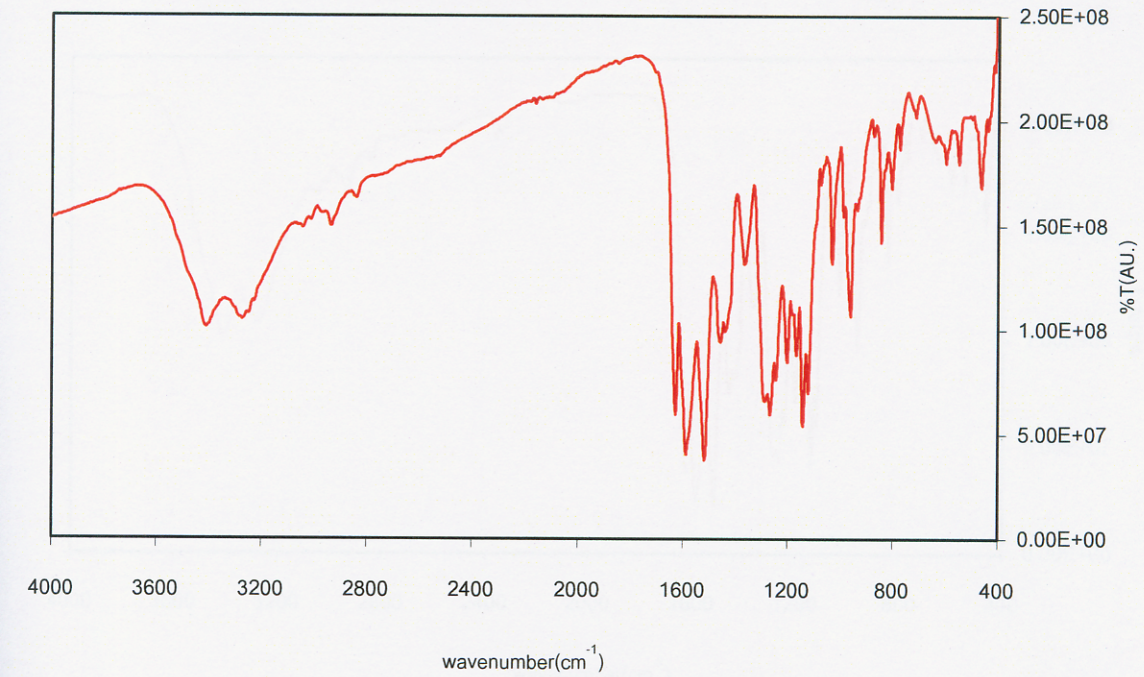

Figure 31 IR spectrum of La-CU

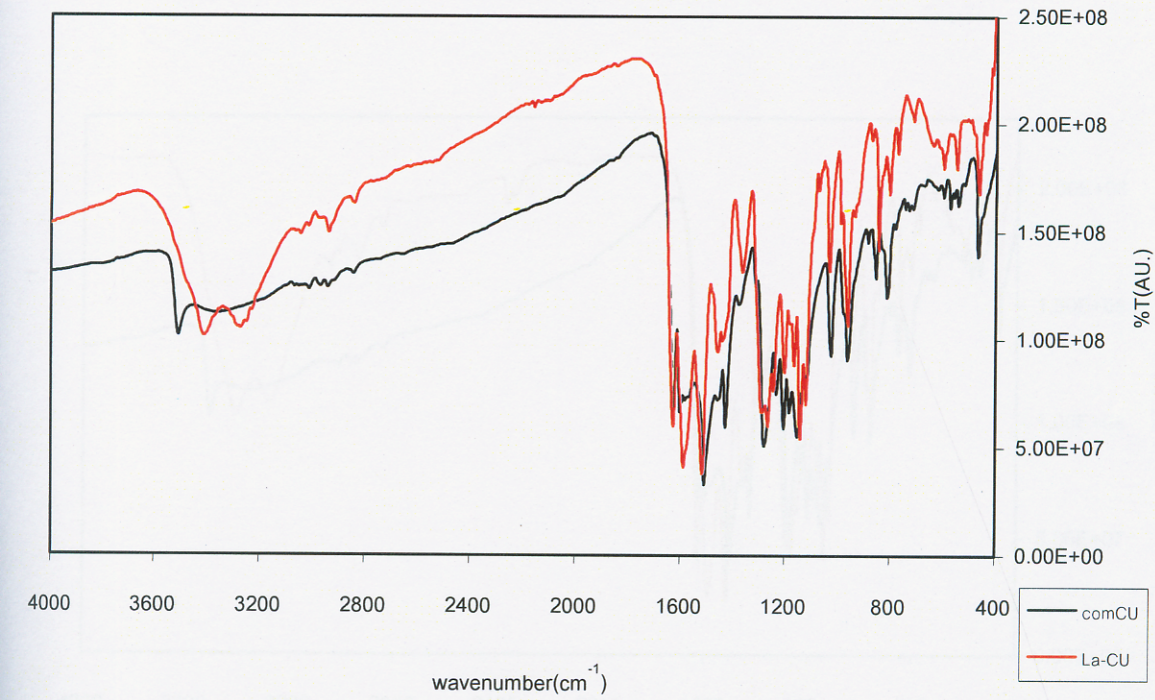

Figure 32 IR spectra of La-CU and commercial curcumin.

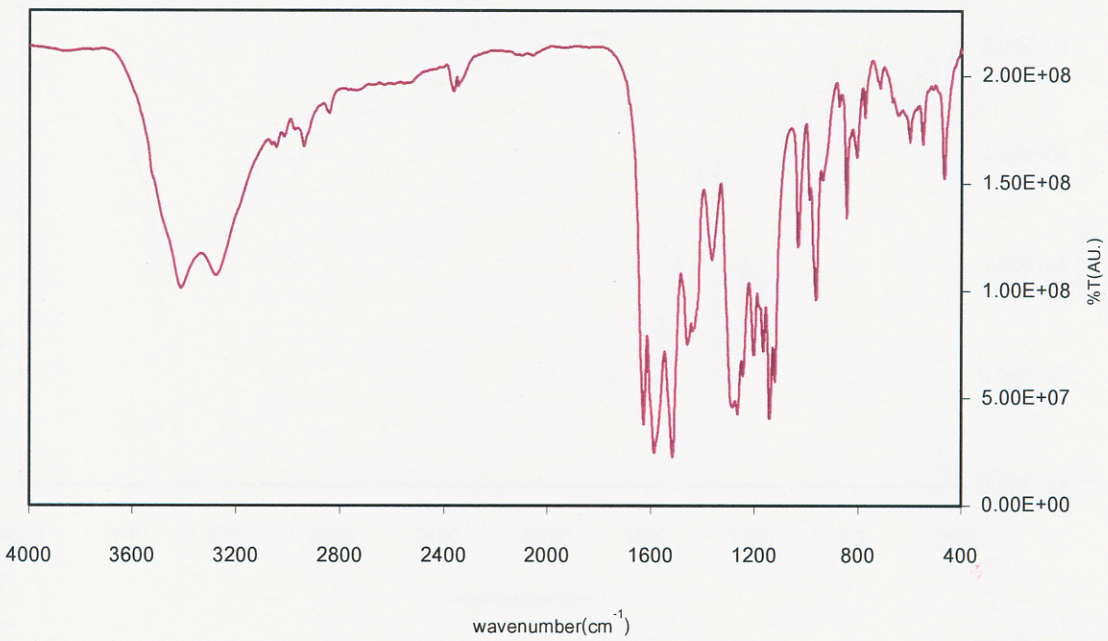

Figure 33 IR spectrum of Nd-CU

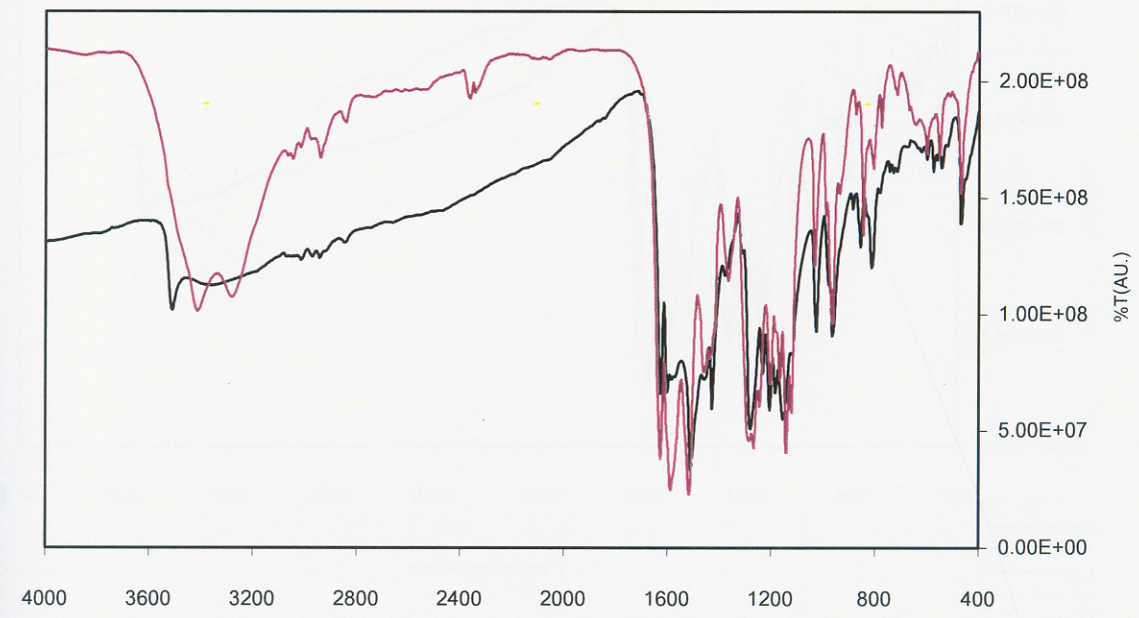

Figure 34 IR spectra of Nd-CU and commercial curcumin.

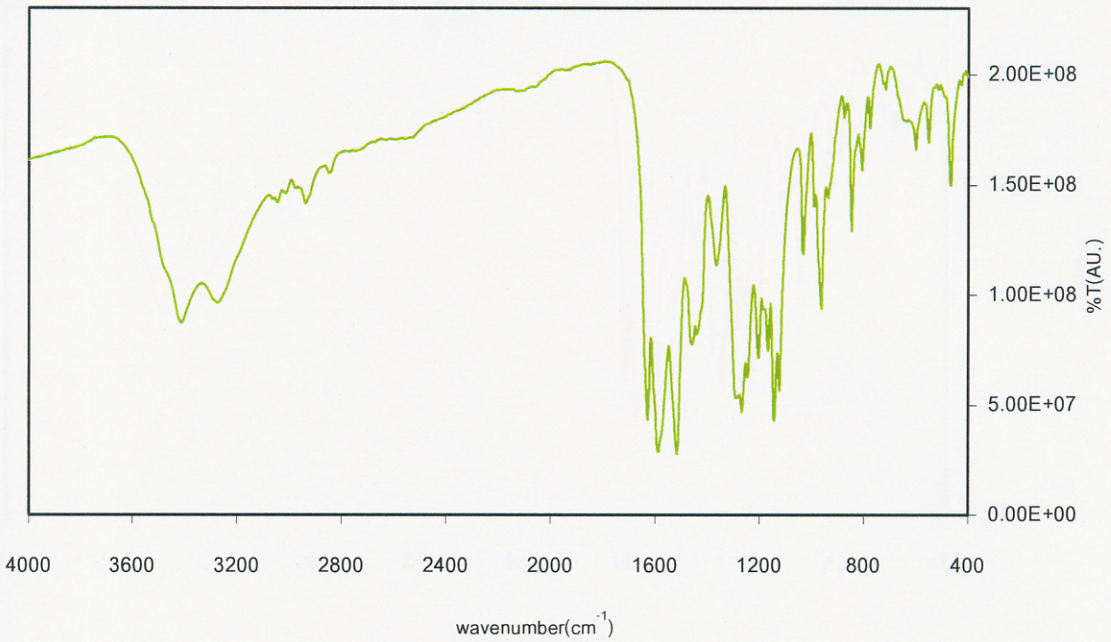

Figure 35 IR spectrum of Pr-CU

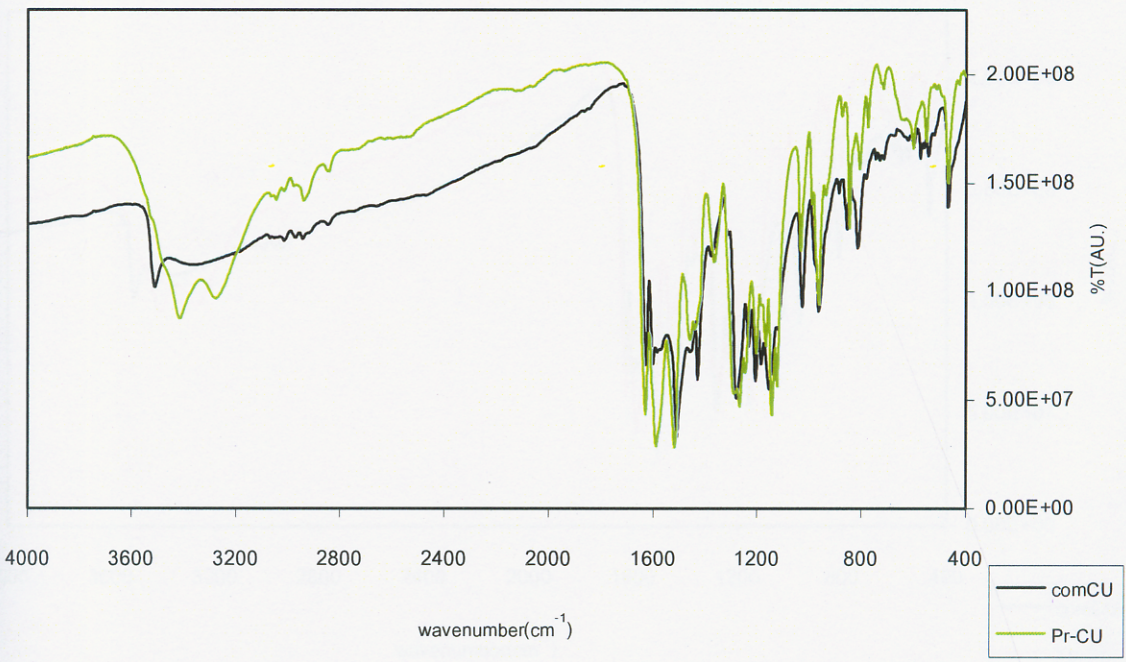

Figure 36 IR spectra of Pr-CU and commercial curcumin.

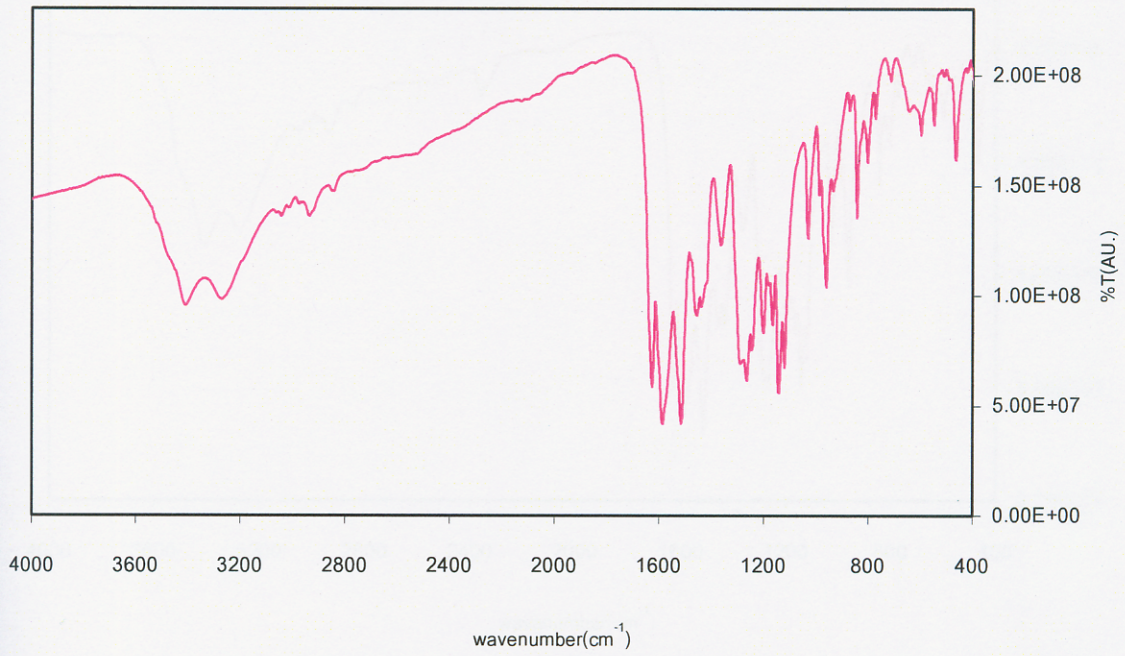

Figure 37 IR spectrum of Yb-CU

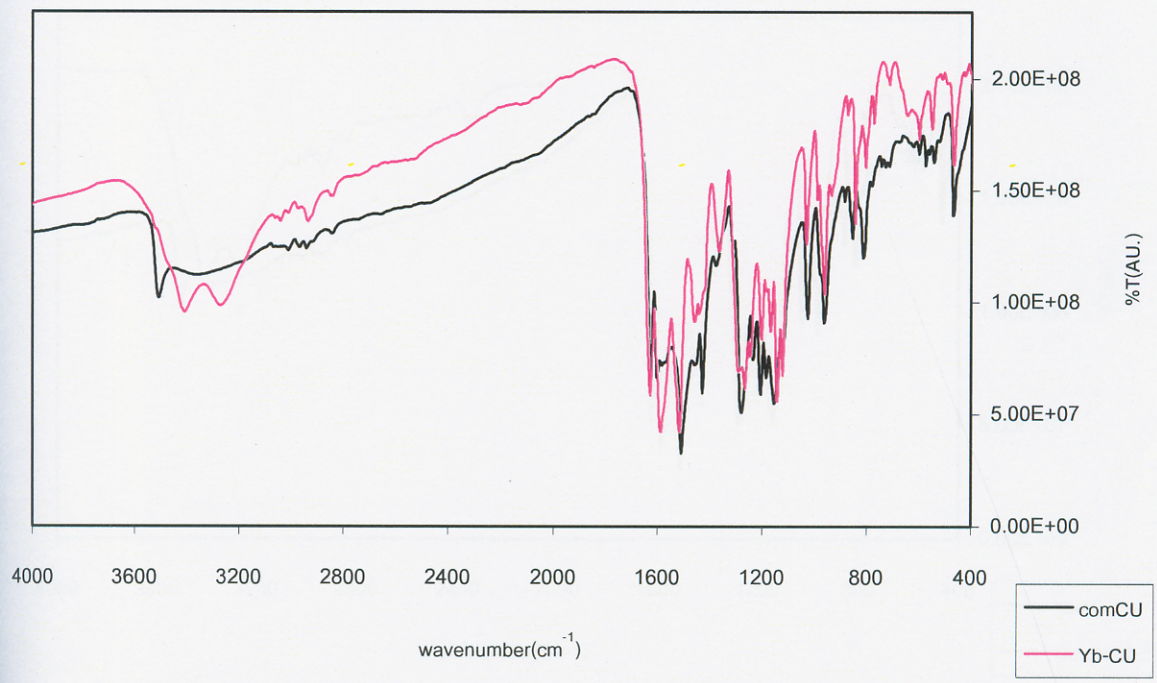

Figure 38 IR spectra of Yb-CU and commercial curcumin.

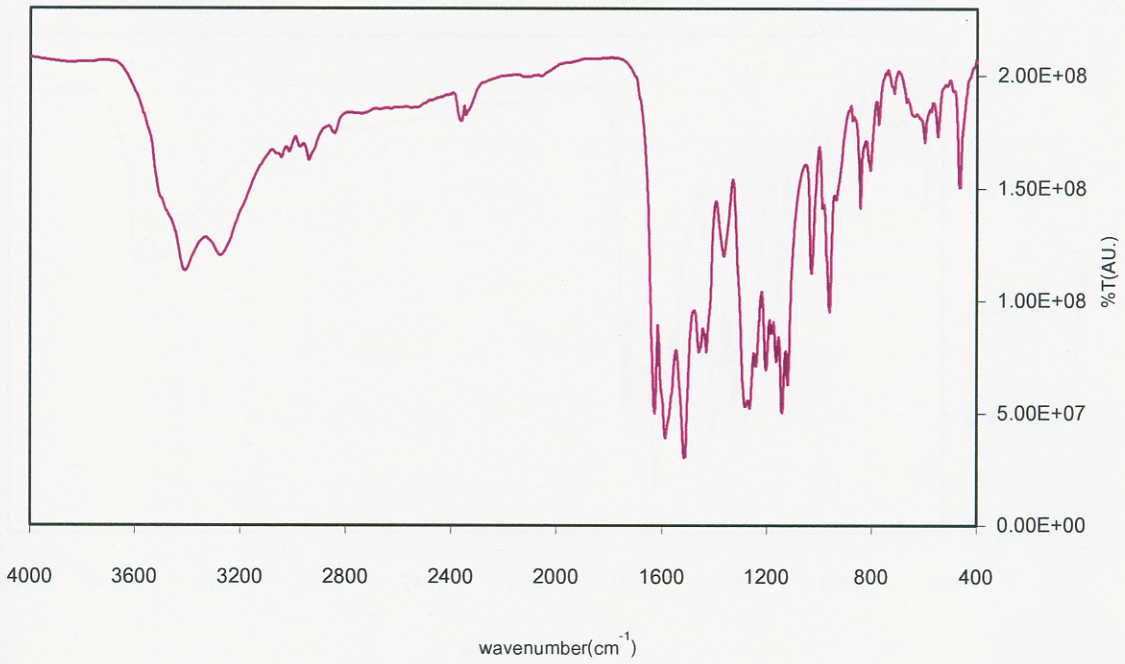

Figure 39 IR spectrum of Sm-CU(0.5)

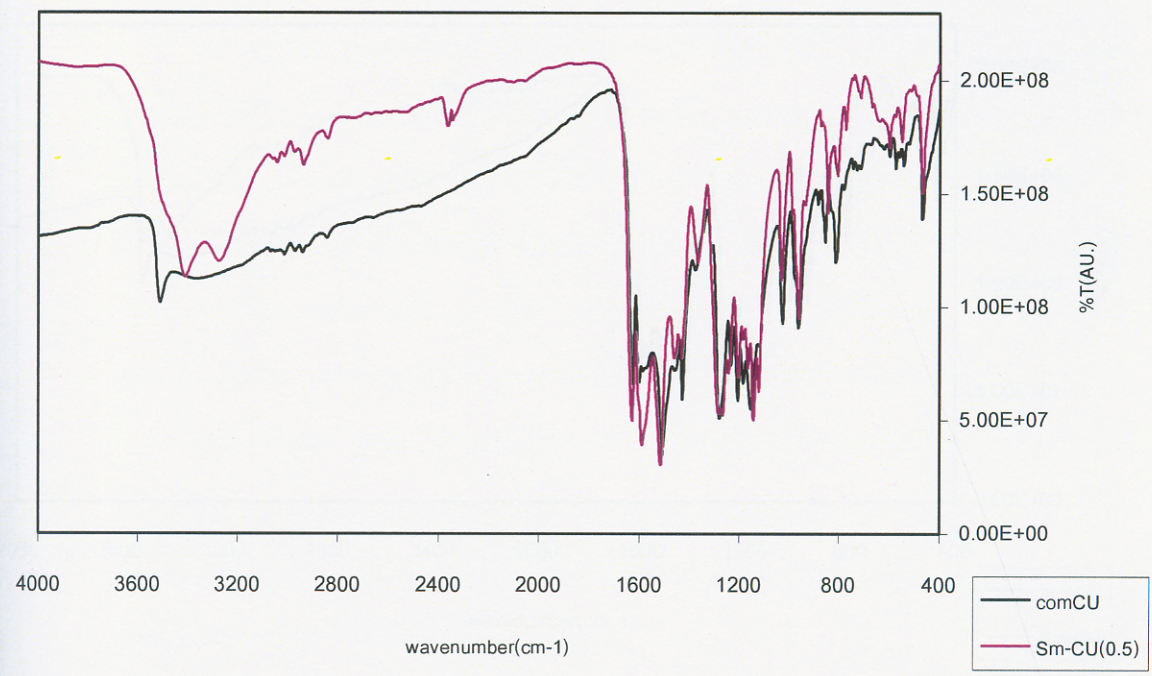

Figure 40 IR spectra of Sm-CU(0.5) and commercial curcumin.

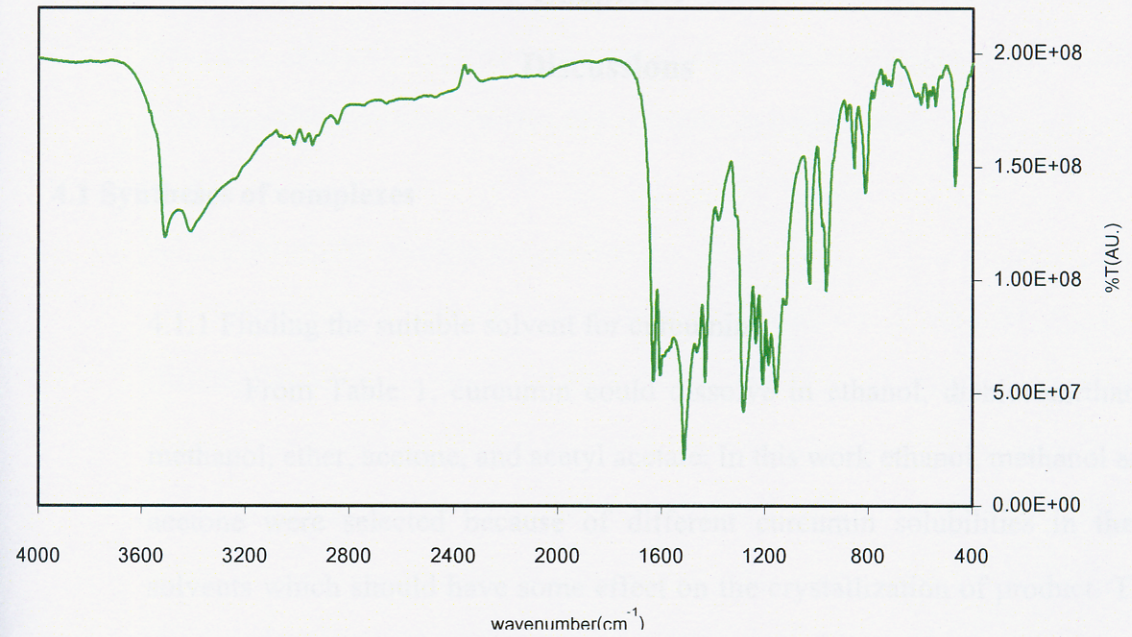

Figure 41 IR spectrum of Sm-CU

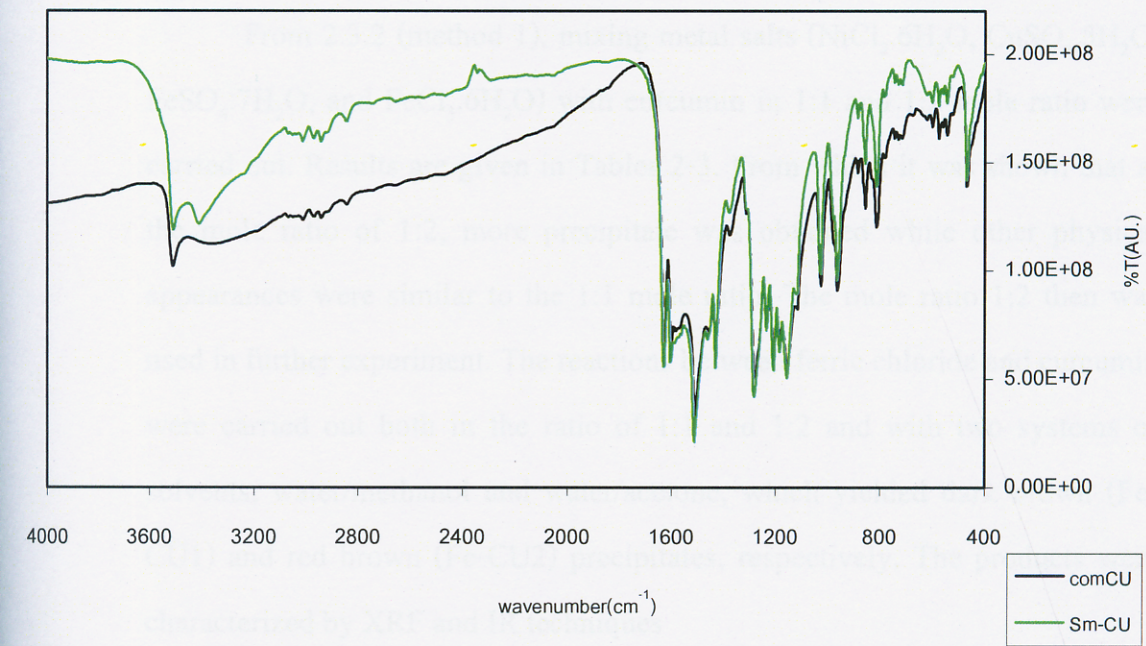

Figure 42 IR spectra of Sm-CU and commercial curcumin.