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Synthesis of Metallo Flavones and Ultrasonic Studies on Chrysin and Morin

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Metallo flavones are synthesized and characterized by UV and IR spectral studies. Ultrasonic studies are conducted on certain flavones.

Key Words: Flavones, Ultrasonics, Chrysin and Morin.

INTRODUCTION

Flavonoids have been reported to have numerous medicinal effects, including antioxidant, vasoprotective, anti-inflammatory, mutagenic, anti-viral, anti-bacterial and anti-tumour[1, 2]. Thus, they help protect against cancer and heart diseases. Dietary intake of flavonoids is estimated to be between 23 mg/day to 1000 mg/day[2]. They are absorbed from the gastrointestinal tract and excreted either unchanged or as metabolites in urine and feces. However, little is known about the mechanisms of absorption and metabolism of flavonoids. Several investigations have determined the correlation between flavonoid structure features and anti-oxidative and free radical scavenging properties[1–7].

Flavonoids, also known as bioflavonoids, are colourful antioxidants found in plants. They are responsible for the colours of fruits (*e.g.*, the red or blue of grape and berry skins) and vegetables. Twelve basic classes (chemical types) of flavonoids have been recognized: flavones, isoflavones, flavanones, flavanols, flavanolols, anthocyanidins, catechins (including proanthocyanidins), leukoanthocyanidins, chalcones, dihydrochalcones and aurones. Anthocyanidins and closely related flavonoids such as proanthocyanidins may collectively be referred to as anthocyanosides. The human body cannot produce bioflavonoids, so they must be supplied in the diet. Bioflavonoids are not tree vitamins in the strictest sense, they are sometimes referred to as vitamin P.

A bioflavonoid called chrysin has shown potential as a natural aromatase-inhibitor. Chrysin, for example, is also a potent antioxidant that possesses vitamin-like effects in the body. It has been shown to induce an anti-inflammatory effect. Chrysin has one other property that could add to its libido-enhancing potential.

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Morin is a pentahydroxy flavone. Similar to other flavones, it has both antitumour and antioxidative activities[8–10], but these are not outstanding. Morin might be used as a chemoprevention drug of cancer[11].

EXPERIMENTAL

All chemicals are of Analytical grade and used as received without further purification. IR spectra were recorded on FTIR spectrophotometer model Shimadzu 8700 using KBr disc method. The UV-Vis spectra in 200–700 nm range were recorded on a shimadzu UV-160 A spectrophotometer.

A multifrequency ultrasonic interferometer (Millal Enterprises, New Delhi, Model Mx-4) operating at a frequency of 3 MHz was used to measure the ultrasonic velocity of the experimental solutions. The maximum uncertainity of the velocity was ± 0.1 ms^{-1}.

Preparation of Chrysin Complexes

Cu(II) complexes of chrysin: 2 mmol of chrysin was dissolved in 20 mL of ethanol. To this solution, 1 mmol of copper acetate in water was added and pH was increased to 10 by using 20% (w/w) sodium hydroxide. The solution was boiled and refluxed for 8 h. The mixture was then cooled to room temperature and poured into 500 mL of distilled water. The final mixture was laid for 48 h, then filtered and washed three times with 1 : 3 (v/v) ethanol : H_2O. Pale brown crystals were obtained.

Ni(II) complexes of chrysin: 2 mmol of chrysin was dissolved in 20 mL of ethanol. To this solution, 1 mmol of nickel acetate in water was added. The same procedure as above was adopted and pale violet crystals were obtained.

Preparation of Morin Complexes

Cu(II) complexes of morin: 2 mmol of morin was dissolved in 20 mL of ethanol. To this solution 1 mmol of copper acetate in water was added. The same procedure was adopted as in case of chrysin complex and pale brown crystals were obtained.

Ni(II) complexes of morin: 2 mmol of morin was dissolved in 20 mL of ethanol. To this solution 1 mmol of nickel acetate in water was added. The same procedure was adopted and pale pink crystals were obtained.

RESULTS AND DISCUSSION

The UV-Vis spectra of the chrysin and morin complexes were recorded in ethanol. For both morin and chrysin the band around 263 and 254 nm may be related to cinnamoyl system[12] and the other band around 346 and 350 nm is related to the benzoyl system. After complexation the second piece shifts slightly (7–14 nm) and the second peak shifts by 26–30 nm suggesting the formation of metal-oxygen bond.

The IR spectral data of chrysin, morin and its complexes are given in Table-2. By comparing the spectra of morin with that of the complexes, important

information can be obtained : ν(M—O) peaks appeared at 514, 517 cm^{-1} while the ligand exhibited no such bands. The characteristic ν(C=O) frequency of the ligand carboxyl group[13] (1652 cm^{-1}) changed upon complexation, indicating that this group is formed.

TABLE-1
UV-VIS SPECTRAL DATA OF FLAVONE AND ITS COMPLEXES

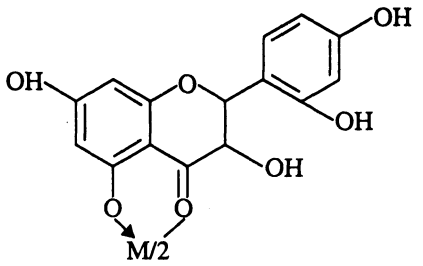
S. No.	Compound	λ_{max} (nm)	
1.	Morin	263	350
2.	Morin-copper complex	270	377
3.	Morin-nickel complex	274	380
4.	Chrysin	254	346
5.	Chrysin-copper complex	260	372
6.	Chrysin-nickel complex	268	374

TABLE-2
IR SPECTRAL DATA (cm^{-1}) OF FLAVONES AND ITS COMPLEXES

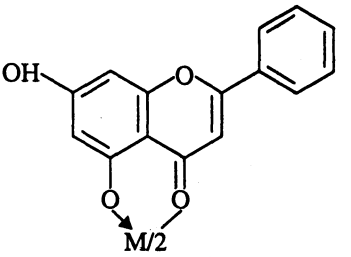
S. No.	Compound	ν(OH)	ν(C=O)	ν(C=C)	ν(C—O—C)	ν(M—O)
1.	Morin	3452 (s)	1652	1570	1245	—
2.	Morin-copper complex	31150 (s)	1420	1554	1243	520
3.	Morin-nickel complex	31172 (s)	1412	1550	1244	517
4.	Chrysin	3320 (sh)	1620	1562	1220	—
5.	Chrysin-copper complex	3100 (s)	1422	1534	1218	515
6.	Chrysin-nickel complex	3122 (sh)	1430	1490	1216	510

Metal oxygen bonds with metal ion (nickel and copper) by deprotonation of the 3-OH or 5-OH groups. However, the ν(C—O—C) frequency[14] remains almost same in the complexes, suggesting the non-coordination of the 3-OH and 2′-OH group of the ligand with the metal(II) ion to form M—O bond in the complexes. The γ ring frequency decreases to 1550, 1554 cm^{-1} in the complexes. This red shift is due to the increase of conjugate effect when the complexes are formed to give new ring.

The IR spectral data of chrysin complexes show that the carbonyl group involved in metal coordination is indicated by the decrease of ν(C=O) group (1430–1422 cm^{-1}). Further, a sharp peak arises at 3450 cm^{-1} which may be due to free hydroxyl group at the 7th position. Further, ν(C=C) decreases to 1490, 1534 cm^{-1} in the complexes. This red shift is due to increase of conjugate effect when the complexes are formed to give new ring. Based on the above spectral evidence, the tentative structures for the flavone complexes may be assigned as



Morin complex M = Cu(II), Ni(II)



Chrysin complex M = Cu(II), Ni(II)

Ultrasonic studies of flavones

The acoustical parameters of morin and chrysin are given in the Tables-3 and 4. In all the flavones, the ultrasonic velocity decreases with increase in concentration. This may be due to strong solute-solvent interaction.

TABLE-3
ACOUSTICAL PARAMETERS OF MORIN-ETHANOL SYSTEM AT 303 K

Concentration ($\times 10^{-4}$ M)	U (m/s)	β ($\times 10^{-10}$ m^2 N^{-1})	Z ($\times 10^6$ kg m^2 s^{-1})	L_f (nm)
1	920	12.72	0.854	0.0707
2	932	12.09	0.887	0.0690
3	958	11.17	0.934	0.0663
4	990	10.19	0.990	0.6330
5	1026	9.24	1.053	0.0603
6	1052	8.73	1.088	0.0586
7	1086	8.11	1.134	0.0565
8	1120	7.62	1.171	0.0547
9	1142	7.30	1.197	0.0536
10	1167	6.99	1.225	0.0524

TABLE-4
ACOUSTICAL PARAMETERS OF CHRYSIN-ETHANOL SYSTEM AT 303 K

Concentration ($\times 10^{-4}$ M)	U (u/s)	β ($\times 10^{-10}$ m^2 N^{-1})	Z ($\times 10^6$ k gm^2 s^{-1})	L_f (nm)
1	945	12.06	0.877	0.0689
2	972	11.12	0.925	0.0661
3	998	10.29	0.973	0.0636
4	1028	9.45	1.029	0.0610
5	1050	8.83	1.078	0.0589
6	1074	8.37	1.111	0.0574
7	1102	7.88	1.150	0.0557
8	1136	7.40	1.188	0.0540
9	1163	7.04	1.732	0.0526
10	1198	6.63	1.276	0.0511

The adiabatic compressibility factor decreases with increase of concentration, may be due to solvation of flavones. The specific acoustic impedance for all flavones increases with increase of concentration. This suggests that the intermolecular attraction is higher in lower concentration than in higher concentration. The free length in all the flavones decreases with increase of concentration. The decrease in free length and increase of ultrasonic velocity suggest that there may be strong molecular interaction between solute and solvent. Due to strong molecular interaction the structural arrangement in the neighbourhood of constituent ion is considerably affected.

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