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COMPLEXATION OF BAICALIN WITH FERROUS (II) AND ITS CHARACTERIZATION

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The complexation of baicalin with ferrous (II) and its characterization are reported. A orthogonal test was used to optimize the conditions of the complexation of baicalin and ferrous (II). The composition and structure of baicalin-ferrous (II) complex were characterized by elementary analysis, TG-DTA methods, and IR- and UV-spectral analysis. Coordination bonding is dependent on the nature of the baicalin and ferrous (II) ion, their ratio, the pH of the solution, etc. The strongest complex forms between baicalin and ferrous (II) (2:1 ratio).

Key words: complexation, baicalin, ferrous (II), characterization.

Scutellaria Baicalensis Georgi (SBG) is the dry root of the labiate plant, the active constituents of which includes baicalin, baicalein, wogonoside, wogonin, and so on. The most important effective component among them is baicalin, a famous natural medicinal herb which has several important biological activities. Moreover, some metal ions have physiological activity, and they are useful for human health. At present, it has been proved that some complexes of baicalin and metal ions have many pharmacological functions [1–6], such as the function of clearing away the superoxygen radical, the functions of antiinflammation and antimetamorphosis, bacteriostasis, etc. The ferrous (II) can enrich the blood. In order to enhance the medicine efficacy of baicalin and the function of enriching the blood by ferrous (II), baicalin was chosen to coordinate with ferrous (II) in this work. The complexation of baicalin and ferrous (II) is an effective method for researching and preparing new medicines.

In this paper, the optimal conditions for the complexation of baicalin and ferrous (II) determined by the L_9 (3^4) orthogonal experimental table and factor significance analysis were as follows: pH of the solution adjusted to 9 with 40% NaOH, baicalin:ferrous (II) = 1:1.5 (mole ratio), ferrous (II):ascorbic acid = 1:1.5 (mole ratio), and reaction at 65° for 6 h. Under these optimal conditions, the yield of baicalin–ferrous (II) complex was 53.05%, and RSD was 5.39% (n = 3). The composition and structure of baicalin–ferrous (II) complex were characterized by elementary analysis, TG-DTA methods, and IR- and UV-spectral analysis.

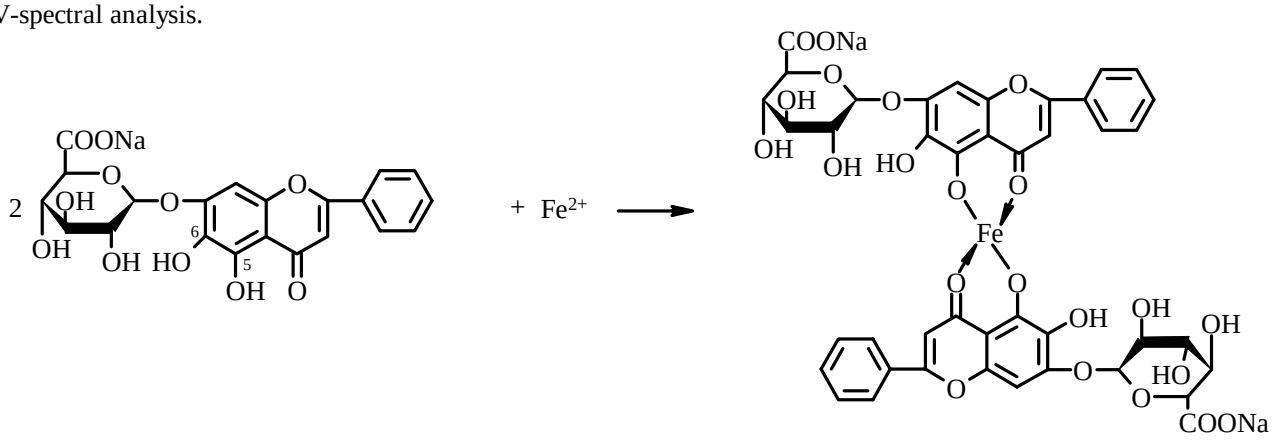

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TABLE 1. Determination Results of Baicalin-Ferrous (II) Complex

Element	C	H	O	Fe	Na
Found, %	45.13	3.74	39.27	5.07	6.79
$Fe(NaL)_2 \cdot 5H_2O$ Calculated, %	46.67	3.88	40.00	5.18	4.26

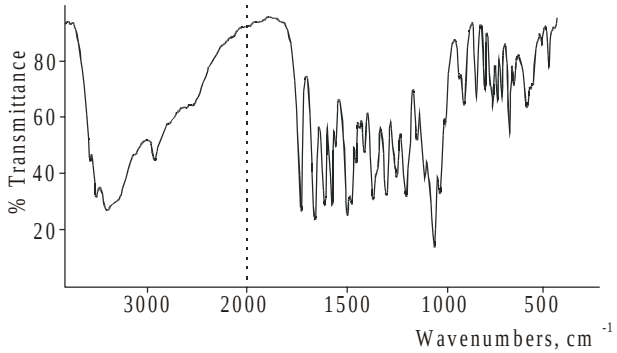

Fig. 1

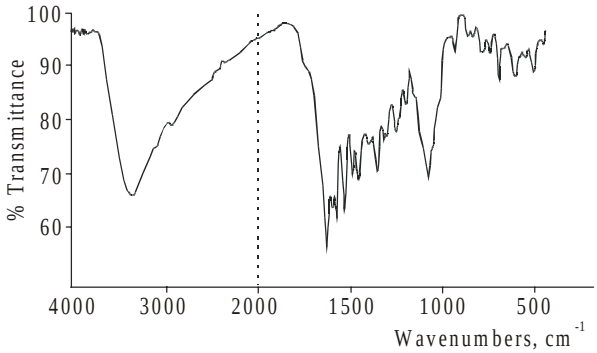

Fig. 2

Fig. 1. The infrared spectrum of baicalin standard.

Fig. 2. The infrared spectrum of baicalin–ferrous (II) complex.

The baicalin–ferrous (II) complex was determined by atomic absorption spectrometry and elementary analysis in order to get the composition of baicalin–ferrous (II) complex. The determination results are shown in Table 1.

As shown in Table 1, the determination value of Na is more than the theoretical calculated value, which was possibly caused by the residual sodium hydroxide, and the determination values of other elements were in accord with the theoretical calculated values basically. As mentioned above, it can be proved preliminarily that the composition ratio of baicalin and ferrous (II) in the complex was 2:1. Because the complex was synthesized in pH 9, the glucuronic acid in the baicalin molecule changed into sodium glucuronate, then reacted with ferrous (II) to form baicalin–ferrous (II) complex.

The infrared spectra of baicalin standard and baicalin–ferrous (II) complex are showed in Fig. 1 and Fig. 2, respectively.

Comparing the infrared spectrum of baicalin standard with the infrared spectrum of baicalin–ferrous (II) complex, it can be seen that the position changes of some characteristic absorption peaks are obvious. In the infrared spectrum of baicalin standard, the peak at 1660 cm^{-1} is due to the quinoid carbonyl group in the baicalin molecule stretching vibration, and the peak at 1726 cm^{-1} is due to the carbonyl group of the carboxyl of the glucuronic acid in the baicalin molecule stretching vibration. But in the infrared spectrum of baicalin–ferrous (II) complex, the peak at 1726 cm^{-1} disappears. It is clear that the glucuronic acid in the baicalin molecule changed into sodium glucuronate. In addition, the new peaks at 1527 cm^{-1} and 1450 cm^{-1} also prove that the glucuronic acid in the baicalin molecule changed into sodium glucuronate. The peak at 1660 cm^{-1} shifts to 1625 cm^{-1}, and the shift to lower frequencies is 35 cm^{-1}, which is due to the formation of the coordination bond of the quinoid carbonyl group in the baicalin molecule and ferrous (II). It reduces the electron cloud density of the quinoid carbonyl group in the baicalin molecule. In the infrared spectrum of baicalin standard, the broad absorption band in the range 3383~3490 cm^{-1} is assigned to the mixed vibration of OH-groups at the C5 and C6 carbon atoms in the baicalin molecule, but it undergoes some changes in the infrared spectrum of the baicalin–ferrous (II) complex because the baicalin molecule coordinates with ferrous (II). From the above, it can be proved that bacailin already coordinates with ferrous (II) to form baicalin–ferrous (II) complex.

The ultraviolet spectra of baicalin standard and baicalin–ferrous (II) complex are shown in Fig. 3.

Comparing the ultraviolet spectra of baicalin standard with baicalin–ferrous (II) complex, it can be seen that in the ultraviolet spectrum of baicalin standard there are two bands at 250 nm and 361 nm except the end absorption; the former originates from a $\pi \rightarrow \pi^*$ transition, termed the B band, and the latter originates from an $n \rightarrow \pi^*$ transition, termed the R band. In the ultraviolet spectrum of baicalin–ferrous (II) complex, the B band at 250 nm shifts to 254 nm, and the R band at 361 nm shifts to 364.5 nm. The position changes of the absorption peaks might be assigned to the coordination of baicalin with ferrous (II) to form baicalin–ferrous (II) complex because the error in the wavelength determined by using a Hitachi U-3010 UV-Vis spectrophotometer in this work was ±0.3 nm.

TABLE 2. The Theoretical and Determination Values of the Weightlessness

Temperature ranges, %	30~184	184~352	352~450
Found weightlessness	8.17	31.24	45.02
Calculated weightlessness	8.33	30.74	45.55

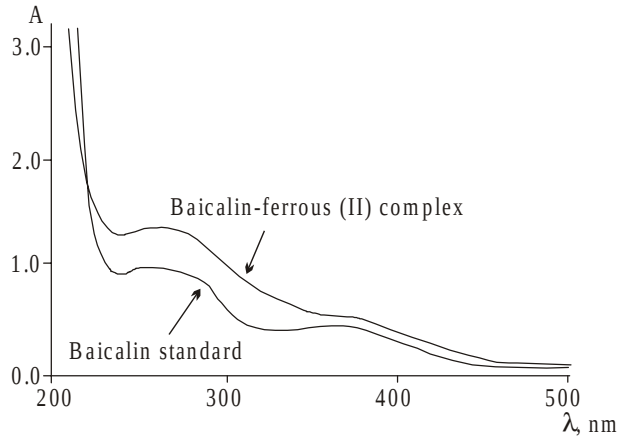

Fig. 3

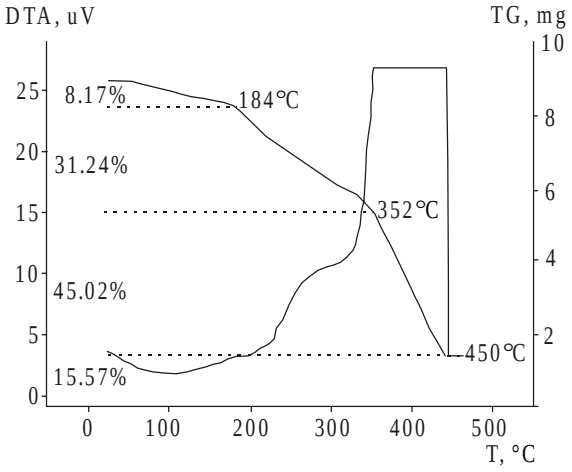

Fig. 4

Fig. 3. The ultraviolet spectra of baicalin standard and baicalin–ferrous (II) complex.
Fig. 4. The TG-DTA curve of baicalin–ferrous (II) complex.

The simultaneous TG-DTA curve for baicalin–ferrous (II) complex is shown in Fig. 4.
As shown in Fig. 4, the weight-loss data (TG curve) from a 8.24 mg sample run under atmosphere pressure and with 10°/min of heating rate showed the slow loss of 5 mole of water from 30°C to 184°C, one mole of carbon dioxide, and 16 moles of water from 184°C to 352°C, and finally the loss of 41 moles of carbon from 352°C to 450°C. In comparison with the DTA curve, the very large exotherm from 352°C to 450°C is due to a combustion reaction, and the relatively small endotherm from 30°C to 184°C is due to water evolved.

With this information the thermal decomposition reactions and phase changes are:

$Fe(NaL)_2 \times 5H_2O\ (s) \rightarrow Fe(NaL)_2\ (s) + 5H_2O\ (g)$

$Fe(NaL)_2\ (s) \rightarrow \frac{1}{2}\ Fe_2O_3\ (s) + Na_2CO_3\ (s) + 41C\ (s) + CO_2\ (g) + 16H_2O\ (g)$

$\frac{1}{2}Fe_2O_3\ (s) + Na_2CO_3\ (s) + 41C\ (s) + 41O_2\ (g) \rightarrow \frac{1}{2}Fe_2O_3\ (s) + Na_2CO_3\ (s) + 41CO_2\ (g)$

In the above formula, the “L” in molecules represents baicalin. It is obviously that the baicalin–ferrous (II) complex loses all of the crystal water from 30°C to 184°C, all of the oxygen and hydrogen from 184°C to 352°C, and finally all of the carbon is burn away from 352°C to 450°C.

The theoretical and determination values of the weightlessness at given temperatures are shown in Table 2.
As shown in Table 2, the theoretical calculated values of the weightlessness are in accord with the determination values of the weightlessness, proving that the composition and structure of baicalin–ferrous (II) complex and its thermal decomposition reactions are reliable.

EXPERIMENTAL

Procedure: Place 0.4230 g of baicalin in a three-necked flask and, add 50 mL of 60% aquecus ethanol solution and 0.4392 g of ascorbic acid. Adjust the pH of the solution to 9 with 40% NaOH, then add 0.3965 g of $Fe_2SO_4 \times 7H_2O$. The reaction was carried out under stirring at 65°C for 6 h. After cooling, filter the contents of the flask and wash the precipitate three times with de-ionized water, then desiccate to constant weight at 50°C in a thermostat. A baicalin–ferrous (II) complex (black powder) was obtained.

Elementary analysis: The contents of C, H and O elements in the baicalin–ferrous (II) complex were determined by a CAROL-ERBA-1106 elementary analyzer, and the contents of Fe and Na elements were determined by a Hitachi Z-8000 polarized zeeman atomic absorption spectrophotometer.

The ultraviolet spectra of baicalin standard and baicalin–ferrous (II) complex were determined by a Hitachi U-3010 UV-Vis spectrophotometer in 1 cm quartz cuvettes.

The infrared spectra of baicalin standard and baicalin–ferrous (II) complex were determined by a Nicolet 210-FTIR spectrophotometer.

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