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Thermal behavior of five free anthraquinones from rhubarb

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Abstract The thermal behavior of five free anthraquinones (chrysophanol, emodin, physcion, aloe-emodin, and rhein) from rhubarb had been investigated using TG, DTG and DTA technique. The results show that all the free anthraquinones have the similar TG and DTG curve shapes, however, due to the substituted groups attached on the skeleton of 1,8-dihydroxy anthraquinone are different, every anthraquinone has different mass loss features. Moreover, all the DTA curves of these free anthraquinones have two obviously characteristic peaks, but with special curvilinear types, peak location and peak values. Therefore, thermal analysis (TA) characteristics of anthraquinones above mentioned could be established, and it is possible to easily distinguish these anthraquinones by using TA technique.

Keywords Free anthraquinones · Rhubarb · Thermal analysis

Introduction

Rhubarb is a famous pharmaceutical plant (named Dahuang in Chinese) that displays diverse pharmacological activities such as bacteriostatic, antiviral, antifungal, anti-inflammatory, antitumor etc. [1–5]. It contains a variety of free anthraquinone compounds (chrysophanol, emodin, physcion, aloe-emodin, and rhein) and their corresponding glycosides, the total content of which varies from 2% to 5% [6]. They are known as the major active constituents of rhubarb. The structures of these free anthraquinones are shown in Scheme 1. The skeleton of these compounds is anthraquinone with hydroxyl groups at C-1 and C-8 positions.

In the recent years, thermal analysis (TA) technique is increasingly recognized as an important analytical technique because of its simple, high-efficiency, ultra-small sample volume, and ease of sample preparation as well as curve analysis [7, 8]. Thus, TA has been widely applied in the drug analyzing fields such as chemical identification, determination of the physical and chemical constants, the investigation of active compounds of natural products and quality controlling of medicinal herbs [9–11], and it is playing a more important role in medical research and quality-testing of drug. Furthermore, applications of thermoanalytical techniques in pre-formulation stages in solid dosage form development have increased immensely. In particular differential scanning calorimetric have been proposed as a rapid method for evaluating physicochemical interactions between components of the formulation and therefore selecting excipients with suitable compatibility [12]. HPLC has always been used for the analysis of free anthraquinones from rhubarb [13, 14], but there are little reports on the thermal characterization of these chemical components. In our previous paper [15], the thermal behavior of aloe-emodin, chrysophanol and physcion and their kinetics have been investigated under non-isothermal conditions by means of different thermal analysis (DTA) and thermogravimetry (TG), the aim of this paper was to put emphasis on thermal decomposition kinetics. In this work, the characteristic patterns of five free anthraquinones from rhubarb were studied employing TG, DTG and DTA

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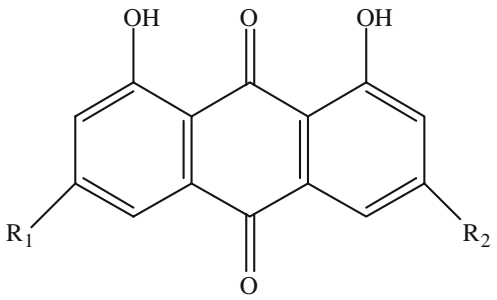

No.	Samples	R_1	R_2
A	Chrysophanol	CH_3	H
B	Emodin	CH_3	OH
C	Physcion	CH_3	OCH_3
D	Aloe-emodin	H	CH_2OH
E	Rhein	H	COOH

Scheme 1 Structures of five free anthraquinones

techniques in order to establish a simple and effective method to identify these products quickly.

Experimental

Materials and chemicals

The chrysophanol (No. 0795-9803), emodin (No. 110756-200110), physcion (No. 110758-200307), aloe-emodin (No. 07959803), rhein (No. 110756-200110) are standard samples purchased from National Institute for the Control of Pharmaceutical and Biological Products. The purity of all the five free anthraquinones was more than 99% wt, and their melting points were measured with XT-4A micro-melting point apparatus.

Thermogravimetric analysis

TG, DTG and DTA curves were obtained simultaneously by using a Pyris/Diamond TG analyzer (produced from Perkin-Elmer, USA). The measurements were carried out under a dynamic atmosphere of dry nitrogen at a flow rate of 150 ml/min over a temperature interval of 25.0–700.0 °C at a heating rate of 10 °C/min. Platinum crucibles were used to hold 5.0 ± 0.5 mg samples for analysis. Highly sintered α-Al_2O_3 was used as the reference material.

Elemental analysis

The contents of carbon (C%, mass basis) and hydrogen (H%, mass basis) were performed in elemental analysis instrument of elementar Vario EL (made in Germany) for the residue of compound D (aloe-emodin).

Results and discussion

TG characteristic of five free anthraquinones

The TG curves of five free anthraquinones from rhubarb are shown in Fig. 1. The analytical results obtained from TG curves are given in Table 1. As shown in Fig. 1 and Table 1, there are both similarities and differences concerning the characteristic curves and decomposition process because these free anthraquinones have the same skeleton (1,8-dihydroxy anthraquinone), but different groups. The chrysophanol (curve A), emodin (curve B), physcion (curve C) and rhein (curve E) have one stage decomposition process, with mass loss of 93.4%, 98.3%, 99.5% and 93.9%, respectively. But the aloe-emodin (curve D) shows a two stage mass loss process, the first stage of which is in the temperature range of 243–369 °C, with a mass loss of 41.7% and the other stage of decomposition process occurs in the temperature range of 465–640 °C, with a mass loss of 8.3%. From the aspect of element constitutes, aloe-emodin residue at the various temperatures are mainly composed of carbon, oxygen and hydrogen. The contents of carbon (C %), hydrogen (H %) and oxygen (O %) in the residue at the temperature of 600 °C is as follows: found for C 76.56, H 3.61; calculated for O 19.83. Compared with aloe-emodin (curve D), the mass loss of other free anthraquinones are relatively high.

Furthermore, the chrysophanol, emodin and physcion which contain the same substituted group R_1 (CH_3), but different groups R_2 such as H, hydroxyl and methoxy display distinguishing temperature of extrapolated onset and stability. From their TG curves, it is shown that the decomposition point of chrysophanol is near to physcion

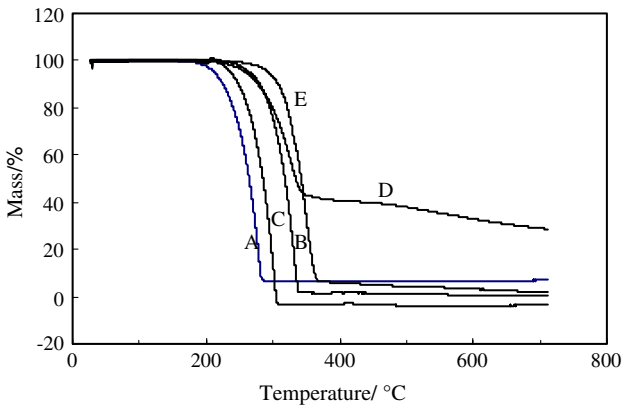

Fig. 1 TG curves of five free anthraquinones (*A*) Chrysophanol; (*B*) Emodin; (*C*) Physcion; (*D*) Aloe-emodin; (*E*) Rhein

Table 1 Characteristic data of the thermal analysis for five free anthraquinones

Samples	Melting point (°C)	Temperature of the extrapolated onset (°C)	Mass loss temperature range (°C)	Mass loss (%)
Chrysophanol	196–198	231	189–293	93.4
Emodin	256–257	281	245–352	98.3
Physcion	203–207	248	200–317	99.5
Aloe-emodin	223–224	276	243–369	41.7
			465–640	8.3
Rhein	321–322	312	252–384	93.9

Table 2 Temperatures of five free anthraquinones at different mass loss

Samples	$T_{5\%}$ (°C)	$T_{25\%}$ (°C)	$T_{50\%}$ (°C)	$T_{75\%}$ (°C)	$T_{90\%}$ (°C)
Chrysophanol	212	246	264	276	281
Emodin	265	300	317	329	334
Physcion	236	267	284	296	301
Aloe-emodin	259	307	334	–	–
Rhein	294	326	342	353	362

and their mass loss occur between 189–293 °C and 200–317 °C, but the emodin is stable before 281 °C and its temperature range is 245–352 °C due to the substituted group hydroxyl. Aloe-emodin and rhein with the different substituted group (hydroxymethyl and carboxyl) display considerable differences regarding to the temperature of the extrapolated onset (Table 1) (276–312 °C), and mass loss (41.7 and 93.9%). In addition, the temperatures of five free anthraquinones at different mass loss are shown in Table 2.

DTG characteristic of five free anthraquinones

The DTG curves of five free anthraquinones from rhubarb were represented in Fig. 2. As known, the sharp of the DTG curve is related with the thermal decomposition process of the sample. It can be seen that the DTG curves of chrysophanol, emodin, physcion and rhein are similar with each other, each having a sharp and high DTG peak, with the peak temperature of 281, 335, 303 and 352 °C, respectively. However, the DTG curve of aloe-emodin displays a blunt and low DTG peak, whose peak temperature (first peak) is 325 °C. When TG curves have different initial-end mass loss temperature and mass loss, their DTG curves have relevant peak location and peak intensity. As for aloe-emodin, it has two DTG peaks and behaved differently when compared with the other free anthraquinones. The first peak is broader and stronger, by contrast, the second one is so flattened that almost could not be noticed. These differences are also attributed to the differences of

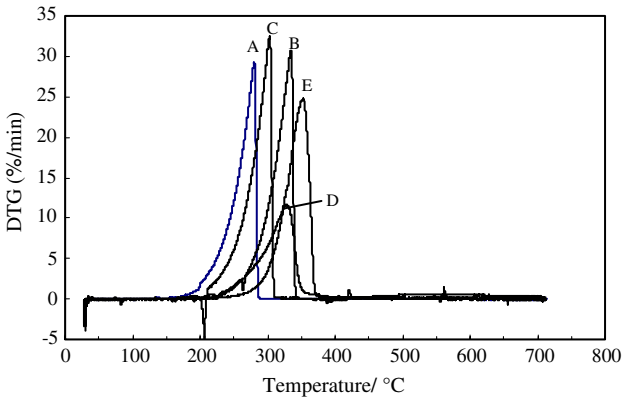

Fig. 2 DTG curves of five free anthraquinones (*A*) Chrysophanol; (*B*) Emodin; (*C*) Physcion; (*D*) Aloe-emodin; (*E*) Rhein

R_1 and R_2 groups attached on the same skeleton (1,8-dihydroxy anthraquinone). Hence, by analyzing the parameters of DTG peak temperature, intensity and initial-end mass loss temperature, the five free anthraquinones could be distinguished easily.

DTA characteristic of five free anthraquinones

The DTA curves of five free anthraquinones from rhubarb were represented in Fig. 3. As can be seen, the DTA curves of all of chrysophanol, emodin, physcion and rhein show two obviously endothermic peaks, the first of which is sharp and strong while the second one is a bit flatted and weak. The first peak temperature and the melting point are very close to each other, which indicated that the melting process causes the first endothermic peak. Furthermore, the second DTA peak temperature approaches to the DTG peak temperature, illustrating that the second endothermic peak was caused by the thermal decomposition process. However, the temperature of two peaks and the temperature gap between two peaks are different from one sample to another, so they could be distinguished clearly. As for aloe-emodin, it has two DTA peaks as well, the first one (a endothermic peak) is also caused by the melting process similarity, and the second one (a exothermic peak) could be explained by the fact that residual chemical components

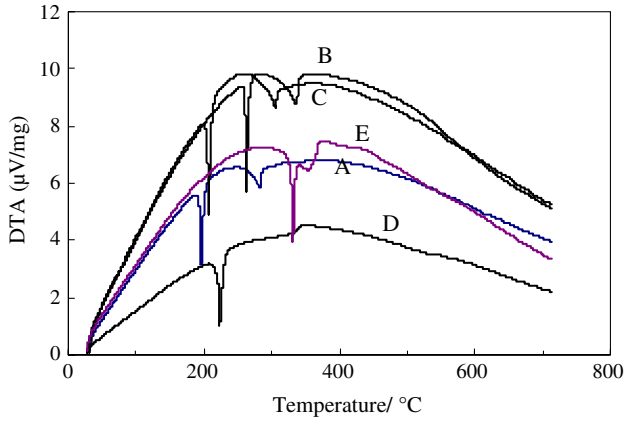

Fig. 3 DTA curves of five free anthraquinones (*A*) Chrysophanol; (*B*) Emodin; (*C*) Physcion; (*D*) Aloe-emodin; (*E*) Rhein

Table 3 Characteristic data of DTA for five free anthraquinones

Samples	Melting point (°C)	DTG peak temperature (°C)	T_1 (°C)	T_2 (°C)
Chrysophanol	196–198	281	196	282
Emodin	256–257	335	262	336
Physcion	203–207	303	206	305
Aloe-emodin	223–224	325	223	350
Rhein	321–322	352	331	354

T_1 temperature of the first DTA peak

T_2 temperature of the second DTA peak

decompose or react with heat evolving. Thus the DTA curve of aloe-emodin is quite distinct when compared with other free anthraquinones'. The difference of DTA curves of five free anthraquinones depends on the substituted groups and their position attached on the same skeleton (1,8-dihydroxy anthraquinone), which made a notable impact on curve shape, peak temperature and location. Specific parameters of DTA peak was given in Table 3. According to these values, these five free anthraquinones could be distinguished clearly.

Conclusions

Five free anthraquinones (chrysophanol, emodin, physcion, aloe-emodin, and rhein) from rhubarb having the same skeleton (1,8-dihydroxy anthraquinone), but due to the different substituted groups, they exhibit different thermal properties. By analyzing the parameters of thermal analysis, combined with peak patterns, peak position and peak values of the DTA and DTG peaks, these five free anthraquinones can be clearly distinguished. Therefore, the thermal analysis is an effective method for distinction and identification of these free anthraquinones on the basis of their characteristic patterns.

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