ELSEVIER

Thermochimica Acta 392–393 (2002) 79–84

thermochimica acta

www.elsevier.com/locate/tca

Thermal characterization of the quercetin and rutin flavonoids

Everaldo Moreira da Costa, José Maria Barbosa Filho, Ticiano Gomes do Nascimento, Rui Oliveira Macêdo*

Laboratório de Tecnologia Farmacêutica/UFPB, Campus I, João Pessoa, Paraíba, CEP 59059-900, Brazil

Received 7 November 2000; accepted 22 July 2001

Abstract

The objective of the present work was to characterize rutin and quercetin by thermogravimetric (TG) and DSC coupled to a photovisual system. The kinetic parameters, rate constant (k), activation energy (E) and reaction order (n) were determined by isothermal and dynamic TG measurements. The results from the TG curves showed the decomposition of the two substances occurring in four stages. The DSC data reveal the presence of several phase transitions for the two compounds. The DSC–photovisual method confirmed the decomposition and polymorphic process for the quercetin and rutin, respectively, according to the literature.

Keywords: TG; DSC–photovisual; Quercetin and rutin flavonoids

1. Introduction

The chemical structures of natural products have been an important contribution in the investigation of traditional medicinal plants. The extraction and purification methods used for plant compounds have an influence on the physical and chemical stability of the pharmaceutical compounds presented. The action of the elevated temperature can cause alterations at the original chemical composition in that part of the plant that is being studied.

The studies concerning the thermal behavior of naturally occurring substances, using thermal techniques, are quite rare in the literature. Thermal studies using terpenoids [1] and gallic acid [2] have been presented as examples for studying natural product chemistry. The objective of this work was to determine the thermal parameters of quercetin and rutin flavonoids using thermogravimetric (TG) and DSC coupled to a photovisual system, which are complementary techniques, in the identification of these products.

2. Experimental

The flavonoid, quercetin dihydrate, and rutin dihydrate were acquired from MERCK.

The TG curves were obtained using a Shimadzu thermobalance, model TGA-50H, using an alumina cell, with heating rates of 5.0, 10.0, 15.0, 20.0 °C/min, in nitrogen and air atmospheres, at a gas flow of 20.0 ml/min over a temperature interval of 25.0–900.0 °C. The amount of sample used was 10.0 mg. The TG-isothermal curves were obtained over 4 h at temperatures before the thermal decomposition reaction, as observed in the TG dynamic profiles. The DSC curves were obtained using a Shimadzu calorimeter, model DSC-50 coupled to the photovisual system composed of an Olympus microscope connected to

* Corresponding author.
E-mail address: ruimacedo@ltf.ufpb.br (R.O. Macêdo).

0040-6031/02/$ – see front matter
PII: S0040-6031(02)00087-4

a Sanyo camera, model VCC-D520, with a nitrogen atmosphere of 50.0 ml/min, a heating rate of 10.0 °C/min, up to the temperature of 500.0 °C. The samples were packed in an aluminum cell with a mass about 2.10 mg. The images were captured from the DSC coupled to the photovisual system at a similar temperature and time compared to the conventional DSC. The TG and DSC curves were analyzed with the aid of the TASYS software by Shimadzu.

The kinetic parameters, activation energy (E), reaction order (n) and pre-exponencial factor (A) were obtained by the methods of Ozawa [3](OZ), Coats and Redfern [4](CR), Madhusudanan et al. [5](MD), Horowitz and Metzger [6] (HM) and Van Krevelen et al. [7](VK). The rate constant (k) for the thermal decomposition reaction was calculated using the classical Ahrrenius' equation.

3. Results

The TG curves for quercetin and rutin showed that thermal decomposition for both of these substances occurred in four stages, and whose mass loss depended on the gaseous atmosphere used and the heating rate (Table 1).

The DSC curve for quercetin presented three phase transition peaks. The first, at 116 °C was the water loss. The shoulder of this peak with onset temperature at 73 °C with a direction change calculated by the tangent method at 94 °C, suggested that one molecule rearranged, corresponding to a transformation of the molecules hydrated in the anydrous form, confirming the thermal behavior mentioned by the literature [8].

The comparison of the TG/DSC curves and DSC photovisual (Figs. 1 and 2), where picture A (room temperature) and B (125 °C) of the quercetin showed that the shoulder in the first peak of phase transition (DSC curve), at 94 °C, occurred without a mass loss (TG curve) but with heat variation evidencing structural changes.

Rutin presented a different calorimetric behavior, where several phase transition were observed. The DSC curves reveal the presence of rutin polymorphism. The comparison of the TG and DSC curves with the DSC–photovisual picture of the rutin (Fig. 2) reveals that the rutin suffers molecular transformation with a mass loss in the first two stages (TG curve) which are related to the loss of two water molecules to become anhydrous [8].

Figs. 3 and 4 represent the TG-isothermal curves for quercetin and rutin, respectively.

Table 2 shows the kinetic parameters, reaction order (n), activation energy (E) and pre-exponencial factor (A) for the quercetin and rutin. These verifies that the rutin presents a major contribution to the activation energy.

Table 1
Thermogravimetric characteristics of the quercetin and rutin

Atmosphere	Decomposition stage			
	First	Second	Third	Fourth
Air				
Quercetin				
Temperature interval (°C)	103–342	342–428	428–605	–
Mass losses (%)	10.0	18.8	71.2	–
Rutin				
Temperature interval (°C)	50–117	117–261	261–422	422–604
Mass losses (%)	3.1	4.3	23.1	69.5
Nitrogen				
Quercetin				
Temperature interval (°C)	29–136	136–366	366–529	529–874
Mass losses (%)	7.9	15.1	20.4	13.31
Rutin				
Temperature interval (°C)	25–139	139–304	304–511	511–892
Mass losses (%)	5.0	15.8	15.5	13.3

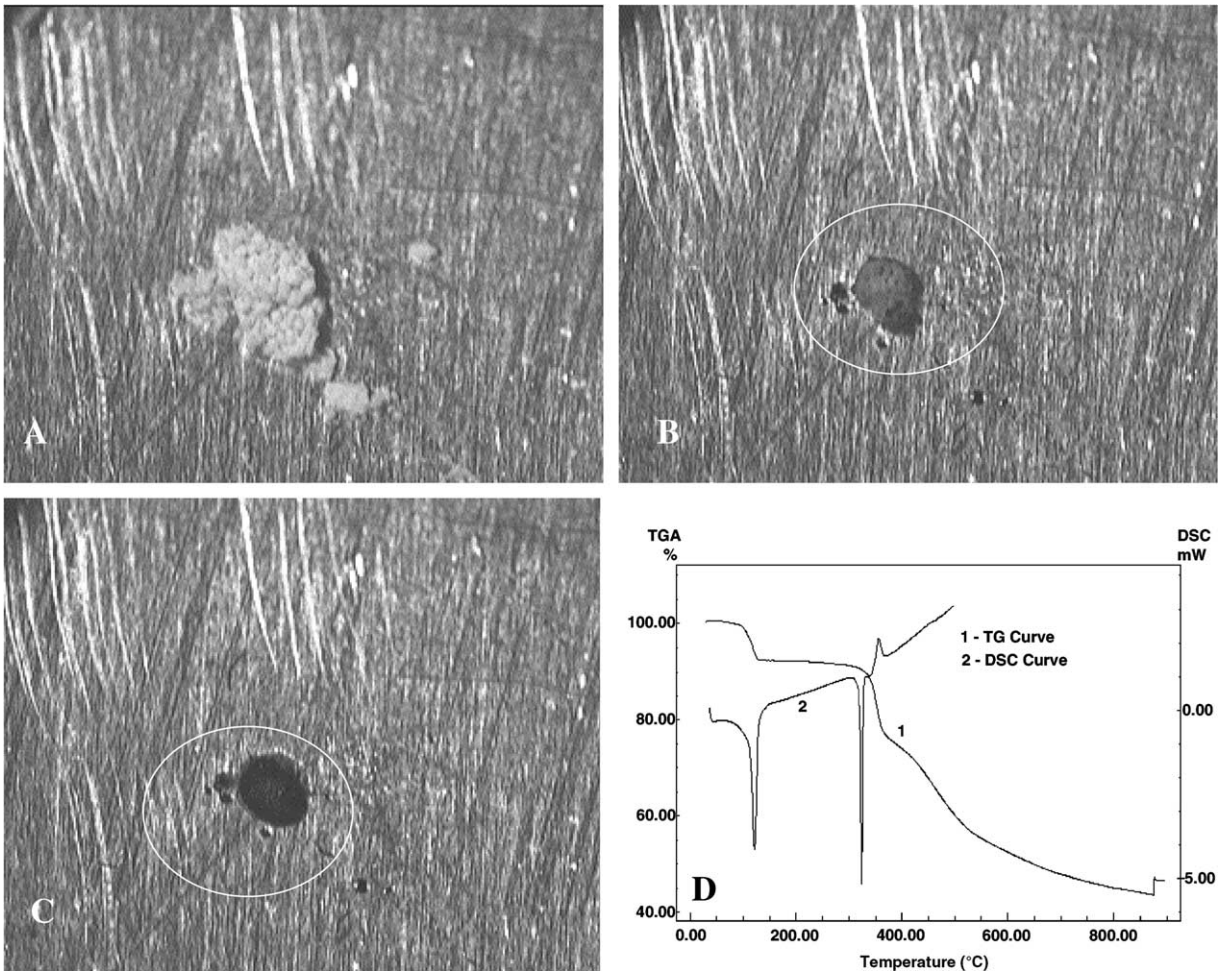

Fig. 1. Pictures: (A) room temperature; (B) 125 °C; (C) 314 °C and (D) TG/DSC curve of the quercetin under nitrogen atmosphere.

Table 2
Kinetic characteristics for the quercetin and rutin

Substance	Methods				
	OZ	CR	MD	HM	VK
Quercetin					
n	0.6	0.5	0.6	0.6	0.6
E (kJ/mol)	103.7	102.6	104.9	117.4	108.6
A (s^{-1})	2.7×10^{13}	3.0×10^{11}	6.7×10^{11}	3.3×10^{13}	3.1×10^{17}
Rutin					
n	1.3	1.3	1.4	1.3	1.3
E (kJ/mol)	122.9	123.6	128.3	132.0	123.4
A (s^{-1})	4.6×10^{15}	1.0×10^{14}	4.5×10^{14}	1.2×10^{15}	1.5×10^{19}

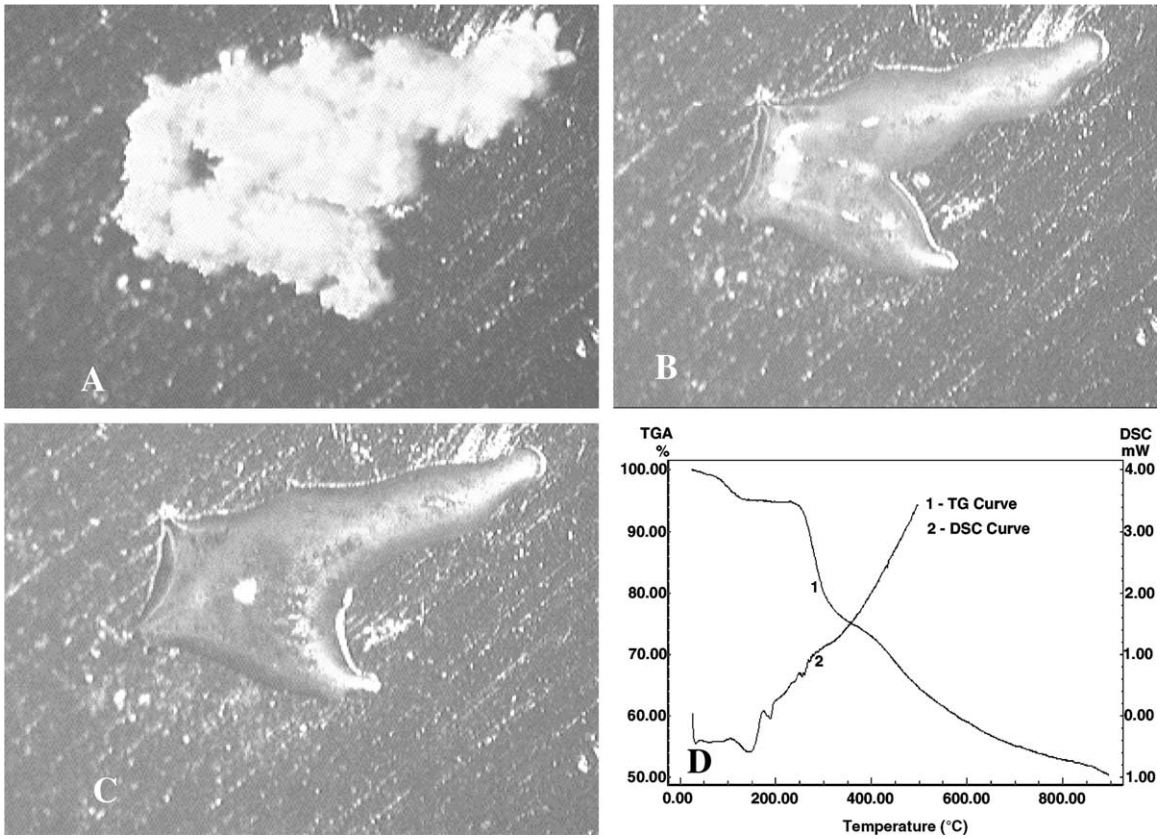

Fig. 2. Pictures: (A) room temperature; (B) 180 °C; (C) 214 °C and (D) TG/DSC curve of the rutin under nitrogen atmosphere.

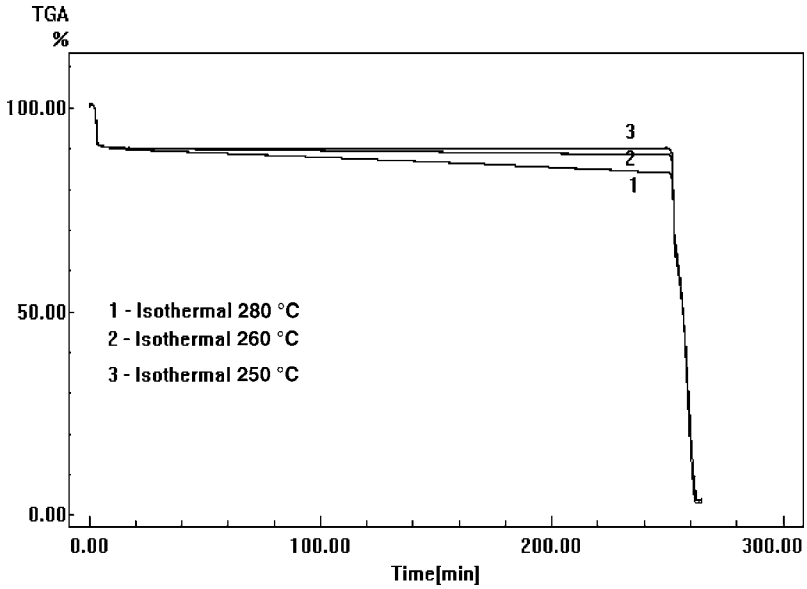

Fig. 3. TG-isothermal curves for the quercetin.

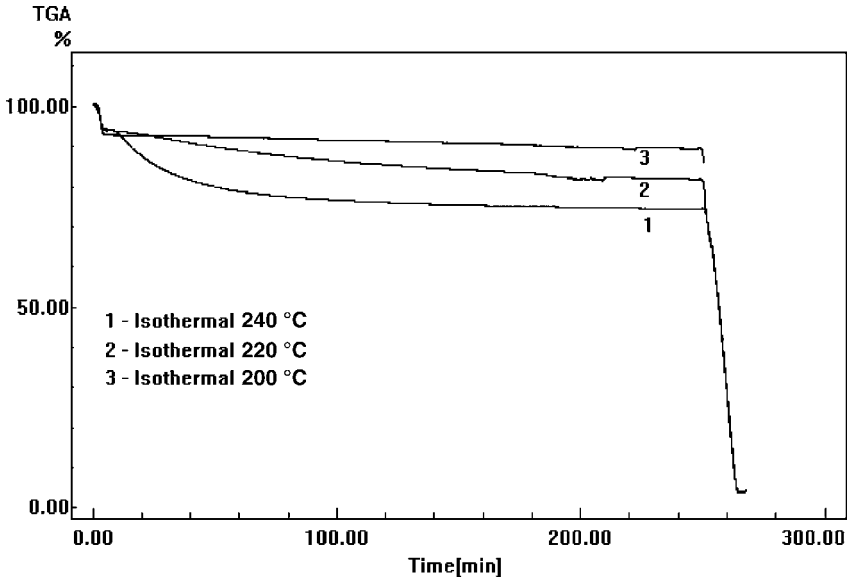

Fig. 4. TG-isothermal curves for the rutin.

Table 3
Rate constants for the thermal decomposition reactions

Temperature (°C)	Rate constant for the thermal decomposition reaction (k, s^{-1})	
	Quercetin	Rutin
200	–	1.79×10^{-6}
220	–	1.91×10^{-5}
240	–	1.22×10^{-4}
250	4.54×10^{-7}	–
260	1.21×10^{-6}	–
280	1.35×10^{-5}	–

Table 3 shows the rate constants (k) for the thermal decomposition reaction for the quercetin and rutin. The TG data treated statistically showed that the thermal decomposition obeyed a zero-order reaction. The rate constants calculated by Arrhenius expression evidenced larger values for rutin as compared to quercetin, thus indicating that quercetin is more stable than rutin.

4. Discussion

The comparison of the TG data for quercetin and rutin, in air atmosphere, reveals that the substances show different thermal behaviors. This fact can be explained by the presence of sugar in the rutin molecule. Another aspect observed was that the stoichiometry for decomposition reaction, where the mass losses in the first three stages for the quercetin and rutin, respectively, one 62.2 and 30.5%. This corresponds to 62.2% of the common structure between these two substances, and provides evidence that the sugars in the rutin are decomposed in the fourth stage (Table 1).

The photovisual system (Fig. 1) showed that the first peak of quercetin, at 116 °C, is related to a decomposition process with water loss. This is confirmed by the mass loss verified in the TG curve. In picture B a volume decrease of the sample is not observed, however, a coloration change was verified. Picture C reveals a volume reduction with a coloration change at 314 °C for the quercetin. The phase transition peak in conventional DSC at 323 °C seems to be characteristic of a melting point and occurs without mass loss in the TG curve. The third peak at 344 °C, a exothermal peak, corresponds to the initial decomposition process for the quercetin [8].

The rutin presented in the photovisual system the first peak of the phase transition (DSC curve) at 177 °C and picture B at 180 °C confirms the change in the sample behavior that should be related to the

molecular rearrangement of the rutin polymorph in a plastic substance. The subsequent peaks of phase transition at 214, 230, 240, 248 °C (DSC curve) and picture C at 214 °C provide evidence for the boiling process with chemical reaction without mass loss in the TG curve. The data obtained in the DSC curve are coherent with those presented by the literature [5] that shows the decomposition of rutin occurring at 214 °C with effervescence (Fig. 2).

The TG isothermal profile for quercetin showed that this flavonoid presents only one decomposition step, but the rutin flavonoid presented two decomposition stages as determined by the tangent TG analysis (Fig. 4). The sugar in the rutin flavonoid could change the thermal decomposition rate in this compound, thus decreasing the decomposition temperature and the isothermal profile.

The kinetic parameters obtained by dynamic and isothermal TG methods allowed one to compare the activation energy with the rate constant values that showed corresponding agreement with the classical Arrhenius equation.

5. Conclusion

The analysis of the TG, DSC and DSC–photovisual data, obtained for quercetin and rutin allows one to characterize the thermal processes involved in the thermal decomposition reaction between these two compounds.

The thermal characteristics of the flavonoids quercetin and rutin did not allow the determination of the melting point and degree of purity as a function of the decomposition which occurs before the melting of the substances.

Acknowledgements

The authors wish to thank CNPq and MS/ANVS and FINEP for the financial support given for this research.

References

[1] R.O. Macêdo et al., J. Therm. Anal. Calorimetry 56 (1999) 1353–1357.
[2] R.O. Macêdo et al., Anais da Assoc. Bras. de Química 47 (1998) 313–315.
[3] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881.
[4] A.W. Coats, J.P. Redfern, Nature 201 (1964) 68.
[5] P.M. Madhusudanan, K. Krishnan, K.N. Ninan, Thermochim. Acta 221 (1993) 13.
[6] H.H. Horowitz, R. Metzger, Anal. Chem. 35 (1964) 10.
[7] W. Van Krevelen, C. Van Heerden, F. Hutjens, Fuel 30 (1951) 253.
[8] The Merck Index, An Encyclopedia of Chemicals, Drugs and Biologicals, 12th edition, Merck & CO Inc., Whitehouse Station, NJ, 1996.