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Characterization of enalapril maleate: An approach using thermoanalytical, thermokinetic and spectroscopic techniques

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Abstract: Enalapril maleate is a widely used drug for the treatment of cardiovascular diseases. Its mechanism of action is to inhibit the angiotensin-converting enzyme selectively. Therefore, it is metabolized to enalaprilat by liver cells. The thermal behaviour of enalapril maleate was investigated by simultaneous thermogravimetry and differential scanning calorimetry (TG-DSC), as well as with evolved gas analysis by simultaneous thermogravimetry and differential scanning calorimetry coupled infrared spectroscopy (TG-DSC–FTIR). The results provided information on thermal stability, purity, thermal decomposition steps and the main products formed in the heating. The enalapril maleate was found to be stable up to 148 °C. Above this temperature causes thermal degradation of the substance, which occurs in two stages in an inert atmosphere (N_2) and three stages in an oxidizing atmosphere (air). Through the TG-DSC–FTIR the released gases were identified as maleic anhydride as a thermal decomposition intermediate. DSC analysis showed that the material obtained 99.5 % purity, which indicates high purity. Employing both the Kissinger and Friedman equations, alongside model fitting methods, the study reveals key insights. The Kissinger method unveils an apparent activation energy of 47.07±15.45 kJ mol^{-1} for the complete thermal breakdown, a finding corroborated by the Friedman method. Model fitting methods, the article applies them, yielding an apparent activation energy of 55.7±3.4 kJ mol^{-1} with a three-dimensional diffusion thermal degradation model.

Keywords: thermal stability; thermal decomposition; kinetic characterization.

INTRODUCTION

Enalapril maleate (Fig. 1) is a prodrug of (*Z*)-but-2-enedioic acid; (2*S*)-1-{(2*S*)-2-[((2*S*)-1-ethoxy-1-oxo-4-phenylbutan-2-yl)amino]propanoyl}pyrrolidine-2-carboxylic acid-1-[2-(1-ethoxycarbonyl-3-phenyl-propyl)aminopropanoyl]

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pyrolidine-2-carboxylic acid ((*Z*)-carboxylic acid), which undergoes hydrolysis of the ethyl ester in hepatic cells and is converted to enalaprilat, considered its bioactive form. Its main indication is for use in cases of heart disease, such as systemic arterial hypertension and congestive heart failure. It acts by inhibiting the angiotensin-converting enzyme, competitively by inhibiting the biotransformation of angiotensin I in angiotensin II, which promotes the therapeutic effect.[1–8]

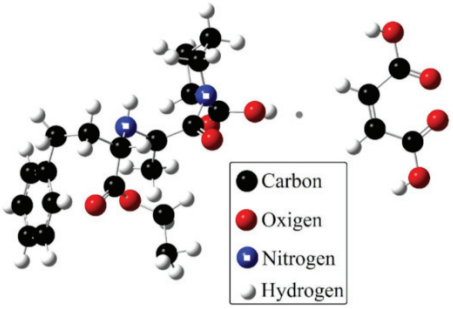


Fig. 1. Structural representation of enalapril maleate.

For the drug to be safe and effective, strict quality control must be done, which may be realized through thermoanalytical techniques. The literature demonstrates the importance of thermal analysis to characterize and evaluate the purity of drugs, active pharmaceutical ingredients (IFAs), excipients and medications since thermogravimetry and DSC are analytical, quantitative and comparative techniques.[9] These techniques are considered capable of quickly and reproducibly producing the expected results. DSC is used in the pharmaceutical industry as an important analytical tool to identify and test the purity of active principles, and it produces results quickly and efficiently. DSC is already accepted in countries such as the United States of America for quality control of raw materials used in pharmaceutical products.[8–11]

The use of analytical techniques to characterize pharmaceuticals is important. An example of this importance that can be cited is that by DSC curves, infrared, and Raman spectra, it was possible to elucidate two polymorphic forms of enalapril.[12,13]

Thus, given the importance of quality control of raw materials and pharmaceutical products, the objective of this study was to perform thermal characterization and determine the purity of the raw material, enalapril maleate, which is one of the most prescribed drugs for cardiovascular changes. In this way, to obtain information not yet described in the literature. Such as thermal and chemical stability, thermal decomposition, and the main products and gaseous intermediates released during the thermal decomposition process.

EXPERIMENTAL

Enalapril maleate was purchased commercially in a compounding pharmacy and stored in an amber bottle for further analysis.

The DSC curves were obtained in a DSC-Q200 calorimeter (TA Instr. Co., USA), which was calibrated according to the manufacturer's recommendation, and a standard indium 99.99 % purity, m.p. 156.6 °C and $\Delta H = 28.56$ J g^{-1} were used to check the calibration. A mass sample was around 2 mg and the sample was heated from 130 to 180 °C using an aluminium crucible with a perforated lid with a 1.0 mm orifice, under an N_2 atmosphere, with a flow rate of 50 mL min^{-1} and a heating rate of 1 °C min^{-1}. Universal Analysis software was used to determine the purity of the sample.[14,15]

Simultaneous TG-DTG–DSC curves were obtained on a thermal analysis System, TG--DSC1, Mettler Toledo. The purge gases were dried in air and N_2 with a flow of 50 mL min^{-1}, with a heating rate of 10 °C min^{-1}, weighing about 10.0 mg. Alumina crucibles were used to record the DSC and TG curves.[16]

The thermokinetic study was conducted using the thermal decomposition curves obtained through thermogravimetry on a calibrated Netzsch STA 449 F3 Jupiter® apparatus following the manufacturer's instructions. The analyses adhered to the recommended parameters in the literature,[17-20] with a sample mass of approximately 1.0±0.1 mg. The temperature range spanned from 30 to 700 °C in an inert N_2 atmosphere (99.99 %), employing the following heating rates: 2, 4, 6, 8 and 10 °C min^{-1}. The thermokinetic treatment was performed with THINKS, free open-source thermokinetic software.[21]

The analysis of the detected gases (TG-DSC–FTIR) was performed using a thermogravimetric analyser coupled to a Nicolet FTIR spectrophotometer with gas cells and a DTGS detector. The oven was coupled to the heated gas cell (250 °C) through a heated current (225 °C) stainless steel transfer line with 3.0 mm diameter and 120 cm length, both purged with 50 ml min^{-1}. The identification of the gaseous products was based on the reference spectra available in the spectrometer software (Omnic 8.0) and literature data.[14–16]

RESULTS AND DISCUSSION

Thermoanalytical and spectroscopic study

The purity determination of enalapril was based on the assumption that an impurity will depress the melting point of a pure material for which the fusion was characterized by melting point (T_0) and a melting enthalpy ($\Delta H_{\text{melt.}}$). The effect of a T_0 impurity on enalapril was determined by the DSC method based on the Van't Hoff equation (Eq. (1)).[16,22] The DSC curve obtained shows an endothermic event corresponding to the melting point of enalapril at 154 °C ($\Delta H_{\text{melt.}} = 29.6$ kJ mol^{-1}); the purity was 99.5 %, indicating the high purity of the material:

$$\ln \frac{k_2}{k_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad (1)$$

The simultaneous TG-DSC curves in dynamic dry air and N_2 atmospheres of enalapril are shown in Fig. 2a and b. In both conditions studied (Pyrolysis (N_2) and oxidation (air)), enalapril was stable up to 148 °C and, above this temperature, the TG-DSC curves showed that the thermal decomposition occurs in two (N_2) and

three (air) stages between 148–330 °C and 148–605 °C, respectively, the with total mass loss of 99.85 (N_2) and 99.95 % (air). The percentages indicated that the compound has no inorganic impurities.

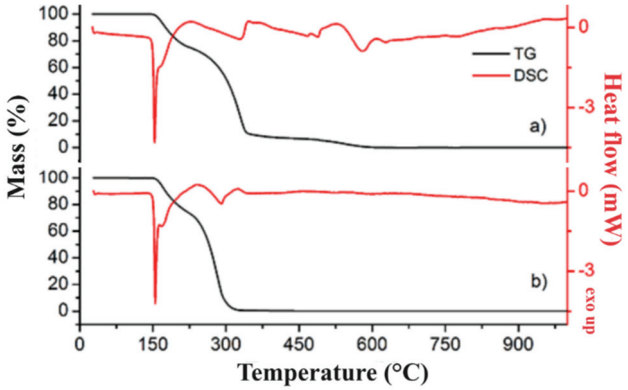


Fig. 2. Enalapril maleate TG-DSC simultaneous curves in dynamic dry air (a) and N_2 (b) atmosphere (mass (air) = 10.225 mg, mass (N_2) = 10.125 mg).

The TG-DSC curves indicate that the first mass loss occurred slowly between 148 and 230 °C (air) and 148 and 220 °C (N_2), with loss mass of 25.4 and 25.5 %, respectively. At this stage, for both analysis conditions (air and N_2) the DSC curves have an endothermic peak at 154 °C with a shoulder at 169 °C, attributed to the melting followed by thermal decomposition of Enalapril maleate, respectively. To check these attributions, the sample was heated in a glass tube until 169° C, and as indicated by the TG-DSC curves, and melting followed by thermal decomposition was observed. The infrared spectrum of the product condensed on the wall of the glass tube after the thermal decomposition of enalapril maleate was obtained (Fig. 3) and the maleic anhydride was identified as a decomposition gas product at this stage ($\Delta m_{Calc.}$ = 26.04%, Δm_{TG} = 25.4 % (air), 25.5 % (N_2)). The TGA also identified maleic anhydride at 170 °C, as the gas product from the thermal decomposition at this stage, as shown in Fig. 3.

The residue mass obtained at the end of the first mass loss stage (220 (N_2) and 230 °C (air)) indicates the formation of "pure" enalapril, the proposed mechanism for this step is shown in Scheme 1 ($\Delta Resid._{Calc.}$ = 76.74 %, $\Delta Resid._{TG}$ = 74.6 % (air), 74.5 % (N_2)).

In the air atmosphere, the second step occurs rapidly between 220 and 350 °C, with a mass loss of 66.90 %, associated with an endothermic peak at 331 °C, attributed to the "pure" enalapril thermal decomposition and the formation of carbonaceous residue at the end of the process. The formation of carbonaceous residue was confirmed by visual inspection, heating the samples to 350 °C, as indicated by the TG-DSC curves.

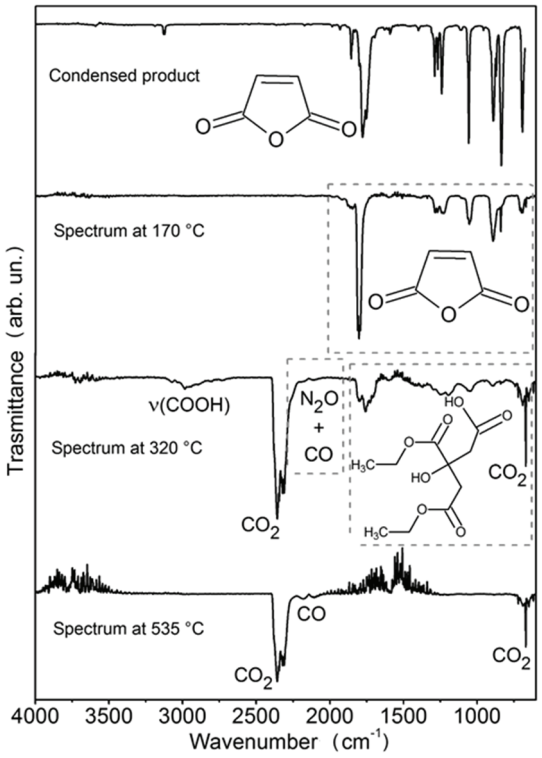
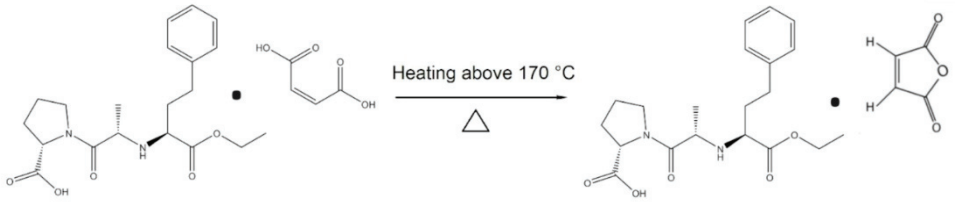


Fig. 3. Infrared FTIR spectra obtained during the thermal decomposition of enalapril maleate in air and N_2.



Scheme 1. Proposed mechanism for the first stage of thermal decomposition.

The last step of mass loss in the TG curve between 350-605 °C (Δm_{TG} = = 9.05 %), corresponding to exothermic peaks in the DSC curve at 475, 527 and 607 °C, is attributed to the oxidation of the carbonaceous residue formed in the previous step and/or to the gaseous products that evolved during thermal decomposition.

Regarding gases released during thermal decomposition, the main gaseous products identified by TGA were 1,2-diethyl citrate, CO, CO_2 and N_2O in the second step, and CO_2 and CO in the third stage.

In the pyrolysis condition (nitrogen atmosphere), the second and last step (pure enalapril thermal pyrolysis) in the TGA curve occurs rapidly between 220––330 °C ($\Delta m_{Calc.}$ = 76.74 %, Δm_{TG} = 73.35 %), associated with the endothermic peak in the DSC curve at 290 °C, attributed to the thermal decomposition and the pyrolysis of the material. Due to the absence of oxygen, parallel reactions are avoided, o which prevents the formation of carbonaceous residue. The infrared spectrum obtained during this thermal decomposition step by EGA is shown in Fig. 3. The main gaseous products released were CO_2, N_2O, 1,2-diethyl citrate and maleic anhydride.

Thermokinetic study

The thermal decomposition of enalapril occurs in consecutive mass loss steps; thus, a thermokinetic study was applied to all stages of thermal decomposition. Isoconversional analysis studies were conducted using the methods of Friedman and Kissinger,[23,24] as well as through model fitting (linear regression).[18,19,25] Fig. 4 shows the results obtained through the application of isoconversional analysis.

The Kissinger and Friedman equations are fundamental tools in isoconversional kinetic analysis, providing valuable insights into the thermal degradation kinetics of various materials. The Kissinger method, also known as the Kissinger––Akahira–Sunose (KAS) method, is widely used to determine the kinetic parameters of a reaction. It involves plotting the heating rate's logarithm against the temperature's reciprocal at the maximum degradation rate for different conversions. The slope of the resulting linear relationship yields the activation energy, while the intercept provides the pre-exponential factor. However, it is important to note that in cases where the isoconversional activation energy varies significantly, the Kissinger plots may appear almost perfectly linear, potentially failing to detect the inherent complexity of the processes.[24] The Friedman method is a widely used differential isoconversional for analysing thermal degradation kinetics. This method involves plotting the temperature at a given conversion against the heating rate. The resulting linear relationship provides the means to determine the activation energy and pre-exponential factor.[26]

The isoconversional analysis demonstrated an apparent activation energy for the complete thermal decomposition of enalapril maleate of 47.07±15.45 kJ mol^{-1} with an R^2 of 0.945.

Fig. 5 shows the results of the thermal kinetic analysis through model fitting. The application of various methods to determine the kinetic parameters of thermal decomposition processes is involved in model fitting. Both model-free (isoconversional) and model-fitting methods were used for this purpose, each with its advantages and limitations. Model fitting methods have been a subject of debate within the thermal analysis community, with the interests about the reliability of deriving

kinetic parameters from a single heating rate, which can lead to some unreliable and nonsensical results.[27]

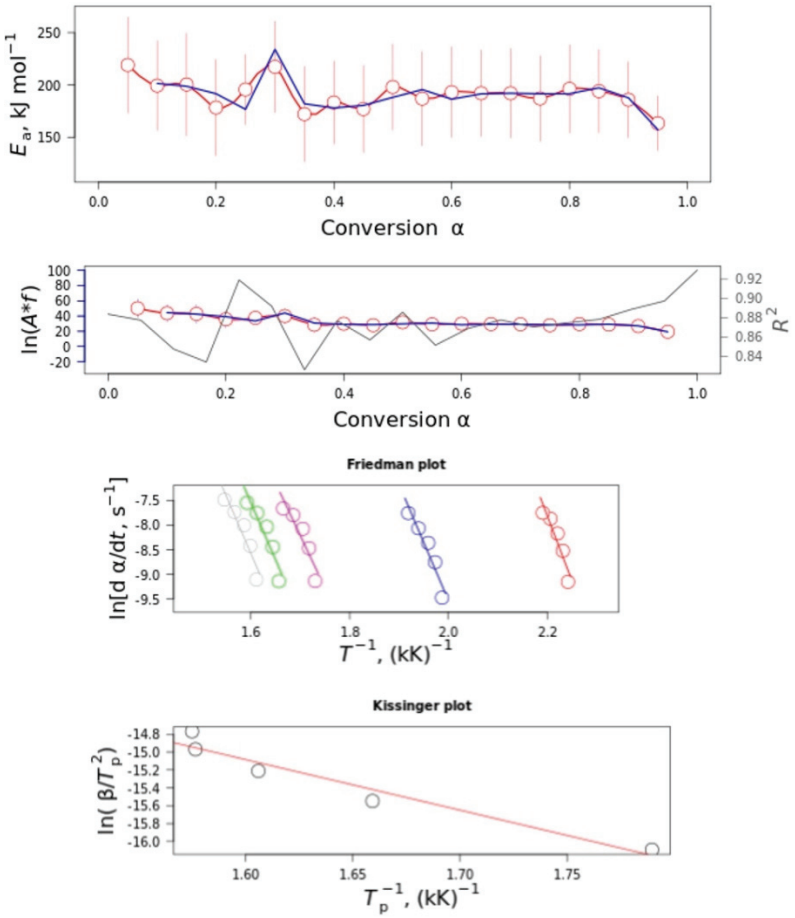


Fig. 4. Results obtained through the application of isoconversional analysis, Friedman plot, and Kissinger plot of thermal decomposition of enalapril.

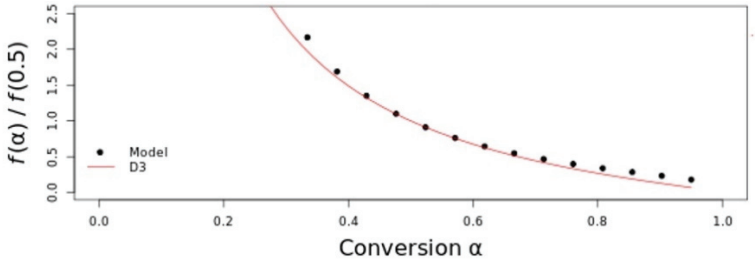


Fig. 5. Results of the thermal kinetic analysis through model fitting of thermal decomposition of enalapril.

However, model fitting methods have historically been widely used in solid-state kinetics and have shown excellent fits to experimental data, although they may produce uncertain kinetic parameters, especially for nonisothermal conditions.[28] The model fitting methods have been used to predict different reaction mechanisms for thermal disintegration processes.[29] Additionally, the model fitting methods have been employed to estimate the kinetic parameters of complex solid-state reactions.[30,31] The kinetic parameters for enalapril maleate demonstrate an apparent activation energy of 55.7±3.4 kJ mol^{-1} with a three-dimensional diffusion thermal degradation model, where $f(\alpha) = 3(1–R)^{2/3}/(2(1–(1–R)^{1/3}))$.

CONCLUSION

When submitted to heating, certain drugs undergo a series of chemical and physical reactions, including decomposition reactions, resulting in compounds different from the original. Thermal analysis can be employed to monitor the sample, while it undergoes the described processes. Thermal analysis was also effective in determining the purity of enalapril maleate.

The thermoanalytical and spectroscopic study of enalapril maleate was conducted to ascertain its purity and thermal behaviour. Purity determination, based on melting point and melting enthalpy, yielded a purity of 99.5 %. The Van't Hoff equation applied to the DSC curve confirmed the high purity, showcasing a melting point at 154 °C with a corresponding $\Delta H_{\text{melt.}}$ of 29.6 kJ mol^{-1}. Simultaneous TG-DSC curves in dynamic air and N_2 atmospheres revealed enalapril's stability up to 148 °C, beyond which thermal decomposition occurred. In air, three decomposition stages were observed between 148–605 °C, with the identified products including maleic anhydride and carbonaceous residue. In N_2, two decomposition stages occurred between 148 and 330 °C. The second step involved thermal decomposition and pyrolysis, releasing CO_2, 1,2-diethyl citrate, N_2O and maleic anhydride.

The thermal decomposition of enalapril maleate was systematically investigated through isoconversional analysis using both the Kissinger and Friedman equations, alongside model fitting methods. The Kissinger method identified an apparent activation energy of 47.07±15.45 kJ mol^{-1} for the complete thermal decomposition, exhibiting an R^2 value of 0.945. The application of the Friedman method supported these findings. Additionally, model fitting methods, despite historical debates regarding their reliability, were employed and resulted in an apparent activation energy of 55.7±3.4 kJ mol^{-1}. The chosen model involved a three-dimensional diffusion thermal degradation model.

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ИЗВОД

КАРАКТЕРИЗАЦИЈА ЕНАЛАПРИЛ-МАЛЕАТА: ПРИСТУП КОЈИ КОРИСТИ ТЕРМОАНАЛИТИЧКЕ, ТЕРМОКИНЕТИЧКЕ И СПЕКТРОСКОПСКЕ ТЕХНИКЕ

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Еналаприл-малеат је лек који се широко користи за лечење кардиоваскуларних болести. Његов механизам деловања је да селективно инхибира ензим који конвертује ангиотензин. Због тога се ћелијама јетре метаболише у еналаприлат. Термичко понашање еналаприл-малеата је испитивано симултаном термогравиметријом и диференцијалном скенирајућом калориметријом (TG-DSC), а анализом еволуираног гаса симултаном термогравиметријом и диференцијалном скенирајућом калориметријом са инфрацрвеном спектроскопијом (TG-DSC–FTIR). Резултати су дали информације о термичкој стабилности, чистоћи, корацима термичке декомпозиције и главним производима насталим током загревања. Утврђено је да је еналаприл-малеат стабилан до 148 °C. Изнад ове температуре долази до термичке деградације супстанце, која се дешава у два степена у инертној атмосфери (N_2) и три степена у оксидационој атмосфери (ваздух). Ослобођени гасови, интермедијери термичке разградње, су идентификовани као анхидрид малеинске киселине. DSC анализа је указала на високу чистоћу материјала (99,5 %). Применом Кисинцерове и Фридманове једначине, заједно са методама уклапања модела, одређена је привидна енергија активације од 47,07±15,45 kJ mol^{-1} за потпуно термичко разлагање. Применом метода уклапања модела са тродимензионалним дифузионим моделом термалне деградације добија се привидна енергија активације од 55,7±3,4 kJ mol^{-1}.

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