Thermal analysis kinetics of dioscorea saponin by mechanical activation

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Abstract. Dioscorea saponin isolated from the rhizome of Dioscorea nipponica Makino was activated by AGO mill. On the basis of TG–DSC analysis, two endothermic peak of dioscorea saponin after mechanical activation both moved back, and it had finished weightlessness in advance due to the accelerated decomposition. According to thermal analysis kinetics, the average thermal decomposition activation energy of dioscorea saponin after mechanical activation increased, and the maximum activation energy at different conversion rates moved back. According to the determining results of kinetic mechanism function, the thermal decomposition kinetics mechanism functions of dioscorea saponin before and after mechanical activation both fitted the Jander formula. After mechanical activation, the thermal decomposition kinetic mechanism of dioscorea saponin transformed from three–dimensional to two–dimensional diffusion.

1. Introduction

Dioscorea saponin, a type of white crystal, is made by the raw material of dioscorea nipponica, and it is obtainable by separation and purification. Dioscorea saponin can increase coronary flow, improve coronary circulation, and resist atherosclerosis in arterial circulation. Water–soluble and active dioscorea saponins are favored by the market because they can be easily absorbed by receptors [1–3]. Dioscorea saponin can also be used to prepare dioscorea diosgenin, which is the initial material used for synthetic steroid hormone drug intermediation and thus regarded the “mother” of the hormone [4, 5]. Considerable researches on dioscorea saponin have focused on its pharmacological effects [6, 7], but no relevant articles have been reported on its mechanical activation. The activation of dioscorea saponin not only improves the effects of efficacy, but also speeds up the hydrolysis process, increases hydrolysis rate, and reduces acid dosage, which can subsequently reduce the preparation cost of dioscorea diosgenin and reduce the pollution of the environment. In this study, dioscorea saponin isolated from the laboratory was mechanically activated, and the thermal decomposition kinetics mechanism functions of dioscorea saponin before and after mechanical activation were analyzed.
2. Materials and methods

2.1. Materials
The dioscorea rhizomes of Dioscorea nipponica Makino were purchased from Yangjiang (Guangdong Province, China). The content of each basic component of the dioscorea rhizome is shown in Table 1.

| Component      | Content/% |
|----------------|-----------|
| Fiber          | 30–35     |
| Starch         | 40–45     |
| Protein        | 5–10      |
| Saponin        | 5–10      |
| Water soluble  | 10–15     |
| Others         | 5         |

Isolated in the laboratory, dioscorea saponin is a white crystalline with chemical formula of C_{45}H_{72}O_{16}, molecular weight of 869.05, and melting point of 294 °C–296 °C. Dioscorea saponin is soluble in acetic acid, methanol, and ethanol; and slightly soluble in acetone and samy alcohol; insoluble in water, petroleum ether, and benzene. Dioscorea saponin is a screw–type saponin, and the structure formula of dioscorea saponin is shown in Figure 1.

2.2. Mechanical activation method
Dioscorea saponin (10 g) was taken from the tank and ground by AGO mill for two minutes. Then, the mechanically activated dioscorea saponin was placed into a dryer for detection. Dioscorea saponin before mechanical activation was represented by S_a, and dioscorea saponin after mechanical activation was represented by S_b.

2.3. Thermal decomposition method
The temperature and heat coordinates were calibrated with high purity indium, and the whole process was conducted under the drying nitrogen. The purge nitrogen flow rate was 20ml/min. Dioscorea saponin samples before and after mechanical activation (5.0±0.1) mg were accurately weighed, and placed into aluminum crucibles whose lids with hole in the center. The same empty crucibles were used as the reference. Then heating rates (5 °C, 10 °C, 15 °C, and 20 °C) were set respectively, heated to 600 °C, and kept the temperature for five minutes.

3. Results and discussion

3.1. TG–DSC analysis
The TG–DSC curves of dioscorea saponin are shown in Figure 2(a). Two obvious endothermic peaks appear on DSC curves. One of the endothermic peaks (358 °C) represents the bond rupture between RMB glycosides and sugar–based glycosides. The other endothermic peak (498 °C) represents the pyran ring ready to be opened. The TG curve of dioscorea saponin before 300 °C corresponds to 5% weightlessness (i.e., moisture volatilized weightlessness). After 300°C, the dioscorea saponin began to rapidly lose weight due to the disintegrating sugar–based glycosides. Then, much more decomposition, material carbonization, and gasification were observed. Before reaching 580 °C, the cumulative weightlessness of the sample was 99%. The TG–DSC curve of the dioscorea saponin after mechanical activation is shown in Figure 2(b), in which two endothermic peaks move toward 343 °C and 463°C. Before reaching 480 °C, the mechanically activated sample had 99% weightlessness, which was ahead of the 100 °C.
3.2. Kinetic analysis

3.2.1. Kinetic data processing method.
According to the isothermal kinetics theory, the dynamic formula of solid decomposition reaction can be expressed as follow Formula 1. In the formula, \( \alpha \) is conversion rate (\%); \( A \) is pre–exponential factor; \( E \) is thermal decomposition activation energy (kJ·mol); \( R \) is universal constant; \( T \) is temperature (K); and \( f(\alpha) \) is differential form of kinetic mechanism function.

\[
\frac{d\alpha}{dt} = A e^{\frac{E}{RT}} \cdot f(\alpha)
\]  

(1)

In the thermal analysis test, the heating rate is a fixed value \( \beta = \frac{dT}{dt} \), which is substituted into Formula 1, can obtain the non–isothermal kinetic formula as in Formula 2.

\[
\frac{d\alpha}{dt} = \left( \frac{A}{\beta} \right) e^{\frac{E}{RT}} \cdot f(\alpha)
\]  

(2)

After derivation of Formula 2 through differential and deformation, formulas corresponding to Flynn–Wall–Ozawa method and Friedman method can be obtained \([8,9]\) as in Formula 3 and Formula 4.

\[
2\ln \ln \frac{5.3305}{R} \frac{1}{T_0^2} \frac{E}{RT} \beta = \ln A - \ln f(\alpha)
\]  

(3)

\[
\ln \left[ \frac{d\alpha}{dt} \right] = \ln A \left[ f(\alpha) \right] - \frac{E}{RT}
\]  

(4)

Through substituting \( \alpha = \frac{H}{H_0} \) (\( H_0 \) is the total heat, \( H_i \) is the heat at a certain temperature) and \( T = T_0 + \beta t \) (\( T_0 \) is the starting point temperature) into Formula 1, the formula of the Kissinger maximum rate method can be deduced after differentiation and deformation as in Formula 5.

\[
\ln \beta_i \frac{1}{T_{\text{max} i}^2} = \ln \left( \frac{A_\alpha R}{E_k} \right) \frac{1}{T_{\text{max} i}^2}
\]  

(5)

Formula 4 can also be changed as in Formula 6.
\[
\ln \left( \frac{d\alpha}{dt} \right) \beta - \ln f(\alpha) = \ln A_s - \frac{E_s}{RT}
\]  

(6)

In the thermal decomposition curve of \( \beta_i \) (i=1, 2, 3...), the corresponding \( E_s \) and \( A_s \) can be calculated by 30 kinds of common kinetics mechanism functions (as shown in Table A of appendix). If \( E_s \) meet the conditions \( (0 < E_s < 400 \text{ kJ}\cdot\text{mol}) \), the \( E_s \) and \( \ln A_s \) would be considered reasonable \[10, 11\]. \( E_s \) was compared to \( E_0 \) (the average thermal decomposition activation energy calculated by the Flynn–Wall–Ozawa method and Friedman method), and kinetics mechanism functions which met the conditions \( \left| \frac{E_s - E_0}{E_0} \right| \leq 0.1 \) would be found out. \( \ln A_s \) was compared to \( \ln A_h \) (calculated by the Kissinger method), and kinetics mechanism functions which met the conditions \( \left| \frac{\ln A_s - \ln A_h}{\ln A_h} \right| \leq 0.2 \) would be found out. According to the \( R^2 \) value, the comparison results of \( E_s \) and \( E_0 \), \( \ln A_s \) and \( \ln A_h \), the best screening result of the thermal decomposition kinetic mechanism function of Dioscorea saponin would be determined.

3.2.2. Kinetic parameters calculation

Graphing \( \ln \beta \) of \( \frac{1}{T} \) and \( \ln \left( \frac{d\alpha}{dT} \right) \beta \) of \( \frac{1}{T} \) according to multivariate linear fitting by Flynn–Wall–Ozawa method and Friedman method (\( \alpha \) in the range of 0.2–0.8), the thermal decomposition activation energy (E) can be obtained. Diagrams of \( \ln \beta \) plotted against \( \frac{1}{T} \) (Flynn–Wall–Ozawa method) and \( \ln \left( \frac{d\alpha}{dT} \right) \beta \) plotted against \( \frac{1}{T} \) (Friedman method) of Dioscorea saponin before and after mechanical activation in different \( \alpha \) are shown in Figure 3.

![Figure 3](image)

Figure 3. TG–DSC processing datas of Dioscorea saponin before and after mechanical activation were plotted against \( \frac{1}{T} \) (a \( \ln \beta - \frac{1}{T} \) (Flynn–Wall–Ozawa, S_a), b \( \ln \left( \frac{d\alpha}{dT} \right) \beta - \frac{1}{T} \) (Friedman, S_a), c \( \ln \beta - \frac{1}{T} \) (Flynn–Wall–Ozawa, S_b), d \( \ln \left( \frac{d\alpha}{dT} \right) \beta - \frac{1}{T} \) (Friedman, S_b))

The fitting curves of thermal decomposition activation energy at different conversion rates obtained by Flynn–Wall–Ozawa method and Friedman method are shown in Figure 4. The thermal decomposition activation energy of Dioscorea saponin after mechanical activation at different conversion rates was higher than that of Dioscorea saponin. The maximum value of Dioscorea saponin
after mechanical activation had been reached when the conversion rate of increment was 0.5, which was 0.15 ahead of dioscorea saponin.

Figure 4. Fitting curves of thermal decomposition activation energy of different conversion rates of dioscorea saponin before and after mechanical activation (a (Flynn–Wall–Ozawa, $S_a$), b (Friedman, $S_a$), c (Flynn–Wall–Ozawa, $S_b$), d (Friedman, $S_b$))

Figure 5. TG–DSC processing datas of dioscorea saponin before and after mechanical activation were plotted for

\[
\frac{1}{T} \ln \frac{\beta_i}{T_{\text{max}}^2} - \frac{1}{T_{\text{max}}} \quad (\text{Kissinger, } S_a)
\]

\[
\ln \frac{\beta_i}{T_{\text{max}}^2} - \frac{1}{T_{\text{max}}} \quad (\text{Kissinger, } S_b)
\]

The thermal decomposition activation energy calculated results of two calculation methods are listed in Table 2. The results ($\bar{E}$) calculated by Flynn–Wall–Ozawa method and Friedman method were similar whether dioscorea saponin mechanically activated or not. The average thermal decomposition activation energy of dioscorea saponin ($\bar{E}_{a0}$) was 86.60±3.74 kJꞏmol. After mechanical activation, the average thermal decomposition activation energy ($\bar{E}_{b0}$) was 100.73±3.57 kJꞏmol.

Table 2. Results of the thermal decomposition activation energy of dioscorea saponin before and after mechanical activation calculated by Flynn–Wall–Ozawa method and Friedman method

| Activation energy | $S_a$ Flynn–Wall–Ozawa | Friedman | $S_b$ Flynn–Wall–Ozawa | Friedman |
|-------------------|-------------------------|----------|-------------------------|----------|
| $\bar{E}$ /kJꞏmol | 88.98±2.8 | 84.22±3.37 | 102.69±3.04 | 98.77±3.22 |
| $\bar{E}_0$ /kJꞏmol | 86.60±3.74 | 100.73±3.57 |

Graphing $\ln \left( \frac{\beta_i}{T_{\text{max}}^2} \right)$ of $\frac{1}{T_{\text{max}}} \quad (\text{Kissinger})$ according to linear fitting by Kissinger method (α in the range of 0.2–0.8), the thermal decomposition activation energy $E_k$ can be obtained. Diagrams of $\ln \left( \frac{\beta_i}{T_{\text{max}}^2} \right)$ plotted against $\frac{1}{T_{\text{max}}} \quad (\text{Kissinger})$ of dioscorea saponin before and after mechanical activation in different α are shown in Figure 5.

The calculated results of Kissinger method are listed in Table 3. The thermal decomposition activation energy of dioscorea saponin ($E_{a0}$) was 91.32 kJꞏmol. After mechanical activation, the
thermal decomposition activation energy ($E_{ak}$) was 103.43 kJ·mol. The result of $\ln A_{ak}$ was 9.21 min$^{-1}$, and $\ln A_{bk}$ was 14.38 min$^{-1}$. The variances ($R^2$) were 0.9889 and 0.99794.

Table 3. Results of dioscorea saponin before and after mechanical activation calculated by Kissinger method

|                | $S_a$ | $E_a$/kJ·mol | $\ln A_a$/min$^{-1}$ | $R^2$ | $S_b$ | $E_b$/kJ·mol | $\ln A_b$/min$^{-1}$ | $R^2$ |
|----------------|-------|---------------|----------------------|-------|-------|--------------|----------------------|-------|
| Value          | 91.32 | 9.21          | 0.98889              | 103.43| 14.38 | 0.99794      |                      |       |

3.2.3. Kinetic mechanism function determination

Combined with 30 kinds of common kinetics mechanism functions $f(\alpha)$, the thermal decomposition activation energy $E_a$ can be obtained through graphing $\ln \left[ \left( \frac{d\alpha}{dT} \right) \beta \right] - \ln f(\alpha)$ of $\frac{1}{T}$ according to multivariate linear fitting. The calculated results ($E_a$, $\ln A_a$, and $R^2$) are shown in Figure 6.

The value of No.5, No.12, No.14, No.17 and No.23 ($E_{as}$) were close to $E_{a0}$ in Figure 6a, and only No.5, No.12 and No.23 met the requirements ($0 < E_{as} < 400$ kJ·mol$^{-1}$ and $\frac{\ln A_{as} - \ln A_{ak}}{\ln A_{as}} \leq 0.2$).

The value of No.5, No.12, No.14, No.17 and No.23 ($\ln A_{as}$) were close to $\ln A_{ak}$ in Figure 6b, and only No.5, No.12, No.14 and No.23 met the requirements ($\frac{\ln A_{as} - \ln A_{ak}}{\ln A_{as}} \leq 0.2$). According to the $R^2$ value in Figure 6c, and refer to the comparison results of $E_{as}$ and $E_{a0}$, $\ln A_{as}$ and $\ln A_{ak}$, No.5 was the best screening result of the thermal decomposition kinetic mechanism function of dioscorea saponin. In the same way, No.6 was the best screening result of the thermal decomposition kinetic mechanism function of dioscorea saponin after mechanical activation.

According to Table A of appendix, the thermal decomposition kinetics mechanism functions of No.5 and No.6 both were Jander formula. The kinetic mechanism function of dioscorea saponin was $f(\alpha) = 6 \left( 1 - \alpha \right)^{2/3} \left[ 1 - \left( 1 - \alpha \right)^{1/3} \right]^{1/3}$, and this was regarded the mechanism of three-dimensional diffusion. After mechanical activation, the kinetic mechanism function of dioscorea saponin was $f(\alpha) = 4 \left( 1 - \alpha \right)^{1/2} \left[ 1 - \left( 1 - \alpha \right)^{1/2} \right]^{1/2}$, and this was regarded the mechanism of two-dimensional diffusion.
Figure 6. Diagram of $E_a$, $\ln A_a$ and $R^2$ obtained from 30 kinds of kinetics mechanism functions of dioscorea saponin before and after mechanical activation (a $E_a$, b $\ln A_a$, c $R^2$, d $E_{bs}$, e $\ln A_{bs}$, f $R^b$)  

a,d The red lines represent the average thermal decomposition activation energy of dioscorea saponin ($E_{a0}$ and $E_{b0}$) in Figure 6a and Figure 6d

b,e The red lines represent the value of $\ln A_{ak}$ and $\ln A_{bk}$ in Figure 6b and Figure 6e

c,f The red lines represent $R^2$ wireless approaching the value 1 in Figure 6c and Figure 6f.

4. Conclusion

(1) According to the TG–DSC analytical results, two endothermic peaks of dioscorea saponin after mechanical activation moved back 15 °C and 35 °C respectively, and it had 99% weightlessness ahead of 100 °C. After mechanical activation, the thermal decomposition of dioscorea saponin was accelerated.

(2) According to the results of thermal analysis kinetics, the average thermal decomposition activation energy of dioscorea saponin before and after mechanical activation were $86.60 \pm 3.74 \text{kJ/mol}$ and $100.73 \pm 3.57 \text{kJ/mol}$, which showed $13.45 \text{kJ/mol}$ activation energy of dioscorea saponin increased after mechanical activation. The maximum activation energy at different conversion rates also changed, which moved from 0.65 to 0.5.

(3) According to the determining results of kinetics mechanism functions, the thermal decomposition kinetics mechanism functions of dioscorea saponin before and after mechanical activation both fitted Jander formula. The kinetic mechanism function of dioscorea saponin was 

$$ \alpha = 6 \left(1 - \alpha\right)^{2/3} \left[1 - \left(1 - \alpha\right)^{1/3}\right]^{1/3}, $$

and the kinetic mechanism function of dioscorea saponin after mechanical activation was 

$$ \alpha = 4 \left(1 - \alpha\right)^{1/2} \left[1 - \left(1 - \alpha\right)^{1/2}\right]^{1/2}. $$

After mechanical activation, the decomposition mechanism of dioscorea saponin transformed from three-dimensional to two-dimensional diffusion.

Appendix

Table A. 30 kinds of common kinetics mechanism functions

| No. | Name | Mechanism | $f(\alpha)$ |
|-----|------|-----------|-------------|
|     |      |           |             |
| 1 | Parabola rule | One–dimensional diffusion, 1D | $1 / 2\alpha^{-1}$ |
| 2 | Valensi formula | Two–dimensional diffusion, Cylindrical symmetry, 2D | $\left[1 - \ln \left(1 - \alpha\right)\right]^{-1}$ |
| 3 | G–B formula | Three–dimensional diffusion, Cylindrical symmetry, 3D | $3 / 2 \left(1 - \alpha^{1/3} - 1\right)^{-1}$ |
| 4–5 | Jander formula | Three–dimensional diffusion, 3D | $3 / n \left(1 - \alpha\right)^{2/3} \left[1 - \left(1 - \alpha\right)^{1/3}\right]^{(n-1)}$ (n=2,1/2) |
| 6 | Jander formula | Two–dimensional diffusion, 2D | $4 \left(1 - \alpha\right)^{1/2} \left[1 - \left(1 - \alpha\right)^{1/2}\right]^{1/2}$ |
| 7 | Jander formula | Three–dimensional diffusion, Sphere symmetry, 3D | $3 / 2 \left(1 - \alpha\right)^{2/3} \left[1 + \alpha^{1/3} - 1\right]^{-1}$ |
| 8 | Z–L–T formula | Three–dimensional diffusion, 3D | $3 / 2 \left(1 - \alpha\right)^{4/3} \left[1 / \left(1 - \alpha\right)^{1/3} - 1\right]^{-1}$ |
| 9 | Mample single rule | Random nucleation and growth, each particle should has only one core | $1 - \alpha$ |
| 10–16 | Avrami–Erofeev formula | Random nucleation and growth, Auto–catalysis, Ramifor nucleation, $A_u$ | $1 / n \left(1 - \alpha\right)\left[-1\ln \left(1 - \alpha\right)\right]^{(n-1)}$ (n=2,3,1/2,1/3,4,1/4,2,3) |
| 17 | P–T formula | | $\alpha \left(1 - \alpha\right)$ |
| 18–22 | Reaction series | $n=1/2,3,2,4,1/3,1/4$ | $1 / n \left(1 - \alpha\right)^{(n-1)}$ (n=3,2,4,1/3,1/4) |
| 23–27 | Mampel Power rule | $n=1/3,2,1/2,1/3,1/4$ | $1 / n\alpha^{(n-1)}$ (n=1,3/2,1/2, 1/3,1/4) |
| 28 | Second order | Chemical reaction, $F_2$ | $\left(1 - \alpha\right)^2$ |
| 29 | Contraction cylinder | Phase boundary reaction, Cylindrical symmetry, $R_2$ | $2 \left(1 - \alpha\right)^{1/2}$ |
| 30 | J–M–A formula | Random nucleation and growth, $A_3$ | $2 / 3 \left(1 - \alpha\right)\left[-1\ln \left(1 - \alpha\right)\right]^{1/3}$ |

References

[1] Lina Xu, Yongli Wei, Jingyong Peng. (2015) Advances in study of Dioscrea natural product. Chinese Materia Medical, 40: 36–41.
[2] Xiaopeng Wang, Xian Lu. (2004) New progress in the study of bioactivity of dioscrea saponin. Foreign Medical Sciences: Traditional Chinese Medicine, 5: 138–141.
[3] Trouillas P, Corbieri C, Liagre B. (2005) Structure–function relationship for saponin effects on cellcycle arrest and apoptosis in the human 1547 osteosarcoma cells: a molecular modelling
approach of natural molecules structurally close to diosgenin. Bioorg Med Chem, 13:1141–1149.

[4] Kanaika PATEI, Manoj GADEWAR. (2012) A review on pharmacological and analytical aspects of diosgenin: a concise report. Nat. Prod. Bioprpspect, 2: 46–52.

[5] Jingzhou Dong, Can Lei, Dayan Lu. (2014) Direct biotransformation of dioscin into diosgenin in rhizome of Dioscorea zingiberensis by Penicillium dioscin. Indian J Microbiol, 6: 22–26.

[6] Edwards A L. (2002) Presence of diosgenin in Dioscorea batatas (Dioscoreaceae). Economic Botany, 56: 204–206.

[7] V. V. Panina, O. S. Madaeva. (1968) Preparation of diosgenin by the hydrolysis of rhizomes of Dioscorea at a high temperature. Pharmaceutical Chemistry Journal, pp.334–335.

[8] Rongzhu Hu, Qizheng Shi. (2001) Thermal analysis kinetics. Science press, Beijing.

[9] Britto D D, Campana–filho S P. (2007) Kinetics of the thermal degradation of chitosan. Thermochim Acta, 465: 73–82.

[10] Ning Ren, Jianjun Zhang. (2006) Progress in Datum Treatment Methods of Thermal Analysis Kinetics. Progress in Chemistry, 18: 410–416.

[11] Feixiong Chen. (2014) Study on crystallization thermodynamics and thermal decomposition performance of diosgenin. Master's thesis of Zhengzhou University, Zhengzhou.