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Kinetics of Thermal Decomposition of Dioscorea Saponin after Mechanical Activation

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Abstract

Dioscorea saponin isolated from the rhizome of *Dioscorea nipponica* Makino was investigated by performing grain size, SEM, XRD, FTIR and TG–DSC analysis. The sizes of D_{50} for the Dioscorea saponin sample activated by AGO mill decreased to as low as 10.03 μm. According to SEM and XRD, the granularity and structures of Dioscorea saponin samples with and without mechanical activation significantly differed, and the crystalline of Dioscorea saponin was significantly converted into amorphous state after mechanical activation. On the basis of TG–DSC analysis, two endothermic peak of Dioscorea saponin after mechanical activation moved back 15 and 35 °C respectively, and it had 99 % weightlessness ahead of 100 °C due to the accelerated decomposition. According to thermal analysis kinetics, the average thermal decomposition activation energy of Dioscorea saponin after mechanical activation was increased 13.45 kJ/mol, and the dynamic mechanism function of Dioscorea saponin was $f(\alpha) = 6(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{1/3}$, and this was regarded the mechanism of three-dimensional diffusion. With mechanical activation, the dynamic mechanism function was $f(\alpha) = 4(1 - \alpha)^{1/2}[1 - (1 - \alpha)^{1/2}]^{1/2}$, and this was regarded the mechanism of two-dimensional diffusion. The result of transformation from three-dimensional to two-dimensional diffusion mechanism was consistent with XRD analytical result of transformation from original ordered crystalline structure to amorphous state after mechanical activation. None of the functional groups of the mechanically activated Dioscorea saponin disappeared, and no new functional groups appeared, which indicate that mechanical activation does not induce a chemical transformation of Dioscorea saponin.

Key words: Dioscorea saponin, mechanical activation, thermodynamic, kinetics

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 improve coronary circulation and resist atherosclerosis in arterial circulation. Water-soluble and active Dioscorea saponins are favoured because they can be easily absorbed by receptors [1–3]. Dioscorea diosgenin, which is obtained by hydrolysing Dioscorea saponin, is the initial material used for synthetic steroid hormone drug intermediation and thus regarded the "mother" of the hormone [4, 5]. Considerable research 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 it 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 activat-

TABLE 1
Basic components of dioscorea rhizome

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

ed. The mechanical activation mechanism was further analyzed by integrating the thermal decomposition kinetic mechanism, particularly for the pre- and post-activated states of Dioscorea saponin.

MATERIALS AND METHODS

Materials

A dioscorea rhizome of *Dioscorea nipponica* Makino was purchased from Yangjiang (Guangdong Province, China). The content of each basic component of the dioscorea rhizome is shown in Table 1.

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

Main equipment

The following equipment were used: planetary mill AGO-2 (Russia), Mastersizer 2003 laser particle size analyzer (China), JMS-6360LV scanning electron microscope (JEOL Ltd.), sharp shadow Empyrean X-ray diffractometer (Panaco, Netherlands), STA449F3 synchronous thermal analyzer (Nextel, Germany), IRAffinity Fourier transform infrared spectrometer (Shimadzu, Japan).

Mechanical activation method

Dioscorea saponin (10 g) was taken from the tank and ground with AGO for 2 min. Then, the mechanically activated saponin was placed into a dryer for detection. Dioscorea saponin before mechanical activation is represented by S_a, and Dioscorea saponin after mechanical activation is represented by S_b.

RESULTS AND DISCUSSION

Grain size analysis

The particle size of the mechanically activated Dioscorea saponin sample was analyzed, and the result is shown in Fig. 2. The D_{50} particle size is 10.03 μm. In the process of mechanical activation, the size of the Dioscorea saponin crystal decreased continuously under the action of shear, shock, and other mechanical forces. A fine Dioscorea saponin powder was obtained after performing mechanical activation.

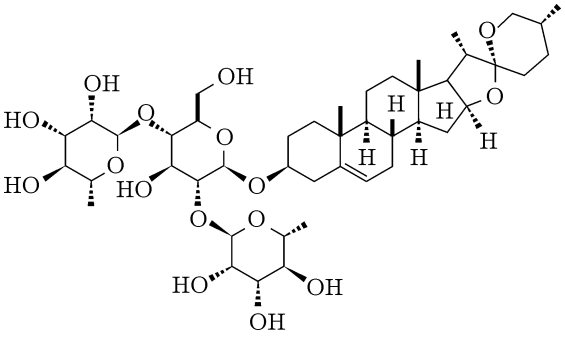

Fig. 1. Structure of Dioscorea saponin.

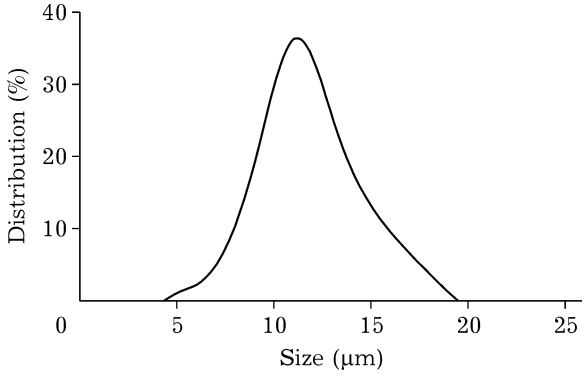

Fig. 2. Particle size distribution of S_b.

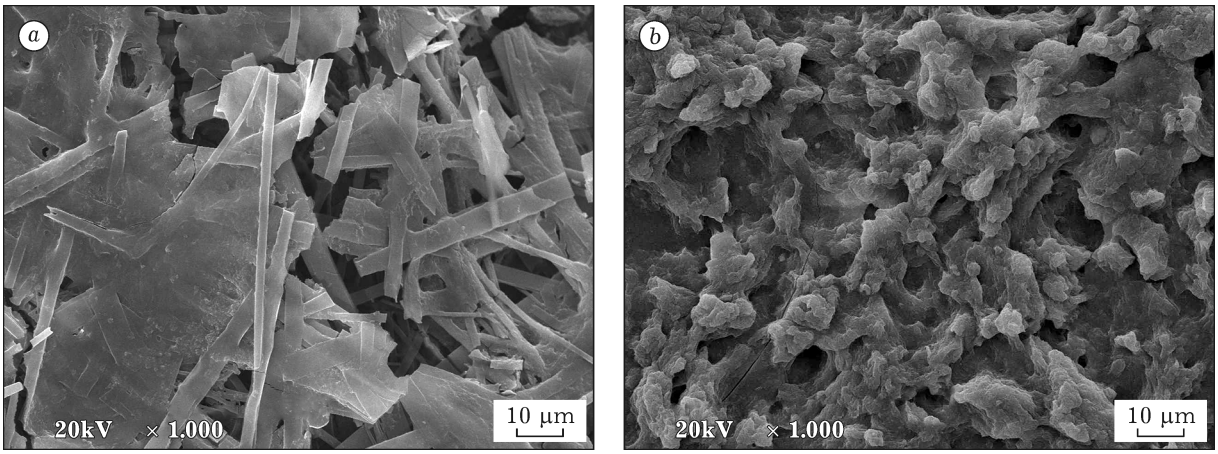

Fig. 3. Microscopic morphology (magnification: 1000×): *a* – S_a, *b* – S_b.

SEM analysis

SEM was used to observe Dioscorea saponin samples before and after mechanical activation. The morphology of Dioscorea saponin is shown in Fig. 3, *a*. Dioscorea saponins are striped crystals. After mechanical activation, the Dioscorea saponin was pulverized, as shown in Fig. 3, *b*. The mechanically activated Dioscorea saponin has no large blocks.

XRD analysis

An XRD analysis of the Dioscorea saponin samples before and after mechanical activation was conducted, and the results are shown in Fig. 4. The pre-activation sample exhibited three distinct peaks, indicating certain crystal surface characteristics (see *a* curve in Fig. 4). After mechanical activation, the characteristic peak of Dioscorea saponin disappeared and instead presented a single low-intensity dispersion peak (see *b* curve in Fig. 4), which indicate non-crystalline characteristics. In the process of mechanical activation, the shock, shear, and compression forces resulted in crystal lattice distortion. This distortion changed the crystal surface spacing and increased the half-peak width of the diffraction peak, and gradually transformed the directional crystal structure of Dioscorea saponin to an indefinite shape.

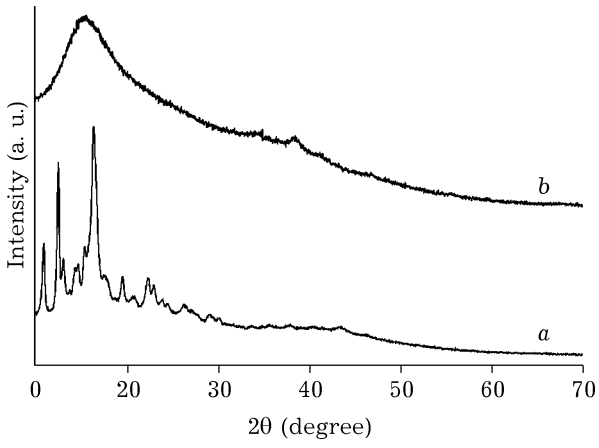

Fig. 4. XRD analytical patterns: *a* – S_a, *b* – S_b.

FTIR analysis

FTIR analysis was conducted to characterize the Dioscorea saponin samples before and after mechanical activation (Fig. 5). The characteristic absorption peaks of Dioscorea saponin before and after mechanical activation were 3400 cm^{-1} (stretching vibration absorption peak of −OH), 2950 cm^{-1} (stretching vibration absorption peak of −CH), 1650 cm^{-1} (deformation vibration absorption peak of −OH), 1450 cm^{-1} (bending vibration peak of C−H), 1150 cm^{-1} (stretching vibration absorption peak of $-CH_3$), 1050 cm^{-1} (stretching vibration absorption peak of ether bond (C−O) in the five-element ring), and 980 cm^{-1}(stretching vibration absorption peak of ether bond (C−O) in pyran ring). No significant movements were observed. In additional, none of the functional groups of the me-

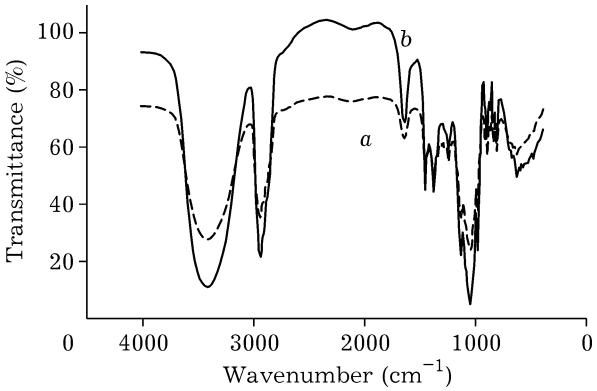

Fig. 5. IR spectra: *a* – S_a, *b* – S_b.

chanically activated Dioscorea saponin disappeared, and no new functional groups appeared, which indicate that mechanical activation does not induce a chemical transformation of Dioscorea saponin.

TG–DSC analysis

The TG–DSC curves of Dioscorea saponin are shown in Fig. 6, *a*. Two obvious endothermic peaks appear on of DSC curves. One of the endothermic peaks (358 °C) represent 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 weight loss of the sample was 99 %. The TG–DSC curve of the mechanically activated Dioscorea saponin is shown in Fig. 6, *b*, in which two endothermic peaks move toward 343 and 463 °C. Before reaching 480 °C, the mechanically activated sample has 99 % weightlessness.

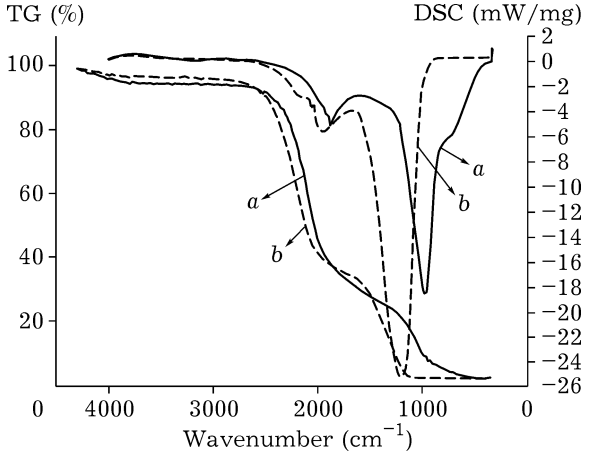

Fig. 6. TG–DSC curves: *a* – S_a, *b* – S_b.

Thermal decomposition kinetic analysis

The thermal decomposition activation energy (E) of Dioscorea saponin was calculated on the basis of the samples' TG–DSC curves with different heating rates (5, 10, 15, and 20 °C) and by using the Flynn–Wall–Ozawa method, the Friedman method, and the Kissinger maximum rate method with their respective integral formulas [8–10] as follows:

$$\ln \beta = \ln\left(\frac{AE}{RG(\alpha)}\right) - 5.3305 - 1.0516\frac{E}{RT} \quad (1)$$

$$\ln\left[\left(\frac{d\alpha}{d\beta}\right)\beta\right] = \ln\left[Af(\alpha)\right] - \frac{E}{RT} \quad (2)$$

$$\ln\frac{\beta_i}{T_{max}^2} = \ln\left(\frac{A_k E}{E_k}\right) - \frac{E_k}{R}\frac{1}{T_{max}} \quad (3)$$

The calculated results of the three calculation methods are listed in Table 2. The average thermal decomposition activation energy of Dioscorea saponin was $\overline{E_0}$ = 88.18 kJ/mol. After mechanical activation, the average thermal decomposition activation energy was 101.63 kJ/mol.

Formula (1.2) was substituted with Formula (1.4), and 30 kinds of thermal decomposition kinetic functions $f(\alpha)$ were considered to obtain the thermal decomposition activation energy (E_s) of the different kinetic models. In this study, the group whose E_s value is close to $\overline{E_0}$, and whose deviation is small can be selected for the investigation of the kinetic mechanism function of the thermal decomposition of Dioscorea saponin before and after mechanical activation.

$$\ln\left[\left(\frac{d\alpha}{d\beta}\right)\beta\right] - \ln f(\alpha) = \ln A - \frac{E_s}{RT} \quad (4)$$

TABLE 2

Results of the thermal decomposition activation energy of Dioscorea saponin before and after mechanical activation

Activation energy (kJ/mol)	Flynn–Wall–Ozawa	Friedman	Kissinger	$\overline{E_0}$
E_a	88.98±2.8	84.22±3.37	91.32	88.18
E_b	102.69±3.04	98.77±3.22	103.43	101.63

On the basis of the calculation, the thermal decomposition kinetic mechanism function of Dioscorea saponin before and after mechanical activation fitted the Jander equation. The dynamic mechanism function of Dioscorea saponin was $f(\alpha) = 6(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{1/3}$, and this was regarded the mechanism of three-dimensional diffusion. After mechanical activation, the dynamic mechanism function of Dioscorea saponin was $f(\alpha) = 4(1 - \alpha)^{1/2}[1 - (1 - \alpha)^{1/2}]^{1/2}$, and this was regarded the mechanism of two-dimensional diffusion.

According to the thermal decomposition kinetics analysis of Dioscorea saponin before and after mechanical activation, Dioscorea saponin after mechanical activation changed from three-dimensional diffusion mechanism to two-dimensional diffusion mechanism, which was consistent with the conclusion that Dioscorea saponin changed from original ordered crystalline structure to amorphous state after mechanical activation.

CONCLUSION

The physical and chemical properties of Dioscorea saponin before and after mechanical activation were investigated. The main conclusions are as follows.

1. According to the SEM results, a significant change in the morphology of Dioscorea saponin can be observed before and after mechanical activation. After mechanical activation, Dioscorea saponin was transformed from massive crystals into minute particles. The D_{50} size of the mechanically activated Dioscorea saponin was 11.43 μm, and the particle size distribution was markedly narrow.

2. According to the XRD analytical results, the Dioscorea saponin samples had three distinct peaks. After mechanical activation, the peaks of Dioscorea saponin disappeared from the XRD diffraction map. The resultant wide single low-intensity peak indicates that the crystalline of Dioscorea saponin was significantly converted into amorphous state after mechanical activation.

3. According to the FTIR analytical results, none of the functional groups of the mechanically activated Dioscorea saponin disappeared, and no new functional groups appeared, which indicate that the mechanical activation does not induce a chemical transformation of Dioscorea saponin.

4. According to the TG–DSC analytical results, two endothermic peak of Dioscorea saponin after mechanical activation moved back 15 and 35 °C respectively, and it had 99 % weightlessness ahead of 100 °C due to the accelerated decomposition.

5. According to the results of thermal analysis kinetics, the average thermal decomposition activation energy of Dioscorea saponin after mechanical activation was increase 13.45 kJ/mol, and show a transformation from three-dimensional to two-dimensional diffusion mechanism.

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