Study on Thermal Decomposition Behavior of Tea Saponin from Camellia Oleifera Cake

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Abstract. Different contents of tea saponin (CZS-1 and CZS-2) from Camellia oleifera Cake were prepared via ethanol extraction method, and thermal degradation temperature and thermal degradation kinetics of the CZS-1 and CZS-2 were studied by thermogravimetric analyzer method. The results indicate that the thermal degradation of CZS-2 involves three steps, the thermal degradation of CZS-1 involve four steps. The thermal decomposing temperature <430℃, thermal stability of CZS-2 was worse; while the thermal decomposing temperature >430℃, the relationship was just opposite. With the heating rate increasing, thermal decomposing temperature of CZS-1 and CZS-2 were increased gradually. The thermal degradation kinetics of CZS-1 and CZS-2 were studied by Kissinger’s method. It was found that thermal degradation activation energy of CZS-1 and CZS-2 were 43.6 kJ/mol and 30.7 kJ/mol at the first and second steps, respectively.

1. Introduction
Camellia oleifera Abel, a theaceous evergreen tree, is distributed and cultivated widely in the central and south China. The seeds are important oil material in China used extensively for producing a kind of tea oil, whose beneficial unsaturated fatty acids are comparable to those of olive oil [1]. To get one ton of tea oil, four times of residue composing of the remaining grounded fruit and shell will be produced, which is called “seed cake” of C. oleifera. As a big amount of by-product, the seed cake of C. oleifera is normally used as detergent, animal feeds, or organic fertiliser, due to the containing of rich polyphenols, saponins, protein, polysaccharide, etc [2].

Tea saponin is a kind of triterpenoid saponin mixture, which is composed of hydrophobic ligands, hydrophilic sugar bodies and organic acids [3-5]. It is a kind of biomass raw material with excellent biological activity and surface activity, due to the characteristics of mild, degradable, non-toxic and so on. And that is widely used in medicine, detergent, textile, flame retardant and other fields [6-10].

Up to now, the study on tea saponin mainly focus on extraction, separation and biological activity, while as biomass raw material are very few, especially in the field of flame retardant. Through the preliminary test, it was found that the thermal stability of tea saponin with the same purity produced by different manufacturers was significantly different, which may be caused by different extraction
processes. Therefore, thermogravimetric analyzer and Kissinger method were used to analyze the thermal stability of tea saponin with different contents under the same extraction process, so as to provide scientific basis for the application of tea saponin in the field of flame retardant.

2. Materials and methods

2.1. Main reagents and instruments

The Camellia oleifera Cake was purchased from a tea oil factory in Guizhou Province, China, where C. oleifera has been planted widely for producing tea oil. Anhydrous ethanol was obtained from Tianjing fuyu fine chemical co., LTD. XFB-500 high speed TCM pulverizer (Jishou zhongxiang pharmaceutical machinery factory); AL204 -IC electronic balance (Mettler Toledo, Switzerland); N-1000S-WA rotary evaporator (Tokyo rikaji apparatus co., LTD); PC 101NT chemical diaphragm pump (vacuubrand, Germany); Discovery thermogravimetric analyzer (TA, USA).

2.2. Extraction of tea saponin

Take a certain amount of cold-pressed Camellia oleifera Cake which has been crushed through a 40-mesh sieve, reflux for 1h with 5 times the amount of petroleum ether at 50℃, remove tea oil, filter, and get degreased Camellia oleifera Cake by volatile petroleum ether. Add 20g degreased Camellia oleifera Cake to 500 ml round bottom flask, the extraction was heated by electric heating jacket according to the extraction process (ethanol mass fraction 84%, extraction temperature 80℃, extraction time 3h and liquid-solid ratio 10:1), Strike filter, washed residue and combine filtrate; When the filtrate was concentrated into a slurry, stop heating, add alum 10% of the weight of the slurry filtrate, stir it for 15 min thoroughly, then the sediment that named the crude tea saponin was separated after standing for 1 h, recorded as CZS-1 after drying. CZS-1 and 5% calcium oxide were added to the round bottom flask, stirred for 15min thoroughly, filtered and separated after standing for 1 hour, then, ammonium bicarbonate was added into the precipitate to transform CZS-1 into liquid, filtered, recorded as CZS-2 after drying. Formula 1 was used to calculate the extraction rate of tea saponin.

\[
Y_1 = \frac{m}{M} \times 100\%
\]  

Where \(Y_1\), \(m\) and \(M\) are the extraction rate, the quality of tea saponin and the degreased Camellia oleifera Cake, respectively.

2.3. Content determination of tea saponin

Refer the SN/T 1852-2006 method [11] to improvement: the samples were precisely weighed about 1.5g and placed in triangle flask, add 12ml hydrochloric acid after dissolve with 10ml deionized water, reflux at 100℃ for 2h, filtered at room temperature and washed to neutral; the remaining steps were basically the same as the SN/T 1852-2006 method. Formula 2 was used to calculate the content of tea saponin.

\[
Y_2 = \frac{(m_3-m_2-m_0) \times 1223.54}{501 \times m_1} \times 100\%
\]  

Where \(Y_2\), \(m_0\), \(m_1\), \(m_2\) and \(m_3\) are the tea saponin content, blank residue quality, sample quality, receiving bottle mass and receiving bottle and extract mass after constant weight, respectively.

2.4. Thermogravimetric analyses

Thermogravimetric analyses were performed on the CZS-1 and CZS-2 samples in a thermobalance TA Instruments Discovery. The samples were submitted to nitrogen atmospheres under a flow rate of 10℃/min under standard temperature and pressure conditions (273 K and 101,325 Pa). They were heated from 40℃ to 800℃under a heating rate equal to 10, 20, 40℃/min, respectively. For each experiment, around 5 mg of samples were placed in the crucible of the thermobalance.
Thermogravimetric experiments were repeated at least three times for each sample with good repeatability.

3. Results and discussion

3.1. Content of CZS-1 and CZS-2

The market price of tea saponin is relatively high, and the price of tea saponin with 60% content is as high as 50 million yuan/ton. Given that, the determination of tea saponin content is very necessary. Therefore, the content of CZS-1 and CZS-2 were determined, and the results were shown in table 1.

| Sample | Content / % | Extraction yield / % |
|--------|-------------|---------------------|
| CZS-1  | 63.92       | 13.52               |
| CZS-2  | 86.24       | 6.14                |

3.2. Thermal decomposition characteristics of CZS-1 and CZS-2

Fig. 1 presents the overall thermogravimetric decomposition process of CZS-1 and CZS-2 at a heating rate of 10℃/min. As shown in Fig. 1, thermal degradation of CZS-1 can be broadly divided into four stages. The first stage is a dehydration stage with a temperature range from 210 to 220 ℃, presumably due to a large number of hydroxyl groups on tea saponin glycoside were removed, resulting in H₂O releasing, and making the most weight loss. At the second stage ranging from 270 to 290℃, triterpene structure of CZS-1 was degraded into CO₂ and H₂O, then released. What’s more, the third thermal degradation stage among the temperature ranging from 430 to 450 ℃ with a slow weight loss, may be accompanied by some volatile small molecules released. The final stage of thermal decomposition is among the temperature ranging from 470 to 600℃, due to the thermal hysteresis of the material. Meanwhile, similar results were obtained from the thermal degradation of CZS-2 in Fig. 1, showing three stages with the decomposition temperature mainly ranging from 210 to 450 ℃, which was basically consistent with reported results of CZS-1. However, the thermal degradation of CZS-2 tends to be constant after 600℃, and the carbon residual was about 24.6% at 600℃ compares to only 3.5% for CZS-1. In addition, as seen from Fig. 1, it was interestingly found that the thermal decomposing temperature <430℃, thermal stability of CZS-2 was worse; while the thermal decomposing temperature >430℃, the relationship was just opposite.

![Fig. 1 Thermal degradation curves of CZS-1 and CZS-2](image-url)
3.3. Thermal degradation kinetics of CZS-1 and CZS-2

As shown in Fig. 2, with the heating rate increasing, thermal decomposing temperature of CZS-1 and CZS-2 were increased gradually. Decomposition temperature of CZS-1 and CZS-2 with t10%, t20%, and t50% were 209.4, 242.4, 350.7 °C and 203.9, 233.5, 345.3 °C at a heating rate of 10 °C/min, respectively; while at a heating rate of 40 °C/min, decomposition temperature of CZS-1 and CZS-2 with t10%, t20%, and t50% were 221.0, 250.9, 342.4 °C and 217.2, 243.2, 346.6 °C, respectively.

![Thermal degradation curves of CZS-1(a) and CZS-2(b) at different heating rate](image)

To explore the activation energy of CZS-1 and CZS-2 at the first and second thermal degradation stage, thermal degradation kinetics of CZS-1 and CZS-2 were studied by Kissinger’s method. Formula 3 was used to calculate the activation energy of CZS-1 and CZS-2.

\[
\ln \left( \frac{\beta}{T_{\text{max}}^2} \right) = \ln \left( \frac{AR}{E} \right) - \frac{E}{RT_{\text{max}}} 
\]

Where \( E \) is the activation energy (kJ/mol), \( R \) is the gas constant (8.314 J/K mol), \( A \) is the pre-exponential factor (min\(^{-1}\)), \( T \) is the absolute temperature (K), \( \beta \) is the heating rate.

Fig. 3 shows the linear plots of \( \ln \left( \beta/T_{\text{max}}^2 \right) \) versus \( T_{\text{max}}^{-1} \) for CZS-1 and CZS-2 from the Kissinger method. Activation energy is the minimum energy for thermal degradation of materials [12], which reflect the thermal stability of the material. The higher the value, the higher the thermal stability. Even though Kissinger’s method is a special case in determining \( E \) and it may not display overall trend of \( E \) due to the fact that only data from a certain conversion rate is used. In this study, it was found that thermal degradation activation energy of CZS-1 and CZS-2 were 43.6 kJ/mol and 30.7 kJ/mol at the first and second steps, respectively. This was basically consistent with the conclusion of thermal decomposition characteristics for CZS-1 and CZS-2.

![Thermal degradation kinetic curves of CZS-1 and CZS-2 at the first (a) and second (b) thermal degradation stage](image)
4. Conclusion
1) The thermal degradation of CZS-2 involves three steps, the thermal degradation of CZS-1 involve four steps. The thermal decomposing temperature <430℃, thermal stability of CZS-2 was worse; while the thermal decomposing temperature >430℃, the relationship was just opposite.
   2) With the heating rate increasing, thermal decomposing temperature of CZS-1 and CZS-2 were increased gradually. The thermal degradation kinetics of CZS-1 and CZS-2 were studied by Kissinger’s method. It was found that thermal degradation activation energy of CZS-1 and CZS-2 were 43.6 kJ/mol and 30.7 kJ/mol at the first and second steps, respectively.

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References
[1] Long, Z. H., Wang, D. P. Chemical constituents of olive oil and from Camellia oleifera seed oil [J]. Journal of the Chinese Cereals and Oils Association, 2008, 23, 121-123.
[2] Wang, T. J., Wei, F. F. The value of comprehensive utilization of oil cake and summary of methods [J]. Journal of East China College of Geology, 1990. 13, 57-62.
[3] Murakami T, Nakamura J, Masuda H, et al. Bioactive saponins and glycosides. XV. Saponin constituents with gastroprotective effect from the seeds of tea plant, Camellia sinensis L. var. assamica Pierre, cultivated in Sri Lanka: structures of assamsaponins A, B, C, D, and E [J]. Chemical & Pharmaceutical Bulletin, 1999, 47 (12): 1759-1764.
[4] Jiang Heyuan, Zhang Jianyong, Gao Qingqing. The properties, preparation and application of tea saponin [J]. China Tea, 2007, 29(3): 14-16.
[5] Xie Qiuying, Huang Yuying, Song Zhenrong. Purification and quantitative determination of tea saponin in extracted from finished product [J]. Journal of Fujian Fisheries, 2010, 32(6): 14-17.
[6] Guo Xia, Xu Rongnian, Qin Zhirong, et al. Research progress of a novel nonionic surfactant of tea saponin[J]. Journal of China Detergent Industry, 2011(2): 43-46.
[7] Huang Jiguang, Chen Xiuxiao, Xu Hanhong, et al. The antibacterial activity of tea saponin against twelve plant pathogenic fungi [J]. Journal of Huazhong Agricultural University, 2013, 32(2): 50-53.
[8] Liao Xiaoxia, Zhu Liwei, Peng Qian, et al. Study on surface activity of Gleditsia Saponin and Camellia Saponin [J]. Chemistry and Industry of Forest Products, 2009, 29(2): 69-74.
[9] Chen L Y, Chen J, Xu H H. Sasanquasaponin from Camellia oleifera Able. induces cell cycle arrest and apoptosis in human breast cancer MCF-7 cells [J]. Fitoterapia, 2013, 84: 123-129.
[10] Hou Ruyan, Wan Xiaochun, Wen Han. Research progress of chemical structure and biological activity of saponins [J]. Journal of Anhui Agricultural University, 2005, 3(3):369-372.
[11] SN/T 1852-2006 Determination of saponin content in tea saponin for export [S].
[12] Galwey A K. Is the science of thermal analysis kinetics based on solid foundations. A literature appraisal [J].
[13] Thermochim Acta, 2004, 413: 139-183.