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Studies on the highly efficient catalyzation of sesamin to asarinin by phosphotungstic acid

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Abstract

The conversion of sesamin to asarinin is a promising route for the production of asarinin. This work reports the affection of acid type and strength of the catalyst on the conversion of sesamin to asarinin and the effect of various reaction conditions in anhydrous ethanol using phosphotungstic acid (HPW) as catalyst. The experimental results indicate that the activity of sesamin conversion is determined by strong B acids. L acids are not active for the reaction, and do not show synergy with B acids for the formation of asarinin. Reaction time, HPW dosage and temperature have significant effects on sesamin conversion. A maximum asarinin yield of 57.93% was achieved. The reaction kinetics in the temperature range 55-75 °C were studied. The kinetic curves can be successfully fitted with an opposing first-order reaction model. The activation energy (Ea) for this reaction is found to be 105.2 ± 0.4 kJ/mol.

Keywords: sesamin; asarinin; phosphotungstic acid; activation energy; acid catalysts.

Practical Application: Phosphotungstic acid, as a strongly acidic solid acid, can catalyze the conversion of sesamin to asarinin with high efficiency, which provides a reference for the production of sesame oil rich in asarinin and a new direction for the industrial large-scale preparation of asarinin.

1 Introduction

Sesame seeds are one of the most important and oldest oil crops in the world, cultivated in many countries and areas (Wan et al., 2015). About 70% of the world's sesame seed production is used to extract oil for food product (Nikzad et al., 2021), which are widely used in East Asian countries (Japan, Indian and China). The strong stability of sesame oil compared to other edible oils may be related to the presence of lignans, including sesamin, sesamolin and asarinin. Actually, asarinin is rarely found in unrefined sesame seed oil but is generated in equivalent amounts from sesamin by isomerization during the acid-clay bleaching of the oil (Fukuda et al., 1986).

Asarinin is a trace compound which is mainly found in the roots of asarum, with a content of about 0.1~0.2% (Xiao et al., 2021). Asarinin also have been reported from zanthoxylum, sesame seeds and other medicinal plants (Nooreen et al., 2019), with a much lower content than in asarum. Various studies demonstrate that asarinin has excellent anti-inflammatory (Zhang et al., 2014; Dai et al., 2020), antibacterial (Bussey et al., 2014; Hou et al., 2020), immunosuppression (He et al., 2021; Dai et al., 2019) and anti-tumor (Cai et al., 2008; Jeong et al., 2018) effects, and thus can play an important role in human health. Due to its remarkable pharmacological effects, asarinin has attracted tremendous research interest of scientists in recent years. So far, asarinin has been produced by extraction and separation methods from asarum using organic solvents, a time-consuming process of low yield and high cost, which obstructs the large-scale production and application of asarinin to some extent.

Li et al. (2005) reported that sesamin could be converted into asarinin under acidic conditions (Figure 1), and the yield reached more than 50%. Sesamin is one of the major lignans in sesame seed and oil, the content of sesamin in sesame seed is 0.3~1.0% (Moazzami et al., 2007; Zhou et al., 2010; Hemalatha & Ghafoorunissa, 2004). As the major source of sesamin, sesame seed are widely distributed and the global production of sesame seeds is high (Capellini et al., 2019; Buranachokpaisan et al., 2021). Moreover, there is already a large amount of plants to engage in the extraction and isolation of sesamin, such as Magnolia sp., Piper sp., Virola sp. and Camellia sp. (Dar & Arumugam, 2013). Thus, sesamin could be another raw material for asarinin with wider availability and larger amount of supply than asarum. Furthermore, this technology can be seamlessly integrated with present sesame oil industry.

In the earlier researches, liquid mineral acids, such as HCl and H_2SO_4, were used as catalysts for sesamin conversion to asarinin (Kuo et al., 2011; Chen et al., 2018; Tsai et al., 2020). Nevertheless, the intrinsic catalytic activities are relatively low, and the use of these conventional mineral acids causes several problems such as environmental problems, corrosion problems, as well as difficulties of separation from products for reuse. In this regard, the development of novel solid catalysts as alternatives of conventional mineral acid ones is highly desirable considering

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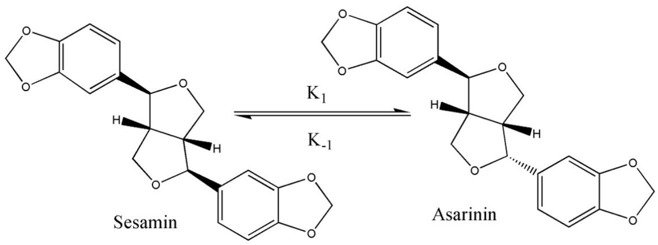

Figure 1. The structure of sesamin, asarinin and the mutual isomerization.

environmental friendliness and industrial benefits. Furthermore, some fundamental mechanism issues about this catalytic reaction have not yet been revealed. As we all know, the catalytic activity of acids strongly depends on the acid type (Brønsted or Lewis acid, B or L), acid strength and acid concentrations (Gardy et al., 2019; Silva & Oliveira, 2018). Although several research articles have reported the conversion of sesamin to asarinin by solid acids (Yu et al., 2022), there are both L and B acids in the catalysts. It is still not clear which type of acid is more catalytically active or if there is a synergy between the two type acids, and if the stronger the acidity, the better it is for this catalytic reaction or there is a best value of a moderate acid strength.

Based on the discussion above, a series of catalysts with L, B or both acids and different acid strength were used to catalyze the conversion of sesamin to asarinin in anhydrous ethanol solvent in this study. The affections of acid type, acid strength and acid concentration on the catalytic activity for this reaction were investigated. On the basis of these experiments, we choose phosphotungstic acid (HPW), a solid acid with super strong B acidity (Alazman et al., 2019; Meireles et al., 2021), as the catalyst for the conversion of sesamin to asarinin for the first time. The effect of various conditions, such as catalyst amount, reaction time, reaction temperature and initial sesamin concentration was investigated. The reaction kinetics and the relevant kinetic parameters such as reaction rate constant were obtained through fitting the kinetic curves with an opposing reaction model. The activation energy for this catalytic system was also obtained by using the Arrhenius theory.

2 Materials and methods

2.1 Chemicals and reagents

Sesamin (98%) used as feedstock in this study was supplied by Macklin Biochemical Co. Ltd. Shanghai, China. HPW was supplied by Inokai Technology Co. Beijing, China. Methyl alcohol (Chromatographic grade) was supplied by Sigma-Aldrich chemical Co. Ltd. Anhydrous ethanol (analytical grade) was supplied by Tianjin Comeo Reagent Co. Ltd. Tianjin, China.

2.2 Preparation of catalyst

γ-Al_2O_3, Nb_2O_5 calcined at 550 °C for 1 h with a ramp rate of 2 °C min^{-1} in a muffle furnace in static air. The prepared catalysts were labeled as γ-Al_2O_3* and Nb_2O_5*, respectively.

Preparation of SO_4^{2-}/Nb_2O_5, SO_4^{2-}/TiO_2: Nb_2O_5 or TiO_2 (1 g) was added to 10 mL of 2.5 mol/L H_2SO_4, and stirred vigorously for 2 h. The resulting precipitated solid was filtered, subsequently dried at 120 °C for 12 h and calcined at 500 °C for 3 h in static air (Yang et al., 2015).

Preparation of SiO_2/γ-Al_2O_3: γ-Al_2O_3 (1 g) was added to 20 mL of 0.2 mol/L oxalic acid, reflux at 100 °C for 1 h, then dried. Subsequently, 0.2 mol/L tetrathoxysilane (TEOS) was added and stirred vigorously for 30 min, ultrasonic for 30 min, dried at 80 °C and added 0.5 mL of water, ultrasonic for 30 min again, dried at 100 °C. The dried solid was calcined for 1 h at 550 °C.

2.3 Acid-catalyzed conversion of sesamin

The reactions were performed in a 50 mL three-necked flask equipped with a reflux condenser and a magnetic stirrer. Typically, a certain amount of sesamin and a certain volume of anhydrous ethanol were put in a three-necked flask, the three-necked flask is connected to the condenser and thermometer. After heating to the target temperature in the oil bath, catalysts were immediately put into three-necked flask while the mixture was stirred magnetically during the reaction. After reaction, samples were cooled down in a cold ice bath to immediately terminate the reaction, then samples were treated and analyzed with high performance liquid chromatography (HPLC).

2.4 Quantitative analysis of the product using HPLC

The amounts of sesamin and asarinin in the reaction mixture were quantified using HPLC. The HPLC was equipped with a Waters Sun Fire® C18 analytical column (250 mm × 4.6 mm, 5 μm) and a Waters 2695 high performance liquid chromatographic system with a Waters 2489 UV/Vis detector (Waters, CA, USA), wavelength 287 nm. The mobile phase consisted of pure water and methanol (30:70 v/v) at a flow rate of 0.80 mL/min. The column was operated at 30 °C. The retention times of sesamin and asarrinin are 17.7 and 20.6 min, respectively. The yield of asarinin was calculated as follows (Equation 1):

$$Yield\ of\ asarinin(\%) = \frac{concentration\ of\ asarinin\ in\ the\ product}{concentration\ of\ sesamin\ in\ the\ feed} \times 100 \qquad (1)$$

3 Results and discussion

3.1 Effect of acid type on the yield of asarinin

As known in some other isomerization reactions, L acid is always essential (Cho et al., 2015; Gounder & Davis, 2013). Sesamin isomerization to asarinin is an acid-catalyzed reaction. Although most catalysts used for this reaction have been reported as B acids in previous literatures, the effectiveness of L acid for this reaction has not been studied yet. To elucidate this point, a series of homogeneous and heterogeneous catalysts with only L acids were chosen to catalyze the conversion of sesamin to asarinin in anhydrous ethanol. The effect of the acid type on asarinin yield is shown in Table 1. As can be seen from Table 1, in the presence of several L acid catalysts (γ-Al_2O_3, B_2O_3 and BF_3) (Feng et al., 2014), asarinin was not detected in the reaction and sesamin was not converted at all, which means L acid alone is not active to catalyze the conversion of sesamin to asarinin. To further investigate the effect of acid type on asarinin yield, a series of well-known monolithic catalyst containing

Table 1. Effect of acid type on the yield of asarinin (reaction conditions: sesamin 50 mg, catalyst 100 mg, anhydrous ethanol 10 mL, 78 °C, 1 h).

Catalysts	Acid type	Yield of asarinin (%)
γ-Al_2O_3	L acid	Nd[a]
γ-Al_2O_3*	L acid	Nd
B_2O_3	L acid	Nd
BF_3	L acid	Nd
Nb_2O_5	L and B acid	Nd
Nb_2O_5*	L and B acid	Nd
TiO_2	L and B acid	Nd
SiO_2/γ-Al_2O_3	L and B acid	Nd
SO_4^{2-}/Nb_2O_5	L and B acid	0.73
SO_4^{2-}/TiO_2	L and B acid	2.09

[a]Nd = no detection; *Represents catalyst calcined at 550 °C for 1 h.

both L acid sites and B acid sites (Nb_2O_5, TiO_2, SiO_2/γ-Al_2O_3, SO_4^{2-}/Nb_2O_5 and SO_4^{2-}/TiO_2) were prepared and used to catalyze the conversion of sesamin to asarinin. In these heterogeneous catalysts, the central metal M (M=Nb, Al or Ti) act as L acids, and the protons on terminal or bridging hydroxyls play the role of B acids. It can be seen asarinin was still not detected when Nb_2O_5, Nb_2O_5*, TiO_2 and SiO^{2-}/γ-Al_2O_3 were used as catalysts. Only small amounts of asarinin (2.09% and 0.73%) were formed in the presence of SO_4^{2-}/TiO_2 and SO_4^{2-}/Nb_2O_5, which was attributed to the stronger B acidity on the surface of them than the others. These results indicate that neither L acid alone nor the combination of L and weak B acid can converse sesamin to asarinin. The isomerization of sesamin to asarinin requires strong B acid catalyst, which will be further elucidated in the following experiments.

3.2 Effect of acid strength on the catalytic activity

The catalytic activities of B acids with different acid strengths (HPW > H_2SO_4 > HCl > HNO_3 > H_3PO_4 > H_3BO_3) on the conversion of sesamin to asarinin were examined. As seen in Figure 2, no formation of asainin was detected by using H_3BO_3 (a weak B acid, $pK_a = 9.2$) and H_3PO_4 (a medium strength B acid, $pK_a = 2.1$) as catalysts. When the acid strength was increased to be as strong as HNO_3 ($pK_a = -1.3$), a small amount of asarinin was obtained after a reaction time of 1 h. The turnover number (TON) which indexes the intrinsic activity of catalyst was calculated as 0.36 mol asarinin per mol H^+. When HCl was used as the catalyst ($pK_a = -7$), the TON was increased to 0.70. When H_2SO_4 was employed to catalyze ($pK_a = -9$) the conversion of sesamin to asarinin, the TON was further increased to 1.53. Then we take HPW (a well-known solid super acid, $pK_a = -13$) as the catalyst, the TON was increased to a level as high as 19.70 mol asarinin per mol H^+. It indicates that weak B acids cannot converse sesamin to asarinin and only strong B acids can catalyze the isomerization. The catalytic activity is positively correlated with the B acid strength. The higher B acid strength, the more efficient the catalyst is in terms of sesamin conversion.

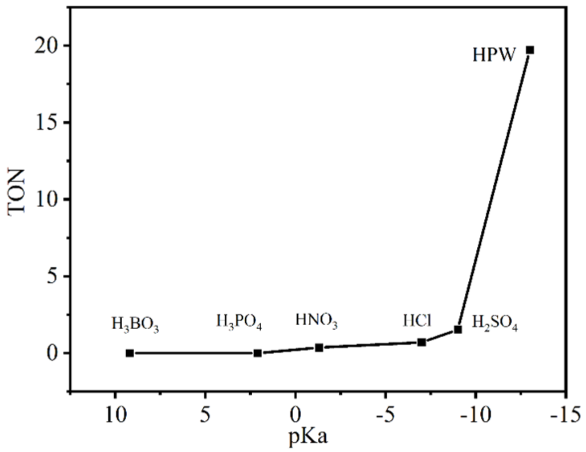

Figure 2. Effect of acid strength on the yield of asarinin (reaction conditions: 0.2wt% sesamin, 10wt% catalyst, 78 °C, 1 h).

3.3 Effect of B and L acid synergy

In some reactions, catalyst exhibits high catalytic activity only in the presence of both B acid and L acid (Gallo et al., 2013). For the conversion of sesamin to asarinin, experiments above have shown that only strong B acids can catalyze this reaction, L acids alone do not work. However, it has not been revealed yet if L acid can act as an additive to increase the catalytic activity of strong B acid and present some kind of B/L acid synergy. In the following study, the conversion of sesamin to asarinin was examined over strong B acid catalysts alone and combinated B/L acid catalysts. The results are shown in Figure 3. When $FeCl_3$, a pure L acid (Azizi et al., 2017; Tomifuji et al., 2018), was added to combine with the strong B acid catalysts of H_2SO_4, HCl, HNO_3 and HPW, there was no significant increase in the yields of asarinin as compared to that using B acid catalysts alone. The small differences are within error range. It unambiguously demonstrates that L acid does not play a role in the reaction. No synergy happens between B and L acid catalysts for the isomerization of sesamin to asarinin. Not only the L acid alone cannot catalyze the conversion, but also it cannot help the strong B acid to increase the catalytic activity. The isomerization of sesamin to asarinin can only be catalyzed by strong B acids.

3.4 HPW-catalyzed conversion of sesamin

Bases on the results above, it can be concluded that strong B acid is the dominating factor for the sesamin conversion to asarinin. Considering the catalytic activity and easy recovery, the solid acid HPW was chosen as the catalyst and the reaction conditions was modified and investigated in the following study.

Effect of the initial sesamin concentration on asarinin yield

To evaluate the affection of initial sesamin concentration on the reaction effect, asarinin yields of initial sesamin concentrations of 0.1-0.5wt% were investigated at 5wt% HPW and 78 °C for 3 h reaction time. The results are presented in Figure 4. At sesamin

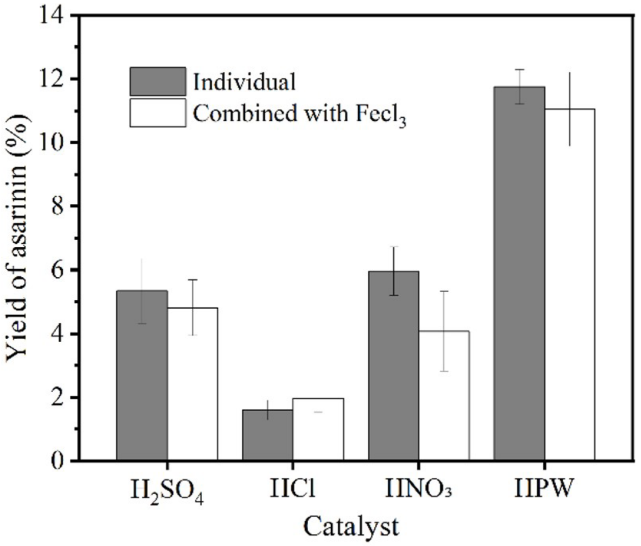

Figure 3. Comparison of the yields of asarinin using individual B acid catalysts and combined B/L acid catalysts (reaction conditions: 0.2wt% sesamin, catalyst to $FeCl_3$ molar ratio of 1:1, 78 °C, 1 h).

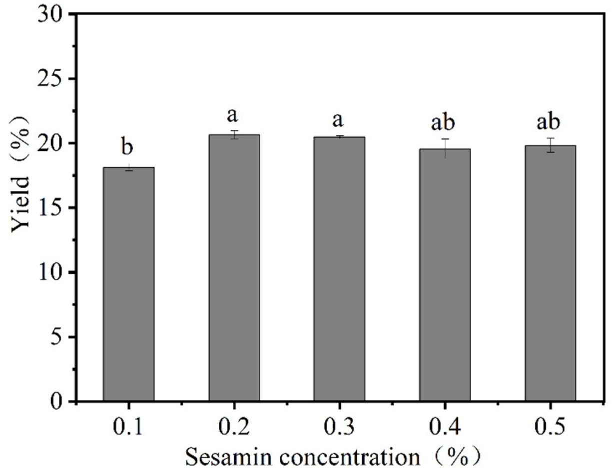

Figure 4. Effect of initial sesamin concentration on asarinin yield. Values with different letters are significantly different ($P < 0.05$). Values with the same letter are not significantly different ($P > 0.05$).

initial concentration range of 0.2-0.5wt%, the obtained asarinin yield ranged from 19.55% to 20.65%, which was not significant ($P > 0.05$). These results indicated that initial sesamin concentration have no significant effects on sesamin conversion. At sesamin concentration of 0.2wt%, the conversion of sesamin and the yield of asarinin was the highest. Henceforth, 0.2wt% was used as the optimum reaction parameter for further reaction studies.

Effect of acid concentration on asarinin yield

Catalyst dosage is an important factor which affects conversion of sesamin and the catalyst cost. The effect of acid concentration on the asarinin yield was studied with 0.2wt% initial sesamin at 78 °C for 3 h. The yields of asarinin obtained from sesamin by using different percentage HPWs are provided in Figure 5.

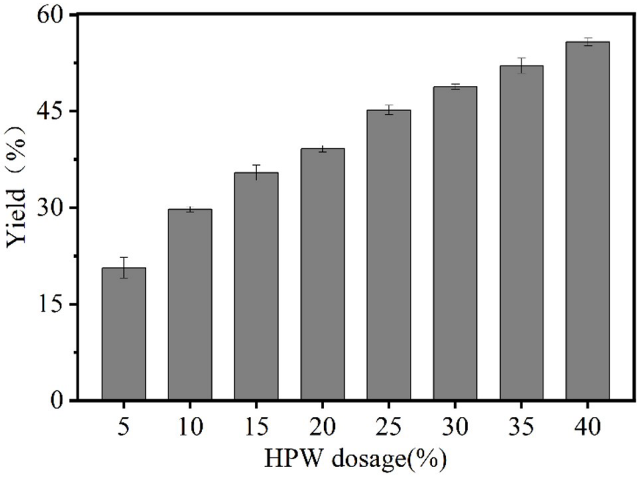

Figure 5. Effect of HPW dosage on asarinin yield.

When the HPW dosage was increased from 5 to 40wt%, the yield of asarinin increased from 20.65% to 55.76%. It indicates that HPW dosage has significant effects on sesamin conversion. The isomerization reaction of sesamin was found to be accelerated by increasing the HPW dosage. This is attributed to an increase in the acid concentration and thus the available number of active sites with increased catalyst dosage. In general, an increment in the catalyst excess results in an increasing viscosity of the reaction system which decreases the yield of asarinin. Owing to the excellent solubility of HPW in anhydrous ethanol, the increase of HPW has little effect on the viscosity of the reaction system, the yield of asarinin did not decrease even when the HPW dosage reached 40wt%. However, when HPW exceeded a certain amount, it triggered the formation of by-products. The dosage of HPW can be chosen as 5-10wt%, taking into account the catalytic efficiency and product selectivity.

Effect of the reaction time on asarinin yield

In general, there is a positive correlation between reaction time and reactivity, i.e., the product yield gradually increases with increasing reaction time, but there is an optimal reaction time for each reaction in terms of productivity. The effect of reaction time on sesamin conversion at 78 °C with 8wt% HPW and 0.2wt% sesamin was investigated. As seen in Figure 6, the conversion of sesamin can be roughly divided into two stages. The yield of asarinin increased sharply with increasing the reaction time from 1 to 12 h in the first stage, while further increasing the reaction time from 12 to 24 h only led to a marginal increase in the asarinin yield in the second stage. The conversion rate of sesamin in the first 12 h was higher than that in the last 12 h. This is because the isomerization of sesamin to asarinin is an opposing reaction, and asarinin and sesamin can be converted to each other. In the early stage of the reaction, the concentration of sesamin in the reaction system is kept at a high level and the concentration of asarinin in the reaction system is at a low level, so that the forward reaction carries out quickly while the reverse reaction proceeds slowly. With the increase of time, the concentration of sesamin decreases and the concentration of

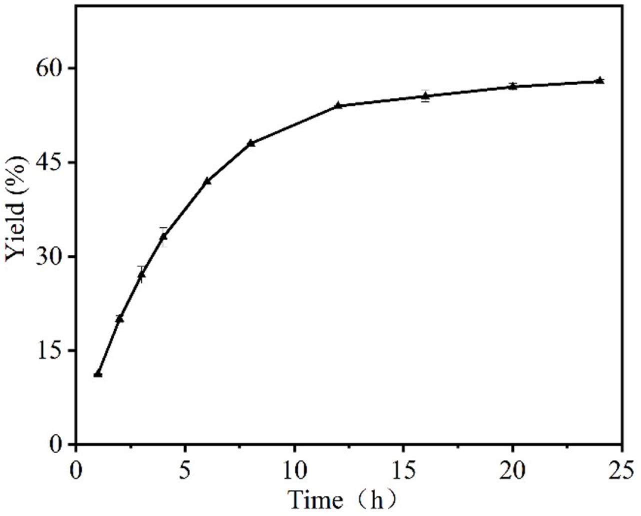

Figure 6. Effect of reaction time on asarinin yield.

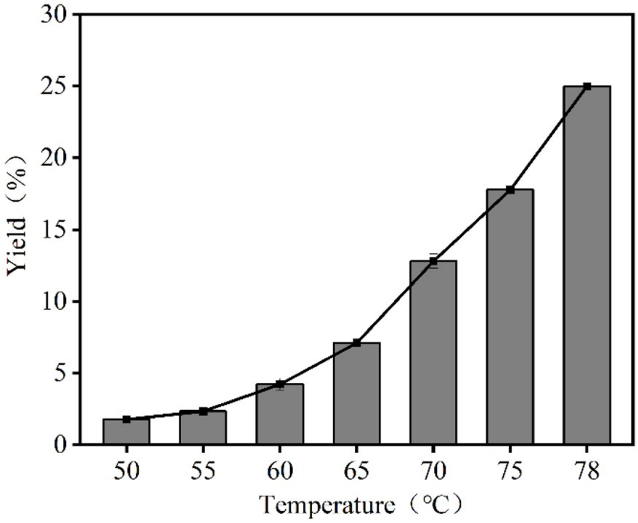

Figure 7. Effect of reaction temperature on asarinin yield.

asarinin increases, leading to the decrease in forward reaction rate and the increase in reverse reaction rate. The reaction gradually reaches an equilibrium state. At 24 h reaction time, the asarinin yield reached 57.93%, which was in good agreement with the literature report (Li et al., 2005). A too long reaction time is meaningless in the asarinin production, thus, 12 h may be an optimal reaction time at this reaction condition.

Effect of the reaction temperature on asarinin yield

The reaction temperature is another important factor on the conversion of sesamin. It can not only affect the reaction rate, the equilibrium constant and the byproduct, but also the energy cost in production. A wide range of reaction temperature for the conversion of sesamin to asarinin in anhydrous ethanol was investigated. The reactions were carried out at an initial sesamin concentration of 0.2wt% and reaction time of 3 h with 8wt% HPW as the catalyst. The results are shown in Figure 7. The yield of asarinin is barely visible at the lower temperature (50 °C), indicating a high stability of sesamin at this temperature and it is almost the lower boundary for sesamin conversion. With increasing of reaction temperature from 50 °C to 75 °C, the yield of asarinin increased slightly from 1.79% to 17.78%. At the boiling point of anhydrous ethanol (78 °C), the yield of asarinin reached 25.05% and no byproduct was observed. These results demonstrate that the asarinin yield grows monotonously with the reaction temperature in the tested range. The higher the reaction temperature is until the boiling point of anhydrous ethanol, the better it is for the yield of asarinin.

3.5 Kinetic studies

The reaction kinetic is very important both for understanding the fundamental reaction mechanism and for practical production (Sun et al., 2022; Xiong et al., 2022). Isomerization of sesamin to asarinin is a reversible reaction as schemed in Figure 1. The kinetic equations in differential and integrated form can be expressed as follows based on the first-order opposing reaction model (Equations 2-4):

$$\frac{dc_B}{dt} = k_1\left(c_{A,0} - c_B\right) - k_{-1}c_B \tag{2}$$

$$c_B = -\frac{k_1 c_{A,0}}{k_1 + k_{-1}} e^{-t\left(k_1 + k_{-1}\right)} + \frac{k_1}{k_1 + k_{-1}} c_{A,0} \tag{3}$$

When the reaction reaches equilibrium,

$$k_{-1}c_{B,e} = k_1(c_{A,0} - c_{B,e}) \tag{4}$$

Where $c_{A,0}$, c_B and $c_{B,e}$ are the initial concentration of sesamin, concentration of the asarinin after reaction time *t* and concentration of asarinin in equilibrium, respectively. k_1 is the kinetic constant for the forward reaction, while k_{-1} is the kinetic constant for the reverse reaction.

Sesamin conversion reactions in anhydrous ethanol were performed at a temperature range of 55-75 °C for a reaction time varying from 1 hour to 12 hours with a catalyst dosage of 8wt%. The results are shown in Figure 8a. The obtained kinetic constant k_1 is 0.0076, 0.0237 and 0.0701 at 55 °C, 65 °C and 75 °C (Table 2), respectively, through exponential fittings and calculations using Equation 3-4.

Further, the kinetic constant for temperature dependent reaction can be modeled by the Arrhenius equation (Equations 5-6),

$$k = A^{-\frac{Ea}{RT}} \tag{5}$$

$$\ln k = \ln A - \frac{Ea}{RT} \tag{6}$$

Where *k* is the kinetic constant, R is the universal gas constant, T is the reaction temperature (in Kelvin), Ea is the activation energy and A is the Arrhenius factor.

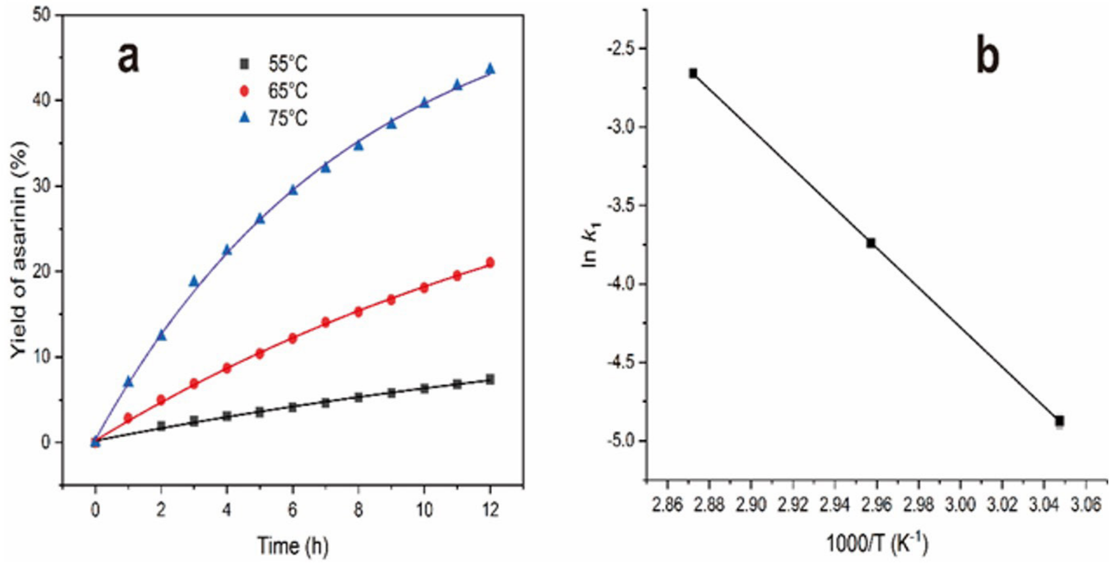

Figure 8. Kinetic plot at reaction temperature of 55 °C (black ▪), 65 °C (red ●) and 75 °C (blue ▲) and the corresponding exponential fittings (solid lines) (a). The Arrhenius plot for the kinetic constant k_1 (b).

Table 2. Reaction rate constants for conversion of sesamin over HPW catalyst.

Temperature (°C)	k_1	Coefficient of determination (R^2)	Ea (kJ/mol)
55	0.0076	0.9962	105.2 ± 0.4
65	0.0237	0.9992	
75	0.0701	0.9986	

The lnk_1 plot against 1/T and the linear fitting using Equation 6 were shown in Figure 8b. The Ea for sesamin conversion to asarinin in anhydrous ethanol in the presence of HPW catalyst was calculated as 105.2 ± 0.4 kJ/mol (Table 2).

4 Conclusion

A series of catalysts with Lewis (L), Brønsted (B) or both acids and different acid strength were used to catalyze the conversion of sesamin to asarinin in ethanol solvent in this study. The results suggest that strong B acids are essential for the catalytic conversion of sesamin to asarinin, while L acids are not active, and no synergic effects are found in this reaction. Furthermore, the catalytic activity was found to be higher with stronger B acid. On the basis of these findings, the solid super B acid, HPW, was used to catalyze the conversion of sesamin to asarinin for the first time. The effect of various conditions, such as catalyst amount, reaction time, reaction temperature and initial sesamin concentration was investigated on the sesamin conversion to asarinin. The HPW was found to have much higher intrinsic catalytic activities than previously reported mineral acid catalysts for this reaction. We also investigated the reaction kinetics and got the relevant kinetic parameters such as reaction rate constant through fitting the kinetic curves with an opposing reaction model. The activation energy for this catalytic system was obtained to be 105.2 ± 0.4 kJ/mol by using the Arrhenius theory. Due to its high acidity, strong stability, ease of preparation and recyclability, HPW will be a promising catalyst for the conversion of sesamin to produce asarinin on a large scale.

Acknowledgements

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