Preparation of Epoxy Wilsoniana Fruit Oil with Peracetic Acid

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Abstract: In this study, epoxy wilsoniana fruit oil (EWFO) was prepared using peracetic acid. The reaction time, temperature, and amounts of acetic acid, hydrogen peroxide, and concentrated sulfuric acid were studied for their influence on the epoxy value of the products. The optimum reaction conditions of EWFO were obtained by using the orthogonal experiment method. The structure and properties of the products were characterized by IR, 1H NMR, and GPC. Results showed that the optimum reaction conditions are as follows: mass ratio of (WFO):(acetic acid):(hydrogen peroxide):(concentrated sulfuric acid) of 30:11:28:0.1, reaction temperature of 75 °C, and reaction time of 1 h. The epoxy value of EWFO can reach 4.08% under these reaction conditions.

1. Introduction

Wilsoniana belongs to the cornaceae wood deciduous tree, and is an important high oil and low protein woody plant (the oil content of its fruit is more than 30%)[1]. It is widely distributed in the southern region of the Yellow River and around southwest China. In recent years, people have realized the ecological and economic importance of the Swida wilsoniana, thereby boosting interest in its research and development, especially in China. However, no studies have been reported on the epoxidation of Swida wilsoniana fruit oil. In this study, epoxidized Swida wilsoniana fruit oil was prepared from Swida wilsoniana fruit oil in the presence of a peracetic acid catalyst. First, the reaction time, temperature, and amounts of acetic acid, hydrogen peroxide, and concentrated sulfuric acid were studied for their influence on the epoxy value of the products. Then the epoxidation process was optimized by orthogonal experiments, and the reaction conditions were evaluated and analyzed based on the epoxy value of each product. Subsequently, the structure and properties of epoxidized Swida wilsoniana fruits oil were characterized by IR, 1H NMR, and GPC.

2. Experimental

2.1 Materials

WFO (refined, bleached, and deodorized) was provided by the Hunan Academy of Forestry (Changsha, Hunan, China) and was used as supplied. Hydrogen peroxide (30 wt. % in H2O), ethyl acetate (AR, 99%), sodium bicarbonate (AR, ≥99.8%), and magnesium sulfate anhydrous (AR) were purchased from Aldrich Chemical. Tetrahydrofurane (HPLC grade, ≥99.9%) was purchased from Aladdin (China). Glacial acetic acid was purchased from Shanghai Shenbo Chemical Co., Ltd. Concentrated sulfuric acid (AR, 95%-98%) was purchased from Sinopharm Chemical Reagent Co., Ltd. All materials were used as received without further purification.

2.2 Epoxidization of WFO

Epoxidized wilsoniana fruit oils (EWFOs) have been prepared by reacting the unsaturated sites of WFO with a mixture of glacial acetic acid, concentrated sulfuric acid, and hydrogen peroxide, according to a procedure in the literature[10,11]. In brief, WFO (30 g) was added to a 250 mL

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round-bottomed, three-necked flask equipped with a mechanical stirrer, thermometer, and reflux condenser. The reaction system was heated to 40 ℃. Certain amounts of glacial acetic acid, hydrogen peroxide, and concentrated sulfuric acid were placed in a separatory funnel and mixed. Then the mixture was added dropwise from the separatory funnel, and the reaction mixture was maintained at a certain temperature for several hours under vigorous stirring. After the reaction was complete, the crude product was transferred to a separatory funnel. Then, 150 mL of ethyl acetate and 150 mL of distilled water were added, resulting in two layers. The organic layer was washed with an aqueous sodium bicarbonate solution and distilled water several times until a neutral pH was obtained. The organic layer product was then dried over anhydrous MgSO4 and filtered. Finally, clear viscous EWFOs were obtained after removal of the solvent with a vacuum evaporator and analyzed for oxirane content.

2.3 Characterization

2.3.1 Epoxy value

The epoxy value of EWFO was measured by titration using the standard method (acetone-hydrochloride method)[12].

2.3.2 IR spectrum

IR spectra of WFO and EWFOs were acquired on a Nicolet 550 FT-IR spectrophotometer equipped with a deuterated triglycine sulfate detector. Scans were taken in a range of 4000–500 cm−1 at 4 cm−1 resolution at room temperature.

2.3.3 HNMR

All 1H NMR spectra were obtained using a Bruker HW300 MHz spectrometer and recorded in CDCl3 (internal reference 7.26 ppm).

2.3.4 Gel Permeation Chromatography

The molecular weights and molecular weight distributions of WFO and EWFOs were measured by gel permeation chromatography (Waters 1550–2410 system, 1550 HPLC Pump, 2410 refractive index detector, column Styragel HR1 and HR2). All the samples were dissolved in THF (0.5%, w/w), and the injection volume was 1 μL. THF was also used as the eluent with a flow rate of 1 mL/min. The calibration curve was constructed using polystyrene standards with different molecular weights.

3. Results and discussion

3.1 Effect of feed ratio on the epoxy value of EWFO

Epoxidation runs were conducted with the following range of conditions: acetic acid to WFO ratios of 0.3:3 to 1.3:3 by weight; hydrogen peroxide to WFO ratios of 0.8:3 to 3.3:3 by weight; concentrated sulfuric acid to WFO ratios of 0.01:3 to 0.06:3 by weight; reaction temperature 45−85 °C; reaction time 1−6 h; stirring speed 1500 rpm.

3.1.1 Effect of acetic acid-to-WFO mass ratio

To investigate the effect of the mass ratio of acetic acid to WFO on the EWFO epoxy value, the reaction was performed at different WFO ratios ranging from 0.3:3 to 1.3:3. The remaining reaction conditions are presented in Table 1. The influence of acetic acid dosage on the EWFO epoxy value is shown in Fig. 1. The epoxy value is low with low amounts of acetic acid. With increasing amounts of acetic acid, the epoxy value gradually increased. When the mass ratio of acetic acid to WFO was 1.1:3, the epoxy value reaches its maximum. After a further increase in the amount of acetic acid, the epoxy value decreased. Acetic acid plays a role in the transfer of reactive oxygen during the reaction process; hence, when the amount of acetic acid was increased, the epoxy value also increased. However, if the amount of acetic acid is too high, the ring-opening reaction of the

epoxy group will be accelerated. Therefore, the appropriate mass ratio range of acetic acid to WFO was 0.7:3 to 1.1:3.

Table 1 Effects of acetic acid-to-WFO mass ratio on epoxy value

No.	(acetic acid):(WFO)	(hydrogen peroxide):(WFO)	(concentrated sulfuric acid):(WFO)	time/h	temperature/ °C	Epoxy value/%
1	0.3:3	2.3:3	0.03:3	2	65	1.3591
2	0.5:3	2.3:3	0.03:3	2	65	2.6754
3	0.7:3	2.3:3	0.03:3	2	65	2.8165
4	0.9:3	2.3:3	0.03:3	2	65	3.2161
5	1.1:3	2.3:3	0.03:3	2	65	3.9155
6	1.3:3	2.3:3	0.03:3	2	65	3.1162

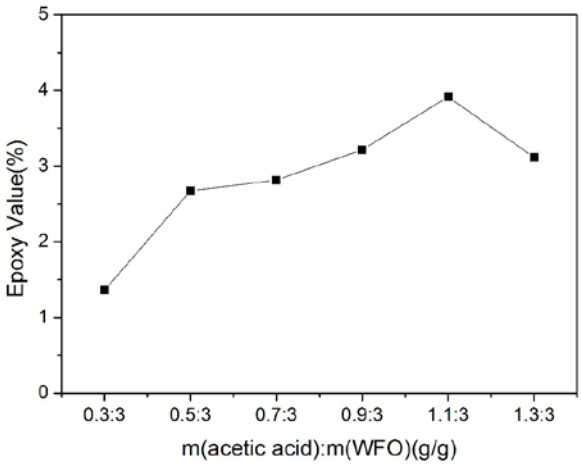

Fig. 1 Influence of (acetic acid):(WFO) on the epoxy value

3.1.2 Effect of hydrogen peroxide-to-WFO mass ratio

The effect of the ratio of hydrogen peroxide to WFO on the epoxy value was studied in the ratio range of 0.8:3 to 3.3:3. The remaining reaction conditions are presented . shows that the epoxy value gradually increased with increasing amount of hydrogen peroxide. An increased amount of hydrogen peroxide promotes the formation of peracetic acid, which is conducive to the epoxidation reaction. When the mass ratio of hydrogen peroxide to WFO is more than 2.3:3, the epoxy value decreases with increasing hydrogen peroxide. This is due to excessive hydrogen peroxide, which results in a large amount of water and leads to ring-opening. Other side reactions also occur. Therefore, the appropriate mass ratio range of hydrogen peroxide to WFO was 1.8:3 to 2.8:3.

3.1.3 Effect of concentrated sulfuric acid-to-WFO mass ratio

The effect of the mass ratio of concentrated sulfuric acid to WFO on the epoxy value was studied in the range of 0.01:3 to 0.06:The remaining reaction conditions are presented. that an increasing amount of concentrated sulfuric acid does not cause an obvious change in the epoxy value. This indicates that concentrated sulfuric acid has a non-significant effect on the epoxidation of WFO. Taking into account the cost of concentrated sulfuric acid and other factors, the appropriate mass ratio of concentrated sulfuric acid to WFO was 0.01:3.

3.2 Effect of reaction temperature on epoxy value

The effect of reaction temperature on the epoxy value was studied at 45, 55, 65, 75, and 85 °C. The remaining reaction conditions are presented . that a rising reaction temperature gradually increases the epoxy value. When the reaction temperature is above 65 °C, the epoxy value decreases with increasing reaction temperature. This is because when the reaction temperature is below 65 °C,

the increase in reaction temperature promotes the formation of peracetic acid, which is conducive to the epoxidation reaction. However, when the temperature of reaction is too high, a large amount of peroxide decomposes and the speed of the ring-opening reaction accelerates, thus leading to the decreased epoxy value. Considering these factors, the appropriate range of reaction temperature was set at 55−75 °C.

3.3 Effect of reaction time on epoxy value

The effect of reaction time on epoxy value was studied in the range of 1−6 h. The remaining reaction conditions.that within 2 h after the reaction began, the epoxy value increases with reaction time. When the reaction time exceeds 2 h, the epoxy value decreased dramatically. An increasing reaction time accelerates the ring-opening reaction under the action of hydrogen ions, and a double hydroxyl side product is formed. Therefore, the appropriate choice of reaction time was in the range of 1−3 h.

3.4 Optimization of experimental conditions

According to the experimental results mentioned above, the influence of the amount of concentrated sulfuric acid on epoxy value is slight.In order to identify the most important factor, the range analysis method was employed. There are two important parameters in range analysis: Ki and Rj. The mean value of the sum values for each level and each factor is defined as Ki. The variation trend of Ki can be used to determine the optimal level. The difference between the maximum and the minimum values of Ki is defined as Rj. The order of Rj is used to evaluate the importance of each factor on the epoxy value. A larger Rj denotes greater importance. All K values and R values of the factors for the L9 (34) matrix were calculated.

4. Conclusion

This article describes the reaction of peracetic acid with WFO, which was used for the synthesis of EWFO without any organic solvent. The results are summarized as follows:

FT-IR, 1H NMR, and GPC analyses indicated that the epoxidation reaction was carried out successfully. This was confirmed with the titration method, which was used to assess the epoxy value of the EWFO.

Under optimal reaction conditions (WFO: acetic acid: hydrogen peroxide: concentrated sulfuric acid = 3:1.1:2.8:0.01, reaction temperature 75 °C, and reaction time 1 h), the epoxy value reaches 4.08%.

An L9 (34) orthogonal experiment was conducted to identify the dominant factor that affects the epoxy value of EWFO. Four factors were examined: reaction time, temperature, and amounts of acetic acid and hydrogen peroxide. The results demonstrated that the relative importance order of the factors was: amount of acetic acid > reaction temperature > amount of hydrogen peroxide > reaction time. The amount of acetic acid was found to be the most significant factor.

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