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Simulated oxidation of insect wax under UV-light and heating catalytic conditions and analysis of the oxidatives

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ABSTRACT

The aim of this study was to explore the role of environmental conditions to insect wax during its storage and application, and determine the types and compositions of the oxidatives. Oxidation of insect wax with UV-light or heating catalyzing were simulated in this paper, and physicochemical parameters, thermogravimetric (TG), infrared spectrum (IR), gas chromatography-mass spectrometry(GC-MS) of the oxidatives were analyzed, respectively. To some extent, it was revealed that UV-light and heating may accelerate the oxidation. The characteristics and the types of the oxidatives were analyzed and summarized. The results showed that the effect of irradiation of 300nm UV-light was approximately equal to that of 50 ℃ thermal catalysis. The wax was oxidized more severe at 100 ℃. Its acid value reached to 69.62mg KOH/g and saponification value reached to 208.36 mg KOH/g. The whole process contained two stages, including degradation and oxidation. The long carbon chains of senior alkyl acid and policosanol shortened during the degradation process, manifested as lower melting peak, increasing of the low-melting point components, altiudinal succession of carbon number of senior alkyl acid and balanced distribution of relative content. During the oxidative degradation, free alkane, policosanol, senior alkyl acid continued to oxidize, characterized by the increase of acid value and saponification value, meanwhile the enhancement and split of characteristic absorption peak of carbonyl in IR spectrum of oxidation products.

Key words: insect wax; simulated oxidation; catalyze; oxidative

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INTRODUCTION

The insect wax was secreted by wax insect, which was a mixture of natural macromolecules. The esters formed by monocarboxylic acids and monohydric alcohol were the main ingredients of it[1-2]. The wax was white, non-toxic, odourless and fragrant, as one of the important characteristics of forest products in China[3]. It was widely used in medicine, food and decoration, etc., because of its properties, such as its unique raw muscle, hemostasis, pain alleviation, tonify deficiency, reinforced bone renewal and excellent sealed container type, assign the light[4-9]. However, the insect wax was not stable because of its structure and components. Its oxidation would occur as the oil rancidity by long time exposure to light, heat, air, etc., and lead to colorizing and odoring. For the most part , these changes affect applied safety of the wax, and become one of the main factors to limit its application and development[10-12]. In fact, ther were many reports about wax insects stocking and applications of insect wax. The chemical composition and the structure of insect wax were also studied clearly[13-17]. But blanks were still remained on researches of the oxidation and its products of the wax.

The study on oxidation of insect wax was an important way and mean to evaluate its stability to the environment, but this process was slow and were caused by multiple factors. These factors not only increased the difficulty and workload of detection but also were difficult to distinguish. So autoxidation had a little value in production practice. The method of simulated oxidation of insect wax was adopted in this study, and the oxidatives were analyzed. The wax was lighted or heated to speed up the process of oxidation under the condition of oxygen. Both of the wax and its oxidatives were characterized and measured after oxidation. On this basis, we needed to determine the impact of environmental factors on insect wax oxidation process, and determine the ingredients and types of oxidatives. The research would provide theory basis on scientific preservation and application of the insect wax.

EXPERIMENTAL SECTION

Theinsect wax was purchased from market of Emei, Sichuan Province.

PHOTOCATALYTIC OXIDATION

To determine the photostability of insect wax, the insect wax powder was taken 3 copies of each 20g and dispersed on the dishes, then the dishes were put under irradiation at UV Transilluminator (300nm, 36w)(WFH-201, Zhejiang Naideike, China). Three days for a cycle, including 2 days irradiation and 1 day pause, the changes on physical and chemical indicators of insect wax were determined after 45 days. Thermogravimetric analyzer(TG209F3, Nestch, Germany) and infrared spectrometer(Tensor-27, Bruck, Germany) were used to analyse the character of oxidation products.

THERMAL OXIDATION

To determine the thermal properties of insect wax, the insect wax powder was taken 3 copies of each 20g and put on the dishes, then the dishes were put in electrothermal blowing dry box. The temperatures of electrothermal blowing dry box were set 50℃、75℃、100℃respectively. The changes on physical and chemical indicators of insect wax were determined after 45 days. Thermogravimetric analyzer, infrared spectrometer and gas chromatograph-mass spectrometer (Clarus 600,Perkin Elmer, America) were used to analyse the character of oxidation products.

ANALYSIS OF PHYSICAL AND CHEMICAL PARAMETERS

According to the standard GH011-80, the fresh insect wax, insect wax after photocatalytic oxidation and thermal oxidation were determined on their acid value, saponification value and iodine value. The roles of various factors on the oxidation of insect wax were analyzed according to the results of the determination.

The insect wax was a kind of esters formed by senior alkyl acid and policosanol, the amount of ester bonds represent the number of insect wax molecules directly. The conditions of saponification and the saponification ability of lye were the same, so we calculated the average molecular weight of insect wax according to the amount of ester bonds. The method we adopt was not accurate enough, but it had strong comparability for fresh insect wax and insect wax after oxidation under the same condition. Therefore, in order to show the change of the molecular structure of insect wax in the process of oxidation directly, the average molecular weight (M) of insect wax under saponification conditions could be calculated according to the following formula:

$$M = \frac{m}{n} \qquad (1)$$

In the formula（1）, M——the average molecular weight of insect wax , g/mol,
m——the quality of insect wax, g,
n——the mole number of insect wax, mol,

the number of insect wax molecules could according to the formula:

$$n = \frac{(A_2 - A_1)\times 10^{-3}}{56.1} \qquad (2)$$

In the formula (1), A_2——saponification value,
A_1——acid value,
56.1——Relative molecular mass of KOH

The average molecular weight (M) of insect wax under saponification conditions could be calculated according to the following formula:

$$M = \frac{56.1}{A_2 - A_1} \times 10^3 \quad (3)$$

ANALYSIS OF THERMOGRAVIMETRIC ANALYZER(TG)

The fresh insect wax, insect wax after photocatalytic oxidation and thermal oxidation were respectively taken 8mg to put in thermogravimetric analyzer, the temperature was kept at 30℃ initially, then increased to 600 ℃ at a rate of 10℃ min^{-1}.

ANALYSIS OF INFRARED SPECTROMETER (IR):

The fresh insect wax, insect wax after photocatalytic oxidation and thermal oxidation were measured in IR with a 4000-400 cm^{-1} scan range.

ANALYSIS OF GAS CHROMATOGRAPH-MASS SPECTROMETER (GC-MS):

Sample preparation

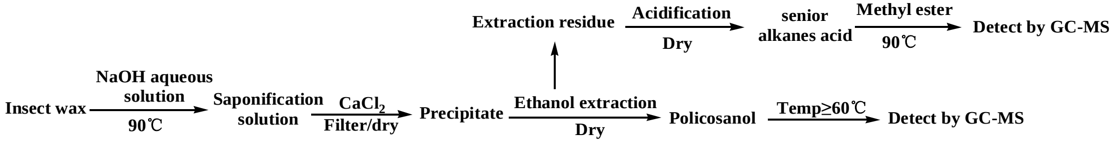


Fig.1Pretreatment method of insect wax before detection by GC-MS

The insect wax powder was put in caustic soda solutions (0.5 mol/L, 90℃) for 24h, then $CaCl_2$ was added to the solution. The solution was filtered and filter cake was put in vacuum drying at 50℃. The dried product was extracted with ethanol at 90℃ and policosanol was obtained. The residues after extraction were acidized by hydrochloric acid and dried, senior alkyl acid was obtained. The samples after methyl esterification at 90℃ were analysed with GC-MS.

GC-MS CONDITIONS

The insect wax after photocatalytic oxidation and thermal oxidation was esterified with methanol in water bath kettle(90℃). GC-MS analysis was performed with a Elite-5 chromatographic column (30 m × 0.32 mm, 0.25 μm). Column temperature was kept at 40℃ initially, then increased to 180 ℃at a rate of 10℃ min^{-1}, held for 3 min, and finally raised to 280℃ at 8℃ min^{-1} for 3 min. Helium was used as the carrier gas at the constant flow of 1.0 mL min^{-1}. Conditions of mass spectrometry for testing was that scan time 0.2 s, interface temperature 250℃, ion source temperature 220℃, mass spectra were recorded in EI mode with a 29-600 amu scan range.

RESUTLS AND DISCUSSION

ANALYSES OF PHYSICOCHEMICAL INDICATORS OF OXIDIZED INSECT WAX

As showed in Table1, the physicochemical indicators of insect wax changed significantly under the given oxidizing conditions. As temperaturerises, acid value and saponification value of oxidizefd insect wax increased significantly.Before and after oxidation, the acid value increased from fresh insect wax 1.87mg KOH/g to 100℃ oxidized insect wax 69.62mg KOH/g and the saponification value increased from 56.64mg KOH/g to 208.36mg KOH/g. It was showed that the free fatty acids in the oxidized insect wax increased markedly at the thermal oxidation process. The changes of iodine value was fluctuant with the increase of temperature. When temperature＜75℃, iodine value decreased significantly and it indicated that some double bonds were oxidized during the oxidation period. But iodine value actually increased when temperature＞75℃ and it indicated that double bonds were generated with vigorous oxidation reaction. Average molecular weight of oxidized insect wax reduced obviously, from 1024g/mol to 404g/mol, and it was suggested that carbon chain of insect wax was degradated in the oxidation process.

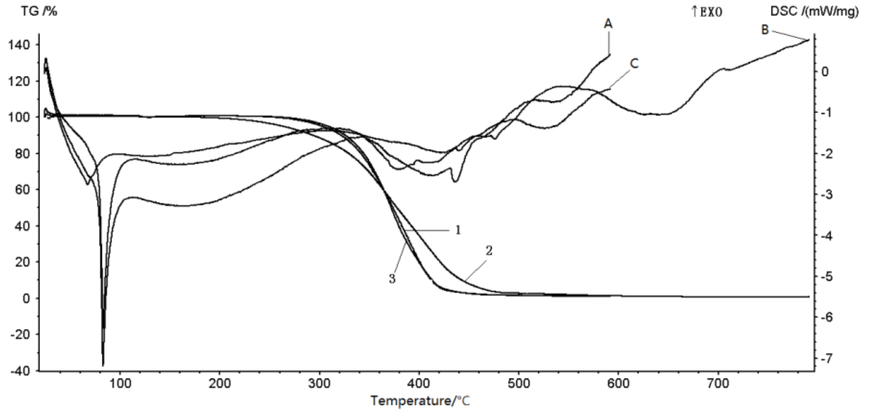
Table1Detection result of insect wax on physicochemical indicators

Sample		Acid value mg KOH/g	Iodine value g I_2/100g	Saponification value mg KOH/g	Averagemolecular weight $\overline{M}$ g/mol
Fresh insect wax		1.87	1.57	56.64	1024
oxidatio ed	50℃	2.07	1.64	78.56	733
	75℃	4.24	0.96	74.94	804
	100℃	69.62	2.59	208.36	404
	uv-light	3.86	0.77	78.77	749

Different from the thermal oxidation, the increased rate of physicochemical indicators of photoxidation insect wax was far less than 100℃ oxidized insect wax. According to the degree of oxidation reflected from the change of average molecular weight, fresh insect wax M=749 g/mol and photoxidation insect wax M=733 g/mol, oxidized effect of 300nm UV-light was similar to the 50℃ thermal oxidation. Therefore, in order to enhance the contrast effect and reveal the oxidation process and characteristics of oxidation products of insect wax, 300nm UV-light and 100℃ thermal oxidation were selected as typical conditions to detect the oxidation products.

THERMAL GRAVIMETRIC(TG) ANALYSIS OF SIMULATED OXIDATION INSECT WAX

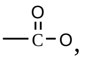
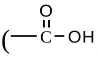
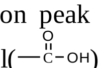
From TG and DSC curves showed in Fig.2, UV-light and thermal oxidation all accelerated oxidation of insect wax. In the melting process, the melting point of insect wax, manifested as A = 84.0 ℃> C = 83.6 ℃> B = 67.2 ℃, consistented with enthalpy of melting peaks, A=6.588mW/mg＞C=6.245mW/mg＞B=2.754mW/mg. This explained that the effect of catalytic oxidation in 100℃ thermal condition was stronger than 300nm UV-light oxidation. A few low melting point components were generated after 100℃ thermal oxidation and the melting point of oxidation insect wax was lower and melting range was wider. In the temperature range of 300-450℃, three kinds of insect wax samples were expressed as the weight loss and the starting point of weightlessness characterized by C=335.5℃＞A=332.0℃＞B=318.1℃. It was showed that UV-light catalysis had an effect to oxidation process of insect wax. Lower weightlessness starting point of oxidation insect wax in 100℃ thermal oxidation indicated that part high boiling substances in the fresh insect wax were oxidized as the low boiling substances in the oxidation process. Weightlessness starting point of UV-light oxidation insect wax rose higher and the reason may be UV-light oxidation reduced iodine value of insect wax(as showed in Table.1). Saturation increased and part of the double bonds were saturated. It is well known that the same numbers of carbon atoms, the boiling point of the saturated carbon chain was higher. Inflection points of weight loss curve manifested as A=379.6℃＞B=372.4℃＞C=371.8℃. It suggested that oxidation leads to lower apparent boiling point of insect wax. The result accord with the judgment that UV-light and thermal oxidation lead to degradation of insectwax.

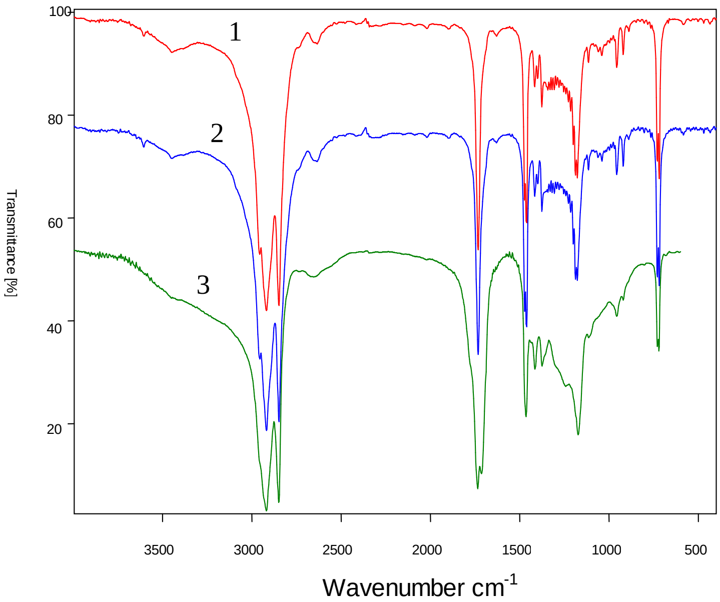


A-DSC curve of fresh insect wax; B- DSC curve of 100 ℃ thermal oxidation products; C- DSC curve of 300nm uv-light oxidation products;1-Weight loss curve of fresh insect wax; 2- Weight loss curve of 100 ℃ thermal oxidation products; 3- Weight loss curve of 300nm uv-light oxidation products;

Fig.2 Contrast of thermal gravimetric curves between fresh insect wax and oxidation products

INFRARED(IR) ABSORPTION SPECTRUM OF SIMULATED OXIDATION INSECT WAX

According to Fig.3, it was coincident among the types of functional groups reflected from IR spectrum of UV-light and thermal oxidation products. Especially, the change between fresh insect wax and UV-light oxidation products was dinky. The result was consistent with 2.2, thermal gravimetric analysis of simulated oxidation insect wax, indicated that the effect of catalytic oxidation in 100℃ thermal condition was stronger than 300nm UV-light oxidation. Differences of IR were exposed between fresh insect wax and UV-light oxidation products. For instance, there was split peaks at 1720 cm^{-1}, absorption peak of stretching vibration of carbonyl, to 100℃ thermal oxidation products. In fresh insect wax, absorption of carbonyl mainly rooted in ester bond carbonyl( $-\overset{O}{\overset{\|}{C}}-O$, 1736 cm^{-1}). In addition, with the thermal oxidation process, a lot of carboxylic acids were generated which contained strong carbonyl absorption( $-\overset{O}{\overset{\|}{C}}-OH$, 1714 cm^{-1}). Secondly, compared with fresh insect wax, there was a obviously enhanced absorption peak at1416cm^{-1}, absorption peak of deformation vibration of hydroxyl. Actually, the absorption peak at1416cm^{-1}happened to be the absorption peak of deformation vibration of hydroxyl(O-H) in carboxyl( $-\overset{O}{\overset{\|}{C}}-OH$). This conclusion was agreement with split peak of carbonyl. Other absorption peaks were attributed as follows: 2918cm^{-1} and 2849 cm^{-1}, stretching vibration absorption peak of C-H bond; 1473 cm^{-1}, deformation vibration absorption peak of CH_2; 1377 cm^{-1}, deformation vibration absorption peak of CH_3; 1188 cm^{-1}, stretching vibration absorption peak of C-O-C in esterfunction; 720 cm^{-1}, deformation vibration absorption peak of more than four successive CH_2.



1-Fresh insect wax; 2-IR of 300nm uv-light oxidation products; 3-IR of 100℃ thermal oxidation products
Fig.3 Infrared absorption spectra of insect wax on simulated oxidation condition

Based on the results of TG and IR, it can be found that there was a little change to functional types and components of insect wax in UV-light oxidation condition. The oxidation effect was very obvious in 100℃ condition and the main oxidation products were carboxylic acids. In order to prove forementioned judgement and confirm species and composition of carboxylic acid, thermal oxidation products was detected by GC-MS and comparison was made between fresh insect wax and oxidation products.

COMPONENT ANALYSIS OF FRESH AND OXIDIZED INSECT WAX BY GC-MS:

ANALYSIS OF POLICOSANOL AND SENIOR ALKYL ACID OF FRESH INSECT WAX BY GC-MS

According to the composition of fresh insect wax showed in Table 2, fresh insect wax comprised main policosanols as hexadecanol, octadecanol, tetracosanol, hexacosanol, octacosanol and a small amount of long-chain alkanes as nonadecane and octacosane. Part of senior alkyl acid included tetradecanoic acid, hexadecanoic acid, octadecanoic acid, docosanoic acid, tetracosanic acid, hexacosoic acid, octocosoic acid and a small amount of 9-octadecenoic acid, eicosanoic acid and carboceric acid. From the content point of view, it was the most content policosanol in fresh insect wax to hexadecanol 32.03%; next, octadecanol 18.96% and tetracosanol 18.68%; the contents of hexacosanol was only 16.16% and octacosanol at least 10.32%. The contents of major policosanols achieved 96.15%＞95%.

Senior alkyl acid of most content in fresh insect wax was hexacosoic acid, achieved 29.43%; next was tetracosanic acid 20.21%. In addition, the contents of senor alkyl acid was more than 10% included tetradecanoic acid 17.10% and hexadecanoic acid 12.63%. It was just 4.48% and 7.30% to the content of octadecanoic acid and octocosoic acid, respectively. The contents of major Senior alkyl acid achieved 91.15%.

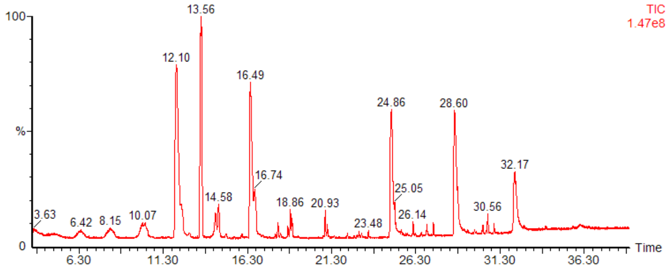


Fig.4 TIC of policosanol of fresh insect wax

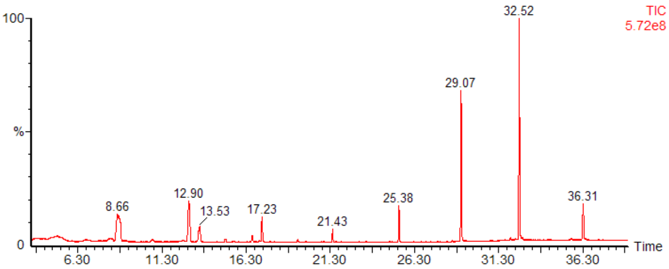


Fig.5 TIC of senior alkyl acid of fresh insect wax

According to Fig.4 and Fig.5, the result was obtained as Table 2.

Table 2 Compositional analysis of fresh insect wax

Policosanol			Senior alkyl acid		
Retention time （RT/min）	Chemical compounds	Relative content %	Retention time （RT/min）	Chemical compounds	Relative content %
12.102	hexadecanol	32.03	8.660	myristic acid	17.10
16.488	octadecanol	18.96	12.897	hexadecanoic acid	12.63
18.114	9-octadecenol	0.70	15.083	15-methy hexadecanoic acid	0.84
18.859	nonadecane	1.18	16.659	9-octadecenoic acid	1.29
20.925	octacosane	0.93	17.234	stearic acid	4.48
24.857	hexacosanol	16.16	19.360	heptacosanoic	0.38
26.958	docosanol	0.51	21.431	eicosanoids	1.74
27.348	Stearaldehyde	0.54	25.377	behenic acid	4.61
28.603	tetracosanol	18.68	29.069	lignoceric acid	20.21
32.175	octacosanol	10.32	32.520	hexacosanoic acid	29.43
-	-	-	36.307	octacosane acid	7.30

ANALYSIS OF POLICOSANOL AND SENIOR ALKYL ACID OF OXIDIZED INSECT WAX BY GC-MS:

ANALYSIS OF POLICOSANOL OF OXIDIZED INSECT WAX BY GC-MS

As it showed in Table 3, after oxidation on 100℃ condition, the content of some policosanols, such as octacosanol, hexacosanol, tetracosanol, hexadecanol, significantly decreased relative fresh insect wax. The type and content of branched alkanols, carbon alcohol and straight-chain aldehyde or ketone increased obviously. Compared with fresh insect wax , except new policosanols of generation, the content of policosanols contained originally in fresh insect wax decreased remarkably. But it was different to decreasing amplitude and policosanols more than twenty-four carbons($\geq C_{24}$) reduced more apparent. For example, the content of policosanols$\geq C_{24}$ in fresh insect wax achieved 45.16% but just for 17.21% after oxidation in 100℃ condition. Among them, the content of octacosanol, hexacosanol and tetracosanol from 10.32%, 16.16%, 18.68% reduced to 7.59%, 1.46%, 8.16%, respectively. policosanols$\leq C_{20}$, as hexadecanol, octadecanol and so on decreased smallerly. For instance, the content of hexadecanol and octadecanol in fresh insect wax was 50.99% but was 44.63% after oxidation. However, some new compounds, such as 2-ethyl decanol, 7- tetradecinol, 2-ethyl decanol, 6-pentadecanol, 2-hexyl decanol, 2-margarone, methyl n-hexadecyl ketone, 2- nineteen ketone, were generated in the oxidation products. According to the change of content of policosanols, it was suggested that the thermal oxidation effect was more prominent to policosanols$\geq C_{24}$ in fresh insect wax. The oxidation way to policosanols was radical oxidation and carbon chain degradation.

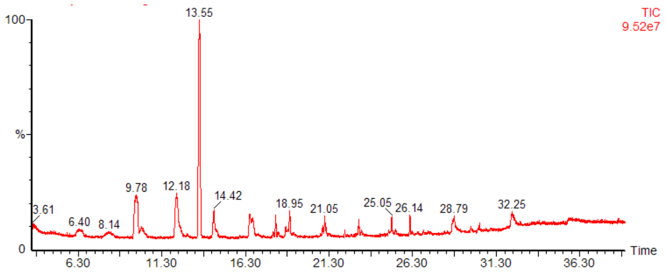


Fig.6 TIC of policosanol of Sichuan insect wax oxidized on 100℃ conditions

According Fig.6, the result was obtained as Table 3.

Table.3 Compositional analysis of policosanol of insect wax oxidized on 100℃ conditions

Policosanols of oxidized insect wax on 100℃ conditions		
Retention time（RT/min）	Chemical compounds	Relative content %
12.177	hexadecanol	28.05
14.418	6-pentadecanol	10.07
16.559	octadecanol	16.58
16.734	2-hexyl decanol	7.65
17.974	7-tetradecinol	1.01
18.829	eicosanol	2.29
20.915	2-ethyl decanol	2.07
21.050	2-heptadecanone	3.47
22.251	9-octadecenol	1.18
23.081	2-nonadecanone	3.26
23.236	hexacosanol	1.46
25.052	methyl *n*-hexadecyl ketone	4.33
26.137	1,22-docosanediol	2.83
28.788	tetracosanol	8.16
32.255	octacosanol	7.59

Based on oxidized condition and products features, it can be summarized as follows(showed in Fig.7):A) carbon chain degradation,B) radical oxidation, to the oxidation of policosanols in fresh insect wax on thermal catalysis condition. In Reason A, degradation reaction was the process that long carbon chain of insect wax was degraded and new carbon chain(shorter than before) was generated. In Reason B, radical oxidation reaction was the process that carbon in the long chain was oxidized as alcohols, aldehyde, ketone or carboxylic acids. Because of different oxidation position, straight chain alcohols, ketone or carboxylic acids was generated when primary carbon was oxidized. If secondary carbon was oxidized, branched chainalcohols, aldehyde or ketone was generated under the oxidation condition.

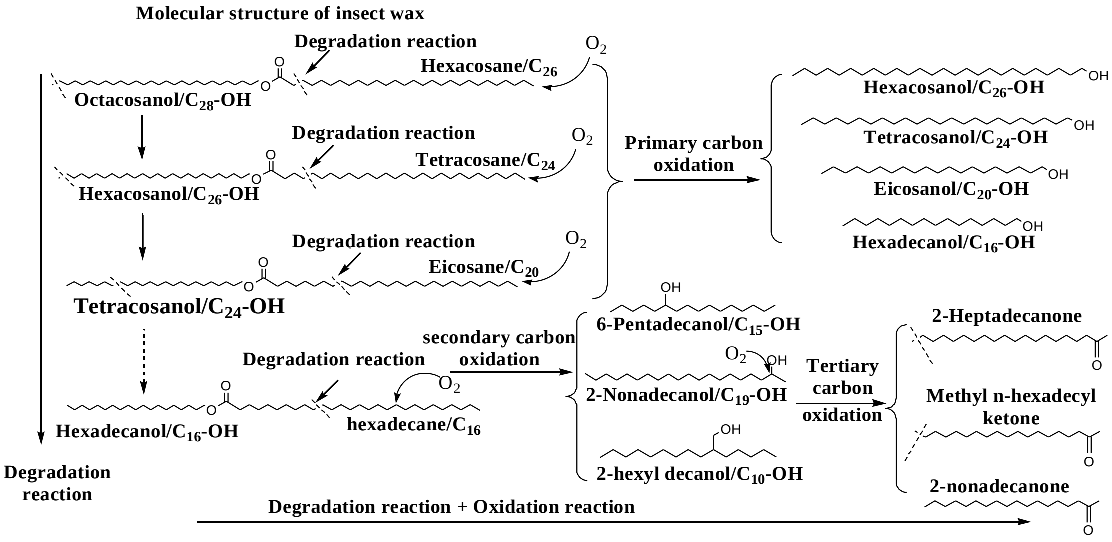


Fig.7 Diagrammatic sketch of oxidation process of insect wax

In conclusion, in the oxidation process of insect wax, the degradation reaction represented by carbon chain fracture mainly occurred on insect wax molecules. It included long carbon chain of policosanols and long carbon chain of senior alkyl acid to the reaction. Oxidation reaction occurred on the different carbons of long-chain molecule generated by degradation reaction. The difference of carbon was primary, secondary or tertiary carbon and it resulted in different oxidation products.

ANALYSIS OF SENIOR ALKYL ACID OF OXIDIZED INSECT WAX BY GC-MS

As it showed in Table 4, the thermal catalytic oxidation of insect wax and products distribution were reflected by species and relative content of senior alkyl acids.Different from the components of fresh insect wax, senior alkyl acids from eleven to twenty-eight carbons were found out in thermal oxidation products. Further more, some senior alkyl acids of odd carbons who were not contained in fresh insect wax were generated, such as hendecanoic, tridecanoic, pentadecanoic, heptadecanoic, nonadecanoic, heneicosanoic, tricosanoic, pentacosane acid. This indicated that long carbon chain was degraded in the process of oxidation of insect wax. The result obtained in the thermal gravimetric analysis in Fig.2 was confirmed again. Appearance of carboxylic acids, especial odd carbon monacid, further proved the conclusion obtained in the IR analysis in Fig.3.

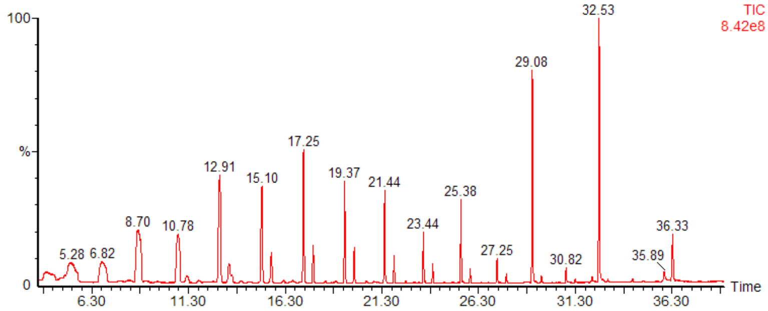


Fig.8 TIC of senior alkyl acid of SiChuan insect wax oxidized on 100℃ conditions

According Fig.8, the result was obtained as Table 4.

Table.4 Compositional analysis of senior alkyl acid of insect wax oxidized on 100℃ conditions

Senior alkyl acid of oxidized insect wax on 100℃ conditions		
Retention time （RT/min）	Chemical compounds	Relative content %
3.969	hendecanoic acid	3.00
5.279	lauric acid	7.24
6.825	tridecanoic acid	5.33
8.700	myristic acid	10.22
10.776	pentadecanoic	6.65
11.226	dodecanoic acid	0.84
12.907	palmitic acid	9.80
13.402	brassylic acid	2.36
15.098	heptadecanoic acid	6.33
15.583	tetradecandioic acid	1.88
17.249	stearic acid	6.55
19.375	nonadecanoic acid	4.11
19.870	hexadecandioic acid	1.41
21.441	eicosanoids	3.54
21.931	heneicosanedioic acid	1.08
23.441	heneicosanoic acid	1.86
23.932	octadecandioic acid	0.78
25.382	behenic acid	3.08
25.862	eicosandioic acid	0.55
27.253	tricosanoic	0.99
27.733	docosandioic acid	0.37
29.079	lignoceric acid	7.93
29.544	triacontanedioic acid	0.27
30.819	pentacosane acid	0.61
32.525	hexacosanoic acid	10.52
35.886	heptacosanoic acid	0.16
36.327	octacosane acid	2.54

However, appearance of many dicarboxylic acids caused supposition to the pattern of broken bond in the oxidation process of insect wax. Overall, the number of carbons of monacids in the oxidatives was highly consecutive, from eleven to twenty-eight carbons. Secondly, types and relative content of dicarboxylic acids was lower than monacids. Based on the two points mentioned above, the critical factor to determine generation of dicarboxylic acids was the content of monacids in the oxidation products. Similar to the result in Fig.6, oxidation reaction of free components was primary in the sample of insect wax. Therefore, as it showed in Fig.9, dicarboxylic acids were generated when the requirement was satisfied as monacids were accumulated continually in the oxidation process of insect wax.

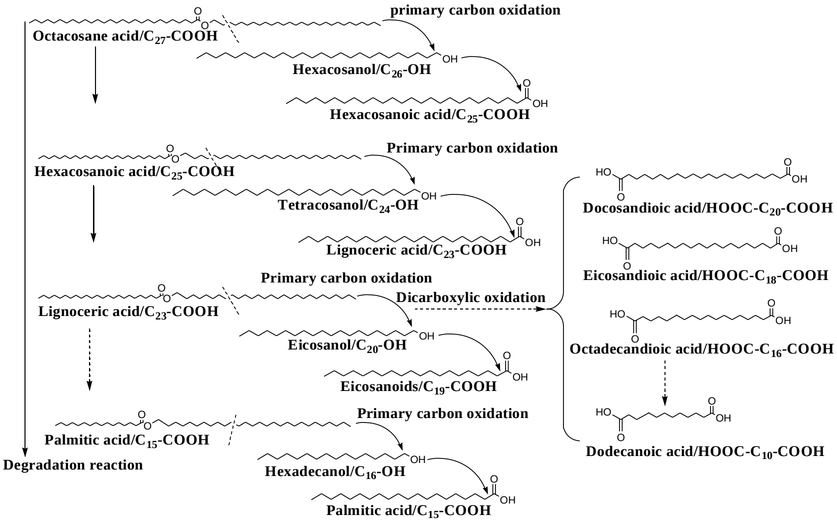


Fig.9 Diagrammatic sketch of oxidation process of insect wax

CONCLUSION

1) Oxidation of insect wax on UV-light or heating catalytic conditions were simulated in this paper. The results demonstrated the effects and the ways of UV-light and heating on accelerating the oxidation of insect wax during its storage and application. Light and heating could accelerate the oxidation of insect wax, but the thermal oxidation was relatively slow when the temperature was less than 75℃. The content of free fatty acids increased and the content of unsaturated double bonds cut down after 45 days, but the changes were slight. The effect of UV-light(300 nm) irradiation was approximately equivalent to that of the thermal catalysis(50℃). The insect wax was oxidized even more severe under the 100℃ condition.

2) Through TG analysis, the results showed that the long carbon chains of senior alkyl acid and policosanol shortened during the degradation process.Lower melting point and small molecular components were obtained in the process. Meanwhile, the types of oxidatives were verified to be alkyl carboxylic acids by IR.

3) The composition of senior alkyl acid and policosanol in fresh insect wax were analysed by GC-MS, the results showed that the main policosanols of insect wax were octacosanol, hexacosanol, tetracosanol, octadecanol, hexadecanol, and the total contents of them reached to 96.15%. The contents of octadecanol and hexadecanol were more than 50%, their carbon number were all less than twenty. The main senior alkyl acid of insect wax were octacosanic acid, hexacosanoic acid, tetracosanoic acid, docosanoic acid, octadecanoic acid, hexadecanoic acid and tetradecanoic acid, the total contents of senior alkyl acids that carbon number greater than twenty-four was 56.94% more than 50%.

4)The results of GC-MS analysis showed that the whole oxidation process of insect wax contains two aspects, degradation and oxidation process. The long carbon chains of senior alkyl acid and policosanol shortened during the degradation process, characterized by lower melting peak value, the increasing of lowmelting point components,altiudinal succession of carbon number of senior alkyl acid and balanced distribution of relative content.During the oxidative degradation, the free alkane, policosanol, senior alkyl acid continued to oxidize. It was characterized by the increase of acid value and saponification value, with the enhancement and split of characteristic absorption peak of carbonyl in IR spectrum of the oxidatives.

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