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ORIGINAL ARTICLE

Natural autoxidation of longifolene and anti-termite activities of the products

Akisato Mukai[1] · Koetsu Takahashi[1,2] · Tatsuya Ashitani[1,2]

Abstract Here, we investigated the reaction mechanism of longifolene autoxidation and the bioactivities of its products. A longifolene sample was autoxidized at 120 °C or room temperature, and the products were analyzed by gas chromatography. Longicamphenylone, norlongilactone, isolongifolic acid, longifolic acid, and longifolene–hydroxy ketone were detected as the products in the autoxidation at 120 °C. During the reaction, longifolene was converted into the other autoxidation products via the formation of longifolene oxide as an intermediate. Anti-termite activities of the longifolene and its autoxidation products were examined against a Japanese subterranean termite (*Reticulitermes speratus* Kolbe) by paper disk methods in Petri dishes. Longifolene and the autoxidation products exhibited anti-*R. speratus* activities, and all the autoxidation products had stronger termiticidal and antifeedant activities than longifolene.

Keywords Bioactivity · Longifolene · Natural autoxidation · Sesquiterpene · Termite

✉ Tatsuya Ashitani
ashitani@tds1.tr.yamagata-u.ac.jp

Akisato Mukai
akisato.mukai@gmail.com

[1] The United Graduate School of Agricultural Science, Iwate University, Morioka 020-8550, Japan

[2] Faculty of Agriculture, Yamagata University, 1-23 Wakaba-machi, Tsuruoka, Yamagata 997-8555, Japan

Introduction

Many components in plant extracts have various functions, including anti-fungal, anti-insect, and insect-attractant functions [1]. However, the functions of some compounds have not been studied in detail, even though they exist in large quantities in plants. Especially, sesquiterpene hydrocarbons are well-known plants components, but studies of their bioactivities are limited. In our previous report, the sesquiterpene hydrocarbons, with high steric hindrances, of caryophyllene and humulene were autoxidized easily by sulfur or oxygen [2, 3]. The oxidized products had anti-termite and anti-tick bioactivities [4, 5]. Other sesquiterpene hydrocarbons with high steric hindrance are also autoxidized easily. For example, longifolene and thujopsene—a tricyclic sesquiterpene—are autoxidized following exposure to air [6–8]. It is one of the characteristic functions of these sesquiterpene hydrocarbons. The oxidation occurred in natural condition is an easy synthesis method to convert into useful bioactive compounds. In addition, the natural autoxidation has the advantage that the reaction proceeds automatically without catalyst and special instrument [7], as compared with other methods such as hydroxylation, isomerization and so on. Therefore, we have investigated the autoxidation to enhance utility of the sesquiterpene hydrocarbons.

Longifolene is a main sesquiterpene component of *Pinus densiflora* and *Pinus thunbergii*, which are widespread in Japan [9, 10]. For example, essential oil of *P. thunbergii* heart wood contained 30.5% of longifolene and component in sesquiterpene, part of the essential oil was almost longifolene in our previous study [11]. Low-polarity extracts of pine wood consist mainly of terpenoid components, and they are useful products. Monoterpenes, such as α-pinene and β-pinene, in the extracts are used as flavor

and/or medical materials, and the resin components of diterpenes are used as sizing reagents during pulping [12]. However, longifolene, which accounts for most of the sesquiterpenes in the extracts, has not been regarded as a useful component compared with the mono- and di-terpenes. Thus, characterization of longifolene will not only lead to the elucidation of the terpenoid reaction, but it will also enhance the use of *Pinus* wood extracts. Longifolene has been reported to undergo oxidation by reacting with lead tetraacetate [13], via ozonolysis in a chloroform solution [14], and by reacting with perbenzoic acid [15] and permanganate [16], which results in oxidation products such as longicamphenylone. Natural autoxidation is an ecologically safe and attractive method for converting longifolene to useful substances because the reaction can be carried out without harmful catalysts and solvents. However, the mechanism for the natural autoxidation of longifolene, as well as the bioactivities of its products, has not been reported in detail. Although longifolene autoxidation has only been examined at room temperature, it is possible that the reaction can be accelerated or controlled by heating. About bioactivity of autoxidation products, we reported that oxidized products had higher termiticidal, anti-feeding, and repellent activities than material in a case of caryophyllene against *Reticulitermes speratus* Kolbe [4]. *R. speratus* is one of the representative termite species for wood material in Japan. *P. densiflora* and *thunbergii* woods are comparatively weaker than other conifer woods such as *Cryptomeria japonica* and *Chamaecyparis obtusa* against the termite. If longifolene contained in the pine woods can be easily converted into anti-termitic substances by autoxidation, it will be important knowledge for development of new methods to improve durability of the pine woods by effective utilization of the extractive components. Therefore, to obtain the fundamental knowledge for longifolene autoxidation, we examined the reaction at high temperatures and the bioactivities of its products against termites.

Materials and methods

Isolation of longifolene

A pine oil sample obtained from the root of *Pinus thunbergii* was supplied by Dr. Nagahama, Professor Emeritus at Sojo University. The sample was subjected to Kugelrohr distillation. The distillate (130–150 °C, 0.2 mm Hg) was separated by silica gel column chromatography with hexane as the solvent to obtain longifolene [98% purity, as assessed by gas chromatography (GC)].

Analysis of compounds

A GC-flame ionization detector (GC–FID) analysis was performed with a Shimadzu GC-2014 gas chromatograph under the following conditions: a DB-1 capillary column (30 m × 0.32 mm inside diameter; 0.25 μm film thickness; J&W Scientific, Folsom, CA, USA); a column temperature ranging from 100 to 200 °C (0 min) at 5 °C/min and from 200 to 320 °C (2 min) at 10 °C/min; an injection temperature of 230 °C; and a detection temperature of 320 °C. GC-mass spectrometry (GC–MS) data were collected with a Shimadzu QP-2010 Ultra gas chromatograph–mass spectrometer under the following conditions: a DB-1 capillary column (0.32 mm i.d. × 30 m; 0.25-μm film thickness; J&W Scientific); a column temperature ranging from 100 °C (1 min) to 200 °C (0 min) at 5 °C/min and from 200 °C (0 min) to 320 °C (2 min) at 10 °C/min; an injection temperature of 250 °C; an interface temperature of 300 °C; and an acquisition mass range of 50–450 atomic mass units using helium as the carrier gas. To analyze carboxylic compounds, a sample was injected into the gas chromatograph after methylation by trimethylsilyldiazomethane (GL Science). Nuclear magnetic resonance (NMR) spectra were measured with a JEOL JNM-EX400 (^{1}H 400 MHz/^{13}C 100 MHz) spectrometer. Longicamphenylone, norlongilactone, and longicamphenylol were identified by comparing the experimental GC–MS data with authentic compounds obtained in our previous study [7].

Autoxidation

Longifolene was stirred in a flask attached to a condenser while exposed to air at 100, 120, or 140 °C in a glycerin bath. A portion of the reaction mixture was collected with a capillary at each reaction time (1, 2, 4, 8, 12, and 24 h). In the non-heating method, longifolene was placed in the dark at room temperature for 3 years. Each reaction product was analyzed by GC–MS and GC–FID. Heneicosane and veratric acid were used as internal standard in GC analysis for neutral and acidic compounds, respectively. The yields of each product and unreacted longifolene were calculated by calibration curves prepared from GC–FID analysis of the internal standard and each compound.

In the heating method, the reaction sample at 120 °C after 24 h was dissolved in ethyl acetate, and the solution was washed with a 1% NaOH solution. The neutral fraction obtained after evaporation of the organic layer was applied to a silica gel column with hexane and ethyl acetate to isolate longicamphenylone and norlongilactone. The acidic fraction obtained after acidification of the alkaline wash-

L   **LC**   **LL**

LA   **LAc**   **isoLAc**

LOX   **LHK**
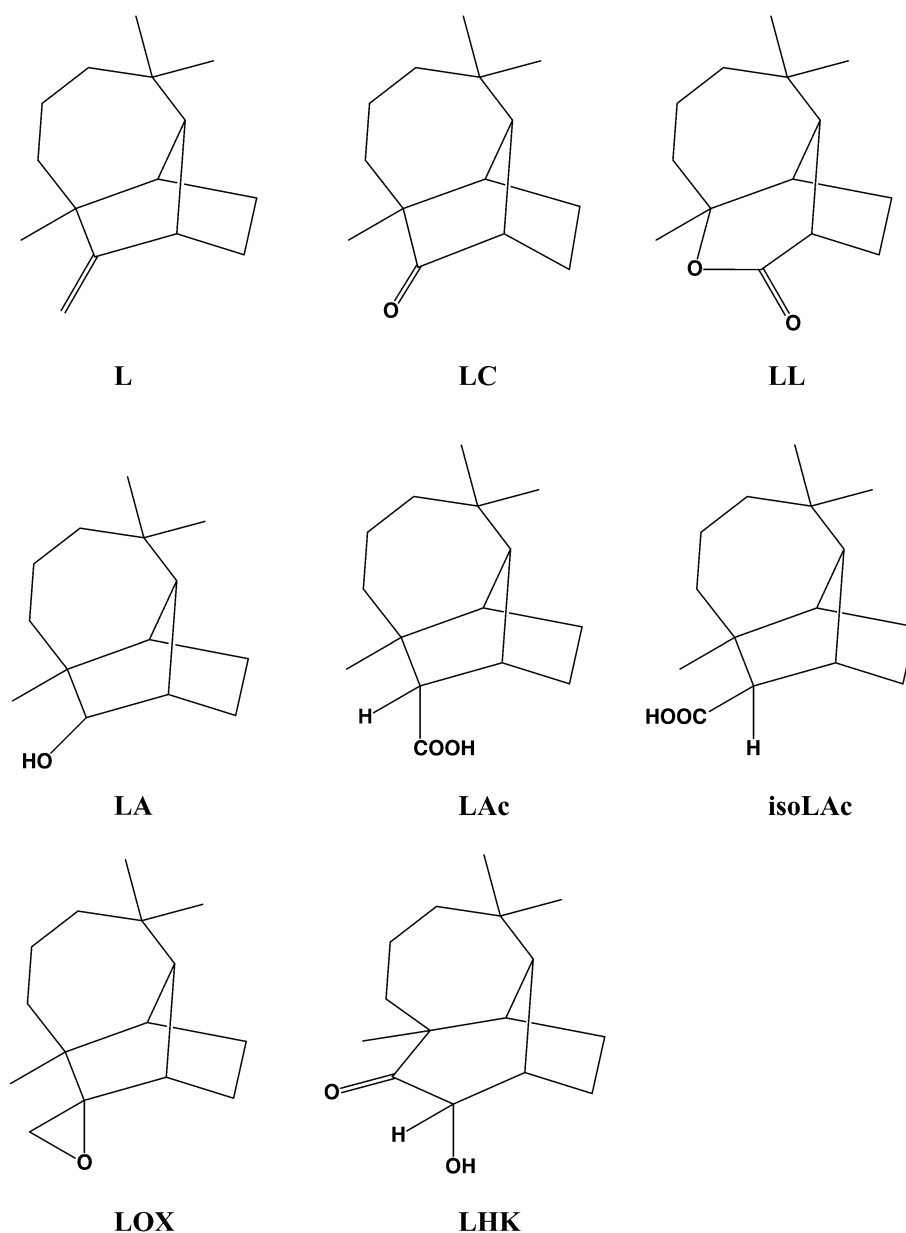
ings was applied to a silica gel column with hexane:diethyl ether (50:4) to isolate longifolic acid and isolongifolic acid. Longifolic acid and isolongifolic acid were identified by comparing their ^{1}H or ^{13}C NMR spectra with reference data [14].

Oxidation of longifolene with *m*-chloroperbenzoic acid

Longifolene was reacted with *m*-chloroperbenzoic acid in benzene or chloroform at room temperature for 24 h according to references [17, 18]. The reaction mixture was washed with 1% NaOH. The solvent was removed under low pressure by a rotary evaporator. The longifolene oxide

was obtained from the reaction in benzene, and identified by comparing its ^{1}H or ^{13}C NMR spectra with reference data. During the reaction in chloroform, longifolene–hydroxy ketone was formed, and it was purified by recrystallization with ethanol. Structural confirmation of the longifolene–hydroxy ketone was obtained by an NMR analysis.

Longifolene–hydroxy ketone

^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.09 (6H, s), 1.15 (3H, s), 1.30–1.40 (2H, m), 1.41–1.85 (8H, m), 2.23–2.30 (1H, m), 2.52–2.60 (1H, m), 3.68 (1H, d, J = 2.5 Hz), 4.58–4.65 (1H, m); ^{13}C-NMR (100 MHz, CDCl$_3$): 21.5 (CH$_2$), 21.9

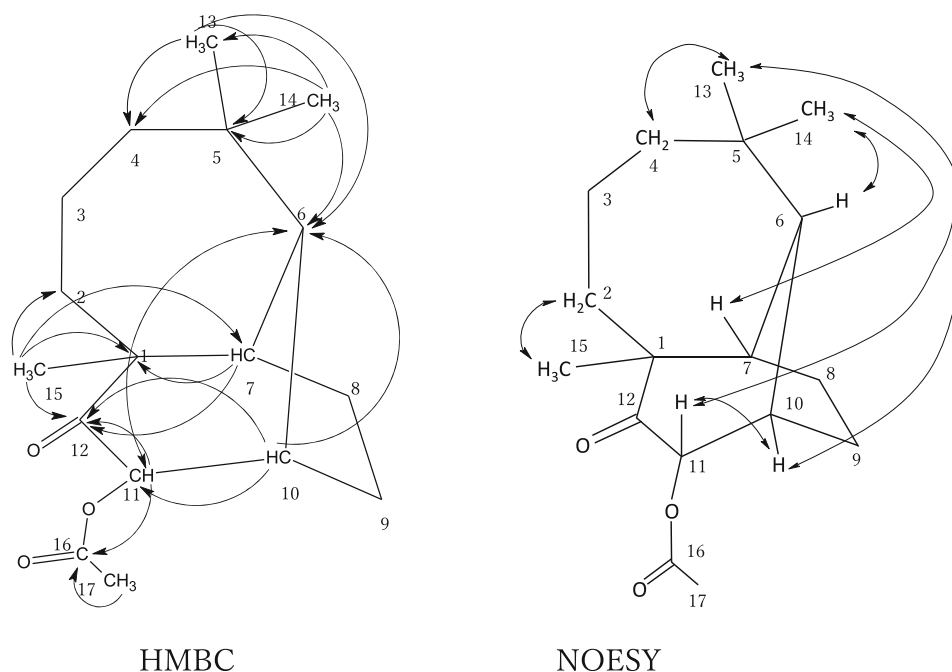**Fig. 2** HMBC and NOESY correlations observed in the NMR analysis of longifolene–hydroxy ketone acetate

HMBC   NOESY

Table 1 Yield* of autoxidation products and unreacted longifolene from reactions at 120 °C and room temperature

Conditions		Products** (%)						Unreacted material** (%)
Temperature	Time	LC	LA	LL	LAc	isoLAc	LHK	L
120 °C	24 h	23	–	4.3	3.0	1.3	2.2	22
Room temperature	3 years	23	2.1	3.0	6.2	1.4	–	46

* Each yield was calculated by dividing the molar amount of product or unreacted longifolene by the molar amount of longifolene before reaction

** **L**, longifolene; **LC**, longicamphenylone; **LL**, norlongilactone; **LA**, longicamphenylol; **LAc**, longifolic acid; **isoLAc**, isolongifolic acid; **LHK**, longifolene–hydroxy ketone; 100% = material longifolene

(CH$_2$), 26.4 (CH$_3$), 27.5 (CH$_2$), 29.6 (CH$_3$), 33.7 (CH$_3$), 34.1 (C), 41.4 (CH$_2$), 42.0 (CH$_2$), 43.3 (CH), 45.1 (CH), 50.7 (C), 56.5 (CH), 73.9 (CH), 217.2 (C).

The longifolene–hydroxy ketone was acetylated by acetic anhydride in pyridine to analyze its configuration. The longifolene–hydroxy ketone acetate product was analyzed by obtaining ^{1}H-NMR, ^{13}C-NMR, heteronuclear multiple quantum correlation (HMQC), heteronuclear multiple bond correlation (HMBC), and nuclear overhauser effect spectroscopy (NOESY) spectra.

Longifolene–hydroxy ketone acetate

^{1}H-NMR (400 MHz, CDCl$_3$): δ 1.07 (3H, s), 1.10 (3H, s), 1.15 (3H, s), 1.48–1.81 (11H, m), 2.13 (3H, s), 2.25 (1H, bs), 2.48–2.50 (1H, m), 5.69 (1H, dd, J = 3.7, 1.3 Hz); ^{13}C-NMR (100 MHz, CDCl$_3$): 20.9 (CH$_3$), 21.3 (CH$_2$), 23.0 (CH$_2$), 26.7 (CH$_3$), 27.5 (CH$_2$), 29.8 (CH$_2$), 33.4 (CH$_3$), 34.2 (C), 41.1 (CH), 41.4 (CH$_2$), 41.7 (CH$_2$), 44.3 (CH), 51.7 (C), 56.7 (CH), 75.9 (CH), 170.4 (C), 210.8 (C).

Termites

Colonies of *R. speratus* Kolbe were collected from the wild in Tsuruoka, Yamagata, Japan, in 2010, and they were maintained in humidified chambers at 26 ± 1 °C.

Anti-termite test

We used no-choice and dual-choice methods for the anti-termite tests, as described previously [4, 19, 20]. The no-choice test was employed to evaluate the termiticidal and antifeedant activity. Test samples were dissolved in acetone and applied to paper disks (8-mm diameter, 1.5-mm thickness) at certain concentrations (sample weight/paper disk weight). The dual-choice test was used to investigate termiticidal and repellent activity. The dual-choice test was performed according to previous studies [4, 18]. A control disk was placed together with a sample-impregnated paper disk on sea sand in a Petri dish. Control disks were dosed only with pure acetone. In control test, a control disk was

Table 2 Time course of the yield* of products during longifolene autoxidation at 120 °C

Time (h)	Products** (%)					Unreacted material** (%)
	LC	**LL**	**LAc**	**isoLAc**	**LHK**	**L**
1	0.50	0.58	–	–	–	<99
2	0.93	0.53	–	–	–	<99
4	2.4	0.86	–	–	–	87
8	7.5	1.7	1.1	–	0.79	71
12	17	3.4	2.3	1.1	1.6	62
24	23	4.3	3.0	1.3	2.2	22

* Each yield was calculated by dividing the molar amount of product or unreacted longifolene by the molar amount of longifolene before reaction

** **L**, longifolene; **LC**, longicamphenylone; **LL**, norlongilactone; **LAc**, longifolic acid; **isoLAc**, iso-longifolic acid; **LHK**, longifolene–hydroxy ketone
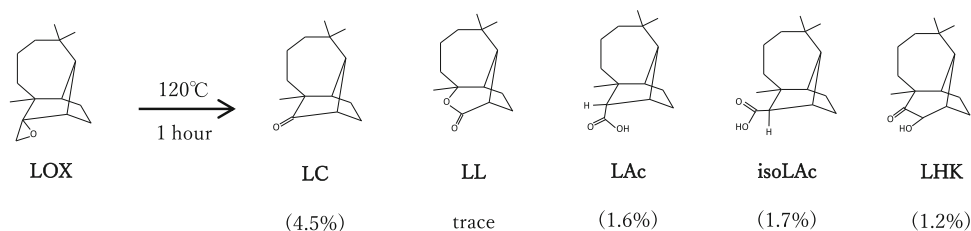
Fig. 3 Autoxidation products of longifolene oxide at 120 °C and their yields. Each yield was calculated by dividing the molar amount by the molar amount of longifolene oxide before reaction. **LC**, longicamphenylone; **LL**, norlongilactone; **LAc**, longifolic acid; **isoLAc**, isolongifolic acid; **LOX**, longifolene oxide; **LHK**, long-folene -hydroxy ketone

placed in each Petri dish. In the no-feed test, no paper disks were placed in the Petri dishes. Ten *R. speratus* workers were placed in each Petri dish, and the dishes were kept in a dark room for 21 days at 26 ± 1 °C. Three replicates of each treatment were prepared. Dead termites were removed daily, and the percent mortality rate was calculated. After 21 days, the sample disks were vacuum dried and weighed, and feeding activity was estimated by calculating the mass loss (percent weight loss) by:

$$\text{Termite mortality}(\%) = 100 \times (\text{Number of dead termites}/ \\ \text{number of initial termites}),$$

$$\text{Mass loss } (\%) = 100 \times (\text{Pre-treatment paper disk weight} \\ - \text{post-treatment paper disk weight})/ \\ \text{pre-treatment paper disk weight}.$$

Statistical analysis

Mortality and weight loss for each treatment were calculated and compared by analysis of variance and a protected Tukey–Kramer test using Statcel 2 software (OMS Inc., Japan). Weight losses in each treatment were compared using a *t* test, and $p < 0.05$ was considered significant.

Results and discussion

Autoxidation of longifolene

We examined longifolene autoxidation by heating and non-heating (room temperature) methods. Figure 1 shows the structures of longifolene (**L**) and the identified autoxidation products in this study. To accelerate and control the autoxidation, **L** was heated in the presence of air, without solvent and catalysis. In the heating method, the reaction temperature was examined from 100 to 140 °C. For the reaction at 140 °C, the rotation of the stirring bar was stopped by the solidification of **L** in the early stage, and the reaction did not proceed. The reaction at 120 °C showed higher product yields than the reaction at 100 °C, as determined by GC. Thus, the reaction at 120 °C was further analyzed. After 24 h, the amount of **L** in the reaction mixture decreased, and longicamphenylone (**LC**), nor-longilactone (**LL**), longifolic acid (**LAc**), isolongifolic acid (**isoLAc**), and longifolene–hydroxy ketone (**LHK**) were produced. **LHK** is a well-known product of several **L** oxidation reactions, but its configuration is unclear [15, 21–23]. We examined the stereo-structure of **LHK** by an NMR analysis of its acetate derivative. Figure 2 shows the HMBC and NOESY spectra of longifolene–hydroxy ketone acetate. NOESY signal was observed between
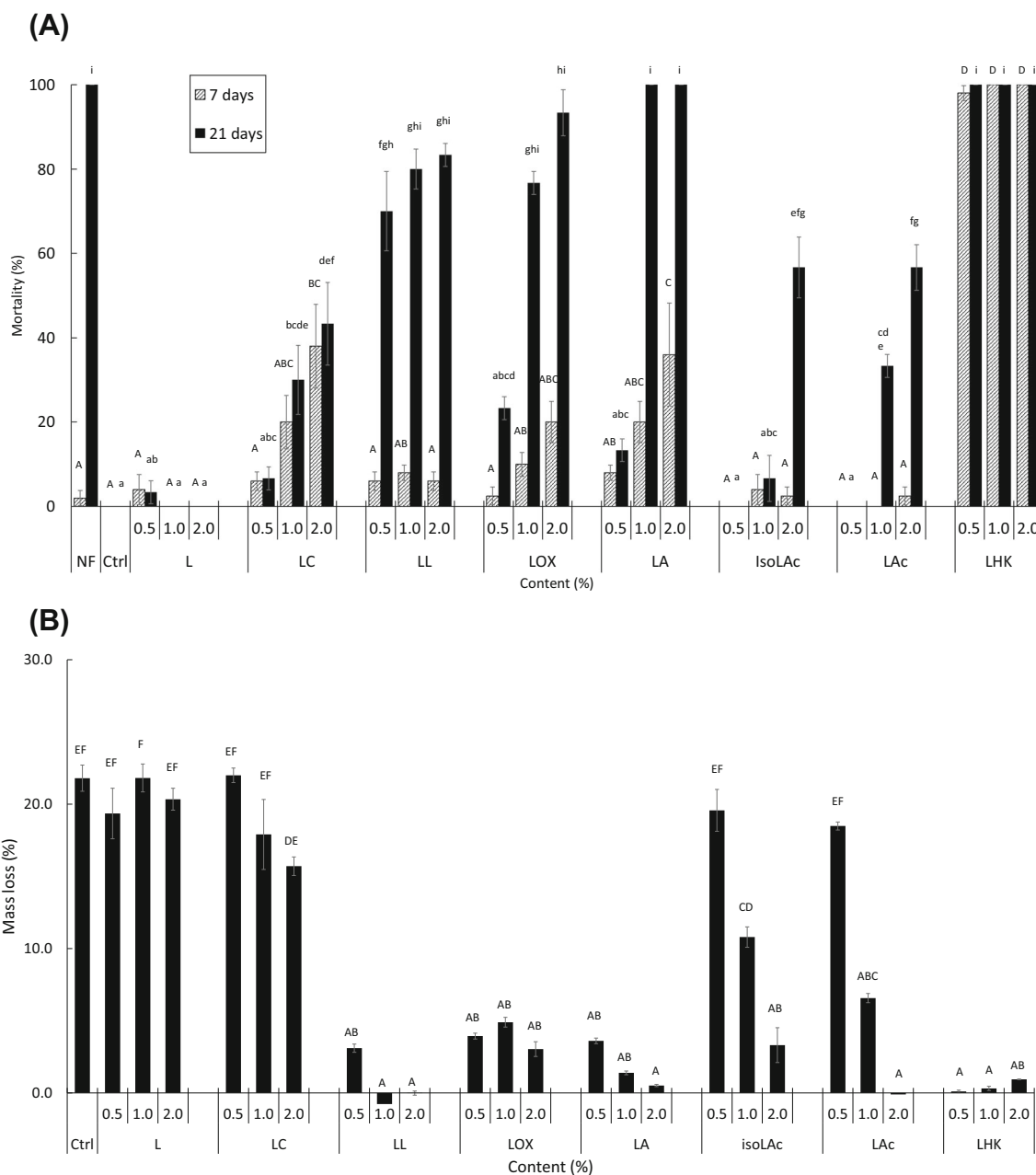
(A)

(B)

Fig. 4 **a** Termiticidal activities after 7 and 21 days and **b** antifeedant activities after 21 days of exposure to compounds in the no-choice test. Ctrl, control test; **L**, longifolene; **LC**, longicamphenylone; **LL**, norlongilactone; **LA**, longicamphenylol; **LAc**, longifolic acid; **LOX**, longifolene oxide; **isoLAc**, isolongifolic acid; **LHK**, longifolene–hydroxy ketone; NF, no-feed test. *Bars* indicate standard errors. *Common letters* indicate that there is no significant difference in the values. *Different letters* indicate statistically significant differences; Tukey–Kramer test, $p \leq 0.05$

hydrogens at 11-C and 13-C in Fig. 2. The configuration of the 11-C bound acetate group was designated as *S* according to the results of the NOESY spectra in Fig. 2 and the structure of **LHK** in Fig. 1.

In the non-heating method, when **L** was placed at room temperature for 3 years, **L**, **LC**, **LL**, **LAc**, **isoLAc** and **LA** were detected as the main products, and **LC** had the highest yield. Table 1 shows the yields of the main

products of **L** autoxidation by the heating and room temperature reactions. **LA** was not detected following autoxidation at 120 °C. It was considered that the **LA** was converted into **LC** by further oxidation under high temperature condition. In contrast, **LHK** was not detected following autoxidation at room temperature. As formation of **LHK**, rearrangement with ring expansion occurred in addition to oxidation. Therefore, high temperature
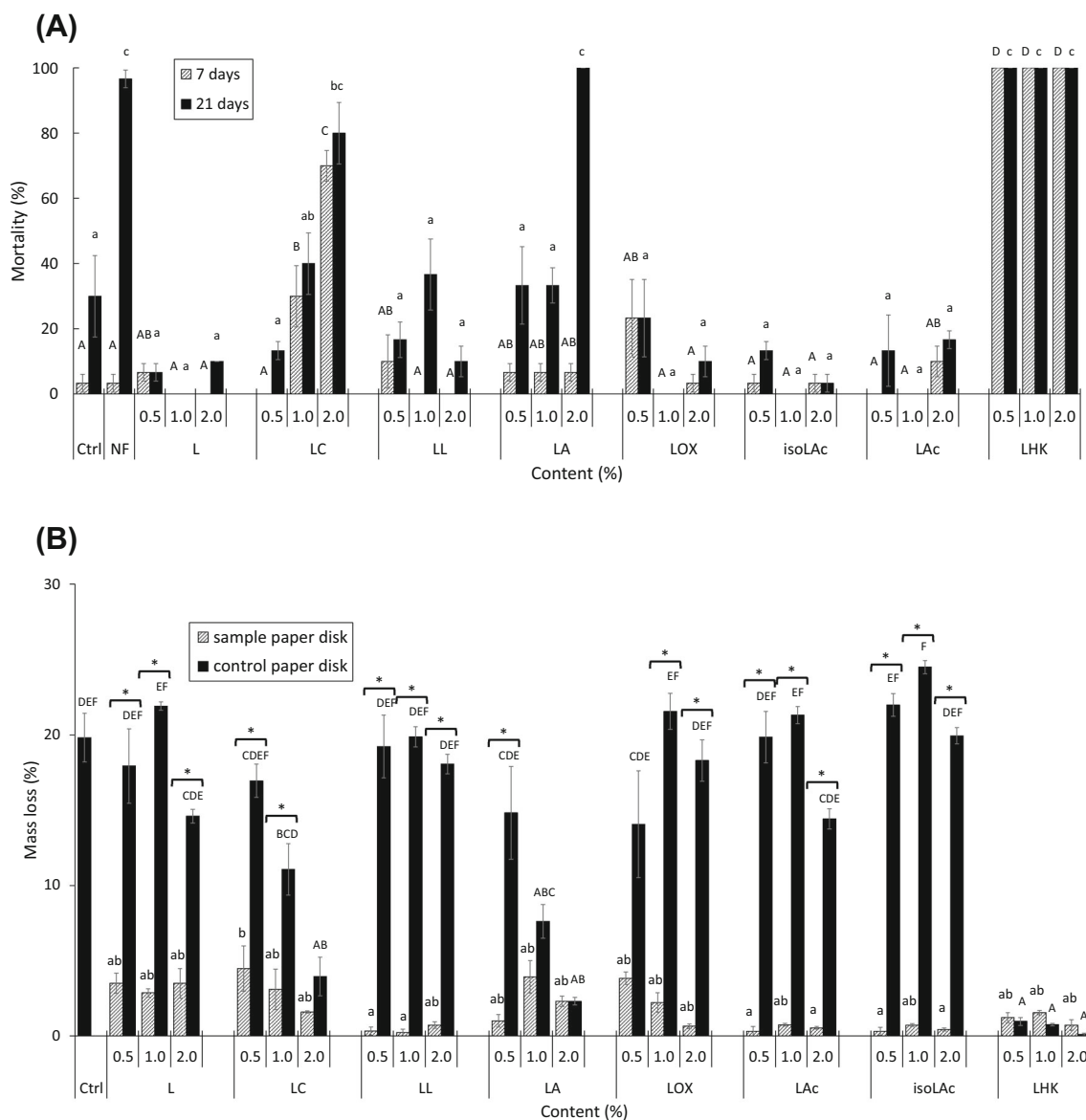
(A)

(B)

Fig. 5 a Termiticidal activities after 7 and 21 days and **b** antifeedant activities after 21 days of exposure to compounds in the dual-choice test. Ctrl, control test; **L**, longifolene; **LC**, longicamphenylone; **LL**, norlongilactone; **LA**, longicamphenylol; **LAc**, longifolic acid; **LOX**, longifolene oxide; **isoLAc**, isolongifolic acid; **LHK**, longifolene–hydroxy ketone; NF, no-feed test. *Bars* indicate standard errors. *Common letters* indicate that there is no significant difference in the values. *Asterisks* denote a significant difference between sample and control papers; Tukey–Kramer test, $p < 0.05$

condition was needed to supply energy for the formation of **LHK**.

Mechanism of longifolene autoxidation

The formation of autoxidation products increased gradually during the reaction at 120 °C (Table 2). To investigate the early stage of the reaction, **L** was autoxidized at 120 °C for 30 and 60 min, and the reaction mixtures were analyzed for minor products by GC–MS. Longifolic acid (**LOX**) was detected within the first 30 min, and then **LC** and other products were detected at 60 min. When pure **LOX** was heated at 120 °C without solvent and catalysis in the presence of air, it was converted into **LC**, **LL**, **LAc**, **isoLAc**, and **LHK** (Fig. 3). These results suggest that **L** was converted into various autoxidation products through the formation of **LOX** as an intermediate. Nayak et al. [15] reported the formation of these products following the oxidation of **L** with perbenzoic acid, and Dimitrov et al. [14] reported that the acidic products **LAc** and **isoLAc** were formed from the ozonolysis of longifolene. Both reports

proposed a common reaction mechanism in which **LOX** served as an intermediate that was cleaved and subsequently oxidized. The proposed mechanism supports our experimental results. In this study, we considered that the natural autoxidation after formation of **LOX** proceeded in the same manner as the perbenzoic acid oxidation and the ozonolysis.

Anti-termite activities of the longifolene (L) autoxidation products

In the no-choice test, all autoxidation products isolated in this study exhibited termiticidal or antifeedant activity, although **L** did not have these activities, compared with the control test (Fig. 4). **LHK** had the highest termiticidal activity in this test, and most of the termites were killed in the early stage at a low concentration (0.5%). Thus, **LHK** is highly toxic to termites. The termiticidal activities of the other products were concentration-dependent. Because the mass loss values of the paper disk were small in the tests of **LL**, **LAc**, and **isoLAc**, depending on their concentration, their termiticidal activities mainly resulted from their antifeedant activities. **LC**, **LA**, and **LOX** exhibited higher termiticidal activities in the no-choice test than in the no-feed test for 7 days. When testing high concentrations of **LA** and **LOX**, almost all the termites died within 21 days, and the mass loss values of the paper disk in the test were small. **LA** and **LOX** were toxic to termites, and they exhibited strong antifeedant activities. **LC** resulted in termite mortality in the early stage (day 7), but the mortality rate did not increase significantly until the end of the test period. Although the mass loss values of the paper disks decreased depending on the **LC** concentration, the values were larger than those of the other autoxidation products. Thus, **LC** exhibited toxicity and weak antifeedant activity for termites.

The dual-choice test was performed to investigate the termiticidal and repellent activities of these compounds. Figure 5 shows the results of the dual-choice test for **L** and its autoxidation products. The repellent activities of the products differed significantly compared with the control paper disk in the same Petri dish, as determined by a t test. **LC**, **LA**, and **LHK** clearly exhibited termiticidal activity. **LHK** had strong lethal activity in both the dual-choice and no-choice tests. **L**, **LC**, **LL**, **LOX**, **LA**, **LAc** and **isoLAc** also exhibited repellent activity. The only anti-termite activity of **L** was its repellent activity. The above results show that the autoxidation products of **L** had various anti-termite activities, such as antifeedant and/or termiticidal activities, as well as repellent activity. This indicates that **L** can be converted easily into more bioactive compounds by autoxidation.

Conclusions

The products of longifolene autoxidation at 120 °C were longicamphenylone, norlongilactone, longifolene oxide, longifolic acid, isolongifolic acid, and longifolene–hydroxy ketone. Longifolene was converted into the autoxidation products via the formation of longifolene oxide as an intermediate. All the autoxidation products had stronger lethal and/or antifeedant activities for termites than longifolene, and longifolene–hydroxy ketone showed potent termiticidal activity. Thus, longifolene can be converted easily into bioactive components by autoxidation.

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