

Research Article

Repellent and Feeding Deterrent Activities of Butanolides and Lignans Isolated from *Cinnamomum camphora* against *Tribolium castaneum*

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Three lignans (1–3) and three butanolides (4–6) were isolated from the lipophilic extract of the *Cinnamomum camphora* stem bark. The six compounds were identified as (-)-sesamin (1), 9 α -hydroxysesamin (2), 9 β -hydroxysesamin (3), obtusilactone A (4), isoobtusilactone A (IOA, 5), and isomahubanolide (6) from their spectroscopic data. Four (1, 2 and 5, 6) of them were evaluated for their repellent and feeding deterrent activities against *Tribolium castaneum*. In this work, the three butanolides (4–6) were confirmed to exist in *C. camphora* for the first time. Results of bioassays indicated that (-)-sesamin (1), IOA (5), and isomahubanolide (6) displayed certain repellent activities against *T. castaneum* at 78.63, 15.73, and 3.15 $\mu\text{g}/\text{cm}^2$ at 2 h after exposure. Among the three compounds, (-)-sesamin (1) and IOA (5) exerted stronger effects and maintained longer duration of repellency. Furthermore, IOA (5) and isomahubanolide (6) showed good feeding deterrent activity against *T. castaneum*. IOA (5) was still potently active at low concentrations with the feeding deterrence index (FDI) ranging from 42.85% to 50.66% at 15–1500 ppm. This work provides some evidence for explaining antiinsect properties of the nonvolatile fraction of the *C. camphora* stem bark and helps promote the development and comprehensive utilization of this tree species.

1. Introduction

Tribolium castaneum (Coleoptera: Tenebrionidae) is one of the widespread and destructive insects infecting stored grain, flour, and many other cereal products [1]. Pest damage in warehouses and grain stores usually results in irretrievable resource wasting and huge economic losses. Currently, synthetic chemical pesticides serve as the main method to control stored-product insects. However, the application of these chemical reagents for decades has led to negative impacts, such as pesticide residue, insecticide resistance, and environmental contamination. All these problems are in conflict with food security and human health we stress today [2, 3]. Therefore, it is necessary to seek for alternative remedies. Botanical pesticides are considered as an eco-friendly and sustainable strategy to control stored-product

pests for their biodegradable property, capacity to alter the behavior of target pests, and broad safety margins for humans, which might play an important role in achieving green revolution for pest management [4].

Cinnamomum camphora (L.) J. Presl is a member of evergreen trees from the genus *Cinnamomum* of the family Lauraceae, mainly distributed in southeastern China, northeastern Australia, and southern Japan [5, 6]. It has been widely cultivated to obtain camphor and essential oils used in the chemical sector and usually planted as ornamental and street trees for its high appreciation and strong resistance.

As early as in the ancient times, people discovered that camphorwood material derived from *C. camphora* can potently repel various insects. The camphorwood with special fragrance is a superior material for construction, furniture, and carvings for its beneficial resistance to

humidity and pests. It was popularly made into a storage box as an essential dowry when a girl gets married in ancient China due to its good practicability of preventing clothing, leather, specimens, archive files, and other items suffering from pests and moulds. Modern research confirmed that the natural extracts from *C. camphora* have insecticidal, repellent [7–10] and antifeedant activities [11] and progeny suppression [12]. Most published articles focus on the essential oil of *C. camphora*. Essential oils are defined as volatile oils produced by secondary metabolic pathways in plants, which are complex mixtures containing multiple components characterized by a low molecular weight [13]. They are generally regarded as volatile fractions extracted from aromatic plants. However, nonvolatile fraction of *C. camphora* was rarely reported about its bioactivities against stored-product insects.

C. camphora is rich in resources, which also provides a favorable material basis for further exploitation and utilization. In this work, lipophilic compounds from its stem barks were evaluated for their repellent and feeding deterrent activities against *T. castaneum*. It was expected to explain antiinsect properties of the *C. camphora* stem bark based on the nonvolatile fraction, thus to fill in the research gaps in this aspect.

2. Materials and Methods

2.1. Equipment and Reagents. EI-MS spectrum was acquired with a GCT CA127 Micronass UK mass spectrometer. ^1H and ^{13}C NMR were performed on a Bruker Avance III NMR spectrometer. Column chromatography was carried out with the silica gel (160–200 mesh), and TLC analysis was carried out on silica gel G plates (Qingdao Marine Chemical Plant, China). Sephadex LH-20 was supplied by Amersham Pharmacia Biotech (Beijing, China). All the analytical grade solvents were produced by Beijing Chemical Works (Beijing, China). The deuterated solvents (CDCl_3 and $\text{DMSO}-d_6$; deuterated ratio, 99.8%) with TMS as the internal reference were purchased from Cambridge Isotope Laboratories, Inc. (Andover, USA).

2.2. Plant Material. Stem barks of *Cinnamomum camphora* were collected in May 2013 from Suzhou (31.97°N latitude, 120.49°E longitude), Jiangsu Province, China. The species was identified by Dr. Q. R., Liu (College of Life Sciences, Beijing Normal University, Beijing, China), and the voucher specimen (BNU-CMH-Dushushan-2013-05-25-005) was deposited at the Herbarium (BNU) of College of Resources Science and Technology, Faculty of Geographical Science, Beijing Normal University.

2.3. Preparation of the Essential Oil and Organic Solvent Extract. The stem barks were air-dried in the room temperature and ground to powder. The essential oil (EO) was available from our previous work [9]. After the preparation of EO, the residual materials were air-dried in the room temperature again and extracted with petroleum ether/ethyl acetate (EtOAc) (1:1) under ultrasound for three replicates

(the liquid-to-solid ratio is 1:10, 1:10, and 1:8, respectively). Extraction lasted for 30 minutes each time, and the solvent was evaporated under reduced pressure; then, the petroleum ether/EtOAc extract (PE) was obtained.

2.4. Isolation of Lignans and Butanolides. PE (19.0 g) was fractionated by silica gel column chromatography with the gradient elution method. Petroleum ether/EtOAc was used as an eluent (concentration ratios: 100:0, 50:1, 20:1, 10:1, 5:1, and 0:100). With the monitoring of TLC, two fractions eluted with 20:1 and 5:1 of petroleum ether/EtOAc were selected as experimental samples at this time, which were separately labelled as S1 (4.51 g) and S2 (2.23 g). S1 and S2 were further separated on a silica gel column with a stepwise gradient of petroleum ether/EtOAc to receive 21 and 15 fractions, respectively. According to similar TLC spots, Fr. 3–8 (2.82 g) of S1 were combined and then subjected to repeated column chromatography on the silica gel (petroleum ether/EtOAc system) and Sephadex LH-20 ($\text{CHCl}_3/\text{CH}_3\text{OH}$ system) column, thus to isolate compound 1 (30 mg), compound 4 (5 mg), compound 5 (40 mg), and compound 6 (45 mg). Fr. 7 of S2 was observed to precipitate white crystals, from which compound 2 (30 mg) and compound 3 (15 mg) were obtained after proper filtration, recrystallization, and column chromatography.

2.5. Structure Determination. The isolated compounds were determined based on the spectroscopic data (EI-MS and ^1H and ^{13}C NMR). The resulting information was matched with the corresponding data in literatures.

(-)-Sesamin (1): white flake crystals, $\text{C}_{20}\text{H}_{18}\text{O}_6$. EI-MS m/z : 377.1 $[\text{M} + \text{Na}]^+$. ^1H -NMR (500 MHz, CDCl_3) δ 6.87 (2H, d, H-2, 2'), 6.80–6.84 (4H, m, H-5, 5', 6, 6'), 5.98 (4H, s, $-\text{OCH}_2\text{O}-$), 4.74 (2H, d, $J = 4.0$ Hz, H-9, 9' β), 4.26 (2H, dt, $J = 7.0, 9.0$ Hz, H-9, 9' α), 3.89 (2H, dd, $J = 3.0, 9.0$ Hz, H-7, 7'), and 3.07 (2H, m, H-8, 8'); ^{13}C -NMR (125 MHz, CDCl_3) δ 148.0 (C-4, 4'), 147.1 (C-3, 3'), 135.1 (C-1, 1'), 119.4 (C-6, 6'), 108.2 (C-5, 5'), 106.5 (C-2, 2'), 101.1 ($-\text{OCH}_2\text{O}-$), 85.8 (C-7, 7'), 71.7 (C-9, 9'), and 54.4 (C-8, 8'). The ^1H and ^{13}C NMR data were in agreement with the reported data [14, 15].

9 α -Hydroxysesamin (2): white needle crystals, $\text{C}_{20}\text{H}_{18}\text{O}_7$. EI-MS m/z : 393.09 $[\text{M} + \text{Na}]^+$. ^1H -NMR (500 MHz, $\text{DMSO}-d_6$) δ 6.83–7.11 (6H, m), 6.70 (1H, d, 9-OH), 6.00 (4H, s, $-\text{OCH}_2\text{O}-$), 5.41 (1H, s, H-9), 4.81 (1H, d, $J = 6.5$ Hz, H-7'), 4.73 (1H, d, $J = 7.0$ Hz, H-7), 4.12 (1H, dd, $J = 6.0, 9.0$ Hz, H-9' α), 3.93 (1H, dd, $J = 2.0, 9.0$ Hz, H-9' β), 3.00 (1H, m, H-8'), and 2.67 (1H, m, H-8); ^{13}C -NMR (125 MHz, $\text{DMSO}-d_6$) δ 148.0 (C-3), 147.8 (C-3'), 147.0 (C-4), 146.8 (C-4'), 137.8 (C-1), 136.8 (C-1'), 120.0 (C-6), 119.7 (C-6'), 108.5 (C-2), 108.2 (C-2'), 107.3 (C-5), 106.8 (C-5'), 101.4 (C-9), 101.3 ($-\text{OCH}_2\text{O}-$), 86.5 (C-7'), 83.0 (C-7), 71.9 (C-9'), 62.6 (C-8), and 53.9 (C-8'). The ^1H and ^{13}C NMR data were in agreement with the reported data [16].

9 β -Hydroxysesamin (3): white needle crystals, $\text{C}_{20}\text{H}_{18}\text{O}_7$. EI-MS m/z : 393.09 $[\text{M} + \text{Na}]^+$. ^1H -NMR (500 MHz, CDCl_3) δ 7.06 (1H, m, H-2'), 6.79–6.91 (5H, m, H-2, 5, 5', 6, 6'), 5.97 (4H, s, $-\text{OCH}_2\text{O}-$), 5.80 (1H, d, $J = 5.5$ Hz, H-9), 5.41 (1H, m, H-7'), 4.98 (1H, d, $J = 6.6$ Hz,

H-7), 4.06 (1H, dd, $J = 8.9$ Hz, H-9' β), 3.97 (1H, dd, $J = 3.9$, 9.2 Hz, H-9' α), 3.30 (1H, m, H-8), and 3.02 (1H, m, H-8'); ^{13}C -NMR (125 MHz, DMSO- d_6) δ 147.9 (C-3), 147.8 (C-3'), 147.0 (C-4), 146.5 (C-4'), 137.6 (C-1), 136.3 (C-1'), 119.9 (C-6), 119.5 (C-6'), 108.4 (C-2), 108.3 (C-2'), 107.0 (C-5), 106.9 (C-5'), 101.3 (-OCH₂O-), 97.7 (C-9), 82.0 (C-7'), 79.3 (C-7), 70.6 (C-9'), 58.4 (C-8), and 55.1 (C-8'). This compound was determined by referring to the ^1H and ^{13}C NMR data in literatures [17, 18].

Obtusilactone A (4): yellowish oil, C₁₉H₃₂O₃. EI-MS m/z : 308.9 [M + H]⁺. ^1H -NMR (500 MHz, CDCl₃) δ 6.69 (1H, td, $J = 7.0$, 1.5 Hz, H-6), 5.12 (1H, s, H-3), 4.89 (1H, dd, $J = 1.7$, 2.8 Hz, H-5'), 4.68 (1H, dd, $J = 1.5$, 2.8 Hz, H-5), 2.77 (2H, m, H-7), 1.51 (2H, m, $J = 7.5$ Hz, H-8), 1.27 (20H, s, H-9 to H-18), and 0.89 (3H, t, $J = 7.0$ Hz, 19-CH₃); ^{13}C -NMR (125 MHz, CDCl₃) δ 165.5 (C-1), 157.6 (C-4), 151.4 (C-6), 126.8 (C-2), 90.3 (C-5), 68.8 (C-3), 31.9 (C-17), 29.7 (C-12), 29.7 (C-13), 29.7 (C-14), 29.6 (C-15), 29.5 (C-11), 29.5 (C-10), 29.4 (C-9), 29.4 (C-16), 29.3 (C-7), 28.3 (C-8), 22.7 (C-18), and 14.1 (C-19). The ^1H and ^{13}C NMR data were in agreement with the reported data [19, 20].

Isobutusalactone A (5): yellowish oil, C₁₉H₃₂O₃. EI-MS m/z : 308.9 [M + H]⁺. ^1H -NMR (500 MHz, CDCl₃) δ 7.08 (1H, td, $J = 7.0$, 1.5 Hz, H-6), 5.26 (1H, d, $J = 8.0$ Hz, H-3), 4.96 (1H, dd, $J = 1.7$, 2.8 Hz, H-5'), 4.74 (1H, dd, $J = 1.5$, 2.8 Hz, H-5), 2.51 (2H, m, H-7), 1.53 (2H, m, $J = 7.0$ Hz, H-8), 1.27 (20H, s, H-9 to H-18), and 0.89 (3H, t, $J = 7.0$ Hz, 19-CH₃); ^{13}C -NMR (125 MHz, CDCl₃) δ 166.9 (C-1), 157.7 (C-4), 150.2 (C-6), 127.4 (C-2), 91.3 (C-5), 66.4 (C-3), 31.9 (C-17), 29.7 (C-7), 29.7 (C-12), 29.6 (C-13), 29.6 (C-14), 29.5 (C-15), 29.4 (C-11), 29.4 (C-10), 29.3 (C-9), 29.3 (C-16), 28.3 (C-8), 22.7 (C-18), and 14.1 (C-19). The ^1H and ^{13}C NMR data were in agreement with the reported data [19, 20].

Isomahubanolide (6): white oil, C₂₁H₃₆O₃. EI-MS m/z : 337 [M + H]⁺. ^1H -NMR (500 MHz, CDCl₃) δ 7.11 (1H, td, $J = 8.0$, 2.0 Hz, H-6), 5.28 (1H, d, $J = 8.0$ Hz, H-3), 4.97 (1H, dd, $J = 2.0$, 2.8 Hz, H-5'), 4.75 (1H, dd, $J = 1.5$, 2.8 Hz, H-5), 2.47 (2H, m, H-7), 1.55 (2H, m, $J = 7.0$ Hz, H-8), 1.28 (20H, s, H-9 to H-18), and 0.90 (3H, t, $J = 6.5$ Hz, 19-CH₃); ^{13}C -NMR (125 MHz, CDCl₃) δ 166.7 (C-1), 157.7 (C-4), 150.3 (C-6), 127.3 (C-2), 91.4 (C-5), 66.5 (C-3), 31.9 (C-19), 29.7 (C-7), 29.7 (C-13), 29.7 (C-14), 29.7 (C-15), 29.7 (C-16), 29.6 (C-17), 29.6 (C-12), 29.5 (C-11), 29.4 (C-10), 29.4 (C-9), 29.4 (C-18), 28.3 (C-8), 22.7 (C-20), and 14.1 (C-21). The ^1H and ^{13}C NMR data were in agreement with the reported data [19, 20].

2.6. Insect Rearing Conditions. *T. castaneum* were sampled in laboratory colonies. They were reared on a mixture of wheat flour and yeast (10:1 w/w) in growth incubators at 28°C–30°C and 70–80% relative humidity. Regardless of gender, adults about 7 ± 2 days old were adopted for bioassays.

2.7. Repellent Bioassay. The repellent assays were referred to the method of Zhang et al. [21]. Petri dishes were used to confine insects here. Testing solutions of EO, PE, and isolated compounds with three concentrations (78.63, 15.73,

and 3.15 $\mu\text{g}/\text{cm}^2$) were prepared in acetone. Acetone was used as the negative control and DEET as the positive control. The filter papers (9 cm in diameter) were cut in half. Each concentration with 500 μL was separately applied to half of a filter paper disc with a micropipette, as uniformly as possible. The other half was treated with an equal volume of acetone. Treated and control halves were air-dried to completely evaporate the solvent. The two halves were attached to their opposites and stuck in Petri dishes. Twenty adults were released at the center of each filter paper disc, and the dishes were covered. Observations on the number of insects present on the treated and control halves were recorded at 2 h and 4 h after exposure. Five replications were used for each concentration.

2.8. Feeding Deterrent Bioassay. The feeding deterrent assays were tested using the method of Liu et al. [22]. The samples of each compound were dissolved in ethanol, and the stock solutions (1 mg/mL) were prepared. 600, 200, 60, 20, and 6 μL stock solutions were drawn, respectively, and then diluted with water and fixed to 2 mL in volumetric flasks. After that, a series of testing solutions for each compound were prepared. They were added into a flask with 400 mg flour and stirred uniformly. The wheat flour suspension with five concentrations (1500, 500, 150, 50, and 15 ppm) was obtained. The control group was prepared with 2 mL water and 400 mg flour by the same procedure. Aliquots of the stirred suspension (200 μL) were placed on the bottom of a clean Petri dish to form testing paste. All pastes were left in the fume-hood overnight to air-dry and then transferred to an incubator to equilibrate at 28°C–30°C and 70–80% relative humidity for 48 h. Twenty adults that starved for 24 h were put inside the glass vial (diameter 2.5 cm, height 5.5 cm, volume 25 mL). Five replicates were carried out for each treatment and control. The empty glass vials were weighed at first, and the pastes were placed in glass vials for weighing. These insects were then added to each vial before further weighing. After weighing, all the experiments were cultured in the constant-temperature incubator. Three days later, the total mass and glass vials containing treated paste but without insects were separately reweighed.

2.9. Data Analysis. In repellent assays, the percent repellency (PR) was determined by the following equation: $\text{PR} (\%) = [(N_c - N_t)/(N_c + N_t)] \times 100$, where N_c = the number of insects on the control half and N_t = the number of insects on the treated half. In feeding-deterrent assays, the feeding deterrence index (FDI) was calculated using the formula: $\text{FDI} (\%) = [(C - T)/C] \times 100$ where C = the consumption of control pastes and T = the consumption of treated pastes.

In the comparative evaluation of repellency for EO and PE, differences between their mean PR values at the same concentration were determined by t -test ($*P < 0.05$). In addition, mean values of PR and FDI of isolated compounds were calculated with data standardization before one-way ANOVA analysis (Tukey's HSD test), respectively. Means in the same column followed by the same letters do not differ significantly ($P > 0.05$) (SPSS V20.0, IBM, NY, USA).

3. Results and Discussion

3.1. Six Compounds Isolated from PE

3.1.1. Structural Determination of Isolated Compounds. There were six compounds isolated from *C. camphora*. By the spectroscopic analysis, it was confirmed that they were (-)-sesamin (1), 9 α -hydroxysesamin (2), 9 β -hydroxysesamin (3), obtusilactone A (4), isoobtusilactone A (5), and isomahubanolid (6), respectively. Among them, one pair of cis-trans isomers (4 and 5) was identified. Their signal assignments were described in "2.5. Structure Determination," and chemical structures are presented in Figure 1.

3.1.2. Butanolides in the Lauraceae. Many members of the Lauraceae family have furan butanolides, especially *Cinnamomum* plants. Butanolides were reported to be distributed in the genus *Cinnamomum* [23–26], *Machilus* [27], *Persea* [28], *Lindera* [19, 29, 30], *Actinodaphne* [31], *Litsea* [32], and *Aiouea* [33] before. Here, *C. camphora* has been proved to contain butanolides as well. They seemed to be characteristic compounds in *Lauraceae* plants. However, Du et al. have also isolated a new butanolide named malleastrumolide A from a Meliaceae plant in recent years [34].

3.2. Bioactivities against *T. castaneum*. Four of the isolated compounds (1, 2 and 5, 6) were evaluated for their repellent and feeding deterrent activities against *T. castaneum*. Another two compounds (3 and 4) failed to be tested due to insufficient amounts obtained, which was a deficiency here. Published articles available about antiinsect activities of these aforementioned compounds are few.

3.2.1. Comparative Evaluation of Repellency for EO and PE. Results of the comparative evaluation are presented in Figure 2. At a maximum testing concentration of 78.63 $\mu\text{g}/\text{cm}^2$, EO showed better repellency than PE did ($P < 0.05$) at 2 and 4 h after exposure according to *t*-test results. At 15.73 and 3.15 $\mu\text{g}/\text{cm}^2$, repellent activities of PE and EO were at the same level throughout the experiments without statistically significant differences between them ($P > 0.05$).

The essential oil from stem bark of *C. camphora* contained large amounts of camphor and other minor monoterpenoids such as 1, 8-cineole and α -terpineol [8, 9]. These volatile compounds were widely reported to have repellent activities against various stored-product insects, including *T. castaneum* [35, 36], *T. confusum* [37], *Lasioderma serricorne* [38], *Stegobium paniceum* [39], *Sitophilus granarius*, *S. zeamais*, and the like. However, these compounds in the EOs are rapidly volatilized [40], so the cases at lower concentrations should be considered and nonvolatile fraction of *C. camphora* deserves further research, which could help promote the investigation of its antiinsect properties.

3.2.2. Repellent Activities of Isolated Compounds. As can be seen in the bar diagrams in Figure 3, (-)-sesamin (1), isoobtusilactone A (IOA, 5), and isomahubanolid (6)

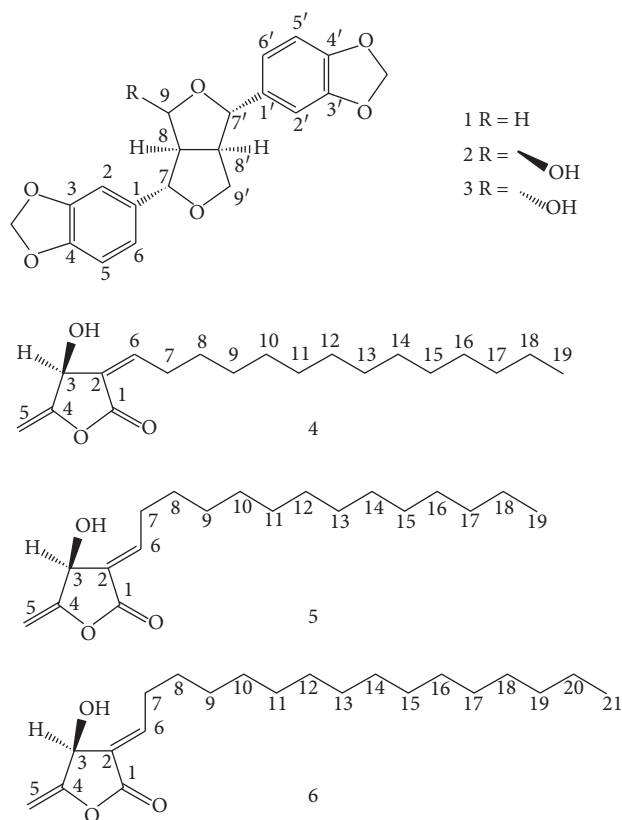


FIGURE 1: Chemical structures of compounds 1–6.

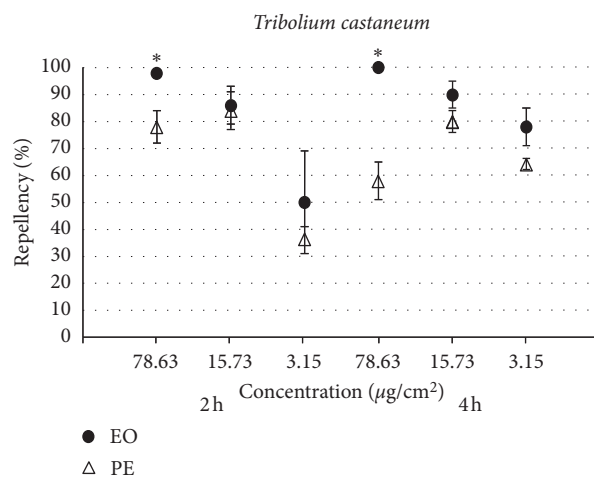


FIGURE 2: Percentage repellency (PR) of EO and PE from the *C. camphora* stem bark against *T. castaneum* at 2 and 4 h after exposure. *Differences between PR values of EO and PE at the same concentration were determined by *t*-test ($*P < 0.05$) (EO: essential oil; PE: petroleum ether/EtOAc extract).

displayed certain repellent activities against *T. castaneum* at all testing concentrations at 2 h after exposure based on PR values. However, 9 α -hydroxysesamin (2) showed weak repellency level at 78.63 and 15.73 $\mu\text{g}/\text{cm}^2$, and it was rather inactive in other cases. Among the four identified compounds, (-)-sesamin (1) and IOA (5) exerted stronger effects

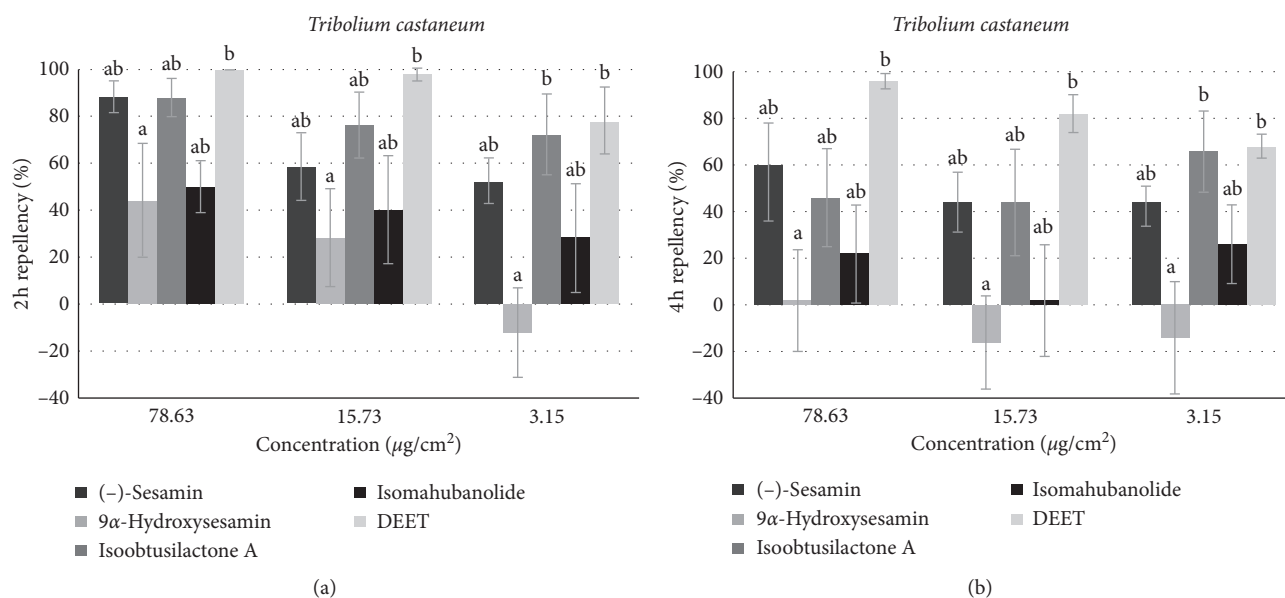


FIGURE 3: Percentage repellency (PR) of two lignans and two butanolides isolated from the *C. camphora* stem bark against *T. castaneum* at 2 h (a) and 4 h (b) after exposure. Means in the same column followed by the same letters do not differ significantly ($P > 0.05$) in ANOVA analysis (Tukey's HSD test).

TABLE 1: Feeding deterrent activities of four compounds isolated from the stem barks of *C. camphora* against *T. castaneum*.

Compound	FDI (%) (mean \pm SE)				
	Concentration ^a (ppm)				
	15	50	150	500	1500
(-)-Sesamin (1)	—	—	8.15 \pm 14.67a	11.41 \pm 12.45b	14.60 \pm 13.90b
9 α -Hydroxysesamin (2)	—	12.77 \pm 9.12a	14.34 \pm 10.89a	18.83 \pm 7.57ab	22.24 \pm 3.69ab
Isoobtusilactone A (5)	42.85 \pm 4.39	45.52 \pm 9.23a	47.60 \pm 9.64a	50.59 \pm 5.67a	50.66 \pm 4.48a
Isomahubanolide (6)	—	26.90 \pm 8.55a	31.48 \pm 8.19a	40.01 \pm 2.19ab	44.26 \pm 3.67ab

^a“—” is for the FDI values considered having no feeding deterrent activity; means followed by the same letters in the same column do not have significant differences ($P > 0.05$) in ANOVA analysis (Tukey's HSD test).

and maintained longer duration of repellency. Notably, at the lowest concentration 3.15 $\mu\text{g}/\text{cm}^2$, the repellency of IOA (5) could be comparable to that of DEET on *T. castaneum* at 2 h and 4 h after exposure.

This work provides some evidence for repellent activities of the nonvolatile fraction of the *C. camphora* stem bark to some degree. Certainly, the bioactivity of a mixture is greatly affected by synergy and antagonism among multiple components [41]. Mutual synergistic or antagonistic interactions among individual constituents need future work.

3.2.3. Feeding Deterrent Activity. Results in Table 1 indicate that butanolides (5-6) exerted stronger effects than lignans (1-2) at high concentrations. (-)-Sesamin (1) showed the weakest feeding deterrence at all testing concentrations. At the lowest concentration, (-)-sesamin (1), 9 α -hydroxysesamin (2), and isomahubanolide (6) were found to have no feeding deterrent activity here, while IOA (5) was rather effective. IOA (5) displayed the strongest activity, whose feeding deterrence index (FDI) at 15–1500 ppm ranged from 42.85% to 50.66% for *T. castaneum*.

It is the first time to assess the feeding deterrent activity of four isolated compounds (1, 2 and 5, 6) against *T. castaneum*. In this work, no enough data were established to speculate the potential structure-activity relationships. Toosendanin is a kind of highly active triterpenoids used as an insect antifeedant agent, whose feeding deterrence index at 25–2000 ppm ranged from 34.20% to 75.52% for *T. castaneum* [42]. Notably, the FDI of IOA (5) could reach over 40% at 15 ppm, while toosendanin arrived the same level at 74 ppm. It was almost five times the concentration of IOA (5). Liu et al. [22] commented that fraxinellone could significantly reduce the food consumption of *T. castaneum* at concentrations of 10 ppm and above, and its FDI value reached about 40% at 30 ppm. As the dose increased, toosendanin and fraxinellone were more active than IOA (5) to *T. castaneum*. It seemed that *T. castaneum* was more sensitive to IOA than to toosendanin and fraxinellone at low concentrations for feeding deterrence.

As for lignans, the feeding deterrent activities of two sesamin-type compounds (1 and 2) were generally poor. However, sesamin was reported to exhibit significant anti-feedant activity towards *Spilarctia obliqua* larvae, and it was

considered as a potent antifeedant principle from *Piper mullesua* [43]. Additionally, a piece of old literature mentioned that sesamin-type lignans could function as active insecticidal synergists for pyrethrins and rotenone without increasing toxicity to mammals [44]. This kind of lignans might play an unexpected role in enhancing the efficacy of botanical insecticides, which requires a substantial of experiments to verify.

4. Conclusions

Three lignans (1–3) and three butanolides (4–6) were obtained from the petroleum ether/EtOAc extract of the *C. camphora* stem bark. Here, butanolides, especially isobtusilactone A (IOA, 5), were proved to exist in *C. camphora* for the first time. Results of bioassays indicated that (-)-sesamin (1) and IOA (5) had effective repellency against *T. castaneum* at 2 and 4 h after exposure. IOA (5) and isomahubanolide (6) showed good feeding deterrent activity against this beetle species, and notably IOA (5) was still potently active at low concentrations. This work provides some evidence for explaining antiinsect properties of the nonvolatile fraction from the *C. camphora* stem bark by bioassays of repellent and feeding deterrent activities against *T. castaneum*.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare no conflicts of interest.

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