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Synthesis, Thermal Behavior, and Pyrolytic Mechanism of 2-Methylpyrrole Citronellol Ester

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ABSTRACT To synthesize new, high temperature stable pyrrole compounds, 4-(methoxycarbonyl)-5-methyl-1-propyl-1H-pyrrole-2-carboxylic acid (**3**) was initially produced as an intermediary using glucosamine hydrochloride as a raw material. In addition, new pyrrole ester derivative 2-(3,7-dimethyloct-6-en-1-yl) 4-methyl 5-methyl-1-propyl-1H-pyrrole-2,4-dicarboxylate (**4**) was made by Steglich esterification of citronellol. Three techniques, namely, thermochemical gas chromatographic spectrometry (Py-GC/MS), differential scan calorimetry, and thermogravimetry were utilized to explore thermal behaviors. **Compound 4** could release citronellol gradually after thermal pyrolysis, and a plausible pyrolytic mechanism was proposed.

KEYWORDS Citronellol, Pyrolytic mechanism, Pyrrole esters, Thermal behavior.

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INTRODUCTION

Pyrrole and its derivatives are one of the main types of heterocyclic compounds because of their various activities,[1,2] good electrical conductivity, good stability, easy preparation, pollution-free, pollution-free, and high safety. These are widely used in medicine,[3-6] materials,[7-12] and agriculture.[13,14] Since most pyrrole esters have a beautiful aroma, they are also used in cigarette flavoring and other fields. New pyrrole alkaloids have been synthesized and are associated with potential antitumor and cancer prevention activities.[15,16] In addition, pyrroles are present in cocoa beans, mushrooms, tobacco, popcorn, and other food products and have unique aroma or sensory properties, making them highly valuable compounds in perfumery. Foods that are prepared by roasting, fermenting, or undergoing prolonged heat treatment during isolation result in odors such as bitter, roasted, peanut, butter, and meaty, so pyrrole is often used as a food flavor additives.[17] With the wide application of pyrrole and its derivatives, the synthesis of new pyrrole compounds has extensively been developed.[18-20] Developing mild and efficient pyrrole synthetic methods has attracted a great attention in recent years, and many synthetic schemes have been reported. In our ongoing efforts to construct aromatic nitrogen-containing heterocyclic compounds, synthesis of new pyrrole ester flavor precursors through cyclization that is highly efficient, environmentally friendly, and new oxidation and esterification using glucosamine hydrochloride as raw material. The new pyrrole ester derivatives synthesized by this method were confirmed by nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR), infrared

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was performed to check when the reaction was finished (petroleum ether/ethyl acetate: 5/1). A solution of ethyl acetate (4 × 10 mL) and water (4 × 10 mL) was added to the evaporated mixture. Separating the organic phase and drying it with anhydrous Na_2SO_4 for the entire night. Column chromatography was used to purify the crude residue over silica gel (100 mesh), then pyrrole ester (**4**) was obtained by using a 20:1 petroleum ether/ethyl acetate ratio to elute the mixture.

Obtained as colorless oil, yied: 61%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (s, 1H), 5.11–5.07 (m, 1H), 4.28–4.21 (m, 4H), 3.80 (s, 3H), 2.56 (s, 3H), 1.99 (td, *J* = 9.1, 5.0 Hz, 2H), 1.78–1.69 (m, 3H), 1.61–1.59 (m, 3H), 1.55–1.50 (m, 1H), 1.38 (dddd, *J* = 13.4, 9.5, 6.5, 5.4 Hz, 2H), 1.26–1.14 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.21, 160.87, 141.43, 131.36, 121.28, 119.40, 112.10, 62.53, 50.94, 46.61, 36.99, 35.56, 29.93, 29.50, 25.68, 25.38, 24.08, 19.45, 17.64, 11.25, 11.04. IR (KBr) *v*: 2957, 1698, 1553, 1448, 1253, 1213, 1157, 1096, 756 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{34}NO_4$ $[M+H]^+$: 364.2488, found $[M+H]^+$: 364.2482.

TG analysis

TG-DTG and DSC curves of the target compounds were detected by a simultaneous thermal analyzer (STA 449 F3, Netzsch, Germany). The standard was spectrally pure Al_2O_3, and each sample was held at 5 mg. Each experiment was carried out in an air environment with a flow rate of 60 mL min^{-1} and was heated between 30 and 450°C at a rate of 10°C min^{-1}.

Pyrolysis analysis

Pyrolysis products of samples were recorded by Py-GC/MS (Pyroprobe 5250T, CDS, Analytical Inc., and Agilent 7890/5975, USA). A 25 mm quartz tube was filled with about 1 mg of each sample for 10 s of cracking at the predetermined temperatures. The pyrolysis temperatures were set at 300, 350, and 400 d°C, respectively. The reactor's temperature was originally maintained at 50°C and heated at a rate of 6°C min^{-1}. The experiments were performed in an atmosphere of air.

For the chromatographic separation, the DB-5MS capillary column (30 m × 250 μm × 0.25 μm) was utilized. The intended injection port temperature was 300°C. The oven's initial temperature was set at 50°C, and it was heated to 80°C at a rate of 6°C per minute, then at a rate of 4°C per minute to 110°C, where it was maintained for 2 min. Finally, the oven was heated to 280°C at a rate of 5°C per minute and maintained there for 2 min. It was determined to utilize splitless helium with a flow rate of 1 mL min^{-1} as the carrier gas.

The separated components were examined using a mass spectrometer. The energy of EI was 70 eV, while the transfer line temperature was 300°C. At 150°C, the quadrupole, and the ion source was maintained at 230°C. From 30 to 500 m/z, mass spectra were obtained and it took 3.9 min for the solvent to delay. The mass spectral library (NIST 2017) connected to the GC/MS apparatus was used to search for the pyrolysis products.

CONCLUSION

new pyrrole ester derivative 2-(3,7-dimethyloct-6-en-1-yl) 4-methyl 5-methyl-1-propyl-1H-pyrrole-2,4-dicarboxylate was devised, synthesized, and investigated for its thermal behavior including pyrolytic mechanism. The results of the Py-GC/MS analysis clearly indicated that the products formed in the pyrolyisis of the synthesized ester are resulted by the breakage of bond O=C-O. The raw materials and substructures, including citronellol and pyrrole derivatives, were safe to use as ingredients in food industry aromas. The outcome of the study supported our initial hypotheses that pyrrole ester derivatives had properties such as thermal stability and release with the characteristic aroma. It has offered technological backing for the flavoring of hot processed foods or tobacco.

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