Short Communication

Serricorone and Serricorole, New Sex Pheromone Components of Cigarette Beetle

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In the course of our chemical studies¹⁾ on the sex pheromone of cigarette beetle (*Lasioderma serricorne* F.), a serious cosmopolitan pest of cured tobacco leaves and almost all dry foodstuffs, the new sex pheromone, serricorone and serricorole, were isolated. In this communication, we wish to report the isolation and structural elucidation of these new compounds, for which the structures suggested that the formation of the sex pheromone components of cigarette beetle might be related to a polyketide biosynthesis.

By preparative GC, compounds A and B were isolated from a polar fraction by silicic acid column chromatography of the hexane extract from female cigarette beetle. Precise mass determination of the molecular ion at m/z 238 in EI-MS established that the molecular formula of compound A was $C_{14}H_{22}O_3$ (Found: 238.1533; Calcd.: 238.1566). The three oxygen atoms in the molecule were attributable to an isolated carbonyl (1730 cm^{-1} , $\nu_{C=O}$), an $\alpha\beta$ -unsaturated carbonyl (1660 cm^{-1} , $\nu_{C=O}$, 1605 cm^{-1} , $\nu_{C=C}$) and an ether oxygen [no IR absorption of a hydroxyl at $3200\sim 3600\text{ cm}^{-1}$, PMR $\delta_{C_6D_6}^{TMS}$ 3.50 (1H, m),

CMR $\delta_{CDCl_3}^{TMS}$ 82.66, 82.96* (-CH-O-)].

Of the four unsaturations in the molecule, three were due to these two carbonyls and the double bond. The remaining one should be derived from a monocyclic structure, because of the absence of any other functional information. By measurements of INEPT-, selective decoupled-CMR and 400 MHz-PMR, five fragments were assigned to be a methyl [δ_C 7.78; δ_H 0.95, 0.97 (3H, t, $J=7.3\text{ Hz}$)] attached to an α -carbonylmethylene [33.9; 2.10 (2H, m)], a methyl [12.7, 12.9; 1.16, 1.18 (3H, d, $J=6.8\text{ Hz}$)] attached to an α -carbonylmethine [49.1, 49.5; 3.11 (1H, q, $J=6.8\text{ Hz}$)] linked to a quaternary carbon, a methyl [9.5; 1.768, 1.773 (3H, s)] attached to a double bond, a methyl [9.7; 0.59, 0.60 (3H, t, $J=7.3\text{ Hz}$)] attached to a methylene [23.3, 23.6; 1.36 (2H, m)] linked to a methine [82.66, 82.96; 3.50 (1H, m)] carrying an ether oxygen and a methyl [9.5; 0.83, 0.85 (3H, d, $J=7.3\text{ Hz}$)] attached to an α -carbonylmethine [42.7; 2.22 (1H, m)] linked to a methine.

In addition to the above data, the presence of intense ions at m/z 153 (relative intensity; 10, $C_9H_{13}O_2$; Found: 153.0922; Calcd.: 153.0916) and 182 (100, $C_{11}H_{18}O_2$; Found: 182.1347; Calcd.: 182.1307), which were caused by a loss of C_5H_9O and C_3H_4O from the molecule, respectively, strongly supported the presence of a 1-methyl-2-oxobutyl moiety in the molecule.

Consequently, these partial structures constituted two possible structures, 2,3-dihydro-3,5-dimethyl-2-ethyl-6-(1-methyl-2-oxo-

* Duplications of CMR- and 400 MHz PMR-signals were due to coexistence of the C-7 epimer.

butyl)-4*H*-pyran-4-one and 2,3-dihydro-3,6-dimethyl-2-ethyl-5-(1-methyl-2-oxobutyl)-4*H*-pyran-4-one.

The final confirmation of the above assignments was obtained from synthesis of the former structure, which was carried out by a synthetic route²⁾ similar to that of stegobinone, the sex pheromone of the drugstore beetle.³⁾

2,3-*cis*-2,3-Dihydro-2,6-diethyl-3,5-dimethyl-4*H*-pyran-4-one [MS: *m/z* (%), 182 (33) = M^+ , 55 (67), 57 (93), 83 (89), 113 (100), 153 (1); PMR $\delta_{CDCl_3}^{TMS}$ 0.98 (3H, t, $J=7$ Hz), 1.03 (3H, d, $J=6$ Hz), 1.14 (3H, t, $J=7$ Hz), 1.73 (3H, s), 2.2~2.4 (3H, m), 4.12 (1H, ddd, $J=8.2, 5.8, 3.1$ Hz); CMR $\delta_{CDCl_3}^{TMS}$ 9.1, 9.5, 9.8, 10.9, 23.6, 25.6, 42.5, 82.0, signals due to the carbons belonged to the carbonyls and the full-substituted double bond were not observed.], prepared from 4-methyl-heptan-3,5-dione and propionaldehyde with $BF_3 \cdot Et_2O$, was treated with propionic anhydride in the presence of $ZnCl_2$ with stirring for 48 hr at 40°C to give 2,3-*cis*-2,3-dihydro-3,5-dimethyl-2-ethyl-6-(1-methyl-2-oxobutyl)-4*H*-pyran-4-one (2,3-*cis*-serricorone).

All spectral data of the synthetic 2,3-*cis*-serricorone were identical with those of the naturally-occurring compound A. In the complete decoupled CMR spectrum of the synthetic 2,3-*cis*-serricorone, some signals were observed as doublets due to coexistence of the C-7 epimer. The complete identity of the PMR and CMR spectra of the synthetic and natural serricorones indicated that the relative configuration at C2 and C3 of the natural serricorone was *cis* and the C7-configuration was epimerized to some extent.

The molecular formula of compound B was deduced to be $C_{14}H_{24}O_3$ (Found: 240.1747; Calcd.: 240.1726), by precise mass determination of the molecular ion. Characteristic IR spectrum and mass-fragmentation indicated that compound B was a compound related to serricorone [IR; 1650 cm^{-1} , 1600 cm^{-1} ; MS, *m/z* (%): 182 (85), 153 (15), 113 (75), 112 (100)]. The absence of IR absorption of an isolated carbonyl at 1730 cm^{-1} and the presence of absorption of a hydroxyl at 3400

cm^{-1} indicated that compound B had a 1-methyl-2-hydroxybutyl moiety instead of a 1-methyl-2-oxobutyl moiety, which was supported by the presence of intense ions at *m/z* 153 ($C_9H_{13}O_2$; Found: 153.0914; Calcd.: 153.0916) and 182 ($C_{11}H_{18}O_2$; Found: 182.1296; Calcd.: 182.1307).

These structural assignments of compound B were confirmed by the synthesis of 2,3-*cis*-2,3-dihydro-3,5-dimethyl-2-ethyl-6-(1-methyl-2-hydroxybutyl)-4*H*-pyran-4-one (2,3-*cis*-serricorole), which was obtained from a $NaBH_4$ reduction of the synthetic 2,3-*cis*-serricorone. All spectral data of the synthetic serricorole were identical with those of the naturally-occurring compound B.

1×10^{-1} μg of the synthetic 2,3-*cis*-serricorone and serricorole elicited typical sex pheromone activity to male cigarette beetle, with a Petridish bioassay method.¹⁾⁾

The structures of serricorone and serricorole were closely related to that of serricornin,¹⁾ the main sex pheromone component of cigarette beetle, as regard to the arrangements of the functional groups and methyl-branches in their structures. Judging from these structural similarities, the sex pheromone components of cigarette beetle might be derived from a polyketide precursor in the pheromone biosynthesis.

Many bioactive substances⁴⁾ of insects, which seem to be related to the polyketide biosynthesis, were reported as defensive substances of opilionids and of mutillid wasp, alarm pheromones of ants, the aggregation pheromone of bark beetle (α -multistriatin) and the sex pheromone of the drugstore beetle (stegobinone).

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