Note

CMR Study on 2,3-Dihydro-2,3,5-trimethyl-6-(1-methyl-2-oxobutyl)-4H-pyran-4-one, the Pheromone of the Drugstore Beetle: Conformation of 2,3-*vic*-Dimethyl Groups

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The sex pheromone secreted by the female drugstore beetle, *Stegobium paniceum* L., was recently isolated,¹⁾ and the structure **1a** was assigned to it on the basis of chemical and spectroscopic evidence.²⁾ However, any conformational information as well as the information on the relative configuration at the 7-position and the absolute stereochemistry at all asymmetric carbons has not been given. More recently, we reported³⁾ a simple synthesis of a stereoisomeric mixture of the pheromone. In the course of our synthetic work, a mixture of 2,3-*trans*-isomers **1b** was separated from a mixture of 2,3-*cis*-isomers. Here we report a 2-axial and 3-equatorial conformation for the *vic*-dimethyl groups of the pheromone, deduced from the comparative CMR study on the 2,3-*cis*-isomeric mixture **1a** and the 2,3-*trans*-isomeric mixture **1b**.

PMR data of the 2,3-*trans*-isomeric mixture **1b** (δ 4.02, dq, $J=14$ & 7 Hz, for a 2-H)³⁾ suggested a probable 2,3-diequatorial conformation for the *vic*-dimethyl groups, while those of the 2,3-*cis*-isomeric mixture **1a** (δ 4.46, dq, $J=7$ & 3 Hz, for a 2-H)³⁾ could not clarify the conformation though they revealed the 2,3-*cis*-stereochemistry.

TABLE I. THE COMPARATIVE CMR DATA

2,3- <i>cis</i> -Isomeric mixture (δ_C)	2,3- <i>trans</i> -Isomeric mixture (δ_C)	carbon	**
207.42 & 207.01	207.45 & 206.98	8	s
197.04 & 196.95	194.87	4	s
168.98	168.87	6	s
109.52 & 109.46	110.19 & 110.10	5	s
77.52 & 77.22	80.03 & 79.91	2	d
49.41 & 49.20	49.46 & 49.29	7 ^a	d
43.73	45.05 & 44.96	3 ^a	d
33.87	33.84 & 33.76	9	t
15.88 & 15.71	19.07	11 ^a	q
12.81 & 12.72	12.81 & 12.67	14 ^{a,d}	q
9.36	10.97 & 10.76	12 ^a	q
9.36	9.51	13 ^{a,b}	q
7.90	7.96 & 7.87	10 ^{a,c}	q

** Multiplicities in the off-resonance spectrum: s, singlet; d, doublet; t, triplet; q, quartet.

^a Assigned by selective proton decoupling experiments.

^b Supported by the absence of long-range coupling ($^2J_{C-H}$ & $^3J_{C-H}$) in a proton coupled spectrum.

^c Confirmed by T_1 measurement.

^d Long-range selective proton decoupling (see ref. 4) at the 7-H (δ_H 3.62 ppm) eliminated fine splittings from this carbon signal.

The comparative CMR data of **1a** and **1b** are summarized in Table I. The remarkable difference between both chemical shifts (δ_C 15.88 & 15.71 for the *cis*-isomeric mixture and δ_C 19.07 for the *trans*-isomeric mixture) of 11-Cs which correspond to the individual 2-methyl carbon atoms, adding to the fact that the *vic*-dimethyl groups of the 2,3-*trans*-isomeric mixture orient to the equatorial direction, indicates the 2-axial and 3-equatorial conformation **2** rather than a 2-equatorial and 3-axial conformation **3** for the *vic*-dimethyl groups of the pheromone **1a**.

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