

ISOLATION AND STRUCTURE OF HEPIALONE;
PRINCIPAL COMPONENT FROM MALE SEX SCALES OF
HEPIALUS CALIFORNICUS (LEPIDOPTERA)

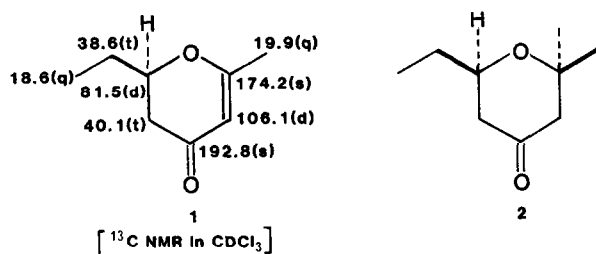
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Abstract: Hepialone, a new sex-pheromonal component produced by the male moth, Hepialus californicus B., was isolated from their hairpencils. The structure was determined to be (2R)-2,3-dihydro-2-ethyl-6-methyl-4H-pyran-4-one (1), a new compound despite its simple structure.

The ghost moth, Hepialus californicus Bdv. (Hepialidae), is among the most primitive of extant Lepidoptera. In contrast to the common mating system of moths, where females produce the primary long-range sex pheromone to which males are attracted, H. californicus possesses a reversed calling system, with males serving to attract females. Male Hepialus may also engage in lekking behaviors, aggregating into small groups of from two to five displaying males. Field observations strongly suggest that males release a sex pheromone from the metathoracic legs which is utilized in the attraction of females as well as in the formation of male aggregations or leks¹. In order to better understand the mating system of this unusual species, we have investigated the chemical components of the male's sex scales or hairpencils which line the surface of the metathoracic tibiae. In this communication we report on the isolation, structure, and absolute configuration of the major component from these hairpencils. We have named this compound hepialone (1).

Hairpencils removed from 70 males were immediately extracted with freshly distilled methylene chloride. After a few minutes the extract was concentrated at 0°C and chromatographed on a silica gel column packed in a tiny pipet using freshly distilled petroleum-ether diethyl ether (3/2) as the eluent. The fraction containing the major component was evaporated at 0°C to give a few mg of pure liquid².



The physical constants of hepialone (1) are as follows: CI-MS m/z 141(MH^+), UV(MeOH) 263 nm(ϵ :12000), IR(neat) 1670 and 1615 cm^{-1} . The relationships of all protons in hepialone were clarified by 400 MHz 1H NMR³ using only 40 μg of sample (see Fig. 1.) The presence of a 'W' type coupling [5.34 ppm(5-H) and 2.35 ppm(3- H_{eq}), $J=0.8$ Hz] and an allylic coupling [5.34 ppm(5-H) and 2.00 ppm(7-Me), $J=0.8$ Hz] provided the key to establish the sequence of protons. The 1H spectral analysis was corroborated by the simulation of the 1H NMR spectrum shown in Fig. 1. The multiplets from the protons attached to carbons C-2, C-3 and C-8 could be reproduced exactly by this method³. The ^{13}C NMR data are shown in (1).⁴ Combination of these data led to the unusual dihydropyranone structure shown in (1). The conformation of the ethyl group should be equatorial because of the presence of the diaxial relationship ($J=12.0$ Hz) between 2-H at 4.31 ppm and 3- H_{ax} at 2.42 ppm. Synthesis of (+)-Hepialone⁵ confirmed our spectral identification as its IR, UV, MS, 1H NMR and ^{13}C NMR were identical to those of the natural hepialone.

The CD spectrum of hepialone in MeOH exhibited two positive Cotton effects at 261 nm ($\Delta\epsilon +2.15, \pi, \pi^*$) and 312 nm ($\Delta\epsilon +0.89, n, \pi^*$) (Fig. 2). Of the two possible absolute configurations, the one depicted (2-R) was chosen on the basis of the rule⁵ for the $n-\pi^*$ band of conjugated carbonyl compounds in which the enone moiety is completely or nearly coplanar. 1H NMR data (zig-zag type coupling) indicate a sofa or slightly distorted sofa conformation in hepialone as shown in Fig. 2. The CD data are compatible with this conformation. This absolute configuration assignment was also supported by octant rule analysis⁷ of the negative Cotton effect observed for the ketone (2) obtained on β -methylation of hepialone.

Biological studies to determine whether pheromonal activity can be demonstrated in the natural and synthetic hepialone, will be reported separately.

Acknowledgment. We thank Professor N. Harada for CD measurements.

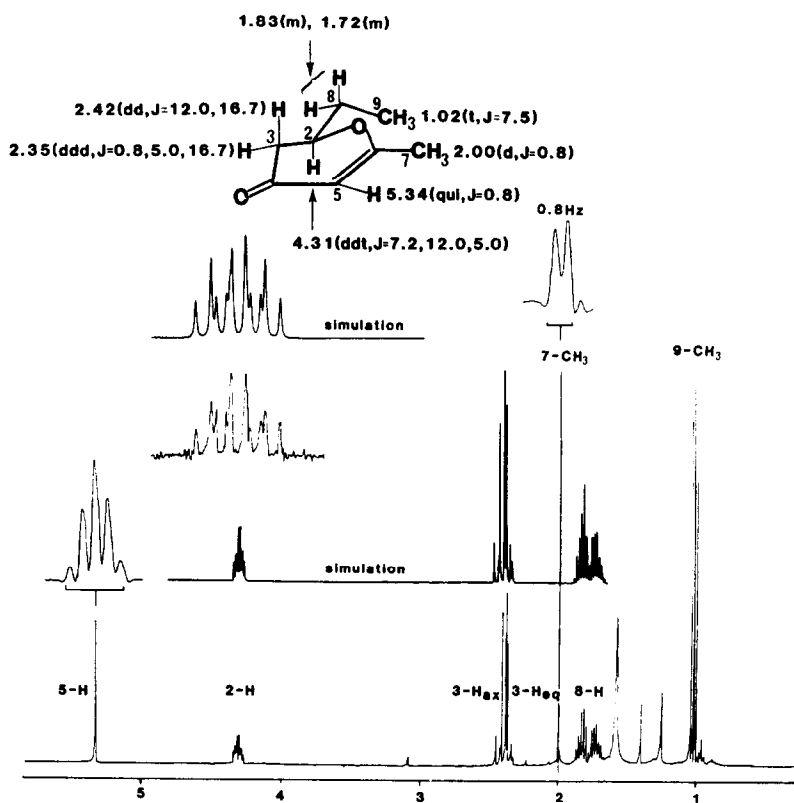


Figure 1. The 400 MHz ^1H NMR spectrum of hepialone (approx. $40\ \mu\text{g}$) and its simulated spectrum, in CDCl_3 .

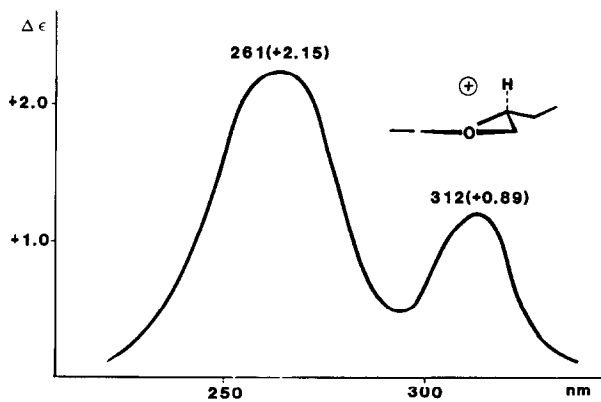


Figure 2. Conformation and CD spectrum of hepialone in MeOH.

References and notes

1. D. Wagner, I. Kubo, T. Matsumoto and J.N. Shoolery, to be published.
2. The purity of this compound was verified by GC using a 2 m X 2 mm Pyrex column packed with 10 Δ carbowax-20 M on 80-100 mesh Supelcoport and programmed from 65 $^{\circ}$ -200 $^{\circ}$ at 10 $^{\circ}$ /min. with a N₂ flow rate of 30 ml/min. The retention time of hepialone is 10 min.
3. The NMR measurements including the spectral simulation were performed on a Varian XL-400 instrument.
4. The ¹³C-NMR data were also obtained with natural hepialone except for the quaternary carbons which were later obtained from the synthetic compound.
5. The synthesis of (+)-hepialone was performed by professor Tadao Kamikawa, Kinki University, Japan. Details of the synthesis will be published elsewhere.
6. J.K. Gawronski, Tetrahedron, 38, 3 (1982), and references therein.
7. The negative Cotton effect of (2) is compatible with the position of the ethyl group in an octant diagram based on the "anti-octant" effect⁸ of the β -axial methyl group and the contribution of the equatorial ethyl group which is two times larger than that of the equatorial methyl group⁹. The oxygen atom of the tetrahydropyran ring does not affect the octant rule analysis since the heteroatom is in the nodal plane of the carbonyl group and does not contribute to the rotatory strength.
8. G. Snatzke, Angew. Chem. Internat. Edn., 18, 363 (1979).
C. Djerassi, J. Am. Chem. Soc., 102, 2737 (1980).
9. J. B. Jones, *ibid.*, 104, 4666 (1982).

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