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ISOLATION OF NEW POLIISOPRENYL KETONE FROM SILKWORM FECES

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A new 43-carbon ketone has been isolated from the unsaponifiable matter of silkworm (Bombix mori L.) feces and identified as a polyisoprenoid compound with 8 isoprene units, each unit having one trans double bond, to which an acetonyl residue is attached at the terminal isoprene unit. The trivial name bombiprenone is proposed for the ketone.

First fractionation of the unsaponifiable matter obtained from lipid extract of silkworm feces was accomplished by molecular distillation. Crude bombiprenone was extracted accompanying solanesol(1) as thiourea inclusion compound from a benzene solution of the fraction, distilled out from 180° ~ 200°C at 10^{-3} Torr. and then, was chromatographed over silica gel. Elution with 5%(V/V) ether in n-hexane yielded bombiprenone in 0.4% yield based on the unsaponifiable matter. Further purification was carried out by crystallization at 0°C from a solution in acetone.

The bombiprenone so far obtained was a white waxy crystal and gave a single spot in TLC and reversed-phase PC in a variety of solvent system, m.p. 46°C, $[\alpha]_D^{25}=0$(Chloroform) Anal. Calcd. for $C_{43}H_{70}O$: C, 85.64: H, 11.70. Found: C, 85.82: H, 11.49.
Treatment of bombiprenone with 2, 4-dinitrophenyl hydrazide gave the monohydrazone, m.p. 57° C.

<u>Anal</u>. Calcd. for $C_{49}H_{74}N_4O_4$: C, 75.24: H, 9.40: N, 7.16. Found: C, 75.10: H, 9.41: N, 7.22. By catalytic hydrogenation with Adams Catalyst and cyclohexane-acetic acid (2:3) as solvent, bombiprenone gave hydrogen uptakes of 9.16 moles of hydrogen/mole at atmospheric pressure (expected 9.0 moles).

Its IR spectrum shows isolated carbonyl group and a polyisoprenoid structure, ν_{max}^{film}, cm^{-1}: 1715(ν.C=O), 1670(ν.C=C of trisubstituted olefin), 3000, 2900, 1460 and 1380 (ν.C-H and σ.C-H) 1445 (σ.C-H of CH_2-C=C) and 800 (σ.C-H of trisubstituted olefin). Its NMR spectrum and its mass spectrum provided enough essential structural information (Table I and Table II).

TABLE I

NMR Spectrum of Bombiprenone*

Peak Position (τ-Value)	Relative Areas Found	Expected	Assignment**
4.85	7.6	8	c
7.50, 7.56, 7.63	2.0	2	d
7.82	3.0	3	e
7.93	29.5	30	a
8.27	27.0	3	the end *cis* b
8.33		24	b, the end *trans* b

* in $CDCl_3$ with TMS as internal reference at 60 Mc/S

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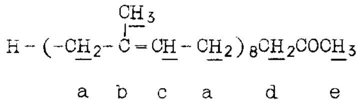

$\mathrm{H-(-}\underset{a}{\underline{\mathrm{CH_2}}}\mathrm{-}\underset{b}{\overset{\underline{\mathrm{CH_3}}}{\overset{|}{\mathrm{C}}}}\mathrm{=}\underset{c}{\mathrm{C\underline{H}}}\mathrm{-}\underset{a}{\underline{\mathrm{CH_2}}}\mathrm{)_8}\underset{d}{\underline{\mathrm{CH_2}}}\mathrm{CO}\underset{e}{\underline{\mathrm{CH_3}}}$

TABLE II

Mass Spectrum of Bombiprenone*

m/e	Relative Intensities	Assignment**
135	100	2b-H
203	21.4	3b-H
262	5.3	M-(a+4b)
272	4.6	4b
330	3.1	M-(a+3b)
341	2.3	a+4b
398	1.9	M-(a+2b)
409	1.3	a+5b
466	1.2	M-(a+b)
477	0.9	a+6b
534	0.7	M-a
603	1.8	M

* the more prominent peaks are listed

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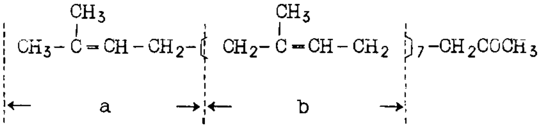

$$\underbrace{CH_3-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-}_{a}[\underbrace{CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2}_{b}]_7-CH_2COCH_3$$

M $C_{43}H_{70}O$(603.03)

Finally, the ubiquinone derivative has been synthesized (2) from 2.3-dimethoxy-5-methylbenzohydroquinone and the vinyl alcohol which was derived from bombiprenone and vinyl magnesium chloride. Anal. Clcd. for $C_{54}H_{82}O_4$: C, 81.58: H, 10.38. Found : C, 81.93: H, 10.27. , m.p. 42~43°C. Its Rf values of TLC and reversed-phase PC in any solvent systems agreed with those of authentic ubiquinone-9. In addition, all spectral data of the ubiquinone derivative were quite identical with data of ubiquinone-9.

On the basis of the data outlined above, bombiprenone has been identified as all-trans 6, 10, 14, 18, 22, 26, 30, 34-octamethyl-5, 9, 13, 17, 21, 25, 29, 33-pentatriacontaoctaen-3-one.

Bombiprenone has been also isolated in 0.002% yield from the leaves of mulberry (Morus bombycis K.), which is the sole diet of silkworm. So, it is clear that bombiprenone in silkworm feces originated from that in leaves of mulberry.

Detailed results will be published elsewhere.

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