

are presented in Figure 2. It is evident that, in the presence of small quantities of cholesterol in lecithin (0.25 and 0.50 molar ratios), the 20 and 45 C transitions of lecithin are eliminated and the phase transition occurs over a wider range of temperature than at higher molar ratios ("intermediate fluid" state of phospholipids).

Some new aspects of the phase transition phenomena may be revealed if the temperatures corresponding to a fixed value of birefringence are plotted vs the molar ratio of cholesterol and lecithin. Thus a set of isorefraction curves are obtained (Fig. 3). At the equimolar ratio of cholesterol and lecithin, a higher temperature is necessary to reach the same value of birefringence as at other ratios. This may reflect a strictly ordered layer of lipid molecules at the equimolar ratio and may be indicative of complex formation between lecithin and cholesterol.

On the basis of these investigations, this simple and rapid method of refractometry seems to be suitable for studying the effect of lipid-soluble and other membrane-active agents upon the physical state and structure of lipid layers.

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Hydrocarbons from Males, Females, and Larvae of Pecan Weevil: *Curculio caryae* (Horn)

ABSTRACT

As part of a program to identify as many as possible of the components of the pecan weevil, *Curculio caryae* (Horn), the hydrocarbons from males, females, and larvae were isolated by solvent extraction and column chromatography and subjected to gas liquid chromatography-mass spectrometry analysis. n-Alkanes from C₁₄-C₃₂ in the larvae and unsaturated and branched chain hydrocarbons from C₂₀-C₃₂ in males and females were found. There are no significant differ-

ences between the hydrocarbons of the male and female pecan weevils.

INTRODUCTION

The adult pecan weevil, *Curculio caryae* (Horn), attacks green maturing nuts in late summer and damages them by making feeding and oviposition punctures. The insect then undergoes an extended life cycle which takes 2-3 years to complete (1). The extended life cycle of the pecan weevil indicates that the role of lipids in this insect is a central one. The importance of lipids in the biochemistry of

insects has been stressed in recent reviews (2,3). Also, extensive studies in the order Coleoptera have been conducted (4-7). Our investigation

was designed to add to the body of general knowledge of insect hydrocarbons and specifically to further the understanding of the hydrocarbons of Coleoptera.

The adult pecan weevils were newly emerged and unfed. The larvae were last instar and about to enter diapause. The experimental procedures were the same as those employed previously (8,9) with these few exceptions. The mass spectra were obtained from a Hewlett-Packard 5930 quadrupole mass spectrometer interfaced with a 5700 A gas chromatograph from a 20 x 1/8 in. 1.5% SE-30 gas chromatographic column at ionizing voltage 70 eV. The gas chromatograph unit was programed from 120-260 C at 4 C/min rate. The final temperature was maintained for 20 min.

TABLE I

Hydrocarbon Composition of Pecan Weevil Larvae

Hydrocarbon ^a	Mol wt	Percent ^b
n-Tetradecane	198	T ^c
n-Pentadecane	212	T ^c
n-Hexadecane	226	0.2
n-Heptadecane	240	0.3
n-Octadecane	254	0.5
n-Nonadecane	268	0.5
n-Eicosane	282	0.7
n-Heneicosane	296	0.8
n-Docosane	310	1.3
n-Tricosane	324	2.4
n-Tetracosane	338	1.9
n-Pentacosane	352	2.9
n-Hexacosane	366	2.1
n-Heptacosane	380	1.5
n-Octacosane	394	10.3
n-Nonacosane	408	2.1
n-Triacontane	422	24.9
Branched C ₃₀ H ₆₂ ^d	422	30.8
C ₃₁ H ₆₄	436	2.1
C ₃₂ H ₆₆	450	3.8

^aMass fragmentation patterns of these compounds corresponded with those published (10).

^bPercent of total hydrocarbons.

^cTrace, present in concentrations of less than 0.1%.

^dFive most abundant fragment ion values plus parent peak observed or inferred. (57, 43, 71, 85, 41, and 422).

RESULTS AND DISCUSSION

The lipid content of the larvae is among the highest ever reported for any stage of any insects (7). This high amount of lipid can be attributed to the larvae feeding on the lipid-rich meats of the pecan, which has been its habitat and sole source of food. The buildup of lipids permits the larvae to survive the long diapause period underground. The hydrocarbon content of the larvae is in the normal range.

The percent total lipids and hydrocarbons of the adult male and female is within the normal range for most other in-season insects. Also, the

TABLE II

Hydrocarbon Composition of Male and Female Adult Pecan Weevils

Hydrocarbon	Mol wt	Male (%) ^a	Female (%) ^a
Eicosene	280	0.2	---
1,3-Henicoadiene ^b	292	0.6	---
3-Heneicosene ^b	294	1.7	1.6
2-Heneicosene ^b	294	---	0.5
1,3-Docosadiene ^b	306	1.8	1.8
3-Docosene ^b	308	---	0.6
Tricosene	322	2.5	2.6
Tetracosene	336	1.7	1.7
Pentacosene	350	0.3	0.3
Hexacosene	364	0.5	0.4
Heptacosene	378	6.8	6.8
4-Methyl hexacosane	380	5.7	5.6
Octacosene	392	1.1	2.5
5-Methyl heptacosane	394	4.6	4.6
4-Methyl octacosane	408	11.5	11.5
5-Methyl nonacosane	422	c	c
11-Methyl nonacosane	422	c	c
13-Methyl nonacosane	422	c	c
15-Methyl nonacosane	422	c	c
C ₃₁ H ₆₂	434	1.7	1.7
C ₃₂ H ₆₄	448	2.2	2.2

^aPercentage of total hydrocarbons.

^bThe geometric isomers of the unsaturated hydrocarbons could not be assigned from the mass spectral data (*cis-trans*).

^cOne gas liquid chromatograph peak contained these four hydrocarbons (36.8%) whose structures were assigned from the mass spectra by the method of Nelson (11).

insects would have just recently emerged from an extended period underground during which they undoubtedly had depleted their lipid reserves for survival. Females contain a slightly larger amount of lipid than males, which is a common occurrence in Coleoptera and in other insects. It is presumed that this higher quantity of lipid is used for reproductive purposes. The investigation of the pecan weevil lipid constituents was done in this laboratory (7).

Table I presents the hydrocarbons of the pecan weevil larvae for which structures were determined. They accounted for 89.1% of the gas liquid chromatographic (GLC) peaks which were presumed to be hydrocarbons. All of the hydrocarbons in the series from C-14-C-32 were present and each, except one, were n-alkyl. In this present work, GLC conditions were adequate to elute hydrocarbons up to C-36, but none above C-32 were observed. The presence of normal chain saturated hydrocarbons probably can be attributed to the larvae feeding on the lipid-rich meats of the pecan. n-Octacosane, n-triacontane, and a branched chain triacontane are the major hydrocarbons of the larvae; they account for 66% of the total hydrocarbons.

Table II lists the total hydrocarbon composition of male and female adult pecan weevils and their percentage distribution. These accounted for 79.7% and 81.2% of the total hydrocarbons amenable to GLC-mass spectrometry in the male and female pecan weevil, respectively. All of the hydrocarbons in series C₂₀-C₃₂ were present in both males and females; all were unsaturated and branched chain hydrocarbons. Five other aliphatic hydrocarbons (C₁₃-C₁₉) also were found in a previous study on the pecan weevil volatiles (12). The mixture of C₃₀ branched chain hydrocarbons in both the male and female which eluted as one GLC peak was resolved by examination of the mass spectral data according to the method of Nelson (11). The C₃₀ hydrocarbons in this mixture included 5-, 11-, 13-, and 15-methyl nonacosane.

In summary, both the larvae and adults contain hydrocarbons through C-32. In contrast, larvae contain only n-alkyl saturated hydrocarbons, except for one branched C-30

hydrocarbon, while adults of both sexes contain only n-alkyl unsaturated and branched chain saturated hydrocarbons. No significant differences between males and females were observed.

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