Advances in Insect Physiology

edited by

J. E. TREHERNE
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Long-Chain Methyl-Branched Hydrocarbons: Occurrence, Biosynthesis, and Function

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1 Introduction

Surface waxes or lipids of all organisms are responsible for the water-repellent character of their surfaces. For example, the skins of higher animals are kept soft, smooth, and free of cracks by lipids [largely squalene, mono-, di-, and triacyl glycerols, wax esters, and fatty acids in man (Nicolaides, 1974)]. By keeping the skin pliable and continuous, microorganisms are unable to penetrate and cause infections, and the skin surface is prevented from drying out and becoming rough and scaly.

Also, the surface lipids of plants (see reviews by Caldicott and Eglinton, 1973 and Kolattukudy, 1975) and insects are important because (1) they allow the uptake of water but prevent excessive water loss when available moisture is low (Beament, 1964, 1967; Browning, 1967); (2) they prevent the penetration of inorganic chemicals (Beament, 1964); (3) they act as a barrier against microorganisms (David, 1967); (4) they affect the absorption of agricultural chemicals (Ebeling, 1964) [in plants, their formation is inhibited by some herbicides (Still *et al.*, 1970; Kolattukudy and Brown, 1974)]; (5) they may serve as a sex attractant (Evans and Green, 1973); and (6) they may serve as a kairomone for insect parasites and predators (Lewis *et al.*, 1975a,b, 1976).

In the present review, I have restricted myself to a consideration of the hydrocarbon components of the surface lipids, particularly to the long-chain internally branched methylalkanes and methylalkenes. These compounds have been extensively investigated since 1970 when di- and trimethylalkanes were identified in an insect (Nelson and Sukkestad, 1970) and the technique of identifying mixtures of the methylalkanes from their mass spectra was elucidated (McCarthy *et al.*, 1968; Nelson and Sukkestad, 1970). The majority of studies of the occurrence and function of the long-chain hydrocarbons has been done with insects. The studies of biosynthesis of alkanes and the origin of the methyl groups have been done largely with plants and microorganisms though some of the more recent investigations have involved insects and other arthropods.

2 Occurrence

2.1 *n*-ALKANES AND *n*-ALKENES

Although in some insects, the surface lipids are mainly long-chain alcohols (Bowers and Thompson, 1965; Bursell and Clements, 1967), ketoesters (Meinwald *et al.*, 1975), and wax esters (Gilby, 1957a,b; Faurot-Bouchet and Michel, 1964, 1965; Brown, 1975), alkanes are a common component of both insect and plant surface lipids and are ubiquitous hydrocarbons in nature. The hydrocarbons of insects usually occur as mixtures, however only *n*-alkanes were reported from the hydrocarbon fraction of the lipids from larval cast skins of the beetle, *Tenebrio molitor* L. (Bursell and Clements, 1967). In addition to the alkanes, alkenes have been reported in the wax of bees, *Apis mellifera* L. (Streibl *et al.*, 1966), the little house fly, *Fannia canicularis* (L.) (Uebel *et al.*, 1975a), the house fly, *Musca domestica* L. (Louloudes *et al.*, 1962; Carlson *et al.*, 1971), the house cricket, *Acheta domesticus* L. (Hutchins and Martin, 1968), the boll weevil, *Anthonomus grandis* Boh. (Hedin *et al.*, 1974), the stonefly, *Pteronarcys californica* Newport (Armold *et al.*, 1969), the cockroaches *Periplaneta australasiae* (F.) and *P. brunnea* Burmeister, and *P. fuliginosa* (Serville) (Jackson, 1970), *P. japonica* Karny and *P. americana* L. (Jackson, 1972), the Argentine ant, *Iridomyrmex humilis* (Mayr) (Cavill and Houghton, 1973), the bull ant, *Myrmecia gulosa* (F.) (Cavill and Williams, 1967), the fleshfly, *Sarcophaga bullata* Parker (Jackson *et al.*, 1974), the stable fly, *Stomoxys calcitrans* (L.) (Uebel *et al.*, 1975b), the face fly, *Musca autumnalis* De Geer (Uebel *et al.*, 1975c). The pecan weevil, *Curculio caryae* (Horn), has alkenes and alkadienes from 20 to 28 carbons in length (Mody *et al.*, 1975) and volatiles of the confused flour beetle, *Tribolium confusum* Jacquelin duVal, contained both 1-alkenes and heptadecadiene (Keville and Kannowski, 1975).

Tridecene constitutes 90 per cent of the defensive secretion from the prothoracic glands of the lacewing, *Chrysopa oculata* Say (Blum *et al.*, 1973). The major hydrocarbon component of the surface lipids of the American cockroach, *Periplaneta americana* L., is *cis,cis*-6,9-heptacosadiene (Baker *et al.*, 1963; Beatty and Gilby, 1969), whereas all other cockroaches studied have methylalkanes as the major components. This diene is changed by ultraviolet light and oxygen into conjugated unsaturated and oxygenated compounds (Beatty and Gilby, 1969), and antioxidants [polyhydric phenols such as 3,4-dihydroxybenzoic acid (protocatechuic acid), which are also involved in tanning] present on the cuticle prevent degradation and the subsequent polymerization (Atkinson and Gilby, 1970; Atkinson *et al.*, 1973). Also, ultraviolet light increases the hydrocarbon content of the cuticular wax (Gingrich, 1975). Alkenes, alkadienes, and alkatrienes and their methyl-branched isomers make up about 90 per cent of the hydrocarbon fraction of the millipede, *Graphidostreptus tumuliporus* (Karsch) (Oudejans, 1973). *n*-Alkenes, 2,(ω-1)-, 2,(ω-2)-, and 3,(ω-2)-dimethylalkenes, and 2- and 3-methylalkenes have been identified in bacteria (Albro and Dittmer, 1969a; Tornabene and Markey, 1971), and polyolefins have been reported from algae (Youngblood and Blumer, 1973) and mosses (Karunen, 1974).

2.2 CYCLOALKANES

Cycloalkanes were reported in *M. domestica* (Louloudes *et al.*, 1962), wool wax (Mold *et al.*, 1964) and tobacco (Enzell *et al.*, 1969); 1-cyclohexylalkanes were found in Nonesuch seep oil (Johns *et al.*, 1966), and 1-cyclopentyl- and 1-cyclohexylalkanes, 7- and 9-cyclohexylalkanes, dicyclohexylalkanes and diphenylalkanes were found in paraffin wax (Levy *et al.*, 1961). In *G. tumuliporus*, cyclopropane alk-1-enes were found only in the female (Oudejans, 1973).

2.3 2- AND 3-METHYLALKANES

Both 2- and 3-methylalkanes (*iso* and *anteiso*alkanes) have been found in meteorites (Oró *et al.*, 1968) [no alkanes were found in lunar samples

(Meinschein *et al.*, 1970) or in parts of graphitetroilite nodules of iron meteorites not exposed to the earth's atmosphere (Oró *et al.*, 1968)], in petroleum (Hills and Whitehead, 1966), in numerous plants (Eglinton and Hamilton, 1967; Weete, 1972; Kolattukudy and Walton, 1973; Kolattukudy, 1975; and references cited therein), in the land snail, *Cepaea nemoralis* (L.) (Van der Horst and Oudejans, 1972), and in the millipede, *G. tumuliporus* (Oudejans, 1972).

2-Methylalkanes were reported from the common house cricket, *A. domesticus* (Hutchins and Martin, 1968; Blomquist *et al.*, 1976), the female tiger moth, *Holomelina opella nigricans* (Reakirt) (Roelofs and Cardé, 1971), the silkworm, *Bombyx mori* L. (Shikata *et al.*, 1974), and the crickets, *Allonemobius fasciatus* (De Geer) and *Gryllus pennsylvanicus* Burmeister (Blomquist *et al.*, 1976).

3-Methylalkanes were reported from the surface lipids of the big stonefly, *P. californica* (Armold *et al.*, 1969), the cockroaches, *P. australasiae*, *P. brunnea*, and *P. fuliginosa* (Jackson, 1970), *P. japonica* and *P. americana* (Jackson, 1972), *L. maderae* and *B. orientalis* (Tartivita and Jackson, 1970), the Mormon cricket, *Anabrus simplex* Haldeman (Jackson and Blomquist, 1976), the fleshfly, *S. bullata* (Jackson *et al.*, 1974), and the fire ants, *Solenopsis invicta* Buren and *S. richteri* Forel (Lok *et al.*, 1975). 3-Ethylhexacosane was reported from the silkworm (Murata *et al.*, 1974), however, their published mass spectrum is more compatible with that of 3-methylheptacosane when compared with spectra of 3-methyl- and 3-ethylalkanes published by the American Petroleum Institute.

It should be noted that in plants (Wollrab *et al.*, 1967), Mollusca and Arthropoda, the majority of the 2-methylalkanes has an odd number of carbon atoms, and the majority of the 3-methylalkanes has an even number of carbon atoms, which would be expected if the methyl branch is derived from the amino acids valine and isoleucine, respectively. Also, 2,(ω-1)-dimethylalkanes were reported in the waxes of the horehound, *Marrubium vulgare* L. (Brieskorn and Feilner, 1968), and dimethylalkenes were reported in bacteria, as noted above (Albro and Dittmer, 1969a; Tornabene and Markey, 1971).

2.4 INTERNALLY BRANCHED METHYLALKANES: ANALYSIS

Recent reports of the occurrence and structural identification of internally branched mono-, di-, and trimethylalkanes have depended upon the use of molecular sieves (1/16 in. pellets of Linde type 5A) to separate the branched alkanes from the *n*-alkanes (O'Connor *et al.*, 1962) and the increased use of improved gas–liquid chromatographic and mass spectrometric methods of analysis. Monomethylalkanes with the methyl branch located on about carbon 7 to over 18 elute from gas–liquid chromatographic columns such as SE-30, OV-17, and OV-101 with an equivalent chain length (Miwa, 1963) 0.6 to 0.7 carbon atoms less than the *n*-alkane with the same number of carbon atoms (Mold *et al.*, 1966; Nelson and Sukkestad, 1970, 1975). Additional internal methyl branches have an additive effect. Thus, two internal methyl branches with isoprenoid spacing decrease the equivalent chain length about 1.4 carbon atoms less than the total number of carbon atoms in the molecule, and three methyl branches cause the equivalent chain length to be about 2.2 carbon atoms less (Nelson and Sukkestad, 1970, 1975).

If the branch point is closer to the end of the chain, the effect of the branch on the equivalent chain length is less (Mold *et al.*, 1966). However, on polar columns such as cyclohexanedimethanol succinate, *iso-* and *anteiso*methyl branches decrease the equivalent chain length 0.65 and 0.75 carbon atoms, respectively, and a centrally located double bond and a terminal double bond decrease it by 0.2 and 0.5, respectively (Albro and Dittmer, 1969a).

The equivalent chain length in conjunction with the carbon number determined by mass spectrometry, gives the number of methyl branches, and the position of the methyl branches is then deduced from the mass spectral fragmentation patterns by comparing the relative intensities of significant adjacent even and odd mass peaks.

Methylalkanes give relatively simple mass spectra, and some mass spectra have been analyzed by plotting the carbon number of the fragment ion vs. the intensity of the fragment ion (Mold *et al.*, 1966; Hutchins and Martin, 1968; Nishimoto, 1974). However, on the basis of such mass spectra alone, one cannot distinguish between an isomeric mixture of internally branched monomethylalkanes and internally branch di- and trimethylalkanes or isomeric mixtures of di- and trimethylalkanes (McCarthy *et al.*, 1968; Nelson and Sukkestad, 1970, 1975).

Biemann (1962) and Hood (1963) noted that internally branched alkanes tended to fragment at the branch point to give a secondary carbonium ion of $[C_nH_{2n+1}]^+$. Formation of the secondary carbonium ion was also accompanied to some degree by the loss of a hydrogen atom to give another secondary carbonium ion of $[C_nH_{2n}]^{\dagger}$ (i.e., a doublet appeared in the mass spectrum that corresponded to the odd-mass secondary carbonium ion and to the even-mass secondary carbonium ion, one mass unit less). Of the two competing reactions (cleavage of the carbon–carbon bond on one side or the other of the branch point) for the formation of the two possible $[C_nH_{2n+1}]^+$ secondary carbonium ions, the preferred cleavage is that which results in the loss of the larger of the alkyl chains (Pomonis *et al.*, 1978). Also, the formation of the primary (straight-chain) carbonium ion is accompanied to some degree by the loss of a hydrogen atom. However, the significance of the loss of the hydrogen atom as an aid to the interpretation of mass spectra was not realized until McCarthy *et al.* (1968) deduced the effects of the size of the straight-chain tail of the secondary carbonium ion and of the presence of other branch points in the secondary carbonium ion on the intensity of the $[C_nH_{2n}]^{+}$ ion (i.e., other branches on the secondary carbonium ion suppressed the formation of the $[C_nH_{2n}]^{+}$ ion). These observations were used to distinguish between the mass spectra expected for 7,9-dimethylhexadecane and that of a mixture of 7- and 8-methylheptadecane (McCarthy *et al.*, 1968) and were later used by Nelson and Sukkestad (1970, 1975), in conjunction with gas chromatographic retention times expressed as equivalent chain lengths, to identify for the first time internally branched di- and trimethylalkanes in insects.

2.5 MONOMETHYLALKANES

Methyl branched alkanes have been identified mainly in arthropods but also in algae, higher plants, and gastropods, in which the methyl branch is located towards the center of the molecule. Alkenes with similar methyl branching have been found in *S. calcitrans* (Uebel *et al.*, 1975b). Similar methylalkenes were found in the millipede, *G. tumuliporus* (Oudejans, 1973).

The identified monomethylalkanes and their sources are summarized in Table 1. The GLC peak number given there is equal to the number of carbons in the backbone of the molecule, and the letter A designates one internal methyl branch. The shorter chain monomethylalkanes (less than 20 carbon atoms such as 5-methylpentadecane and 7- and 8-methylheptadecanes) are present in meteorites (Oró *et al.*, 1968), in a number of algae (Gelpi *et al.*, 1970), and blue-green algae (Han *et al.*, 1968; Fehler and Light, 1970). In Hymenoptera, they were identified in the secretions of Dufour's gland in the ants, *Formica nigricans* Emery, *F. rufa* L., and *F. polyctena* Foerster (Bergström and Löfqvist, 1973), *Camponotus intrepidus* (Brophy *et al.*, 1973), *Pogonomyrmex rugosus* var. *fuscatus* Emery and *P. barbatus rugosus* Emery (Regnier *et al.*, 1973) and in whole body extracts of the Argentine ant, *Iridomyrmex humilis* (Mayr) (Cavill and Houghton, 1973). The 7- and 8-methylheptadecanes were also reported in the lichen, *Siphula ceratites* (Wg.) Fr. though they may have been from the algal symbiont (Gaskell *et al.*, 1973).

Although *n*-alkanes and 2- and 3-methylalkanes have been identified in the waxes of a large number of higher plants, the only internally branched monomethylalkanes reported were in the leaf wax of the walnut tree, *Juglans regia* L. (Stránský *et al.*, 1970), and of wheat (Nishimoto, 1974). A series of methylalkanes from 17 to 34 carbon atoms was present in the walnut leaf wax. In the GLC peaks identified, GLC peak 27-A was a mixture of 7-, 9-, 11-, and 13-methylheptacosane, and GLC peak 29-A was a mixture of 11-, 13-, and 15-

TABLE 1

Occurence and structure of internally-branched monomethylalkanes

Source[a]	GLC peak no.[b]	Methyl-branched components	Major isomer[c]
METEORITES			
Carbonaceous chondrites	15-A	5- and 6-methylpentadecane	?
	16-A	5-methylhexadecane	
PLANTS (Algae)			
C. turgidus	16-A	6- and 7-methylhexadecane	?
C. turgidus, *A. cyanea*, *L. aestuarii*, *Nostoc sp.*	17-A	7- and 8-methylheptadecane	?
C. fritschii	17-A	4-, 7- and 8-methylhepadecane	?
N. muscorum, *P. luridum*, *A. nidulans*, *A. variabilis*	17-A	7- and 8-methylheptadecane	similar
PLANTS (Lichen)			
S. ceratites	17-A	7-, and 8-methylheptadecane	similar
PLANTS (Trees)			
J. regia	27-A	7-, 9-, 11-, and 13-methylheptacosane	13-methyl
	29-A	11-, 13-, and 15-methylnonacosane	11- & 13-methyl
PLANTS (Wheat)			
T. aestivum	23-A	11-methyltricosane	
	25-A	11-methylpentacosane	
	27-A	11-, and 13-methylheptacosane	11-methyl
	28-A	10-, and 12-methyloctacosane	12-methyl
	29-A	11-, and 13-methylnonacosane	11-methyl
	30-A	10, and 12-methyltriacontane	12-methyl
	31-A	11-, 13-, and 15-methylhentriacontane	11-methyl
	32-A	10-, and 12-methyldotriacontane	12-methyl
	33-A	11, 13-, and 15-methyltritriacontane	11- & 13-methyl
	35-A	11-, 13-, 15-, and 17-methylpentatriacontane	11- & 13-methyl
INSECTA (Coleoptera)			
A. grandis	20-A	10-methyleicosane	
P. japonica	22-A	11-methyldocosane	
	23-A	11-methyltricosane	
	24-A	10-, 11-, and 12-methyltetracosane	12-methyl
	25-A	11-, and 13-methylpentacosane	11-methyl
C. caryae	26-A	4-methylhexacosane	
	27-A	5-methylheptacosane	
	28-A	4-methyloctacosane	
	29-A	5-, 11- 13-, and 15-methylnonacosane	?

TABLE 1 (*cont.*)

Source[a]	GLC peak no.[b]	Methyl-branched components	Major isomer[c]
INSECTA (Diptera)			
S. bullata	25-A	5-, 7-, 9-, 11-, and 13-methylpentacosane	?
	27-A	5-, 7-, 9-, 11-, and 13-methylheptacosane	?
	29-A	5-, 7-, 9-, 11-, 13-, and 15-methylnonacosane	?
	31-A	5-, 7-, 9-, 11-, 13-, and 15-methylhentriacontane	?
S. calcitrans	31-A	11-, 13-, and 15-methylhentriacontane	?
	33-A	13-, and 15-methyltritriacontane	?
	35-A	13-, 15-, and 17-methylpentatriacontane	?
	37-A	13-, and 15-methylheptatriacontane	?
INSECTA (Hymenoptera)			
F. nigricans, *F. rufa*, *F. polyctena*, *C. intrepidus*	11-A	5-methylundecane	
P. rugosus	11-A	5-, and 6-methylundecane	?
F. nigricans	12-A	4-methyldodecane	
C. intrepidus	12-A	5-methyldodecane	
P. rugosus, *P. barbatus*	12-A	6-methyldodecane	
F. nigricans, *F. rufa*, *F. polyctena*, *C. intrepidus*, *P. barbatus*	13-A	5-methyltridecane	
P. rugosus	13-A	5-, and 6-methyltridecane	?
P. rugosus, *P. barbatus*	14-A	6-methyltetradecane	
F. nigricans, *C. intrepidus*, *I. humilis*	15-A	5-methylpentadecane	
I. humilis	16-A	4-methylhexadecane	
C. intrepidus	16-A	5-methylhexadecane	
I. humilis	17-A	5-methylheptadecane	
S. richteri	23-A	9-, and 11-methyltricosane	11-methyl
	25-A	11-, and 13-methylpentacosane	11-methyl
A. mellifera (Beeswax)	25-A	9-, and 11-methylpentacosane	11-methyl
	27-A	5-, 7-, 9-, 11-, and 13-methylheptacosane	13-methyl
S. richteri	27-A	11-, and 13-methylheptacosane	13-methyl
S. invicta	27-A	11-, and 13-methylheptacosane	13-methyl
M. gulosa	27-A	9-, 11-, 13-, and 15-methylheptacosane	?
A. mellifera	29-A	11-, 13-, and 15-methylnonacosane	15-methyl
M. gulosa	29-A	9-, 11-, 13-, and 15-methylnonacosane	?
	31-A	9-, 11-, 13-, and 15-methylhentriacontane	?

TABLE 1 (*cont.*)

INSECTA (Lepidoptera)			
H. zea	31-A	7-, 9-, 11-, 13-, and 15-methylhentriacontane	13-methyl
H. virescens	31-A	9-, 11-, 12-, 13-, and 15-methylhentriacontane	?
	32-A	10-, 12-, 13-, 14-, 15-, and 16-methyldotriacontane	?
	33-A	9-, 11-, 13-, 15-, and 17-methyltritriacontane	?
M. sexta	35-A	15-, and 17-methylpentatriacontane	17-methyl
	37-A	13-, 15-, 17-, and 19-methylheptatriacontane	15-methyl
	39-A	13-, 15-, 17-, and 19-methylnonatriacontane	15-methyl
INSECTA (Orthoptera)			
P. australasiae, *P. brunnea*, *P. fuliginosa*	23-A	11-methyltricosane	
	24-A	12-methyltetracosane	
	25-A	13-methylpentacosane	
	26-A	13-methylhexacosane	
L. maderae, *B. orientalis*	27-A	11-, and 13-methylheptacosane	similar
M. sanguinipes	27-A	5-, 7-, 9-, 11-, 13-, and 15-methylheptacosane	11-methyl
M. packardii	27-A	5-, 7-, 9-, 11-, and 13-methylheptacosane	13-methyl
P. japonica	27-A	13-methylheptacosane	
A. simplex	27-A	5-, 7-, 11-, and 13-methylheptacosane	11-methyl
M. sanguinipes	29-A	5-, 7-, 9-, 11-, and 13-methylnonacosane	11-methyl
M. packardii	29-A	7-, 9-, 11-, 13-, and 15-methylnonacosane	9-methyl
P. japonica	29-A	13-methylnonacosane	
A. simplex	29-A	5-, 7-, 9-, 11-, 13-, and 15-methylnonacosane	5-methyl
M. sanguinipes	30-A	8-, 9-, 10-, and 11-methyltriacontane	9-methyl
M. packardii	30-A	8-, 9-, 10-, 11-, 12-, and 13-methyltriacontane	9-methyl
P. japonica	30-A	13-methyltriacontane	
M. sanguinipes	31-A	7-, 9-, 11-, 13-, and 15-methylhentriacontane	11-methyl
M. packardii	31-A	5-, 7-, 9-, 11-, 13-, and 15-methylhentriacontane	11-methyl
A. simplex	31-A	5-, 7-, 9-, 11-, 13-, and 15-methylhentriacontane	7-methyl
M. sanguinipes	32-A	9-, 10-, 11-, and 12-methyldotriacontane	11-methyl
M. packardii	32-A	9-, 10-, 11-, 12-, and 13-methyldotriacontane	11-methyl
M. sanguinipes	33-A	11-, and 13-methyltritriacontane	11-methyl
M. packardii	33-A	11-, 13-, and 15-methyltritriacontane	11-methyl
A. simplex	33-A	7-, 9-, 11-, and 13-methyltritriacontane	9-methyl
A. domesticus	33-A	13-, 15-, and 17-methyltritriacontane	?
S. vaga	33-A	11-, 13-, and 15-methyltritriacontane	13- & 15-methyl
A. domesticus	34-A	13-, 15-, and 17-methyltetratriacontane	?
S. vaga	34-A	13-methyltetratriacontane	
A. simplex	35-A	11-, 13-, and 15-methylpentatriacontane	11-methyl
A. domesticus	35-A	13-, 15-, and 17-methylpentatriacontane	?
S. vaga	35-A	11-, 13-, 15-, and 17-methylpentatriacontane	13-methyl
A. domesticus	36-A	13-, 15-, and 17-methylhexatriacontane	?
S. vaga	36-A	14-methylhexatriacontane	
A. simplex	37-A	11-, 13-, 15-, and 17-methylheptatriacontane	13-methyl
S. vaga	37-A	13-, 15-, 17-, and 19-methylheptatriacontane	13-methyl
	38-A	12-, and 13-methyloctatriacontane	Similar
	39-A	13-, 15-, 17-, and 19-methylnonatriacontane	13-methyl
	41-A	13-methylhentetracontane	

TABLE 1 (*cont.*)

Source[a]	GLC peak no.[b]	Methyl-branched components	Major isomer[c]
INSECTA (Tricoptera)			
P. californica	21-A	9-methylheneicosane	
	23-A	8-, 10-, and 12-methyltricosane	?
	25-A	9-, 10-, and 12-methylpentacosane	?
	27-A	9-, 11-, and 13-methylheptacosane	?
	29-A	7-, 9-, 10-, 12-, and 14-methylnonacosane	?
CHORDATA			
Wool wax	29-A	13-methylnonacosane	
	31-A	11-, 13-, and 15-methylhentriacontane	13-methyl
	33-A	11-, and 13-methyltritriacontane	Similar
	35-A	13-methylpentatriacontane	
	36-A	12-, and 14-methylhexatriacontane	Similar
	37-A	11-, 13-, 15-, and 17-methylheptatriacontane	13-methyl
	38-A	12-methyloctatriacontane	
	39-A	11-, 13-, 15-, and 17-methylnonatriacontane	13-methyl
	40-A	12-, and 14-methyltetracontane	12-methyl
	43-A	13-methyltritetracontane	
PETROLEUM			
Paraffin wax	27-A	4-, and 5-methylheptacosane	4-methyl
	28-A	4-, and 5-methyloctacosane	Similar
	29-A	4-, and 5-methylnonacosane	4-methyl
	30-A	4-, and 5-methyltriacontane	4-methyl
	31-A	4-, and 5-methylhentriacontane	Similar

[a] Meteorites: Oró *et al.*, 1968, *C. turgidus, A. cyanea, L. aestuarii, Nostoc* sp: Gelpi *et al.*, 1970; *N. muscorum, A. nidulans, P. luridum, C. fritschii:* Han *et al.*, 1968; *A. variabilis:* Fehler and Light, 1970; *S. ceratites:* Gaskell *et al.*, 1973; *J. regia:* Stránský *et al.*, 1970; *T. aestivum:* Nishimoto, 1974; *A. grandis:* Hedin *et al.*, 1972; *P. japonica:* Bennett *et al.*, 1972 and Nelson, D. R. (unpublished); *C. caryae:* Mody *et al.*, 1975; *S. bullata:* Jackson *et al.*, 1974; *S. calcitrans:* Uebel *et al.*, 1975b; *F. nigricans, F. rufa, F. polyctena:* Bergström and Löfqvist, 1973; *C. intrepidus:* Brophy *et al.*, 1973; *P. rugosus* and *P. barbatus:* Regnier *et al.*, 1973; *I. humilis:* Cavill and Houghton, 1973; *S. invicta* and *S. richteri:* Lok *et al.*, 1975; Beeswax: Stránský *et al.*, 1966, Streibl *et al.*, 1966; *M. gulosa:* Cavill *et al.*, 1970; *H. zea:* Jones *et al.*, 1971; *H. virescens:* Vinson *et al.*, 1975; *M. sexta:* Nelson and Sukkestad, 1970, Nelson *et al.*, 1972; *P. australasiae, P. brunnea,* and *P. fuliginosa:* Jackson, 1970; *L. maderae* and *B. orientalis:* Tartivita and Jackson, 1970; *P. japonica:* Jackson, 1972; *M. sanguinipes* and *M. packardii:* Soliday *et al.*, 1974; *A. simplex:* Jackson and Blomquist, 1976; *A. domesticus:* Hutchins and Martin, 1968; *S. vaga:* Nelson and Sukkestad, 1975; *P. californica:* Armold *et al.*, 1969; wool wax: Mold *et al.*, 1966; paraffin wax: Levy *et al.*, 1961.

[b] GLC peaks designated as described herein and in Nelson and Sukkestad, 1970, 1975. The number is equal to the number of carbons in the backbone of the molecule, and the letter A designates one internal methyl branch. The monomethylalkanes eluted with an equivalent chain length 0.6 to 0.7 carbon atoms less than the *n*-alkane with the same number of carbon atoms (Mold *et al.*, 1966; Nelson and Sukkestad, 1970; 1975).

[c] Determined from the relative intensities of the major characteristic fragmentation peaks in the mass spectra.

methylnonacosane. Other internally branched monomethylalkanes from 23-A to 35-A were present, including some in which the methyl branch occurred on an even numbered carbon atom (12 or 14). In wheat, the internally branched methylalkane series was from 21 to 37 carbon atoms and consisted of even carbon numbered 11-, 13-, and 15-methylalkanes and odd carbon numbered 10- and 12-methyl alkanes.

Other *Hymenoptera* and the *Coleoptera* had longer chain methylalkanes (over 20 carbon atoms). 10-Methyleicosane was the only methylalkane found in the boll weevil, *A. grandis* (Hedin *et al.*, 1972). The monomethylalkanes 26-A, 27-A, 28-A, and 29-A were identified in whole-body extracts of the pecan weevil, *C. caryae*, (Mody *et al.*, 1975); 27-A, 29-A, and 31-A (each GLC peak consisted of a mixture of isomers) were identified in whole-body extracts of the bull ant, *Myrmecia gulosa* (F.), (Cavill *et al.*, 1970), and the monomethylalkanes 25-A, 27-A, and 29-A were identified in beeswax (Stránský *et al.*, 1966; Streibel *et al.*, 1966); 23-A, 25-A, and 27-A were identified in *S. richteri*, and 27-A was identified in *S. invicta* (Lok *et al.*, 1975) (Table 1).

In *Diptera*, internally branched monomethylalkanes and monomethylalkenes have been reported from the stable fly, *Stomoxys calcitrans*, (Uebel *et al.*, 1975b), which contained methylalkanes from 32 to 38 carbons in chain length and from the fleshfly, *Sarcophaga bullata*, (Jackson *et al.*, 1974), which contained methylalkanes from 26 to 32 carbons in chain length (no methylalkanes with an even-numbered carbon backbone were found) (Table 1). One of the major alkane components of the surface lipids of the female tsetse fly, *Glossina morsitans* Westwood, is 2-methyltriacontane (personal communication, D. A. Carlson, USDA, Insects Affecting Man and Animals Laboratory, Gainesville, Fla.).

Among the *Orthoptera*, the cockroaches, *Periplaneta australasiae*, *P. brunnea*, *P. fuliginosa* (Jackson, 1970), *P. japonica* (Jackson, 1972), *Leucophaea maderae*, and *Blatta orientalis* (Tartivita and Jackson, 1970), have the smallest internally branched monomethylalkanes (between 20 and 31 carbon atoms), followed by the grasshoppers, *Melanoplus sanguinipes* (F.), and *M. packardii* Scudder (Soliday *et al.*, 1974) (between 28 and 38 carbon atoms). The common house cricket, *Acheta domesticus* (Hutchins and Martin, 1968), has monomethylalkanes, from 27 to 39 carbon atoms, and the Mormon cricket, *A. simplex* has monomethylalkanes from 28 to 38 carbon atoms with all the branch points on odd-numbered carbons (Jackson and Blomquist, 1976). The longest chain monomethylalkanes (33 to about 50 carbon atoms) from an orthopteran insect were in the grasshopper, *Schistocerca vaga* (Scudder) (Nelson and Sukkestad, 1975).

Internally branched monomethylalkanes were identified in four Lepidoptera: the tobacco hornworm, *Manduca sexta* (L.) (Nelson and Sukkestad, 1970; Nelson *et al.*, 1971, 1972), the corn earworm *Heliothis zea* (Boddie) (Jones *et al.*, 1971), the tobacco budworm, *H. virescens* (F.) (Vinson *et al.*, 1975), and the silkworm, *B. mori* (Murata *et al.*, 1974). *M. sexta* had monomethylalkanes ranging in chain length from about 20 to 44 carbon atoms, and the major components were GLC peaks 35-A, 37-A, and 39-A. One GLC peak, 31-A, of three GLC hydrocarbon peaks of *H. zea* was identified as a mixture of 7-, 9-, 11-, 13-, and 15-methylhentriacontanes, and the 13-methyl isomer was shown to be a kairomone for the *H. zea* larval parasite, *Microplitis croceipes* (Cresson).

Murata *et al.* (1974) reported finding 9-methyltriacontane in *B. mori*, but their mass spectra leave doubt as to this identification. However, mass spectra that they deduced as coming from 11,12-dimethyloctacosane was completely compatible with the mass spectra expected for a mixture of 11-, 13-, and 15-methylnonacosane. The GLC retention time also appeared to be compatible with that expected for a monomethylalkane chromatographed on OV-1.

Similar homologous series of monomethylalkanes were present in both *M. sexta* and *S. vaga*. A comparison of GLC peaks 35-A, 37-A, and 39-A showed that the peaks from both insects contained the same mixture of isomers, but the major component of each peak from *S. vaga* had the methyl branch on carbon 13, and the major component of each peak from *M. sexta* had the methyl branch on carbon 17 for peak 35-A and on carbon 15 for peaks 37-A and 39-A. Whether this difference is of any significance is not known at present.

The majority of the internally branched monomethylalkanes has the methyl branch located on an odd-numbered carbon atom, and in plants and insects, this is usually either on carbon 11, 13, or 15. Monomethylalkanes with the methyl branch on an even-numbered carbon atom have been reported in only six insects: the boll weevil, *Anthonomus grandis* Boheman, with 10-methyleicosane (Hedin *et al.*, 1972), the grasshopper, *Melanoplus sanguinipes*, with GLC peak 30-A a mixture of 8-, 9-, 10-, and 11-methyltriacontanes and GLC peak 32-A a mixture of 9-, 10-, 11-, and 12-methyldotriacontanes (Soliday *et al.*, 1974), the grasshopper, *M. packardii*, with GLC peak 30-A a mixture of 8-, 9-, 10-, 11-, 12-, and 13-methyltriacontanes and GLC peak 32-A a mixture of 9-, 10-, 11-, 12-, and 13-methyldotricontanes (Soliday *et al.*, 1974), the stonefly, *Pteronarcys californica*, with GLC peak 23-A being a mixture of 8-, 10-, and 12-methyltricosanes, GLC peak 25-A a mixture of 9-, 10-, and 12-methylpentacosanes, and GLC peak 29-A a mixture of 7-, 9-, 10-, 12-, and 14-methylnonacosanes (Ármold *et al.*, 1969a), *Popillia japonica*, with 12-methyltetracosane (Bennett *et al.*, 1972), and *Heliothis virescens*, with possibly 9-, 11-, 12-, 13-, and 15-methylhentriacontanes and 10-, 12-, 13-, 14-, 15-, and 16-methyldotriacontanes (Vinson *et al.*, 1975).

The only report of internally branched monomethylalkanes from a chordate was the finding in wool wax of methylalkanes from 17 to 44 carbon atoms (Mold *et al.*, 1966) (Table 1). The methyl branch occurred mainly at the 13 position for the even-carbon numbered series.