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THE ALKANES OF THE ANT, *ATTA COLOMBICA*

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Abstract—Two homologous series of trimethylalkanes, the 3,7,11-trimethylalkanes ($C_{34}H_{70}$, $C_{36}H_{74}$ and $C_{38}H_{78}$) and the 4,8,12-trimethylalkanes ($C_{35}H_{72}$, $C_{37}H_{76}$ and $C_{39}H_{80}$) are the major constituents of the cuticular alkanes of the ant, *Atta colombica*. Each of these structures combines a reduced polyketomethylene chain and a modified isoprenoid chain, and hence combine structural units from two major metabolic pathways. Hydrocarbons of this type have not been previously isolated from natural sources.

INTRODUCTION

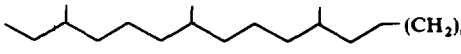
IN RECENT years insects have been used with increasing frequency by organic chemists as source materials for the isolation and characterization of natural products.[1–3] The structures of insect products have provided challenging obstacles to organic synthesis[2,4–7] and have posed some interesting biogenetic questions.[8–11] This paper describes the characterization of the saturated hydrocarbons derived from the Panamanian ant, *Atta colombica* Guerin.[12*] Compounds of a structural type not previously isolated from any natural source make up the bulk of the ant hydrocarbons. These structures raise interesting and fundamental questions regarding the biosynthetic capabilities of insects.

RESULTS

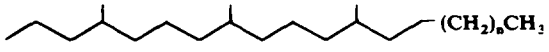
The saturated hydrocarbons of A. colombica. An alkane fraction was isolated from *A. colombica* by a straight-forward procedure in which 30–100 g of ants was homogenized and extracted in a Waring blender, giving a lipid extract from which a pure alkane fraction was easily isolated by chromatography. First a hydrocarbon fraction was obtained by chromatography over Florisil, then alkanes and alkenes were separated by chromatography over silica gel impregnated with silver nitrate. A gas-liquid chromatogram of the alkane fraction so isolated is displayed in Fig. 1.

Insect hydrocarbons are largely of cuticular origin. Extracts of the cuticle surface of *A. colombica* gave an alkane fraction with virtually the same composition as the alkane fraction obtained from an extract of homogenized ants. Thus, the hydrocarbons described in this paper are largely of cuticular origin.

Components 14, 17, 21, 24, 27 and 30 collectively account for 80% (by wt) of the alkanes of *A. colombica*, and it was to the elucidation of the structures of these components that our major efforts were directed. The structures which were ultimately assigned to these substances are indicated in formulas Ia–c and IIa–c.



Ia (Peak 14): n = 17 ($C_{34}H_{70}$)
Ib (Peak 21): n = 19 ($C_{36}H_{74}$)
Ic (Peak 27): n = 21 ($C_{38}H_{78}$)



IIa (Peak 17): n = 17 ($C_{35}H_{72}$)
IIb (Peak 24): n = 19 ($C_{37}H_{76}$)
IIc (Peak 30): n = 21 ($C_{39}H_{80}$)

* The Panamanian variety of this species is accorded subspecific status by some entomologists,[13] by whom it is designated *Atta colombica tonsipes* Santschi.

Two related homologous series are represented by these six substances. Components 14, 21 and 27 are the 34-, 36- and 38-carbon members of the 3,7,11-trimethylalkanes, and components 17, 24 and 30 are the 35-, 37- and 39-carbon members of the 4,8,12-trimethylalkanes. Each of these structures combines a reduced polyketomethylene

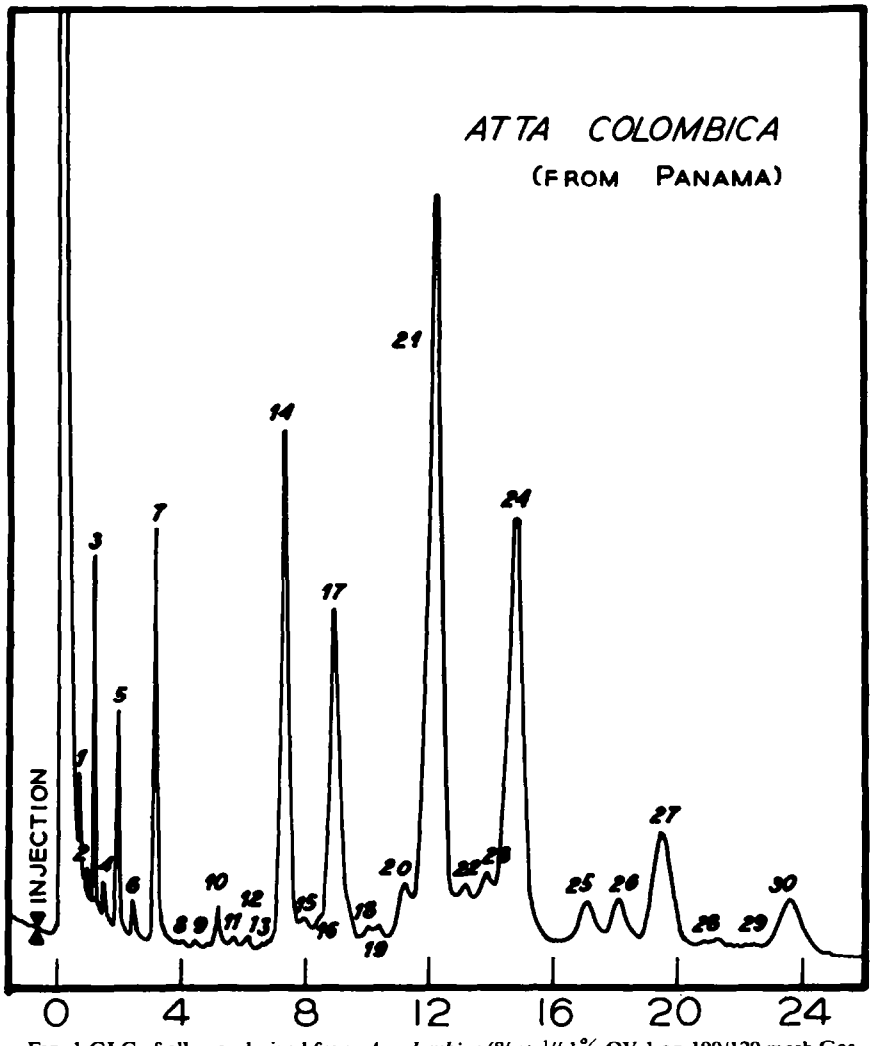


FIG. 1 GLC of alkanes derived from *A. colombica* (8′ × ⅛″ 1% OV-1 on 100/120 mesh Gas Chrom Q, 259°C)

chain with a modified isoprenoid chain. These structures were established by interpretation of mass spectral fragmentation patterns, GLC behavior, chemical degradation, and in one case, comparison with an authentic sample obtained by unequivocal synthesis.

The mass spectra of components 14, 21 and 27 and 17, 24 and 30 are displayed in Figs 2 and 3, respectively. Although the mass spectra do not permit unique structures

to be assigned to each of these six components, they do serve to establish the very important fact that all six are branched alkanes in which the branches are all Me groups. Thus, for component 14, the molecular ion appears at *m/e* 478, establishing that the molecular formula is $C_{34}H_{70}$. Major fragment ions at *m/e* 463

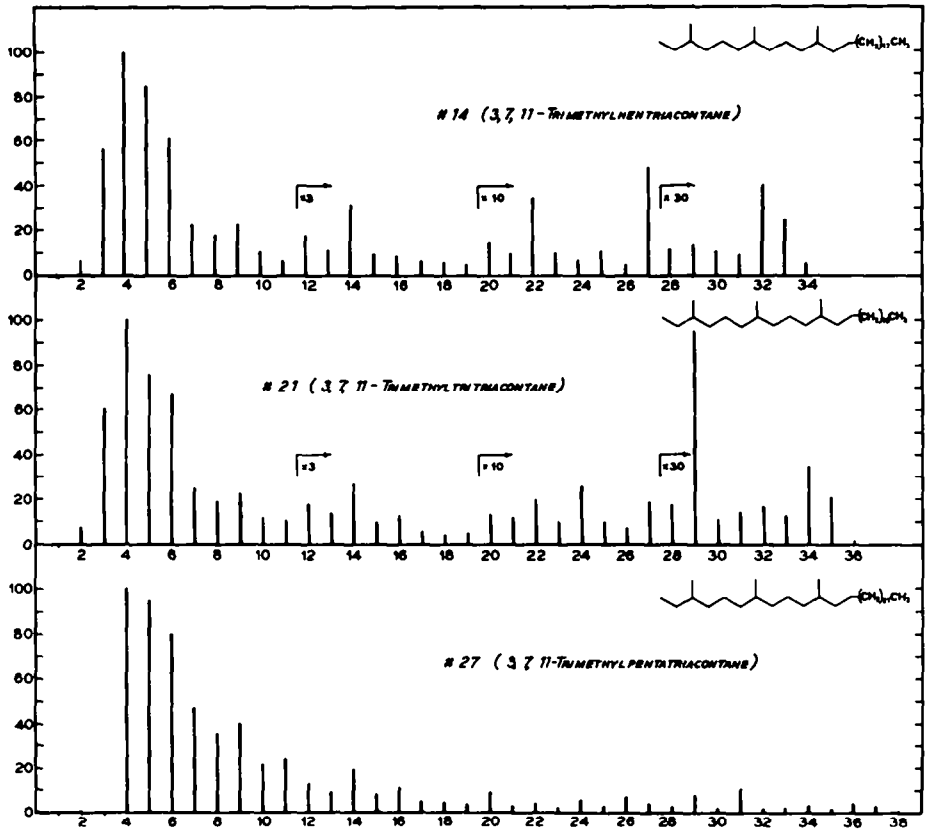


FIG. 2 Mass spectra of components 14, 21, 27.

($C_{33}H_{67}$=M^+—CH_3), 379 ($C_{27}H_{55}$=M^+—C_7H_{15}), 127 (C_9H_{19}=M^+—$C_{25}H_{51}$), 309 ($C_{22}H_{45}$=M^+—$C_{12}H_{25}$) and 197 ($C_{14}H_{29}$=M^+—$C_{20}H_{41}$) require that component 14 incorporate the structural elements indicated in formulas III and IV. Also the fragment ion at *m/e* 449 ($C_{32}H_{65}$=M^+—C_2H_5) indicates the presence of a Me group on C-3, as in structure V. The mass spectrum is not consistent with a structure in which an Et group is attached to any other chain C atom. Loss of a Me group from any one of the structures III–V would account for the fragment ion at *m/e* 463 ($C_{33}H_{67}$). The mass spectra for components 21 and 27 suggest structures very similar to 14, and require the incorporation of the same structural elements, III–V where m = 22, n = 27 and p = 32 for component 21 and m = 24, n = 29 and p = 34 for component 27.

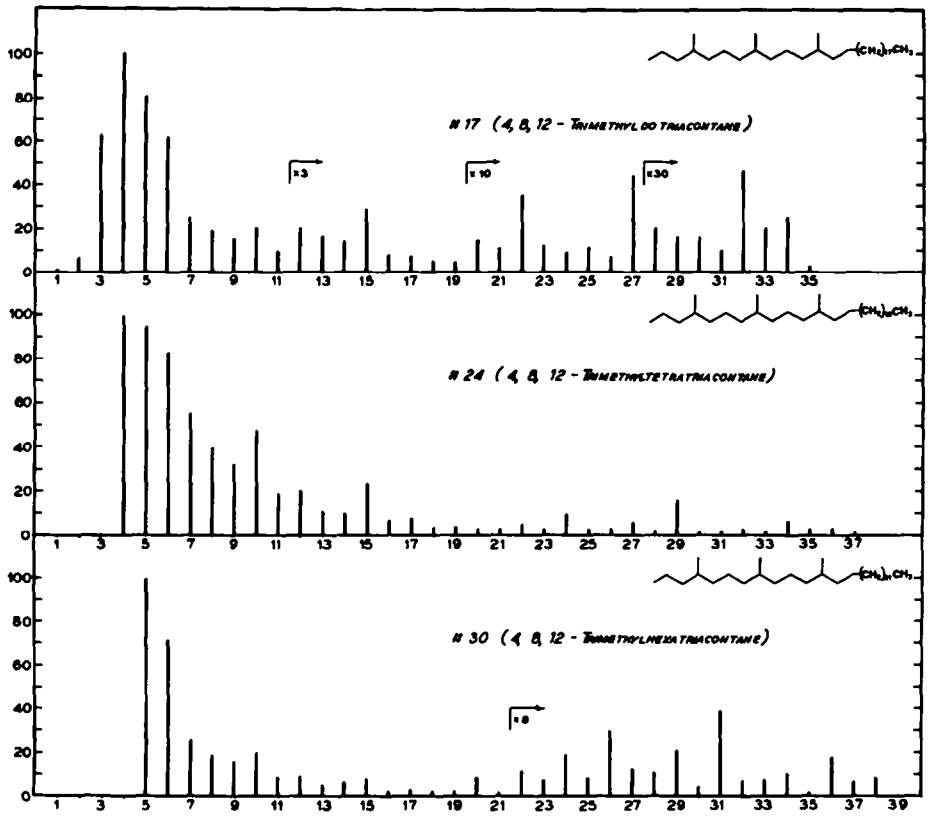
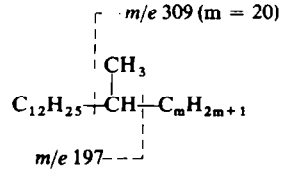
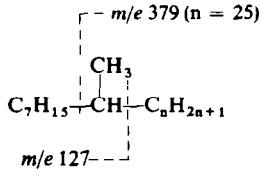


FIG. 3 Mass spectra of components 17, 24, and 30

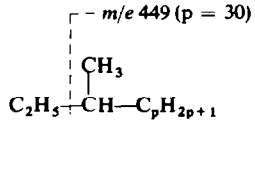
The mass spectra of 17, 24 and 30 require the incorporation of the structural elements VI–VIII. The *m/e* values for the fragments indicated on the structures are for component 17. For 24, m = 22, n = 27 and p = 32 and for 30, m = 24, n = 29 and p = 34.



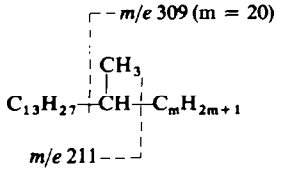
III



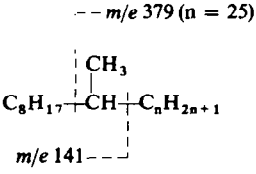
IV



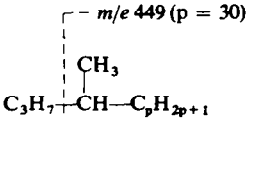
V



VI



VII



VIII

Next, it was determined that all six of the components in question are trimethylalkanes. This was achieved by comparing the retention times on GLC of these materials with those of authentic isomeric standards. Thus, component 14, a 34-carbon alkane, elutes from a GLC column long before the straight-chain isomer, n-tetratriacontane, or an isomeric monomethylalkane. The "effective chain length"[14] of component 14 is 32·4, a value appropriate for a trimethylhentriacontane. The effective chain lengths of components 17, 21, 24, 27 and 30 also point to trimethylalkane structures. Components 14 and 17 were compared directly with authentic trimethylalkanes

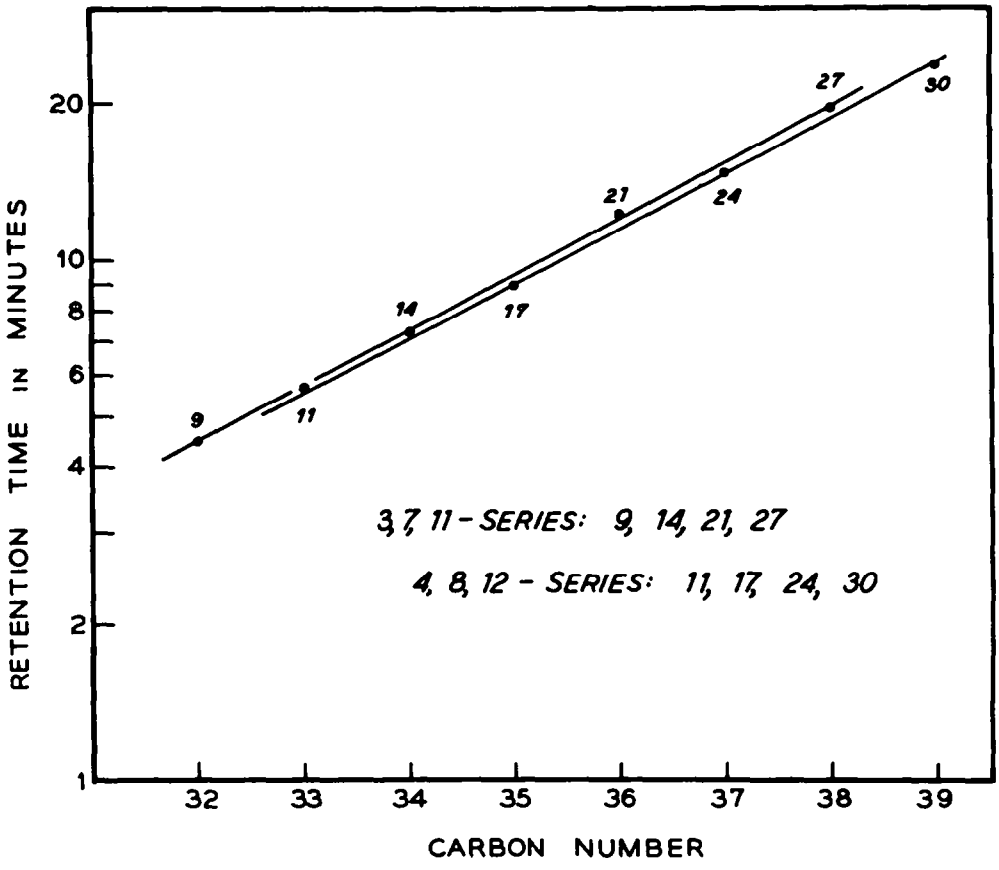


FIG. 4 Log retention times *vs.* carbon number plot for components 9, 11, 14, 17, 21, 24, 27 and 30.

having the same number of C atoms. Component 14 had identical retention times on four different GLC columns as 3,7,11-trimethylhentriacontane, and component 17 had a retention time very close to that of authentic 2,6,10-trimethyldotriacontane.

Components 14, 21 and 27 were shown to be members of one homologous series and components 17, 24 and 30 members of a second homologous series by noting that each set of substances defined a straight line when the logarithm of the retention time was plotted against carbon number[15] (Fig. 4).

Since components 14 and 17 were shown to be trimethylalkanes by direct comparison with standards, and since 14, 21 and 27, and 17, 24 and 30 form two homologous series, obviously all six of these compounds must be trimethylalkanes. It was also noted that the minor components 9 and 11 fall on the lines defined by these six components. Hence, they have been tentatively assigned to these two series.

The mass spectrum of component 14 is in accord with four isomeric trimethylhentriacontanes Ia, IX, X and XI. An oxidative degradation with chromic acid in acetic acid[16] served to establish that Ia was the correct structure for component 14.

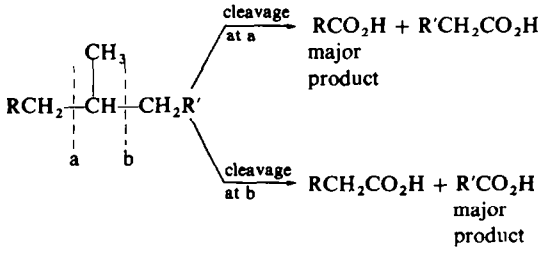
Ia $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_3\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_3\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_{19}CH_3$

IX $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_3\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_{11}\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_{11}CH_3$

X $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_8\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_{11}\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_6CH_3$

XI $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_{16}\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_3\underset{\displaystyle CH_3}{\underset{|}{C}}H(CH_2)_6CH_3$

This reagent is a vigorous oxidizing agent which preferentially cleaves an alkane at branching points. The ultimate products are carboxylic acids (Reaction 1). The oxidation product mixture is a complex one, since there is some cleavage of every C—C bond in the molecule, but since fatty acid mixtures are conveniently analyzed by GLC, it is possible to utilize the method to locate branch points. A sample of component 14 obtained by preparative GLC was oxidized by this method. The major product of the



(Reaction 1)

oxidation was the C_{20} straight-chain acid. There were smaller amounts of the C_{21} straight-chain acid. 4,8-Dimethyldecanoic and 5,9-dimethylundecanoic acids were also major product acids. Of the four possible structures for component 14, only Ia is consistent with the results of this oxidation. Structure IX could not give a straight chain acid with more than thirteen C atoms, and could give only small quantities of 4,8-dimethyldecanoic and 5,9-dimethylundecanoic acids. Structures X and XI cannot give either of these dimethylalkanoic acids, and cannot give a straight-chain acid

with more than eight C atoms. The oxidation, therefore, serve to establish unambiguously that component 14 is 3,7,11-trimethylhentriacontane, Ia.

Further affirmation of the correctness of this structure assignment was obtained by comparing component 14 with synthetic 3,7,11-trimethylhentriacontane. The mass spectra of the two substances are virtually identical. The chromic acid degradation of the natural and synthetic materials gave product mixtures which contained all of the same components, as indicated by GLC. Although there were some differences in the relative amounts of some of the products, doubtless reflecting inconsistencies in the execution and work-up, the same components were major and minor in each product mixture. Finally, component 14 and synthetic Ia were indistinguishable on four different GLC columns.

The mass spectra of components 21, 27, 17, 24 and 30 are, of course, in complete accord with the proposed structures Ib,c and II a–c. Obviously, however, for each of these substances there will be four isomeric trimethylalkanes which could give the observed mass spectrum, just as was the case for component 14. Since oxidative degradations were not carried out on any of these components, no claim can be made that the structures proposed have been rigorously and unequivocally established. However, strong arguments can be marshalled in support of these structures. As has been pointed out, a log retention time *vs* carbon number plot (Fig. 4) reveals that 14, 21 and 27 and 17, 24 and 30 are members of two related homologous series. The fact that each set of three components defines a straight line implies that the three Me groups are identically positioned on the alkane chain of each member of the two series.

There is also a very persuasive biogenetic argument favoring structures Ib and c and IIa–c. Cuticular waxes are generally composed of homologous series of substances of common biogenetic origin. The structure of 14, Ia, obviously incorporates a modified isoprenoid unit. This structural unit is preserved in structures Ib and c and IIa–c. The alternate structures which are permitted by the mass spectra for components 17, 21, 24, 27 and 30 are all nonisoprenoid, and would, therefore, represent end products of quite different metabolic pathways from the ones which must be involved in the synthesis of 14. It would be completely contrary to the biogenetic economy characteristic of living systems to utilize diverse and unrelated metabolic pathways and precursers to synthesize the mixture of homologous materials present in cuticular wax. Component 14 has been rigorously shown to possess structure Ia. Biogenetic principles, therefore, virtually require that components 21, 27, 17, 24 and 30 have the structures suggested, Ib and c, and IIa–c, all of which contain the intact isoprenoid unit.

Peaks 1 through 8 and 10 were identified as n-alkanes. These components were completely removed from the total alkane mixture by treatment with Linde 5 Å molecular sieves. Peaks 2 and 6 were enhanced upon coinjection of authentic samples of n-tetracosane and n-octacosane, respectively. Component 7 was identified as n-nonacosane by comparison of its mass spectrum with the published mass spectrum of n-nonacosane.[17] Finally, the line resulting from the plot of the logarithm of the retention time *versus* carbon number[15] for peaks 1 through 8 and 10 coincided precisely with one constructed from authentic reference samples. Chromatograms obtained at lower temperatures allowed the detection of trace quantities of n-alkanes down to n-pentadecane. The seventeen n-alkanes detected, which includes the

homologous series from n-pentadecane through n-hentriacoutane, collectively constitute 10% (by wt) of the alkanes derived from *A. colombica*. n-Nonacosane, peak 7, is the most abundant n-alkane (4% of the total alkanes).

A complete summary of the composition of the alkanes derived from *A. colombica* is presented in Table 1. Only the minor components 12, 13 15, 16, 18, 19, 20, 22, 23, 25, 26, 28 and 29, collectively accounting for 10% (by wt) of the alkanes, remain unidentified.

TABLE 1. THE ALKANES OF THE ANT *A. colombica*

	n-Alkanes		3,7,11-*Trimethylalkanes*		4,8,12-*Trimethylalkanes*	
C #	%	*Evidence*	%	*Evidence*	%	*Evidence*
15	Trace	*a*	—		—	
16	Trace	*a*	—		—	
17	~0·2	*a*	—		—	
18	<0·1	*a*	—		—	
19	<0·1	*a*	—		—	
20	<0·1	*a*	—		—	
21	<0·1	*a*	—		—	
22	<0·1	*a*	—		—	
23	0·5	*a*	—		—	
24	<0·1	*a, b*	—		—	
25	1·7	*a*	—		—	
26	0·2	*a*	—		—	
27	1·5	*a*	—		—	
28	0·3	*a, b*	—		—	
29	4·1	*a, c, d*			—	
30	<0·1	*a*				
31	0·6	*a*	—		—	
32	—		~0·1	*a*	—	
33	—		—		~0·2	*a*
34	—		12	*a, b, c, d, e*	—	
35	—		—		8·8	*a, c*
36	—		29	*a, c*	—	
37	—		—		18	*a, c*
38	—		6·7	*a, c*	—	
39	—		—		4·4	*a, c*

a Position on log retention time *vs* carbon number plot. *b* Comparison of retention time with that of an authentic sample. *c* Mass spectrum. *d* Comparison of mass spectrum with that of an authentic sample. *e* Oxidative degradation.

The occurrence of the trimethylalkanes in other Atta *species.* The alkanes derived from two other Panamanian species of the ant genus *Atta* were examined for the presence of the 3,7,11-trimethyl- and 4,8,12-trimethylalkanes detected in *A. colombica*. The results of these investigations are summarized in Table 2. In *A. sexdens*, both the 3,7,11- and 4,8,12-trimethylalkanes series' are present, and together account for 61·3% of the total alkanes. n-Alkanes make up 16·2% of the total, In *A. cephalotes isthmicola*, on the other hand, only the 3,7,11-trimethyl series is present, and it accounts for only 15·3% of the total. n-Alkanes make up 17·2% of the alkanes of *A.c. isthmicola*. The very pronounced differences in the alkane distribution patterns

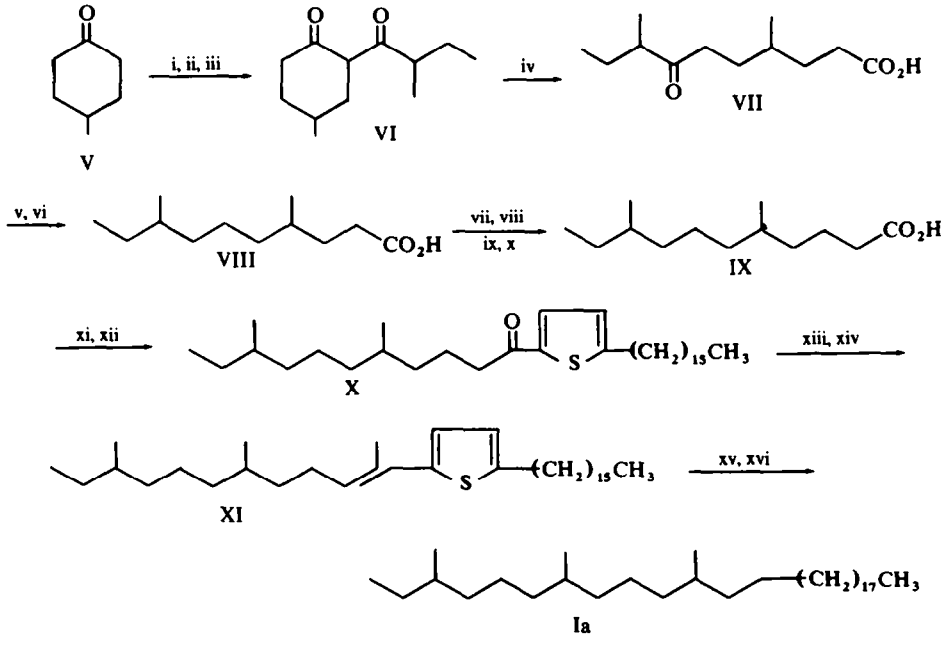
TABLE 2. THE OCCURRENCE OF 3,7,11- AND 4,8,12-TRIMETHYLALKANES IN *A. sexdens* AND *A. cephalotes isthmicola*

	3,7,11-Trimethylalkanes (% of total alkanes)		4,8,12-Trimethylalkanes (% of total alkanes)	
C #	*In A. sexdens*	*In A.c. isthmicola*	*In A. sexdens*	*In A.c. isthmicola*
34	21·6	6·5	—	—
35	—	—	28·1	—
36	7·0	7·5	—	—
37	—	—	3·9	—
38	0·7	1·3	—	—
39	—	—	—	—

observed for these three closely related species suggests the possible utility of insect alkane distribution patterns in insect taxonomy.

The synthesis of 3,7,11-*trimethylhentriacontane.* 3,7,11-Trimethylhentriacontane was synthesized by the route indicated in Chart 1. The final product is doubtless a mixture of diastereometers. No attempt was made to establish the relative amounts of the possible diastereomeric modifications which are present.

Chart 1. The synthesis of 3,7,11-trimethylhentriacontane



Reagents. (i) Morpholine/*p*-toluenesulfonic acid; (ii) d,*l*-2-Methylbutyryl chloride/triethylamine/$HCCl_3$; (iii) 3N HCl; (iv) 5% NaOH/Δ; (v) N_2H_4/diethylene glycol; (vi) KOH/Δ; (vii) LAH/ether; (viii) *p*-Toluenesulfonyl chloride/pyridine; (ix) NaCN/DMSO; (x) $NaOH/H_2O/HOCH_2CH_2OH$; (xi) $SOCl_2$; (xii) 2-Palmitylthiophene/$SnCl_4$; (xiii) MeMgI/ether; (xiv) 0·05 N HCl; (xv) Ni(R)/toluene; (xvi) $Pt/C/H_2$.

DISCUSSION

Cuticular alkanes of both plant and insect origin are invariably complex mixtures. The most ubiquitously encountered components of such mixtures are the n-alkanes, although branched structures are by no means uncommon.[18–21] The branched structures most often encountered are the monomethylalkanes, primarily the 2-Me (iso) and 3-Me (anteiso) compounds,[14, 18, 21–24] although alkanes with a single Me branch at mid-chain positions have been isolated from several sources.[14, 23, 24] Dimethylalkanes have also been reported from several plant waxes.[25, 26] Terpene hydrocarbons are, of course, widely distributed in nature. However, saturated acyclic isoprenoid compounds are not so common. Wool wax[27] and shark liver oil[28] have been found to contain pristane, a modified diterpene. Ancient sediments and oils are among the richest sources of saturated acyclic terpenoid structures.[29, 30]

The alkanes derived from the ant, *A. colombica*, represent a new class of natural products of a type not previously isolated from any natural source. These acyclic saturated hydrocarbons incorporate both a reduced polyketomethylene chain and a reduced and modified isoprenoid chain. This combination of structural units derived from different metabolic pathways poses some interesting biogenetic questions. How are the two structural units combined? Are these structures synthesized by modifications of the same general metabolic pathways operative in the biosynthesis of other long chain alkanes,[31] or are fundamentally different biosynthetic pathways involved? How are the "extra" C atoms added to the sesquiterpene portion of the structure? Is it possible that the apparent sesquiterpene structure is not a product of the mevalonate pathway at all, but rather a product of an entirely unsuspected biogenetic pathway? These questions can only be answered by the isolation of additional related metabolites from the ants, and by suitable studies utilizing labeled precursors. Such efforts would seem quite worthwhile in view of other recent findings which suggest some unusual biochemical capabilities of insects. For instance, the two juvenile hormones of Cecropia are sesquiterpenes with "extra" C atoms.[9, 10] Also, the terpene, canthraridine, the structure of which involves head-to-head, tail-to-tail union of two isoprene units, appears to be derived from a biogenetic sequence which incorporates three, rather than the expected two, mevalonate units.[8]

EXPERIMENTAL

The ants. A. colombica and *A. cephalotes isthmicola* were collected in the vicinity of Gamboa, Canal Zone. *A. sexdens* was collected on the beach near Santa Clara, Panama. All of the ants were collected using a vacuum cleaner apparatus.[32] They were killed with HCN, and were frozen shortly after collection and were kept frozen until extracted.

The isolation of an alkane fraction. In a typical isolation 30 g of ants was homogenized four times in a Waring blendor with a total of 1 l of Et_2O:MeOH (3:1). The resulting suspension was filtered through Celite on a course sintered glass funnel. The organic layer was separated and the water layer was saturated with salt, and washed with ether. The ether wash solns were combined with the organic layer and the combination was dried with $MgSO_4$, and concentrated, leaving 1·8 g of oil. This oil was chromatographed over 100 g of Florisil deactivated with water (7% by wt). Hydrocarbons (100 mg) were eluted with 600 ml of pet. ether (30–60°, redistilled). The hydrocarbon fraction was further chromatographed over silica gel impregnated with 25% $AgNO_3$ (Adsorbosil-CABN, Applied Science Laboratories). Alkanes (63% of the total hydrocarbons) were eluted with pet. ether, alkenes (37%) by ether : pet. ether (1 : 1).

GLC conditions. The chromatogram depicted in Fig. 1 was obtained using an 8′ × ¼″ stainless steel column of 1% methyl silicone gum OV-1 on silanized calcined diatomaceous earth support (Gas

Chrom Q, 100/120), using a Hewlett Packard Model 5750B dual column flame ionization Research Gas Chromatograph. The He flow rate was 30 ml/min and the oven temp was 259°. An excellent chromatogram was also obtained using an 18′ × ⅛″ column of 2·5% methyl vinyl silicone gum UC-W98 on a silanized diatomaceous earth support (Diatoport S, 80/100) at 250°. Samples of components 14, 17 and 21 were obtained by preparative GLC on a 6′ × ¼″ column of 6% methyl silicone gum SE-30 on 80/100 mesh Gas Chrom Q at 300°.

Mass spectra. Mass spectra of components 14, 17, and 21 were obtained on samples obtained by preparative GLC on a Hitachi Perkin–Elmer RMU-6D instrument at the Morgan-Schaffer Corp., Montreal Canada. Mass spectra of components 7, 24, 27 and 30 were obtained on an LKB 9000 Combined Gas Chromatograph-Mass Spectrometer in the Biochemistry Department at Michigan State University, E. Lansing.

The oxidative degradation.[16] A 2–3 mg sample of the ant hydrocarbon (71% component 14, 25% component 17, 2% component 21 and 2% component 24) was oxidized with 7 mg (0·07 mmol) of chromic anhydride in 0·5 ml of glacial AcOH. The oxidiation was conducted in a test tube for 4 hr at 65°. After cooling it was possible to remove a small bead of unreacted organic material from the reaction mixture with a spatula. The AcOH solvent was then removed by evaporation at reduced press. About 3 ml of 14% BF_3 in MeOH was added and the mixture refluxed for several min on a water bath. After cooling, 2–3 vols water was added and the cloudy suspension washed with pet. ether. The pet. ether layer was separated, concentrated and used directly for GLC analysis of the Me esters. The analyses were performed on a 1% methyl silicone gum OV-1 column and a 6% polyester LAC-728 column. Me esters of straight chain acids and of 4,8-dimethyldecanoic and 5,9-dimethylundecanoic acid were identified by comparison with authentic samples.

The synthesis of 3,7,11-*trimethylhentriacontane*

2-(2-*Methylbutyryl*)-4-methylcyclohexanone (VI). Over a 1·5 hr period 25 g (0·207 mol) of d,*l*-2-methylbutyryl chloride (Eastman) in 50 ml $CHCl_3$ was added to a mixture of 22·5 g (0·222 mol) dry Et_3N, 40·7 g (0·225 mol) 1-morpholino-4-methyl-1-cyclohexene,[33] and 120 ml $CHCl_3$ maintained at 35°. The reaction mixture was stirred at 35° for an additional 3 hr. Then 300 ml 3 N HCl was added, and the mixture was heated under reflux for 5 hr. After cooling, the $CHCl_3$ layer was removed, the aqueous layer was brought to a pH of 6 with 20% NaOH, and the mixture extracted with $CHCl_3$. The organic layers were combined, dried and concentrated, and the residue distilled through a spinning band column, giving 23·6 g (58%) of VI, b.p. 65–66°/0·10 mm; λ_{max}^{EtOH} 294 mμ (ε 7210); IR spectrum, 1550–1650 cm^{-1} (broad). (Found: C, 73·09; H, 10·09. $C_{12}H_{20}O_2$ requires: C, 73·43; H, 10·27%).

4,8-*Dimethyl*-7-*ketodecanoic acid* (VII). 2-(2-Methylbutyryl)-4-methylcyclohexanone, 19·1 g (0·098 mol) was heated under reflux for 1·5 hr with 120 ml 5% NaOH. The mixture was washed with ether, and then the pH was adjusted to 1 with conc HCl. The soln was saturated with salt and extracted with ether. The ether extract was dried and concentrated, and the residue was distilled through a spinning band column giving 14·2 g (67%) of acid VII, b.p. 116–125°/0·01–0·15 mm; IR spectrum (neat), 3600–2400 cm^{-1}, 1715 cm^{-1}. (Found: C, 67·48; H, 10·13. $C_{12}H_{22}O_3$ requires: C, 67·25; H, 10·35%).

4,8-*Dimethyldecanoic acid* (VIII). A mixture of 30·3 g (0·142 mol) of VII, 70 g (1·4 mol) 99% hydrazine hydrate and 150 ml diethylene glycol was heated under reflux for 6 hr. Then the mixture was cooled, 30 g (0·45 mol) 85% KOH was added, and the reaction was heated at 190° for 12 hr. About two vols water was then added, and the pH was adjusted to 1 with conc HCl. The mixture was extracted with ether, and the ether extracts were dried, and concentrated. The residue was distilled through a spinning band column giving 21 g (75%) of 4,8-dimethyldecanoic acid, b.p. 99–100°/0·1 mm; IR spectrum (neat), 3600–2400 cm^{-1}, 1715 cm^{-1}; mass spectrum, major signals at *m/e* at 200, 171, 153, 143, 141, 111, 101, 85, 73 (base peak) and 60. (Found: C, 72·06; H, 11·95. $C_{12}H_{24}O_2$ requires: C, 71·95; H, 12·07%).

4,8-*Dimethyl*-1-*decanol.* 4,8-Dimethyldecanoic acid was reduced to 4,8-dimethyl-1-decanol with LAH using the procedures of Nystrom and Brown[34] and Micovic and Mihailovic.[35] The yield of distilled product was 87%, b.p. 72–73°/0·3 mm; IR spectrum, 3350 cm^{-1}, no CO absorption. (Found: C, 77·39; H, 14·00. $C_{12}H_{26}O$ requires: C, 77·35; H, 14·07%).

5,9-*Dimethylundecanoic acid.* A mixture of 8·1 g (0·043 mol) 4,8-dimethyl-1-decanol, 19 g (0·100 mol.) *p*-toluene sulfonyl chloride and 100 ml dry pyridine was allowed to stand at 0–5° for 18 hr. The mixture was then poured onto 600 ml crushed ice, and the suspension was extracted 3 times with ether. The ether soln was washed twice with cold 20% HCl, dried over $MgSO_4$, and concentrated, leaving a clear yellow oil which exhibited characteristic tosylate absorption bands in the IR at 1105 and 1130 cm^{-1}. There was no absorption characteristic of an alcohol.

This tosylate was added dropwise to a stirred soln of 3·0 g (0·061 mol) NaCN in 50 ml dry DMSO at 75°. The mixture was kept at 65–75° for 2 hr, at which time 3 vols water was added, and the mixture was extracted 3 times with ether. The ether extract was washed once with water, dried and concentrated. The residue was distilled giving 7·72 g (91%) 4,8-dimethyldecanenitrile, b.p. 73–75°/0·25 mm; IR spectrum (neat) 2260 cm^{-1}. (Found: C, 80·11; H, 12·80; N, 7·15. $C_{13}H_{25}N$ requires: C, 79·93; H, 12·90; N, 7·17%).

Hydrolysis was carried out by heating 7·2 g (0·036 mol) 4,8-dimethyldecanenitrile with 5·0 g (0·125 mol) NaOH in 25 ml ethylene glycol under reflux for 15 hr. The acid was isolated in the usual way. The yield of IX was 92%; b.p. 110–113°/0·3 mm; IR spectrum, 3600–2400 cm^{-1}, 1715 cm^{-1}; mass spectrum, major signals at *m/e* 214, 185, 178, 171, 115, 97, 85, 71, 69, 57 (base peak) and 43. (Found: C, 73·06; H, 12·22. $C_{13}H_{26}O_2$ requires: C, 72·84; H, 12·23%).

2-Palmityl-5-(5,9-dimethylundecanoyl)thiophene (X). To a stirred mixture of 5·3 g (0·023 mol) acid chloride of 5,9-dimethylundecanoic acid, prepared by heating the acid for 2 hr under reflux with a large excess $SOCl_2$, and 7·2 g (0·023 mol) 2-palmitylthiophene,[36] maintained at 0°, was added 2·6 g (0·01 mol) $SnCl_4$ over a period of 15 min. Stirring was continued at 0° for 45 min and at room temp for 1·5 hr. 1 N HCl (20 ml) was then added, and the mixture extracted with ether. The organic layers were combined and concentrated, giving 7·1 g (60%) of a brown oil which eventually solidified. A pure sample was obtained by evaporative distillation, b.p. 200°/0·01 mm; m.p., 33·5°; IR spectrum (neat), 1665 cm^{-1}. (Found: C, 78·56; H, 12·01; S, 6·28. $C_{33}H_{60}OS$ requires: C, 78·50; H, 11·98; S, 6·35%).

2-Palmityl-5-(1,5,9-trimethyl-1-undecenyl)thiophene (XI). To 0·02 mol MeMgI in ether, prepared in the usual way, was added 5·1 g (0·01 mol) of X in dry ether. The mixture was heated under reflux for 3 hr following completion of addition. Then the mixture was hydrolyzed by the dropwise addition of 50 ml 0·05 N HCl. The organic layer was separated, dried and concentrated, leaving 4·1 g (80%) of an oil which appeared to be very pure XI. A short path distillation afforded an analytical sample, b.p. 200°/0·01 mm. (Found: C, 81·20; H, 12·43; S, 6·37. $C_{34}H_{62}S$ requires: C, 81·03; H, 12·38; S, 6·32%).

3,7,11-Trimethylhentriacontane (Ia). Compound XI, 2·9 g (5·7 mmol), was heated under reflux for 13 hr with 30 g of Raney Ni in toluene. After removal of the catalyst by filtration, and the solvent by evaporation at reduced press, reduction was completed by hydrogenating with 5%Pt-C in isooctane at 50 p.s.i. of H_2. Catalyst was removed by filtration, the product was concentrated, and purified by passage through a column of silica gel impregnated with $AgNO_3$. An analytical sample of 3,7,11-trimethylhentriacontane was obtained by short path distillation (170°/0·02 mm). The product, a mixture of diastereomers, melted between 20° and 30°. (Found: C, 85·11; H, 14·87. $C_{34}H_{70}$ requires: C, 85·26; H, 14·74).

This synthetic material had a mass spectrum virtually identical to that of component 14 (Fig. 1), derived from *A. colombica*. The synthetic and natural materials could not be separated by GLC on 3% methyl silicone gum SE-30, 3% trifluoropropyl methyl silicone oil QF-1, 1% OV-1 methyl silicone gum or 3% methyl phenyl silicone oil OV-17 columns.

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