(Royal Prussian Academy of Science, Berlin, 1831), book 5, chap. 8, pp. 542, A6-10.
4. W. M. Rogoff, A. D. Beltz, J. O. Johnsen, F. W. Plapp, *J. Insect. Physiol.* **10**, 239 (1964).
5. M. S. Mayer and C. W. Thaggard, *ibid.* **12**, 891 (1966); M. S. Mayer and J. D. James, *ibid.* **17**, 833 (1971).
6. D. L. Silhacek, M. S. Mayer, D. A. Carlson, J. D. James, *ibid.*, in press.
7. D. L. Silhacek, D. A. Carlson, M. S. Mayer, J. D. James, *ibid.*, in press.
8. Silica gel G containing 25 percent silver nitrate (Uniplates from Analtech, Inc., Newark, Del.).
9. With a column of Adsorbosil-CABN, 100/140 mesh, 25 percent silver nitrate on silica gel (Applied Science Laboratories, State College, Pa.), paraffins, monoolefins, and polyolefins were eluted with 0, 1, and 10 percent ether in hexane, respectively.
10. F & M Model 810 instrument with a flame ionization detector was equipped with stainless steel columns; 5 percent DEGS on 60/80 Chromosorb G-DMCS (1.8 m by 4 mm i.d.); 3 percent OV-17 on 100/120 Gas Chrom Q (2 m by 4 mm i.d.); 5 percent SE-30 on 100/120 Varaport 30 (1.8 m by 4 mm i.d.).
11. Varian Model 90-P instrument, equipped with thermal conductivity detector and the 5 percent SE-30 column (*10*), was temperature programmed from 150° to 280°C.
12. E. Kovats, *Advan. Chromatogr.* **1**, 229 (1966).
13. M. Beroza and B. A. Bierl, *Anal. Chem.* **39**, 1311 (1967).
14. Samples of (*Z*)- and (*E*)-9-octadecene gave spots at R_F 0.70 and 0.90, respectively, on TLC plates (*8*) developed three times with hexane. The natural olefin gave a spot at 0.70.
15. M. Beroza and R. Sarmiento, *Anal. Chem.* **38**, 1042 (1966).
16. Finnigan Model 1015 mass spectrometer interfaced with a Gohlke glass separator to a Varian GC equipped with 3 percent OV-101 on 80/100 Gas Chrom Q (glass column, 2 m by 4 mm i.d.).
17. (*Z*)-9-Tricosene has been reported as one of the major cuticular hydrocarbons of several cockroach species [L. L. Jackson, *Lipids* **5**, 38 (1970)].
18. Spots at R_F 0.70 and 0.90, obtained as described (*14*), for the (*Z*) and (*E*) isomers, respectively, were eluted and quantified by GC.
19. Determined with a Varian XL 100 instrument. We thank K. Scott of the Department of Chemistry, University of Florida, Gainesville, for determining the spectrum.
20. Perkin-Elmer Model 237 instrument, liquid film on NaCl plates.
21. This and other authentic straight-chain hydrocarbons were obtained from Analabs, Inc., North Haven, Conn.
22. DEGS and SE-30 columns (*10*).
23. From a laboratory colony of house flies resistant to phosphate insecticides (Cradson-P).
24. Hydrolyzed milk protein, Sheffield Chemical Co., Union, N.J.

27 August 1971

Natural Occurrence of Fatty Acid Ethyl Esters

Laseter and Weete (*1*) have recently reported the presence of ethyl esters of long-chain fatty acids in extracts of *Rhizopus arrhizus* and their identification by combined gas chromatography–mass spectrometry. This report is interesting in that it extends the known occurrence of such esters to microorganisms but does not constitute their first identification as natural products since they have already been reported from mammalian (*2*) and insect (*3–6*) sources.

As with *Rhizopus*, Skořepa *et al.* (*2*) could attribute no physiological role to the three ethyl esters of long-chain fatty acids which they identified in extracts of ox pancreas. By contrast, specific roles have been suggested for ethyl esters in insects. Thus Bergström *et al.* (*3*) identified ethyl laurate as a component of the volatile territory-marking scent produced by the bumblebee *Bombus terrestris*, and I (*4*) suggested the same function for the series of ethyl esters, of which ethyl myristoleate was the major component, obtained from *B. lucorum*. Kullenberg *et al.* (*5*) have since distinguished a second race of *B. lucorum*, which employs a different series of ethyl esters and have identified these esters in the scents of two other *Bombus* species. As indicated in the original papers, these findings have additional significance as possibly the first examples of chemical characters supplementing and extending classifications based on classical insect taxonomy. Ikan *et al.* (*6*) have identified ethyl esters of long-chain fatty acids as the greater part of the "assembling scent" of the beetle *Trogoderma granarium*, which scent also acts as a repellent for *Tribolium castaneum*.

It may be conjectured that ethyl esters of this type, possessing advantages of volatility and of specificity as natural products, may be used quite widely in the insect world as compounds modifying behavior, that is, "pheromones" in the broadest sense. It is also likely that rather specific, possibly unusual, biosynthetic mechanisms are operating.

In all the above reports, extensive use has been made of modern analytical techniques, notably combined gas chromatography–mass spectrometry which has yielded unequivocal evidence of structure. Their use in reexamination of data obtained by older, less-refined methods and in other contexts should prove illuminating. It is, for instance, possible to confuse a fatty acid ethyl ester with the methyl ester of the corresponding acid containing one more carbon atom if some gas chromatographic methods are used alone. This may explain why ethyl esters have remained undetected in natural sources until recently.

The presence of ethyl esters of short-chain and other acids in flavor and odor volatiles is, of course, well documented [see for example (*7*)].

D. H. CALAM
National Institute for Medical Research, London, N.W. 7, 1AA, England

References

1. J. L. Laseter and J. D. Weete, *Science* **172**, 864 (1971).
2. J. Skorepa, P. Hrabák, P. Mareš, A. Linnarson, *Biochem. J.* **107**, 318 (1968).
3. G. Bergström *et al.*, *Ark. Kemi* **28**, 453 (1968).
4. D. H. Calam, *Nature* **221**, 856 (1969).
5. B. Kullenberg, G. Bergström, S. Ställberg-Stenhagen, *Acta Chem. Scand.* **24**, 1481 (1970).
6. R. Ikan, E. D. Bergmann, U. Yinon, A. Shulov, *Nature* **223**, 317 (1969).
7. H. E. Nursten and A. A. Williams, *Chem. Ind.* **1967**, 486 (1967).

10 June 1971

Our omission in referencing works by Calam and others stems from the fact (with two exceptions) that no notations of esters of any type were made in their titles, and, therefore, one surveying the literature might easily overlook such information. Two such examples concerning ethyl esters are worth noting at this time. Investigations by Light *et al.* (*1*) demonstrated that cell-free preparations of yeast extract were capable of synthesizing ethyl esters of long-chain fatty acids, while ethanol exogenously added to goat's milk resulted in the synthesis of esters of the same type [Patton (*2*)]. Calam has also related some interesting speculations concerning the functions of ethyl esters of long-chain fatty acids. However, the fungal growth-promoting properties found for the mono- and dienoic C_{18} fatty acid ethyl esters reported by Wardle and Schisler (*3*) and again by Holtz and Schisler (*4*) should not be overlooked. The limited and varied distribution known at this time and the attributed functions of long-chain fatty acid ethyl esters stimulates some interesting questions.

JOHN L. LASETER
Department of Biological Sciences, Louisiana State University, New Orleans 70122

JOHN D. WEETE
Lunar Science Institute, Houston, Texas 77058

References

1. R. J. Light, W. J. Lennarz, K. Block, *J. Biol. Chem.* **237**(6), 1793 (1965).
2. S. Patton and R. D. McCarthy, *Nature* **209**(5023) 616 (1966).
3. K. S. Wardle and L. C. Schisler, *Mycologia* **61**, 305 (1969).
4. R. B. Holtz and L. C. Schisler, *Lipids* **6**(3), 176 (1971).

4 August 1971