and to Dr. N. Danieli for the mass spectra.

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Sativene, Parent of the Toxin from *Helminthosporium sativum*

Sir:

We have previously reported on the isolation and constitution of helminthosporal (1),[1,2] the toxin responsible for widespread destruction and losses of cereal crops.[3] In Western Canada this has amounted to 3–13% of the wheat crop over the last 25 years.[4] The suggestion was made that helminthosporal, itself not a direct farnesyl pyrophosphate cyclization product, might be derived by oxidative cleavage of a carbon–carbon bond in a hypothetical precursor, sativene (2), with an as yet unencountered carbon skeleton. Evidence was provided from labeling experiments to justify this.[5]

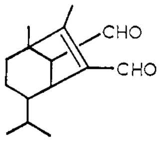
A search among the oxygenated compounds produced by the mold has not yet revealed the presence of any substance with an intact sativane skeleton, although more immediate precursors, such as prehelminthosporol, have been identified.[6] Attention was then given to the very small hydrocarbon fraction accompanying this oxygenated material.

Separation by gas–liquid chromatography gave a homogeneous substance in the yield of 0.5 mg./l. of culture fluid. This compound, $[\alpha]_D$ −186 ± 3°[7] (*Anal.* Found: C, 88.68; H, 11.67; mol. wt., 204[7]), showed absorption at 3060, 1660, and 885 cm.$^{-1}$ (CCl_4), compatible with an exocyclic methylene group. This interpretation was confirmed by the n.m.r. spectrum (τ 5.60 and 5.28; 2 H) which also showed signals at 9.13 (3 H, d, $J \sim 5$ c.p.s.), 9.10 (3 H, d, $J \sim 5$ c.p.s.), and 8.95 (3 H, s) These additional bands suggested the presence of a methyl attached to quaternary carbon, and of an isopropyl group. The derived diol (OsO_4), m.p. 63–64°, $[\alpha]_D$ −68° (*Anal.* Found: C, 74.88; H, 10.72; mol. wt. 238[7]), showed no absorption above 200 mμ in the ultraviolet, requiring the presence of but one double bond in the original hydrocarbon, and periodate cleavage of the diol gave material absorbing at 1740 cm.$^{-1}$.

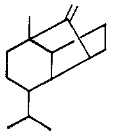
The sum of the available evidence was thus compatible, but merely compatible, with structure 2. Too little material remained for further, degradative, studies to be considered.

Recently the conversion of longifolene into the bromo ester 3 was reported, together with its ring contraction, under the influence of silver ion to isopropyl derivatives including 4.[8,9] We have prepared 3: on distillation from iron powder at 180° (0.2 mm.) 4 is obtained (45%). Hydrogenation gave the saturated methyl ester reduced with lithium aluminum hydride to the alcohol, $[\alpha]_D$ +77° (*Anal.* Found: C, 81.49; H, 11.28); α-naphthylurethan, m.p. 105–106° (*Anal.* Found: C, 80.38; H, 8.63; N, 4.26). The alcohol was acetylated and pyrolyzed in the vapor phase at 550°[11] to give (+)-sativene, $[\alpha]_D$ +191 ± 3°, identical in infrared spectrum (CCl_4) and n.m.r. spectrum with the natural hydrocarbon. It was converted into the diol, m.p. 63–64°, $[\alpha]_D$ +68°, enantiomeric with the diol from the naturally occurring hydrocarbon.

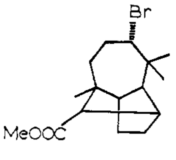
This partial synthesis[12] establishes unequivocally the nature of the natural hydrocarbon isolated from the culture fluid. Its production by the mold adds significant credibility to the biosynthetic scheme suggested for these substances,[5] though it does not require that the specific hydrocarbon itself be the progenitor of the toxins.[16]



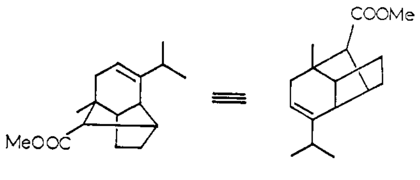
1



2



3



4

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(1) Terpenoids: Part XI.

(2) P. de Mayo, E. Y. Spencer, and R. W. White, *Can. J. Chem.*, **39**, 1608 (1961); **41**, 2996 (1963).

(3) R. A. Ludwig, *Can. J. Botany*, **35**, 291 (1957).

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(6) P. de Mayo, E. Y. Spencer, and R. E. Williams, *Can. J. Chem.*, **43**, 1357 (1965).

(7) Rotations were determined in chloroform. Molecular weights (mass spectrum) were determined by N. S. McIntyre and R. Ryhage.

(8) G. Ourisson, Simonsen Lecture, *Proc. Chem. Soc.*, 274 (1964).

(9) We wish to express our most sincere thanks to Professor Ourisson (Strasbourg) for making experimental data[10] available to us prior to publication, and for his generous scientific good will.

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(11) See, for example, D. H. R. Barton and P. de Mayo, *J. Chem. Soc.*, 887 (1953).

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(13) E. J. Corey, M. Ohno, R. B. Mitra, and P. A. Vatakencherry, *J. Am. Chem. Soc.*, **86**, 478 (1964).

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(15) E. J. Corey and S. Nozoe, *J. Am. Chem. Soc.*, **85**, 3527 (1963).

(16) The authors are glad to acknowledge support for this work under Grant No. EF-00419-01 from the National Institutes of Health.

(17) Holder of a National Research Council of Canada Scholarship.

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Organic Syntheses by Means of Noble Metal Compounds. XII.[1] Reaction of the Cyclooctadiene–Palladium Chloride Complex with Ethyl Malonate

Sir:

It is known that a nucleophilic attack of a hydroxide anion on the ethylene–palladium chloride complex gives acetaldehyde.[2] The reactions of other nucleo-

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