sistent with the hypothesis that the phosphorylation ability of this type of compound is not essential regarding fungitoxicity, but is important in mammalian toxicity. The findings that certain organic phosphoramidothionates, such as I and the phosphonothionates mentioned in the opening sentence of this report, show high fungitoxicity without being effective phosphorylating agents, and that they are less active when converted to their oxygen analogs (phosphoramidates), represent fundamentally new results in the area of pesticidal organophosphorus compounds.

Addendum: Compounds of structures I and IV were prepared by reacting the corresponding intermediates, *N,N*-dialkyl phenylphosphonamidochloridothionate and cyanuric chloride, with imidazole in the presence of a tertiary base as HCl-acceptor (*6, 10*). Compounds of structures II and III were prepared similarly by reacting the respective intermediates, trityl chloride and diethylthiocarbamoyl chloride, with imidazole (*11*). The fungicidal and toxicological test methods used have been reported (*2, 12*).

HENRY TOLKMITH
JAMES N. SEIBER
PAUL B. BUDDE
Edgar C. Britton Research Laboratory, Dow Chemical Company, Midland, Michigan
DORSEY R. MUSSELL
Bioproducts Department, Dow Chemical Company

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Isoprenoid Acids in Recent Sediments

Abstract. *Phytanic acid, pristanic acid, and 4,8,12-trimethyltridecanoic acid have been isolated from three recent marine sediments. The ratio of palmitic to pristanic acid is similar to that encountered in typical marine lipids. This suggests a biochemical origin of these sedimentary acids; phytol is their presumed biochemical precursor. Other isoprenoid acids between C_{11} and C_{22} which are common in ancient sediments have not been found. They are probably geochemical products formed slowly and at a greater depth.*

Biochemical and geochemical conversion products of phytol are among the most ubiquitous compounds in nature. Isoprenoid hydrocarbons occur in terrestrial (*1*) and marine (*2*) plants and animals. They are incorporated into recent sediments (*3*) and persist for geological time spans in sediments (*4*) and petroleum (*5*). Isoprenoid acids are common in zooplankton (*6*), in fishes (*7*), and in marine (*8*) and terrestrial (*9*) mammals. They occur in ancient sediments (*10*) and in petroleum (*11*) but—in contrast to straight-chain acids (*12*) and those with one side chain (*13*)—they have not previously been isolated from recent sediments.

To search for isoprenoid acids in those recent sediments from which we had previously isolated pristane (*3*), we obtained samples from the Wilkinson Basin, a depression in the shelf off Cape Cod, Massachusetts, and from Volden Fjord, Norway. These samples had been selected because of their deposition from waters rich in calanid copepods. A near-shore sample from Tarpaulin Cove, Massachusetts, was included in our study.

The sediments, preserved in the frozen state, were extracted first with methanol and then with benzene-methanol azeotrope. The residue was further digested for 24 hours at 30°C with anhydrous methanol-HCl. This extract was decanted, the residue was washed with methanol, and the washings were added to the extract. The extracts were concentrated either by partitioning between aqueous sodium chloride and chloroform or by distillation after addition of alkali; the residue was acidified and extracted with chloroform. The extracts were esterified with a mixture of methanol and boron trifluoride (*14*) and chromatographed on silica gel deactivated with 5 percent water. Pentane and mixtures of pentane and benzene served as eluents; the presence of esters in the eluates was established by gas chromatography. The chromatograms indicated the presence of many straight-chain, branched, saturated, and olefinic esters. Further concentration of the isoprenoid structures was necessary. Therefore, all ester fractions were combined and hydrogenated in isooctane with platinum oxide at 60°C. The straight-chain and most of the singly branched esters were then removed by urea clathration (*15*). Gas chromatography on unpolar (Apiezon L) and polar (FFAP) substrates (*16*) of the multibranched concentrates gave peaks with values for equivalent chain length (ECL) (*17*) agreeing with those of 4,8,12-trimethyltridecanoic, 2,6,10,14-tetramethylpentadecanoic (pristanic), and 3,7,11,15-tetramethylhexadecanoic (phytanic) acid methyl esters (Table 1). Results of gas chromatography on two different substrates, when used in conjunction with silica-gel chromatography and urea clathration, provide conclusive evidence for the presence of these esters. Isomeric isoprenoid esters whose

Table 1. Gas chromatographic equivalent chain lengths of isoprenoid methyl esters. Temperature, 2°C per minute; steel columns (3.6 m, inside diameter 1.4 mm) with 0.8 percent Apiezon L on Chromosorb G, acid-washed, silicone-treated; 1.5 m of 25 percent FFAP (*16*) on Chromosorb W, acid-washed, silicone-treated. This substrate diluted 1:3 with 100–140 mesh glass microbeads, silicone-treated. Average deviation of unknowns isolated from recent sediments from standards: 0.01 ECL unit; maximum deviation −0.03 (Apiezon L) and +0.04 ECL units (FFAP).

Methyl esters	Apiezon L	FFAP
4,8,12-Trimethyl-C_{13}	14.35	14.03
Pristanate	16.41	15.76
Phytanate	17.50	16.95

Table 2. Determination of isoprenoid and palmitic acid as methyl esters. Conditions as in Table 1. Standards: methyl palmitate and methyl pristanate. Wilkinson Basin, Gosnold Cruise No. 65; 42°22′N,69°29′W; depth approximately 225 m. Volden Fjord, Norway, Chain Cruise No. 13; 63°09.5′N,5°59.8′E; depth 659 m. Tarpaulin Cove, Massachusetts; 41°28′N,70°45′W; depth approximately 18 m. Values include any olefinic acids present.

Methyl esters	Concentration (ppm)		
	Wilkinson Basin	Volden Fjord	Tarpaulin Cove
4,8,12-Trimethyl-C_{13}	0.5	0.7	4
Pristanate	1.7	0.8	7
Phytanate	0.9	1.3	1.8
Palmitate	26	25	150

Table 3. Ratios of palmitic to pristanic acid (I) and pristanic acid to pristane (II).

Source of lipid	I	II (*3*)
Wilkinson Basin	15	130
Volden Fjord	30	47
Tarpaulin Cove	21	
Tuna (*6*)	32	13
Calanus spec.	50	0.5–0.2

methyl groups are displaced by one carbon atom along the chain have ECL values outside the range measured here (*10*).

Olefinic isoprenoid acids, for example, phytenic acid (*9*), are minor constituents of some lipids and could conceivably be present in the sediments. A different isolation procedure, excluding hydrogenation, was chosen to establish the presence in the extracts of the saturated acids. The esters were fractionated on an active silica gel, containing 2 percent water, at a high ratio of adsorbent to sample. Pentane and pentane of low benzene content served as eluents. The C_{16} isoprenoid ester appeared just ahead of the normal C_{14} and C_{15} esters; pristanic and phytanic esters appeared together with the C_{16} through C_{20} straight-chain esters and well ahead of the monounsaturated straight-chain esters. This establishes the presence in the recent sediments of the saturated C_{16}, C_{19}, and C_{20} isoprenoid acids. The great complexity of the olefinic fractions that were eluted later did not permit the identification of possible traces of olefinic isoprenoid esters.

For quantitative determinations, separate samples were processed; to minimize losses, urea clathration was omitted. Hydrogenation was necessary to reduce the complexity of the chromatograms. The values of Table 2 therefore include the concentration of any unsaturated isoprenoid esters that might be present in the sediments.

Terpenoid acids from C_{11} to C_{22} occur in ancient sediments (*15*). Acids other than those reported here were not detected in the recent sediments; if present, they amounted to less than 10 percent of the trimethyltridecanoic acid.

The ratio of palmitic to pristanic acid is similar to that encountered in typical marine lipids (Table 3); this suggests that the isoprenoid acids of recent sediments are directly derived from living organisms. Compared to pristanic acid, pristane is much more abundant in the lipids of *Calanus* than in the sediments. However, the high pristane content of *Calanus* lipids is unusual; it exceeds that of most other marine fats and oils by about two orders of magnitude. The ratio of pristanic acid to pristane in the sediments is much closer to that in the tuna lipids than to those in calanid copepods. This implies that the direct contribution to the sedimentary lipids by *Calanus* is minor, even in regions rich in these copepods.

In these sediments, the absence of the wide range of isoprenoid acids common to ancient sediments suggests that their formation is a slow postdepositional process. This is analogous to our earlier finding that the biochemically derived pristane is present in recent marine sediments but that the phytane of ancient sediments is formed slowly and presumably at depth. These results extend our knowledge of the biogeochemistry of phytol and of the dissemination of its degradation products through the biosphere and geosphere.

MAX BLUMER
W. J. COOPER
Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543

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Synovial Cell Synthesis of a Substance Immunologically Like Cartilage Proteinpolysaccharide

Abstract. *Fluids from joints contain a substance that reacts immunologically like one of two known antigenic components of articular cartilage proteinpolysaccharide. This newly recognized substance occurs in the lining cells of synovial membranes as shown by indirect immunofluorescence. The localization of this substance in tissue culture cells derived from synovial membranes and its identification in the culture medium supports the suggestion that it is synthesized by lining cells. Rheumatoid synovial cells contain less of this substance.*

The matrix of articular cartilage consists largely of collagen and proteinpolysaccharides. These substances are synthesized by the chondrocytes—cells which share a common mesenchymal origin with fibroblasts and surface (lining) cells of the synovial membrane (*1*). Synovial membrane lining cells appear to secrete (*2, 3*) hyaluronateprotein, the major proteinpolysaccharide of synovial fluid. Alterations in these cells derived from mesenchyme and in their secretory products may be significant in the pathogenesis of rheumatoid arthritis. We now describe the apparent synthesis by synovial cells of a substance immunologically identical to a component of articular cartilage matrix, and we note a diminished synthesis of this substance by rheumatoid cells.

The proteinpolysaccharides of cartilage have been extracted, purified (*4*), and shown to be antigenic (*5*). Moreover, they possess at least two antigenic components (*6*). One is present in the proteinpolysaccharides from bovine, porcine, and human cartilage and has been called the common component; the other appears to be unique to each species and has been termed the species-specific component. Antiserums were prepared by immunization of rabbits with purified cartilage proteinpolysaccharides from each species. Species specificity was demonstrated by reactivity between antigen and antiserum that