Keports

Pristane in Zooplankton

Abstract. The hydrocarbon pristane (2,6,10,14-tetramethylpentadecane) occurs in unusually high concentrations (1 to 3 percent of the body fat) in the three copepods Calanus finmarchicus, C. glacialis, and C. hyperboreus. These planktonic crustaceans appear to be the primary source of the pristane in liver oils of sharks and whales.

In a search for the biogenic sources of hydrocarbons in sea water we have analyzed some bulk extracts of zooplankton from the Gulf of Maine and the western North Atlantic. A very large part of the saturated hydrocarbon fraction consists of a single hydrocarbon, which cochromatographs with normal heptadecane on nonpolar gaschromatographic substrates.

Samples for further analysis were prepared by trapping the hydrocarbon as it was eluted from the chromatographic column or by distilling the saturated fraction of the extract in a micromolecular still (1). A molecular weight of 268 was determined by mass

Table	1. F	ristai	ne in	Cald	anus	species	. Coll	ect-
ing lo	ocati	ons:	42°1	4'N,	64°:	30'W,	and	41°
39'N,	65°	07'W.	Col	lectin	ng da	te: At	tlantis	II,
cruise	2, 9) to	17 A	pril	1963.			

Pristane per	Percentage pristane			
individual (µg)	Dry wt.	Total lipids		
Calanus	finmarchicus V			
2.0	0.77	1.5		
C. finma	rchicus, female			
1.2	0.46	1.7		
C . §	glacialis V			
2.3	0.47	0.86		
C. hy	perboreus V			
5.9	0.84	1.6		
C. hyper	<i>boreus</i> , female			
12.2	0.90	2.9		

spectrometry and, together with the near infrared spectrum and the chromatographic behavior, it suggested a highly branched isomer of nonadecane C10H40. The extremely low melting point ---there was no crystallization even at dry-ice temperature-suggested that the hydrocarbon was pristane (2,6,10,14tetramethylpentadecane). This was confirmed by the agreement of the massand infrared-spectra with published data (2, 3) and with spectra obtained on commercial pristane.

In our zooplankton samples pristane occurs mainly in three cogeneric species of copepods, Calanus finmarchicus, C. glacialis, and C. hyperboreus (Table 1), in which it constitutes an appreciable fraction of the total body fat. Other species in the same zooplankton samples (for example, Metridia lucens, Rhincalanus nasutus, Euchirella rostrata, Pleuromamma robusta, Paraeuchaeta norvegica, Nematoscelis megalops, and Meganyctiphanes norvegica) contain, relative to their dry weight, much less pristane, or none at all.

Pristane is a minor constituent of the liver oil of both plankton- and nekton-feeding sharks and whales (4) from which it is commercially isolated (5). Recently it has been found at concentrations up to 0.5 percent in various crude oils (2, 6).

The pristane of sharks and whales has been thought to be already formed in zooplankton or intermediate food animals (7). Our findings confirm this and suggest that the copepods of the genus Calanus are among the major producers of pristane. The structural similarity between pristane and phytol suggests that the hydrocarbon may be derived in Calanus from the chlorophyll of its phytoplankton diet. The pristane of crude petroleum may also be directly derived from zooplankton, though the possible conversion of phytol to pristane in sediments by biotic or abiotic processes should not be ruled out.

A fraction of the pristane formed by the copepods may find its way into the sea water. During the spring bloom, Calanus finmarchicus in Cape Cod Bay (8) reaches a density of up to 2000 individuals per cubic meter. A small part of their total pristane, when dissolved in the water, could be detected by sensitive analytical techniques. As a relatively refractory compound, the pristane might thus tag the water mass in which the copepods live (9).

> MAX BLUMER MICHAEL M. MULLIN DAVID W. THOMAS

Woods Hole Oceanographic Institution, Woods Hole, Massachusetts

References and Notes

- M. Blumer, Anal. Chem. 34, 704 (1962).
 J. G. Bendoraitis, B. L. Brown, L. S. Hepner, Anal. Chem. 34, 49 (1962).
 J. Plivia and N. A. Sörensen, Acta Chim. Scand. 4, 846 (1950).
 N. A. Sörensen and J. Mehlum, Acta Chim. Scand. 2, 140 (1948); Y. Toyama, Chem. Umschau 30, 181 (1923); T. Tsuchiya and R. Kaneko, J. Chem. Soc. Japan 54, 592 (1951).
 M. L. Rosenthal, Robeco Chemicals, New York, private communication.
- W. L. Rostenhar, Robert Chinese, New York, private communication.
 R. A. Dean and E. V. Whitehead, *Tetra-hedron Letters*, 768 (1961).
 J. S. Sörensen and N. A. Sörensen, *Acta Chim. Scand.* 3, 939 (1949). 6. R. 7. J

- Chim. Scand. 3, 939 (1949).
 8. M. Anraku, unpublished manuscript, Woods Hole Oceanographic Institution, 1962.
 9. Supported by a research contract with the United States Office of Naval Research [con-tract Nonr-2196 (00)] and a grant from the National Science Foundation (Nr. 23472). Contribution No. 1384 of the Woods Hole Oceanographic Institution Oceanographic Institution.

9 May 1963

Krypton Fluoride: Preparation by the Matrix Isolation Technique

Attempts to prepare compounds of krypton and fluorine through pyrolysis (1) and photolysis (2) have been unsuccessful. Grosse et al. were able to prepare KrF4 in a high-voltage discharge through a krypton-fluorine gas mixture at -78° C. We now report the preparation of KrF2 by the photolysis of fluorine suspended in a solid mixture of argon and krypton at 20°K. This experimental method is called the matrix isolation technique (3).

In a typical experiment, a gaseous mixture of fluorine, krypton, and argon at mole ratios F2:Kr:Ar of 1:70:220 was deposited slowly upon a CsI window held at 20°K. After an infrared spectrum had been recorded (with a Beckman IR-7 spectrometer), the sample was irradiated at 20°K with the focused light from an AH-4 mediumpressure mercury lamp (without its glass envelope). After photolysis for a period of 3 hours, the infrared spectrum of the sample then showed a relatively sharp (half-width about 3.5 cm⁻¹) absorption at 580 cm⁻¹ (optical density 0.19) and a second band at 236 cm^{-1} (optical density 0.04).

Supporting experiments show that these absorptions can be assigned to krypton difluoride. After 8 hours of photolysis of a fluorine-argon sample (without krypton), no absorptions can be detected. Analogous experiments with mixtures of fluorine, xenon, and argon produce xenon difluoride very readily. The spectrum of xenon tetrafluoride is also detectable in the spectrum of the irradiated matrix samples, but in amounts small compared with XeF₂.

The infrared absorptions of KrF2 can be assigned as the asymmetric stretching and the bending modes of a linear, symmetric molecule. They imply force constants (4) $k_r - k_{rr} = 2.59$ mdy/Å and $k_{\delta}/l^2 = 0.21$ mdy/Å. These force constants are very close to those of XeF2. This is a surprising result since it is implied that the bond energies in KrF2 cannot be greatly different from those of XeF₂.

This work shows that the matrix technique is useful for preparing compounds of inert gases, and it may have unique value for those that are least stable. It is significant, perhaps, that no evidence could be obtained for an argon-fluorine compound by this method (5).

J. J. TURNER* GEORGE C. PIMENTEL Department of Chemistry,

University of California, Berkeley

References and Notes

- A. V. Grosse, A. D. Kirshenbaum, A. G. Streng, L. V. Streng, *Science* 139, 1047 (1963).
 J. L. Weeks, C. L. Chernick, M. S. Matheson, *J. Am. Chem. Soc.* 84, 4612 (1962).
 G. C. Bingerich, *Science herbacking data* 21, 24
- C. Pimentel, Spectrochim. Acta 21, 94 3. G. 1958).
- 4. The force constant notation is that used by Agron et al. in their treatment of XeF2; see P. A. Agron, G. M. Begun, H. A. Levy, A. A. Mason, C. G. Jones, D. F. Smith, Sci-ence 139, 842 (1963).
- 5. This work was presented at the Conference on Noble Gas Compounds, Argonne National Laboratory, 22-23 April 1963, and a more detailed discussion will appear in the Pro-ceedings of the Conference, to be published by the University of Chicago Press. Harkness fellow of the Commonwealth Fund.

14 May 1963

31 MAY 1963

Marsilea vestita: Conversion of the Water Form to the Land Form by Darkness and by Far-Red Light

Abstract. A period in darkness or in continuous far-red light can cause the ferns of the species Marsilea vestita Hook. and Grev. to develop as a land form in a medium which normally allows only the water form to develop. Far-red light is more effective than darkness in causing this conversion. The difference in the quality of light reaching plants growing in water or on land may cause this conversion to occur in nature.

The fern Marsilea, like many other aquatic vascular plants, can exist as a land form or as a water form (Fig. 1A). The factors that determine which form will develop in nature have not yet been resolved. According to Allsopp the osmotic pressure of the cells of the plant is an important factor (1). Under conditions of low osmotic concentration-for example, in nutrient solutions with low glucose concentrations-the water form predominates; when the osmotic concentration of the solution is raised by addition of glucose, a land form develops. Bauer (2) obtained land forms of Ranunculus aquatilis under water by darkening terminal buds with black vaseline and then immersing the buds but not the leaves of the plants. If the leaves were also immersed the production of a land form depended on other factors. This variation in his results was most likely due to nutritional differences. If Marsilea are grown in exact nutrient media, nutritional differences can be ruled out, and the true effect of light on the form of the plant can be evaluated.

In order to study the effect of light on Marsilea, aseptic sporelings of M. vestita Hook. and Grev. were obtained by the method of Allsopp (3). These sporelings were allowed to develop a first leaf and root under weak fluorescent light. Then they were transferred to tubes containing 20 ml of White's nutrient (4) fortified with 5 percent sucrose. Plants kept in this medium under continuous fluorescent lighting (47 days) remained in the water form for the duration of the experiments.

The light energy at the level of the plants was 11,200 erg/cm² sec (5), and the tubes were slanted to expose the plants to the light. Plants placed in darkness or under far-red light became etiolated (6). These etiolated plants had certain characteristics of the land form —a large number of stomatal initials appeared on both sides of the leaf lamina and the petioles were thin and elongated, but they differed from both the land and the water form in that the leaf lamina did not expand and the rhizome was ageotropic. Unless



Fig. 1. (A) The land form of Marsilea vestita (left) has a short rhizome and long petioles. The water form (right) has a long rhizome and short petioles. (B) The etiolated plant (right of arrow) developed into a land form (left of arrow). All plants about 5/8 life size.

