tially 100 °C and increased at a rate of 6 °C min^{-1} to 270 °C. Ten single Dufour glands (6 with sting attached, 4 without) were analyzed and the absolute quantity of each component was determined by using a solution of pentadecane in hexane as an external standard.

Two single Dufour glands and a sample of seven glands were analyzed by GC-MS, on a Hewlett Packard 5890 Gas Chromatograph and 5970B Mass Selective Detector with HP59970C ChemStation. A fused silica capillary column (12 m × 0.2 mm) coated with HP-1 (cross-linked methylsilicone gum ≅ OV – 1) of 0.33-µm film thickness was used. The carrier gas was helium at 10 psi column head pressure (≅ 1 ml min^{-1} flow rate). The samples were introduced by the solid injection method [10] described above. The oven temperature was initially 60 °C and increased at a rate of 4 °C min^{-1} to 250 °C. The mass selective detector was set to monitor m/z 35–350 in the scan mode (≅ 1.5 scan s^{-1}) under 'Autotune' conditions using 70-eV ionization.

Acknowledgments. We thank Dr R. W. Taylor for his help in collecting the ants, Professor W. Francke for helpful discussion on the identification of squalene, the Belgian National Fund for Scientific Research for a travel grant to Australia for J. P. J. B., the British Council for a travel award to J. P. J. B. to visit Keele, the Royal Society for a grant to EDM for GC equipment and the SERC for a grant to EDM for the purchase of the linked GC-MS, and for a research studentship to B. D. J.

* Please address all correspondence to E.D.M., Dept of Chemistry, University of Keele, Staffordshire ST5 5BG, England.

1 Clark, J., Mem. nat. Mus. Vict. *8* (1934) 5.
2 Brown, W. L., and Wilson, E. O., West Aust. Nat. *7* (1959) 25.
3 Taylor, R. W., Science *201* (1978) 979.
4 Clark, J., The Formicidae of Australia, I. Subfamily Myrmeciinae, p. 18, CSIRO, Melbourne 1951.
5 Hölldobler, B., and Taylor, R. W., Insectes Soc. *30* (1983) 384.
6 Ward, P. S., and Taylor, R. W., J. Aust. ent. Soc. *20* (1981) 177.
7 Kugler, C., J. Aust. ent. Soc. *19* (1980) 263.
8 Billen, J. P. J., in preparation.
9 Attygalle, A. B., and Morgan, E. D., Chem. Soc. Revs *13* (1984) 245.
10 Morgan, E. D., and Wadhams, L. J., J. Chromatogr. Sci. *10* (1972) 528.
11 Anet, E. F. L. J., Aust. J. Chem. *23* (1970) 2101.
12 Burger, B. V., le Roux, M., Spies, H. S. C., Truter, V., and Bigalke, R. C., Z. Naturforsch. *36C* (1981) 340–343.
13 Burger, B. V., personal communication.
14 Attygalle, A. B., Vostrowsky, O., Bestmann, H. J., and Morgan, E. D., Insect Biochem. *17* (1987) 219.
15 Cavill, G. W. K., and Williams, P. J., J. Insect Physiol. *13* (1967) 1097.
16 Blum, M. S., and Hermann, H. R., in: Arthropod Venoms, chapt. 25, p. 801, Ed. S. Bettini. Springer-Verlag, Berlin 1978.
17 Vander Meer, R. V., in: Fire Ants and Leaf-Cutting Ants, p. 316. Eds. C. S. Lofgren and R. K. Vander Meer. Westview Press, Boulder and London 1986.

0014-4754/88/080715-05$1.50 + 0.20/0

Marine eicosanoids: Occurrence of 8-(R)-HETE in the starfish *Patiria miniata*

M. V. D'Auria, L. Minale, R. Riccio and E. Uriarte [1]

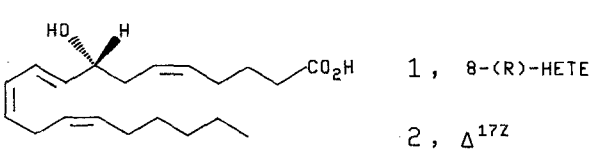
Dipartimento di Chimica delle Sostanze Naturali, Università di Napoli, Via L. Rodinò, 22, I-80138 Napoli (Italy)
Received 28 March 1988; accepted 2 May 1988

Summary. The first isolation of 8-(R)-hydroxy-5Z, 9E, 11Z, 14Z-eicosatetraenoic acid [8-(R)-HETE] from a marine source, the pacific starfish *Patiria miniata,* is reported. 8-(R)-HETE occurs together with 8-(R)-hydroxy-5Z, 9E, 11Z, 14Z, 17Z-eicosapentaenoic acid.
Key words. Starfish; 8-(R)-HETE; arachidonic acid metabolism; marine prostanoids biosynthesis.

Marine prostanoids, first discovered in a gorgonian [2], have since been isolated from octocorals [3–5] and from red algae [6]. A feature of the octocoral-derived clavulones [3], claviridenones [4] and punaglandins [5] and the algal metabolite, hybridalactone [6] is C-12 oxygenation. This led Corey [7] to suggest a distinctive biosynthetic pathway for these marine eicosanoids. More recently, biosynthetic experiments with two different species of coral, *Clavularia viridis* and *Pseudoplexaura porosa,* have shown the intermediacy of 8-(R)-HPETE [i.e., 8-(R)-hydroperoxy-5,11,14(Z), 9 (E)-eicosatetraenoic acid] in the conversion of arachidonic acid to pre-clavulone [8, 9], from which clavulones and possibly other prostanoids as well can arise by a series of hydroxylations, esterifications etc. These results led Corey and Matsuda [10] to propose a new biosynthetic pathway for marine prostanoids through the 2-oxidopentadienyl cation, totally different from the biosynthetic path to mammalian prostanoids. Bundy et al. [11] discovered an arachidonic acid C-8 lipoxygenase in the gorgonian coral *Pseudoplexaura porosa,* capable of converting exogenous arachidonic acid into 8-(R)-HPETE, and this gives further support to the importance of the 8-oxygenation pathway in the biosynthesis of marine prostanoids. The corresponding alcohol, 8-HETE, has been previously obtained by a variety of procedures: enzymatically [12], after in vivo stimulation by a tumor promoter [13], chemically via regio-random oxidation [14] and via total chemical synthesis [15], but has not yet been identified in marine organism extracts.

In this paper we report the isolation of 8-(R)-HETE (**1**) along with its 17,18-didehydro derivative (**2**) from the starfish *Patiria miniata.* The recent discovery that 8-(R)-HETE triggers oocyte maturation in starfish [16] provides still another reason for interest in this result.

The compounds **1** and **2** were purified from the aqueous extracts of the animals (3.5 kg fresh wt), collected from the Gulf of California, by the following successive chromatographic steps: recovery of the polar material on a column of Amberlite XAD-2, chromatography of methanol eluates on a column of Sephadex LH-60 (eluent: methanol-water, 2:1) to separate the steroidal glycosides from the eicosanoids, which were eluted as the last moving compounds, chromatography on silica gel (eluent: chloroform-methanol, 98:2) and finally HPLC (C_{18} µ-Bondapak, 75% aq. methanol) to obtain 8-(R)-HETE (0.5 mg) and **2** (1 mg).



250 MHz ^{1}H-NMR data for 8-(R)-HETE (**1**) and (**2**)

H at C	1	2
2	2.28 t (6)	2.28 t (6)
3	1.69 qui (6)	1.69 qui (6)
4	2.12 m	2.12 m
5, 6	5.40–5.49	5.40–5.49
7	2.32 t (6)	2.32 t (6)
8	4.16 q (6)	4.16 q (6)
9	5.70 dd (15,6)	5.70 dd (15,6)
10	6.57 dd (15,10)	6.58 dd (15,10)
11	6.00 dd (10,10)	6.01 dd (10,10)
12	5.40 m	5.40 m
13	2.96 t (6)	3.00 t (6)
14, 15	5.40–5.49	5.40–5.49
16	2.12 m	2.86 t (6)
17	1.35 m	5.40–5.49
18	1.35 m	5.40–5.49
19	1.35 m	2.12 m
20	0.94 t (6)	1.00 t (6)

Measured in CD_3OD; chemical shifts in ppm; coupling constants in Hertz enclosed in parentheses; d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet.

The EI mass spectrum of the 8-HETE methyl ester (diazomethane esterification) gave a small peak at m/z 316 for M^+-H_2O and the base peak at m/z 193 due to the cleavage of C-7/C-8 bond, shifted after trimethylsilylation to m/z 265, diagnostic for 8-HETE structure. Smallest peaks at m/z 171 (methyl ester) and 243 (silylated methyl ester) corresponding to the alternative cleavage of C-8/C-9 bond were also observed. In the spectra of silylated methyl ester of **2** the base peak was observed at m/z 263, indicating the location of an extra double bond on this fragment. The peak due to the cleavage of C-8/C-9 was observed at m/z 243 unshifted relative to the silylated methyl ester of **1**. The UV maximum at 234 (ε = 26 000) nm for both **1** and **2** indicated the presence of a *cis-trans*-conjugated-diene. ^{1}H-NMR double resonance experiments showed that the *trans* double bond was adjacent to the hydroxyl-bearing carbon and also allowed all signals to be assigned (table). Thus the structures **1** and **2** were established. We also note that the spectrum of compound **1** was superimposable on that reported for 8-HETE [11, 13].
The configuration at C-8 in **1** and **2** was determined by the exciton-split c.d. curve of their *p*-bromobenzoates [c.d. in methanol: 227/246, $\Delta\varepsilon$ + 1.2/− 1.6, A = + 2.8 for both **1** and **2**]. We have assumed that the circular dichroic exciton chirality method for determining configuration of acyclic allylic alcohols [17] is extendable to conjugated diene acyclic allylic alcohols. Namely, a predominance of the rotamer with the carbinyl hydrogen and double bond eclipsed should give rise to a negative c.d. when the configuration is R and accordingly a positive c.d. when the configuration is S.

Acknowledgment. Work supported by C.N.R. (ROME) 'Contributo No. 86.01624.03' and Ministero della Pubblica Istruzione (MPI). We are most grateful to Professor William Fenical, Scripps Institution of Oceanography, La Jolla, California, for his invaluable help in collecting and identifying the organism. E.U. thanks 'Xunta de Galicia' for a financial grant. Mass spectral data were provided by 'Servizio di Spettrometria di Massa del C.N.R. e dell'Università di Napoli'. The assistance of Dr A. Milone is particularly acknowledged.

1 On leave from the Departamento de Quimica Organica, Universidad, Santiago de Compostela, Spain.
2 Weinheimer, A. J., and Spraggins, R. L., Tetrahedron *1969*, 5785.
3 Kikuchi, M., Tsukitani, Y., Iguchi, K., and Yamada, Y., Tetrahedron Lett. *23* (1982) 517.
4 Kobayashi, M., Yasuzawa, T., Yoshihara, M., Akutsu, M., Kyogoku, Y., and Kitagawa, I., Tetrahedron Lett. *23* (1982) 533.
5 Baker, B. J., Okunda, R. K., Yu, P. T. K., and Scheuer, P. J., J. Am. chem. Soc. *107* (1985) 2976.
6 Higgins, M. D., and Mulheirn, L. J., Tetrahedron *37* (1981) 4259.
7 Corey, E. J., Experientia *39* (1983) 1084.
8 Corey, E. J., Lansbury, P. T., and Yamada, Y., Tetrahedron Lett. *26* (1985) 4171.
9 Corey, E. J., D'Alarcao, M., Matsuda, S. P. T., and Lansbury, P. T. Jr, J. Am. chem. Soc. *109* (1987) 289.
10 Corey, E. J., and Matsuda, S. P. T., Tetrahedron Lett. *28* (1987) 4247.
11 Bundy, G. L., Nidy, E. G., Epps, D. E., Mizsak, S. A., and Wnuk, R. J., J. biol. Chem. *261* (1986) 747.
12 Goetzl, E. J., and Sun, F. F., J. exp. Med. *150* (1979) 406; Falck, J. R., Siddhanta, A. K., Estabrook, R. W., Capodevila, J., and Mioskowski, C., Tetrahedron Lett. *25* (1984) 1457.
13 Gschwendt, M., Furstenberger, G., Kittstein, W., Besemfelder, E., Hull, W. E., Hagedorn, M., Opferkuch, H. J., and Marks, F., Carcinogenesis *7* (1986) 449.
14 Boeynaems, J. M., Brash, A. R., Oates, J. A., and Hubbard, W. C., Analyt. Biochem. *104* (1980) 259; Porter, N. A., Wolf, R. A., Yarbro, E. M., and Weenen, H., Biochem. biophys. Res. Commun. *89* (1979) 1058; Porter, N. A., Logan, J., and Kontoyiannidou, V., J. org. Chem. *44* (1979) 3177; Teraong, J., and Matsushita, S., Agric. biol. Chem. *45* (1981) 587.
15 Adams, J., and Rokach, J., Tetrahedron Lett. *25* (1984) 35.
16 Meijer, L., Maclouf, J., and Bryant, R. W., Prostaglandins, Leukotrienes Medicine *23* (1986) 179.
17 Gonnella, N. C., Nakanishi, K., Martin, V. S., and Sharpless, K. B., J. Am. chem. Soc. *104* (1982) 3772.

0014-4754/88/080719-02$1.50 + 0.20/0

Communication and synchronized molting in a colonial araneid spider, *Eriophora bistriata*

H. G. Fowler and N. Gobbi

Departamento de Ecologia e Centro para o Estudo de Insetos Sociais, Instituto de Biociências, UNESP, 13.500 Rio Claro, São Paulo (Brazil)
Received 6 October 1987; accepted 20 April 1988

Summary. The colonial orb-weaving spider, *Eriophora bistriata*, coordinates molting cycles through communication. Colonies with differing molting cycles synchronize when combined. Intercycle intervals depend upon food availability. The possible coordination of this synchrony by chemical communication among spiders is discussed.
Key words. Spider; molting; coloniality; Araneidae; synchronization.

In the majority of arthropods, molting is commonly cued by external stimuli [1]. In general, synchrony in molting is achieved only during one molt, for example when the induction of diapause for a specific instar is cued by some phenological cue [2]. In the colonial orb-weaving spider, *Eriophora bistriata*, the instar composition of any colony is essentially