

Review

Demospongiac Acids Revisited

Jean-Michel Kornprobst * and Gilles Barnathan

Groupe Mer, Molécules, Santé MMS/EA 2160, Equipe 7: Lipides marins à activité biologique, Pôle Mer et Littoral, Faculté de Pharmacie, Université de Nantes, France;

E-Mail: gilles.barnathan@univ-nantes.fr

* Author to whom correspondence should be addressed; E-Mail: jean-michel.kornprobst@univ-nantes.fr; Tel.: +33 2 51 12 56 89; Fax: +33 2 51 12 56 79.

Received: 7 September 2010; in revised form: 27 September 2010 / Accepted: 30 September 2010 / Published: 8 October 2010

Abstract: The well-known fatty acids with a $\Delta 5,9$ unsaturation system were designated for a long period as demospongiac acids, taking into account that they originally occurred in marine *Demospongia* sponges. However, such acids have also been observed in various marine sources with a large range of chain-lengths (C_{16} – C_{32}) and from some terrestrial plants with short acyl chains (C_{18} – C_{19}). Finally, the $\Delta 5,9$ fatty acids appear to be a particular type of non-methylene-interrupted fatty acids (NMA FAs). This article reviews the occurrence of these particular fatty acids in marine and terrestrial organisms and shows the biosynthetic connections between $\Delta 5,9$ fatty acids and other NMI FAs.

Keywords: demospongiac acids; marine lipids; sponges; marine invertebrates; non-methylene interrupted fatty acids

1. Introduction

The well-known notion of demospongiac acid appeared for the first time in 1976 in a historical paper from Litchfield and Morales [1], but at that time only as «demospongiae fatty acids». In another paper published in 1980 [2], Litchfield *et al.* used the term «demospongiac fatty acids» probably for the first time. Since then and up until now [3–5], this term has widely been used. However, about 35 years after Litchfield's work on sponge lipids, the notion of demospongiac acid seems to no longer have significance, mainly due to their controversial definition and to their wide distribution among marine invertebrates and some terrestrial plants. At the time, it seemed to be of interest to precisely identify

the function of demospongiic acids, in consideration of their biological activities as topoisomerase inhibitors or against cancer cells as recently reviewed [6], whereas the biological interests of terrestrial short-chain $\Delta 5,9$ fatty acids (FAs) had already been demonstrated [7,8].

2. What Exactly Is a Demospongiic Acid?

The definition of a demospongiic acid has never been very clear [1,2]. In their first papers, Litchfield *et al.* only mentioned very long-chain C_{24} – C_{30} or C_{24} – C_{34} acids with the unusual 5,9 unsaturation pattern, but at that time, only fatty acids with an even number of carbons had been found [1,9]. In the 1980s, a lot of work was published on sponge FAs, and it became apparent that “demospongiic acids” also contained all odd FAs from C_{23} – C_{31} [10]. Within this field of research, a consensus was quickly established that agreed that demospongiic acids were very long-chain fatty acids, mainly C_{24} – C_{30} , with the atypical 5,9-diunsaturation system, independent of the total number of double bonds. Some years later—and due to many papers being devoted to FAs from sponges—it appeared that:

- (i) the distinction between long-chain fatty acids (LCFAs, C_{20} – C_{22} ?) and very long-chain FAs (VLCFAs, $\geq C_{23}$?) is not clear and often depends on the authors’ interpretation [10–17].
- (ii) the presence of the ever-mentioned 5,9-diunsaturation pattern cannot be considered as characteristic of “demospongiic acids” due to the elongation process during their biosynthetic pathways, and diunsaturations such as 5,9-, 7,11-, 9,13-, 11,15-, 17,21-, 19,23-, 21,25- and 23,27- can be considered as being similar [18], but other dienoic patterns with short chains such as 6,11-18:2 and 6,11-20:2 have also been considered as “demospongiic” acids [19]. Furthermore, several “demospongiic acids” display *E* and *Z* configurations for $\Delta 5$ and $\Delta 9$ double bonds [20].

Currently, the best definition for a demospongiic acid would be that of Christie [18], stating “*bis-methylene-interrupted cis-double bonds, ranging in chain-length from C_{16} to C_{34} with a cis,cis-dienoic system, either with the double bonds in position 5 and 9, or derived from 5,9-16:2 by chain elongation*”.

At present, the question is whether such acids are not at all specific to demosponges, but have been found in other groups of sponges, especially among hexactinellida, in different phyla of marine invertebrates and in several species of terrestrial plants, especially conifers, and in some species of Apocynaceae, Malvaceae, and Ranunculaceae.

3. Occurrence of “Demospongiic” Acids among Other Organisms

Table 1 presents a non-exhaustive list of more than 40 FAs that correspond to Christie’s definition of demospongiic acids found in microorganisms, marine invertebrates and terrestrial plants. A particularly interesting point is the presence of 6-Br-5,9-FAs that are very common in demosponges but quite rare in other organisms. To the best of our knowledge only some Cnidaria Hexacorallia were shown to contain these brominated FAs [21–23], which prove the existence of bromoperoxidases in this group of Cnidaria since it has been proved that these brominated demospongiic acids are synthesized by the sponge itself in the final stage of biosynthesis [24].

Table 1. Occurrence of “demospongiac” acids in organisms that are not demosponges.

Acids	Genera/species	Kind of organisms	Ref.
5,9-16:2	<i>Stoichactis helianthus</i>	Cnidaria (Hexacorallia)	[22]
5,9-17:2	<i>Dictyostelium discoideum</i>	Microorganism, soil-living amoeba	[25]
5,9-18:2 taxoleic acid	<i>Condylactis gigantea</i> , <i>Palythoa caribaeorum</i> , <i>Stoichactis helianthus</i>	Cnidaria (Hexacorallia)	[22,23]
	<i>Cellana grata</i> , <i>Collisella dorsuosa</i>	Marine molluscs	[26,27]
	<i>Tripneustes esculentus</i>	Echinoderm	[28]
	<i>Ginkgo biloba</i>	Terrestrial plant	[7]
5,9,12-18:3 pinolenic acid (Z,Z,Z) and/or columbinic acid (E,Z,Z)	<i>Abies</i> sp., <i>Cedrus</i> sp., <i>Cupressus</i> sp., <i>Juniperus</i> sp., <i>Laryx</i> sp., <i>Picea</i> sp., <i>Pinus</i> sp., <i>Sequoia</i> sp., <i>Thuja</i> sp. <i>Anemone leveillei</i> (Ranunculaceae)	Terrestrial plants (conifers, gymnosperms)	[8,29] [30]
5,9,12,15-18:4	<i>Perna canaliculus</i>	Marine mollusc (Lamellibranchiata)	[31]
	<i>Abies</i> sp., <i>Cedrus</i> sp., <i>Cupressus</i> sp., <i>Juniperus</i> sp., <i>Laryx</i> sp., <i>Picea</i> sp., <i>Sequoia</i> sp., <i>Thuja</i> sp.	Terrestrial plants (conifers)	[8,29]
5,9-19:2	<i>Allamanda cathartica</i> (Apocynaceae) <i>Malvaviscus arboreus</i> (Malvaceae)	Terrestrial plants (angiosperms)	[32]
i-5,9-19:2	<i>Allamanda cathartica</i> (Apocynaceae) <i>Malvaviscus arboreus</i> (Malvaceae)	Terrestrial plants (angiosperms)	[32]
ai-5,9-19:2	<i>Allamanda cathartica</i> (Apocynaceae) <i>Malvaviscus arboreus</i> (Malvaceae)	Terrestrial plants (angiosperms)	[32]
5,9,12,16-19:4	<i>Perna canaliculus</i>	Marine mollusc (Lamellibranchiata)	[31]
5,9-20:2	<i>Condylactis gigantea</i> , <i>Palythoa caribaeorum</i> , <i>Stoichactis helianthus</i>	Cnidaria (Hexacorallia)	[22,23]
6-Br,5,9-20:2	<i>Condylactis gigantea</i> , <i>Palythoa caribaeorum</i>	Cnidaria (Hexacorallia)	[22,23]
7,11-20:2	<i>Penaeus setiferus</i>	Arthropod (shrimp)	[33]
5,9-21:2	<i>Condylactis gigantea</i> , <i>Stoichactis helianthus</i>	Cnidaria (Hexacorallia)	[22,23]
6-Br,5,9-21:2	<i>Stoichactis helianthus</i>	Cnidaria (Hexacorallia)	[22]
5,9,12,15,18-21:5	<i>Perna canaliculus</i>	Marine mollusc	[23]
5,9-22:2	<i>Condylactis gigantea</i> , <i>Palythoa caribaeorum</i> , <i>Stoichactis helianthus</i> <i>Cellana grata</i> , <i>Collisella dorsuosa</i>	Cnidaria (Hexacorallia) Marine molluscs	[22,23] [26-27]
6-Br,5,9-22:2	<i>Stoichactis helianthus</i>	Cnidaria (Hexacorallia)	[22]
9,13-22:2	<i>Penaeus setiferus</i>	Arthropod (shrimp)	[33]
5,9,15-22:3	<i>Collisella dorsuosa</i>	Marine molluscs	[27]
5,9,19-22:3	<i>Stoichactis helianthus</i>	Cnidaria (Hexacorallia)	[22]
5,9-23:2	<i>Stoichactis helianthus</i>	Cnidaria (Hexacorallia)	[22]

Table 1. Cont.

5,9-24:2	<i>Condylactis gigantea</i> , <i>Palythoa caribaeorum</i>	Cnidaria (Hexacorallia)	[23]
	<i>Cellana grata</i> , <i>Chromodoris</i> sp., <i>Collisella dorsuosa</i> , <i>Phyllidia coelesti</i>	Marine molluscs	[26,27,34]
5,9,15-24:3	<i>Cellana grata</i> , <i>Collisella dorsuosa</i>	Marine molluscs	[26,27]
5,9,17-24:3	<i>Cellana grata</i> , <i>Collisella dorsuosa</i>	Marine molluscs	[26,27]
5,9,15,18-24:4	<i>Cellana grata</i>	Marine mollusc	[26]
5,9,15,18,21-24:5	<i>Cellana grata</i>	Marine mollusc	[26]
5,9-25:2	<i>Chromodoris</i> sp., <i>Phyllidia coelesti</i>	Marine molluscs	[34]
	<i>Bebryce studeri</i>	Cnidaria (Octocorallia)	[35]
i-5,9-25:2	<i>Phyllidia coelesti</i>	Marine molluscs	[33]
5,9-26:2	<i>Heterochone</i> sp.	Marine sponge, Hexactinellida	[36]
	<i>Chromodoris</i> sp., <i>Phyllidia coelesti</i>	Cnidaria (Octocorallia)	[34]
	<i>Bebryce studeri</i>		[35]
i-5,9-26:2	<i>Chromodoris</i> sp., <i>Phyllidia coelesti</i>	Marine molluscs	[34]
5,9,19-26:3	<i>Bebryce studeri</i>	Cnidaria (Octocorallia)	[35]
5,9-28:2	<i>Aulosaccus</i> cf. <i>mitsukuri</i> , <i>Heterochone</i> sp., <i>Rosella</i> sp., <i>Sympagella nux</i>	Marine sponges, Hexactinellida	[36]
	<i>Bebryce studeri</i>	Cnidaria (Octocorallia)	[35]
5,9,19-28:3	<i>Bebryce studeri</i>	Cnidaria (Octocorallia)	[35]
5,9,23-28:3	<i>Hyalonema</i> sp.	Marine sponge, Hexactinellida	[36]
5,9-29:2	<i>Hyalonema</i> sp.	Marine sponge, Hexactinellida	[36]
5,9,22-29:3	<i>Acanthascus</i> sp., <i>Aulosaccus</i> cf. <i>mitsukuri</i> , <i>Euplectella</i> sp., <i>Heterochone</i> sp., <i>Hyalonema</i> sp.	Marine sponges, Hexactinellida	[36]
5,9,21-30:3	<i>Acanthascus</i> sp., <i>Aulosaccus</i> cf. <i>mitsukuri</i> , <i>Euplectella</i> sp., <i>Hyalonema</i> sp., <i>Heterochone</i> sp., <i>Staurocalyptus</i> sp., <i>Sympagella nux</i>	Marine sponges, Hexactinellida	[36]
5,9,23-30:3	<i>Acanthascus</i> sp., <i>Aulosaccus</i> cf. <i>mitsukuri</i> , <i>Euplectella</i> sp., <i>Farrea</i> sp., <i>Heterochone</i> sp., <i>Hyalonema</i> sp., <i>Ipheteon panicea</i> , <i>Staurocalyptus</i> sp., <i>Sympagella nux</i>	Marine sponges, Hexactinellida	[36]
5,9,25-30:3	<i>Hyalonema</i> sp.	Marine sponges, Hexactinellida	[36]
5,9-31:2	<i>Hyalonema</i> sp.	Marine sponge, Hexactinellida	[36]
5,9,21-31:3	<i>Staurocalyptus</i> sp.	Marine sponge, Hexactinellida	[36]
5,9,22-31:3	<i>Acanthascus</i> sp., <i>Aulosaccus</i> cf. <i>mitsukuri</i> ,	Marine sponges, Hexactinellida	[36]
5,9,23-32:3	<i>Ipheteon panicea</i> , <i>Staurocalyptus</i> sp.	Marine sponges, Hexactinellida	[36]

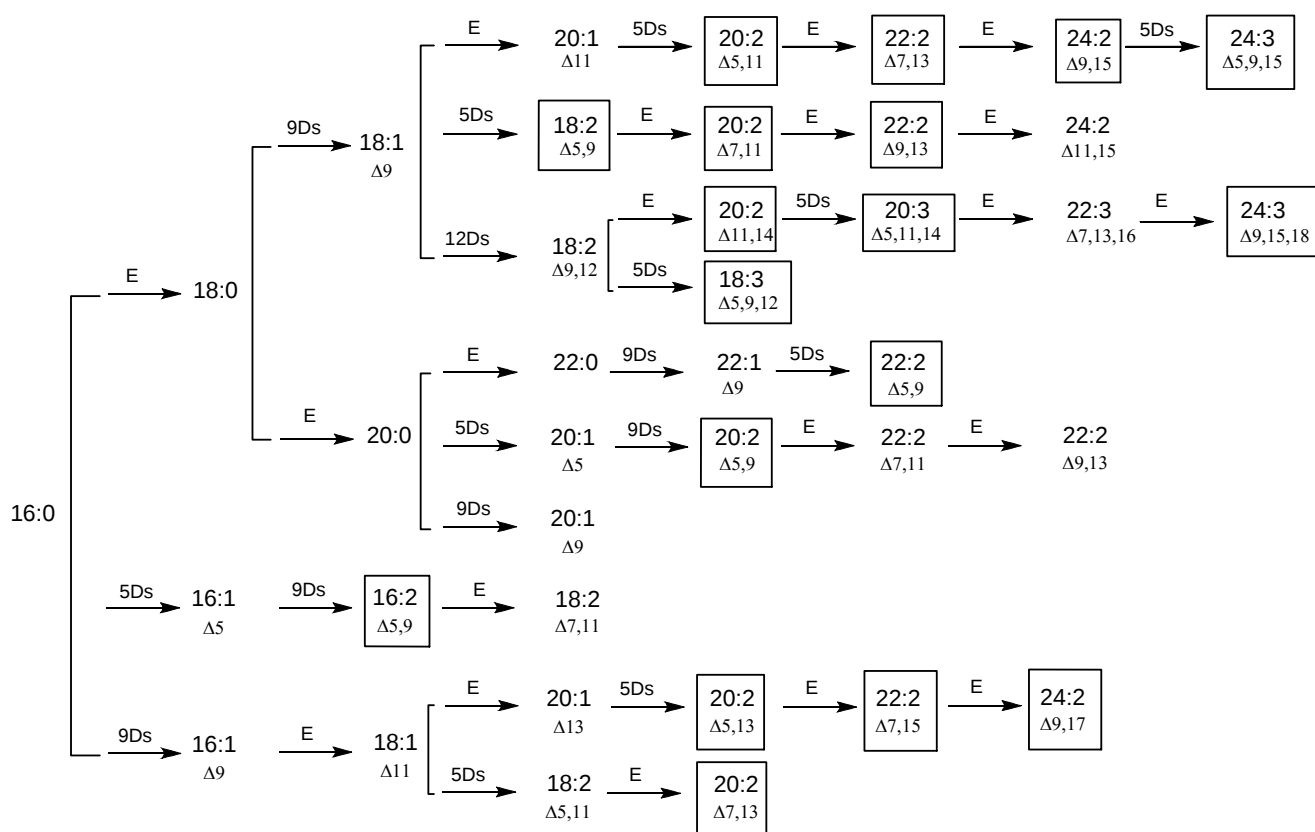
* According to Christie's definition.

4. Towards a Classification of Non-Methylene-Interrupted Fatty Acids?

Demospongiac acids represent a particular type of non-methylene-interrupted FA and, according to Christie's definition, it could be interesting to consider at least three classes of non-methylene-interrupted fatty acids (NMI FAs) depending on the number of methylene groups situated between the

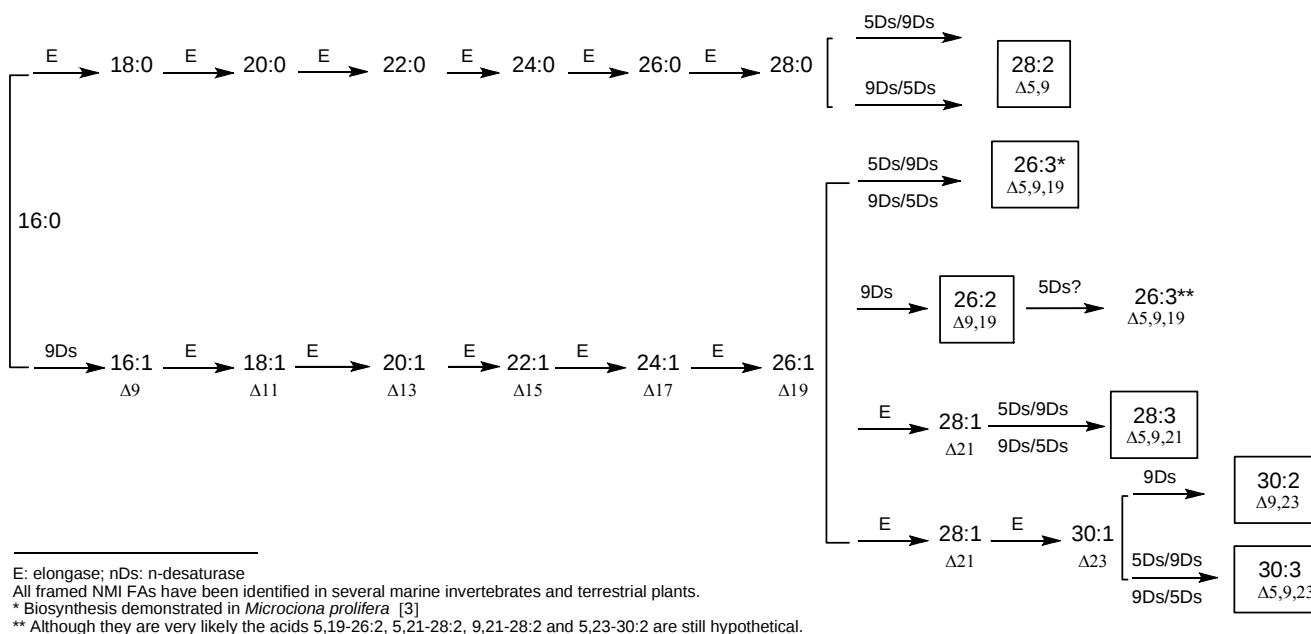
two first double bonds. Then, group 1 would contain all *bis*-methylene-interrupted *cis*-double bonds and would correspond to the series 5,9; 7,11; 9,13... dienoic or polyenoic acids (demospongiac acids). Group 2 would be that of *tetra*-methylene-interrupted *cis*-double bonds and would contain the series 5,11; 7,13; 9,15... NMI FAs, such as the acids 7,13-20:2 found in the Brittle star (Echinoderm, Ophiuroidea) *Ophiura sarsi* [37] and in the maritime pine *Pinus pinaster* [29], or the acid 7,13-22:2 found in the sponge *Petrosia ficiformis* [38]. Finally, group 3 would contain *hexamethylene*-interrupted *cis*-double bonds corresponding to the series 5,13; 7,15; 9,17... NMI FAs, such as the acid 7,15-20:2 found in the sponge *Dysidea fragilis* [39]. Some other acids of these three groups have been identified in marine invertebrates, especially molluscs and arthropods, and in numerous terrestrial plants, especially gymnosperms, and all of them can be deduced from accepted biosynthetic pathways implying elongases and 5- and 9-desaturases. Figures 1 and 2 give an overview of these putative biosyntheses from palmitic acid (16:0), palmitoleic acid (9-16:1) and linoleic acid (9,12-18:2). These schemes are currently used and have appeared recently in several publications, along with recent reviews on elongases and polyketide synthases [3,9,10,12,40–44].

Figure 1. Currently accepted pathways for the main long-chain NMI FAs ($\leq C_{24}$)



E: elongase; nDs: n-desaturase

All framed NMI FAs have been identified in several marine invertebrates and terrestrial plants.

Figure 2. Currently accepted pathways for the main very long-chain NMI FAs ($>C_{24}$)

5. Conclusion

To end this point of view, we think that the former notion of demospongiic acid should no longer be used mainly because *bis*-methylene interrupted 5,9-diunsaturated FAs and related acids are distributed among several phyla of marine organisms and several classes of terrestrial plants. The former “demospongiic acids” can be considered as a particular series of NMI FAs produced by different combinations of elongases and $\Delta 5$ and $\Delta 9$ desaturases on the most common FAs in nature such as palmitic and palmitoleic acids.

References

- 1 Litchfield, C.; Morales, R.W. Are demospongiae membranes unique among living organisms? In *Aspects of Sponge Biology*; Harrison, F.W., Cowden, R.R., Eds.; Academic Press: New York, NY, USA, 1976; pp. 183–200.
- 2 Litchfield, C.; Tyszkiewicz, J.; Dato, V. 5,9,23-Triacontatrienoic acid, principal fatty acid of the marine sponge *Chondrilla nucula*. *Lipids* **1980**, *15*, 200–202.
- 3 Djerassi, C.; Lam, W.-K. Sponge phospholipids. *Acc. Chem. Res.* **1991**, *24*, 69–75.
- 4 Barnathan, G.; Kornprobst, J.-M. Fatty acids from marine organisms: recent research developments. In *Marine Lipids*; Baudimant, G., Guézennec, J., Roy, P., Samain, J.-F., Eds.; Editions Ifremer: Plouzané, France, 2000; pp. 35–43.
- 5 Kornprobst, J.-M. *Encyclopedia of Marine Natural Products*; Wiley-VCH: Weinheim, Germany, 2010; Volume 2, pp. 538–555.
- 6 Carballeira, N.M. New advances in fatty acids as antimalarial, antimycobacterial and antifungal agents. *Prog. Lipid Res.* **2008**, *47*, 50–61.
- 7 Wolff, R.L.; Christie, W.W.; Marpeau, A.M. Reinvestigation of the polymethylene-interrupted 18:2 and 20:2 acids of *Ginkgo biloba* seed lipids. *J. Am. Oil. Chem. Soc.* **1999**, *76*, 273–276.

- 8 Wolff, R.L.; Deluc, L.G.; Marpeau, A.M. Conifer seeds: oil content and fatty acid compositions. *J. Am. Oil. Chem. Soc.* **1996**, *73*, 765–771.
- 9 Ando, Y.; Kawabata, Y.; Narukawa, K.; Ota, T. Demospongiac acids of the marine sponge *Halichondria panicea* from the coast of Hokkaido, Japan. *Fish. Sci.* **1998**, *64*, 136–139.
- 10 Rezanka, T.; Sigler, K. Odd-numbered very-long-chain fatty acids from the microbial, animal and plant kingdoms, *Prog. Lipid Res.* **2009**, *48*, 206–238.
- 11 Bergé, J.P.; Barnathan, G. Fatty acids from lipids of marine organisms: molecular biodiversity, roles as biomarkers, biologically active compounds, and economical aspects. *Adv. Biochem. Eng. Biotechnol.* **2005**, *96*, 49–125.
- 12 Johnson, D.W. Contemporary clinical usage of LC/MS: analysis of biologically important carboxylic acids, *Clin. Biochem.* **2005**, *38*, 351–361.
- 13 Leonard, A.E.; Pereira, S.L.; Sprecher, H.; Huang, Y.-S. Elongation of long-chain fatty acids. *Prog. Lipid Res.* **2004**, *43*, 36–54.
- 14 Tsydendambaev, V.D.; Christie, W.W.; Brechany, E.Y.; Vereshchagin, A.G. Identification of unusual fatty acids of four alpine plant species from the Pamir. *Phytochemistry* **2004**, *65*, 2695–2703.
- 15 Moldovan, Z.; Jover, E.; Bayona, J.M. Gas chromatographic and mass spectrometric methods for the characterization of long-chain fatty acids – Application to wool wax extract. *Anal. Chim. Acta* **2002**, *465*, 359–378.
- 16 Steinberg, S.J.; Wang, S.J.; Kim, D.G.; Mihalik, S.J.; Watkins, P.A. Human very-long-chain acyl-CoA synthetase: cloning, topography, and relevance to branched-chain fatty acid metabolism. *Biochem. Biophys. Res. Commun.* **1999**, *257*, 615–621.
- 17 Rezanka, T. Very-long-chain fatty acids from the animal and plant kingdoms, *Prog. Lipid Res.* **1989**, *28*, 147–187.
18. Christie, W.W. AOCS Lipid Library. http://lipidlibrary.aocs.org/Lipids/fa_conj+/index.htm (accessed on 26 July 2010).
- 19 Kulkarni, B.A.; Chattopadhyay, S.; Chattopadhyay, A.; Mamdapur, V.R. Synthesis of the demospongiac compounds, (6Z,11Z)-octadecadienoic acid and (6Z,11Z)-eicosadienoic acid *Molecules* **1997**, *2*, 3–6.
- 20 Carballeira, N.M.; Shalabi, F. Identification of naturally occurring *trans*, *trans* Δ -5,9 fatty acids from the sponge *Plakortis halichondroides*. *Lipids* **1990**, *25*, 835–840.
- 21 Dembitsky, V.M.; Srebnik, M. Natural halogenated fatty acids: their analogues and derivatives. *Prog. Lipid Res.* **2002**, *41*, 315–367.
- 22 Carballeira, N.M.; Medina, J.R. New Δ 5,9 fatty acids in the phospholipids of the sea anemone *Stoichactis helianthus*. *J. Nat. Prod.* **1994**, *57*, 1688–1695.
- 23 Carballeira, N.M.; Reyes, M. Identification of a new 6-bromo-5,9-eicosadienoic acid from the anemone *Condylactis gigantea* and the Zoanthid *Palythoa caribaeorum*. *J. Nat. Prod.* **1995**, *58*, 1689–1694.
- 24 Lam, W.K.; Hahn, S.; Ayanoglu, E.; Djerassi, C. Phospholipid studies of marine organisms. 22. Structure and biosynthesis of a novel brominated fatty acid from a Hymeniacidonid sponge. *J. Org. Chem.* **1989**, *54*, 3428–3432.

- 25 Schlenk, H. Odd numbered polyunsaturated fatty acids. *Prog. Chem. Fats Other Lipids* **1970**, IX, Part 5, 589–605.
- 26 Kawashima, H.; Ohnishi, M. Occurrence of novel nonmethylene-interrupted C₂₄ polyenoic fatty acids in female gonad lipids of the limpet *Cellana grata*. *Biosci. Biotechnol. Biochem.* **2006**, 70, 2575–2578.
- 27 Kawashima, H. Unusual minor nonmethylene-interrupted di-, tri- and tetraenoic fatty acids in limpet gonads. *Lipids* **2005**, 40, 627–630.
- 28 Joseph, J.D. Distribution and composition of lipids in marine invertebrates. In *Marine Biogenic Lipids, Fats and Oils*; Ackman, R.G., Ed.; CRC Press: Boca Raton, FL, USA, 1989; Volume II, pp. 49–143.
- 29 Asset, G.; Leroy, A.; Bauge, E.; Wolff, R.L.; Fruchant, J.-C.; Dallongeville, J. Effects of dietary maritime pine (*Pinus pinaster*)-seed oil on high-density lipoprotein levels and *in vitro* cholesterol efflux in mice expressing human apolipoprotein A-I. *British J. Nutrition* **2000**, 84, 353–360.
- 30 Sayanova, O.; Haslam, R.; Venegas Caleron, M.; Napier, J.A. Cloning and characterization of unusual fatty acid desaturases from *Anemone leveillei*: Identification of an acyl-coenzyme A C₂₀ Δ^5 -desaturase responsible for the synthesis of sciadonic acid. *Plant Physiol.* **2007**, 144, 455–467.
- 31 Treschow, A.P.; Hodges, L.D.; Wright, P.F.A.; Wynne, P.M.; Kalafatis, N.; Macrides, T. Novel anti-inflammatory γ -3 PUFAs from the New Zealand green-lipped mussel, *Perna canaliculus*. *Comp. Biochem. Physiol.* **2007**, 147B, 645–656.
- 32 Carballeira, N.M.; Cruz, C. 5,9-Nonadecadienoic acids in *Malvaviscus arboreus* and *Allamanda cathartica*. *Phytochemistry* **1998**, 49, 1253–1256.
- 33 Pearce, R.E.; Stillway, L.W. Non-methylene-interrupted and ω 4 dienoic fatty acids of the white shrimp *Penaeus setiferus*. *Lipids* **1977**, 12, 544–549.
- 34 Zhukova, N.V. Lipid classes and fatty acid composition of the tropical nudibranch mollusks *Chromodoris* sp. and *Phyllidia coelestis*. *Lipids* **2007**, 42, 1169–1175.
- 35 Imbs, A.B.; Demidkova, D.A.; Dautova T.N.; Latyshev, N.A. Fatty acid biomarkers of symbionts and unusual inhibition of tetracosapolyenoic acid biosynthesis in corals (Octocorallia). *Lipids* **2009**, 44, 325–335.
- 36 Thiel, V.; Blumenberg, M.; Hefter, J.; Pape, T.; Pomponi, S.; Reed, J.; Reitner, J.; Wörheide, G.; Michaelis, W. A chemical view of the most ancient metazoa: biomarker chemotaxonomy of hexactinellid sponges. *Naturwissenschaften* **2002**, 89, 60–66. Erratum: *Naturwissenschaften* **2002**, 89, 233–234.
- 37 Sato, D.; Ando, Y. Distribution of novel nonmethylene-interrupted fatty acids over neutral and polar lipids of Ophiuroidea (Brittle Star). *J. Oleo Sci.* **2002**, 51, 563–567.
- 38 Ayanoglu, E.; Walkup, R.D.; Sica, D.; Djerassi, C. Phospholipid studies of marine organisms: III. New phospholipid fatty acids from *Petrosia ficiformis*. *Lipids* **1982**, 17, 617–625.
- 39 Christie, W.W.; Brechany, E.Y.; Stefanov, K.; Popov, S. The fatty acids of the sponge *Dysidea fragilis* from the Black Sea. *Lipids* **1992**, 27, 640–644.
- 40 Hahn, S.; Lam W.K.; Wu, I.; Silva, C.J.; Djerassi, C. Unusual pattern of fatty acid biosynthesis. *J. Biol. Chem.* **1989**, 264, 21043–21046.
- 41 Wallis, J.G.; Watts, J.L.; Browse, J. Polyunsaturated fatty acid synthesis: what will they think of next? *Trends Biochem. Sci.* **2002**, 27, 467–473.

- 42 Buist, P.H. Fatty acid desaturases: selecting the dehydrogenation channel. *Nat. Prod. Rep.* **2004**, *21*, 249–262.
- 43 Barnathan, G. Non-methylene-interrupted fatty acids from marine invertebrates: Occurrence, characterization and biological properties. *Biochimie* **2009**, *91*, 671–678.
- 44 Hochmuth, T.; Piel, J. Polyketide synthases of bacterial symbionts in sponges – Evolution-based applications in natural products research, *Phytochemistry* **2009**, *70*, 1841–1849.

© 2010 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).0