Indian Journal of Chemistry
Vol. 45B, February 2006, pp. 433-449

Advances in Contemporary Research

Marine algal natural products: Contributions from India in the global context

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Received 28 March 2005; accepted (revised) 18 August 2005

Several terpenes (mostly sesqui- and diterpenes), steroids, ceramides, nitrogen pigments, heterocyclics, aromatic compounds and polyethers have been reported from Indian marine algae, which is an encouraging feature. The research deserves to be intensified if the ongoing search for drugs has to be amply rewarded.

Keywords: Marine natural products, Marine algae, terpenes, steroids, ceramides, nitrogen pigments, heterocyclics, aromatic compounds and polyethers

IPC: **Int.Cl.**[7] **A 61 K 35/00**

Introduction

Marine natural product research, in India, was started in the late seventies. It was late starting for India, although the country enjoys a strong base in natural product research and in spite of the fact that the country enjoys sizeable resource of marine life forms along its long coastline, from the points of view of biomass as well as biodiversity. In the early phase, marine algae were the first choice for chemical examination since they are operationally easier than animal organisms for handling. At the global level, peak activity in algal natural products research reached early; in India however, considering the vast potential, the peak activity has yet to reach. The marine algal resource of the Indian coast is quite phenomenal with an estimated biomass of about 261×10^3 tons[1]. Macro algae belonging to 217 genera and 844 species occur along the Indian coastline[2]. The three groups of algae that are most important from the occurrence as well as the investigated natural products point of view are the red algae, brown algae, and the green algae. Many of the algal crude extracts show promising biological activities[3-5] spurring investigation of the responsible chemical constituents. The investigation has led to the isolation of several new compounds, and many more known compounds, that at one day can potentially be useful either directly or indirectly.

The coastline of the Tamil Nadu State supports the maximum estimated resource ($\sim90\times10^3$ tons), and the species identified. The Andaman and Nicobar islands vie with Tamil Nadu State for the top position for the estimated resource, but the number of species identified there are only a few, perhaps because a lot of survey yet needs to be done there. The States of Gujarat, and Maharashtra and the Lakshadweep islands are bracketed in the second place with $\sim20\times10^3$ tons each, and the third place goes to the Andhra Pradesh state[1]. The marine algal natural products research in India is largely carried out so far by research groups at the Andhra University (AU) on the east coast, and the National Institute of Oceanography, with contribution also coming from the Indian Institute of Technology, Mumbai on the west coast. Four more laboratories of the CSIR namely the Indian Institute of Chemical Technology (IICT), the Central Salt and Marine Chemicals Research Institute (CSMCRI), the Central Drug Research Institute (CDRI) and the Regional Research Laboratory at Bhubaneshwar (RRL) have also been engaged in marine algal research in India. It is surprising that notwithstanding Tamil Nadu's premier position in the algal resources, there has so far not been an active school of marine natural products research in the State. Researchers far off perform their chemical studies on collections made from the Tamil Nadu coast at centres such as Mandapam. This can perhaps be explained by the fact that the primary concern there is the polysaccharide research, and its commercial offshoot the phycocolloid industry.

Many algal species are common to different parts of the Indian coastline and many more are unique to a given ecosystem, e.g., the green algal *Monostoma*

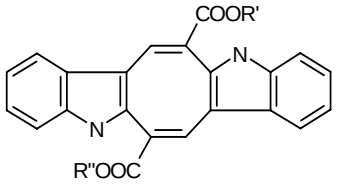
species that is confined to the west coast, and another green alga, *Tydemania expeditionis* which is unique to the Andaman and Nicobar islands' ecosystem. Further, being at the root of the food chain, the algal metabolites are received, concentrated, and transformed within their bodies by the higher organisms, a process that not only satisfies the nutritional requirement, but also the urge for enriching defensive chemicals. A third reason why algal natural products research is an active area of study is the relative ease with which they can be collected and handled as well as the culturing practices to which they can be subjected.

Chemical examination of Indian marine algae

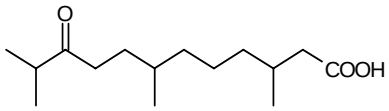
A total of 6 green, 5 brown and 8 red algal species were so far examined. The constituents of a sea hare are also discussed under red algae as the organism derives its chemicals from its red algal diet.

Green Algae

Caulerpa racemosa: Caulerpine **1**, the red pigment of green algae[6] is usually present in most (~80%) of the species of *Caulerpa* that were examined[7]. Anjaneyulu *et al*. (1991) isolated it from *C. racemosa* collected from Visakhapatnam. Along with the pigment which is a symmetrical dimethyl ester, they also isolated the free acid, caulerpinic acid **2** and the monomethyl ester **3**. These pigments are associated with a new sesquiterpene keto acid **4**, and *cis* and *trans* phytols **5** and **6** (ref. 8). They also isolated simple C_6-C_3 phenyl propane dimeric ethers or esters **7-11** (ref. 9) with a C_{18} skeleton. These aromatic compounds, that may be considered as neolignans are



1 R′= Me, R″= Me
2 R′= H, R″= Me
3 R′= Me, R″= H



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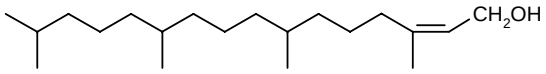

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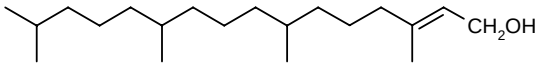

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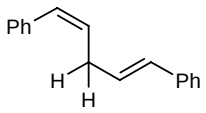

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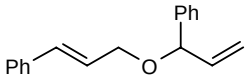

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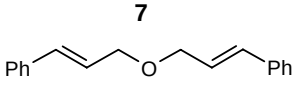

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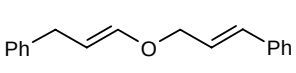

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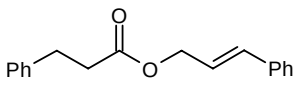

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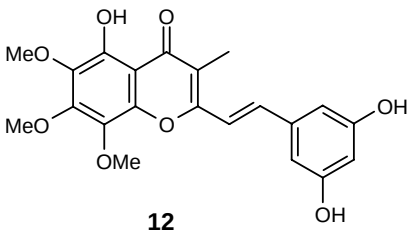

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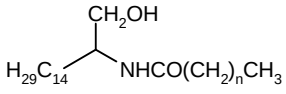
rare for marine algae, although common in land plants. Hormothamnion **12** is a cytotoxic styryl chromone from the marine cyanophyte *Hormothamnion enteromorphoides* that, according to the authors, stands out as an isolated example of such compounds in marine organisms[10].

The algal species from Sri Lanka yielded sphingolipids. The sphingosines are difficult to obtain in pure condition due to the difficulty in separation of the various closely eluting homologues. Hence, from *Caulerpa racemosa*, the 'compound' named as caulerpicin reported as being a three component mixture **13** (ref. 11) was revised[6] as a four component mixture **14** and was later shown to be a mixture of five N-acylsphinganines **15** (ref. 12).

Caulerpa taxifolia: The algae collected from Visakhapatnam afforded[13] the diterpene *trans* phytol **6** which is the ester component of chlorophylls, and its degradation product the C-18 ketone viz., 6,10,14-trimethylpentadecan-2-one **16** and the sterol clinosterol **17**. An Italian group isolated from this alga occurring in the Mediterranean, the glycoglycerolipid **18**, and the stable enols **19** and **20**, which occur in both *E* and *Z* forms[14]. Caulerpenyne **21** is the major metabolite of this alga[15].

Ulva fasciata: Garg's group[16] isolated the sphingosine (ceramide) derivatives **22**, and **23** (ref. 17), the former shown to be antiviral from *Ulva fasciata* collected off Goa. Recently, Siddhanta *et al.* obtained[18] an inseparable mixture of nitrogenous glycerolipids **24-26** from this alga collected off the Gujarat coast. Within the mixture, **25** was the major component.

Ulva lactuca afforded the sterol glycoside, 3-O-β-D-glucopyranosyl stigmasta-5,25-dien **27**, an antimicro



n=23, 24 or 25
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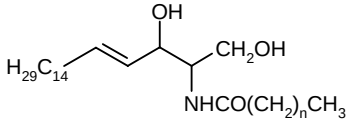

n=12,14, 20 or 22
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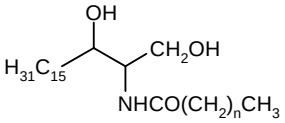

n= 16,18, 20, 22 or 24
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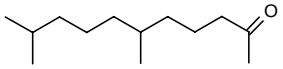

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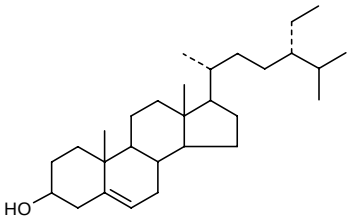

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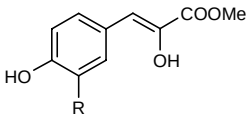
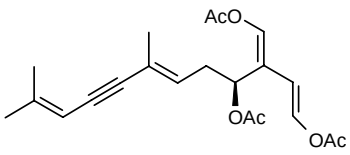


19 R=H
20 R=OH



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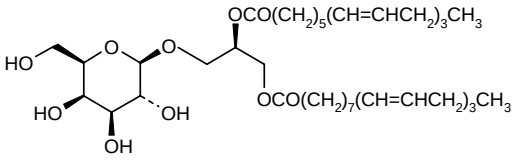

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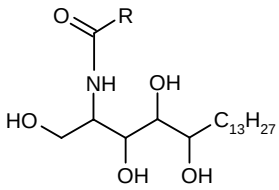
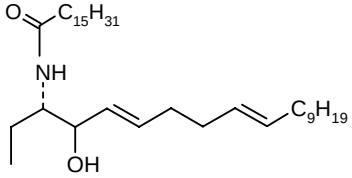


22, R=$C_{14}H_{29}$
115, R=$C_{23}H_{47}$



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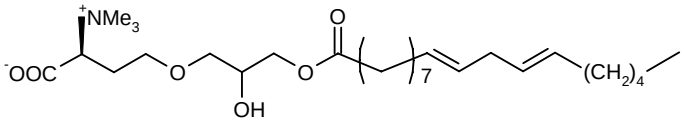

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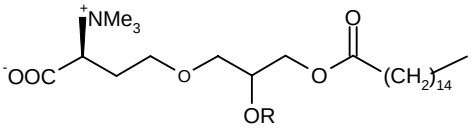
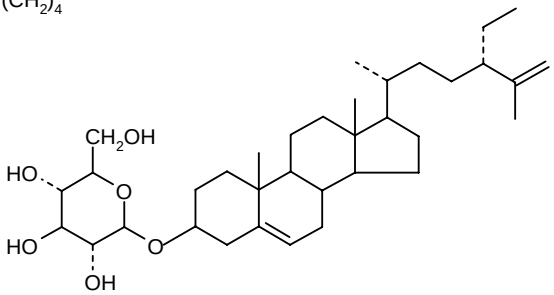


25 R=H
26 R=$CO(CH_2)_{14}CH_3$



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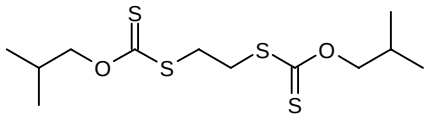

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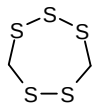

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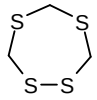

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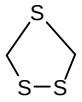

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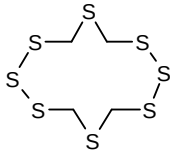

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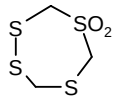

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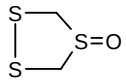

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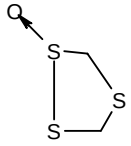

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bial agent in which the side chain is the same as in the *Codium* sterols[19] (see below).

Dictyosphaera favulosa: This alga occurs widely on the shores of the Indo-Pacific and the Southern Atlantic region. The specimen collected from the Andaman Island produced[20] the new symmetrical ethylene bis alkyl xanthate **28**.

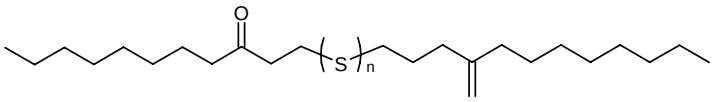
The alkyl xanthates, i.e., sulfur containing lipids are quite rare in marine algae. Prior to *D. favulosa*, the brown algae of the genus *Dictyopteris* were shown to contain cyclic disulfides together with mono, di and tri sulfides[21-23] and the Mexican red algal species *Chondria californica* was shown to contain polysulfides **29-32** including the octasulfide **32**, and sulfones **33-35**[24]. The crude extract of *Chondria californica* exhibited interesting biological properties, presumably due to the cyclic polysulfides and the more polar sulfones.

The brown alga *Dictyopteris* sp. was from the Hawaiian waters and its sulfur containing compounds were S-(3-oxoundecyl) thioacetate **36**, bis (3-oxoundecyl) disulfide **37**, 3-n-hexyl-4,5-dithiacyclohexanone **38** and S-(*trans*-3-oxoundec-4-enyl)thioacetate **39** (ref. 21), bis-(3-oxoundecyl) trisulfide **40**, and the corresponding tetrasulfide **41** (ref. 22), and bis (*cis*-acetoxyundec-5-enyl) disulfide **42** and S-*cis*-acetoxyundec-5-enyl thioacetate **43** (ref. 23).

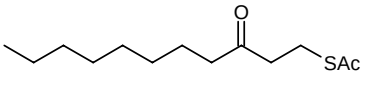
Sacoglossan volvatella: This alga afforded volvatellin **44**, a caulerpenyne **21** related product [25].

Codium decorticatum: This alga, collected from the Gulf of Mannar (Mandapam Camp) afforded the sterols aplysterol **45** and 24(28)-didehydro aplysterol **46** (ref. .26).

Prior to this, sterols were reported from another *Codium* species, viz., *C. iyengarii* from the Karachi coast. Iyengadione **47** and the glycosides iyengarosides A **48**, and B **49** having moderate activity against a range of bacteria were reported [27]. The ring AB oxidation pattern of these sterols is similar to that noticed in clerosterols **50-52**, which



37 n=2; **40** n=3; **41** n=4



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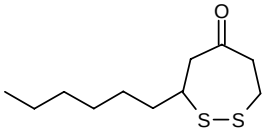

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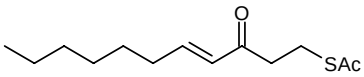

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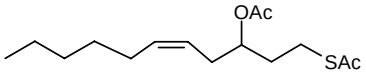

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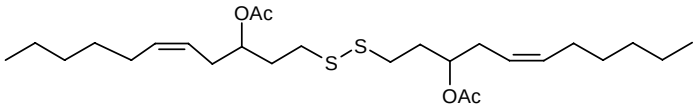

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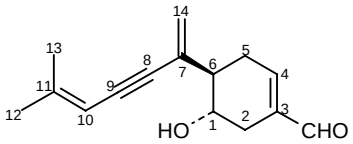

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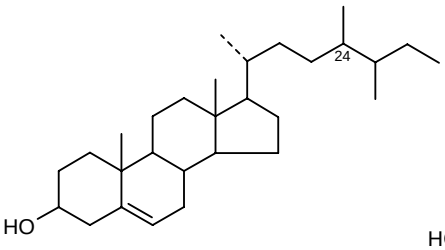

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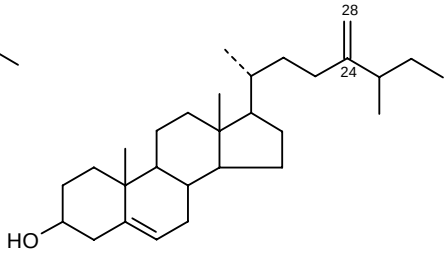

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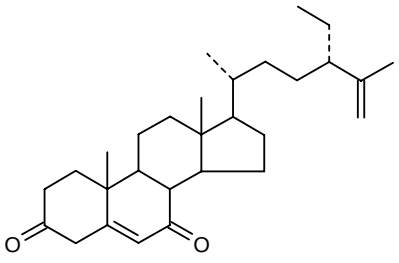

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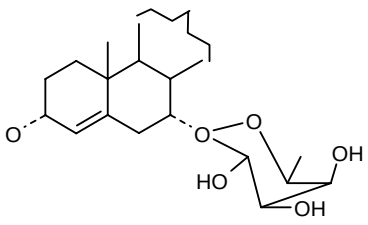

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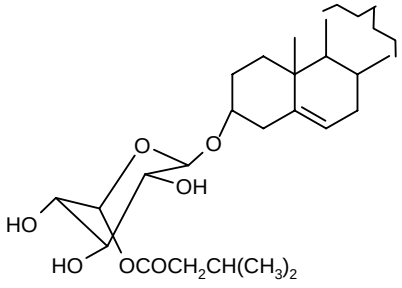

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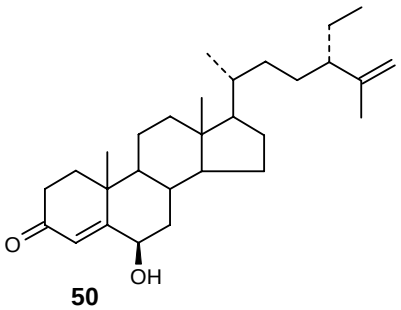
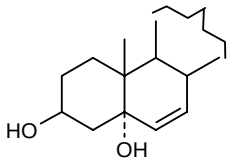


50

have an identical side chain, isolated from *C. arabicum* [28].

Brown algae

Dictyota dichotoma: The alga, collected from the Gulf of Mannar afforded a novel diterpene dictyoxetane **53**, belonging to a new tricyclic carbon skeleton[29]. The alga also contains[30] some sixteen more new diterpenes, fifteen **54-68** of which belong to the familiar dolabellane skeleton, and the sixteenth **69**, a dolastane derivative, that was postulated by the authors to originate from a dolabellane precursor by a



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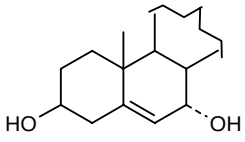

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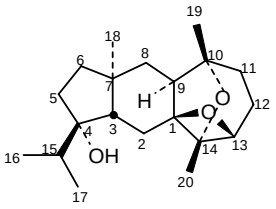

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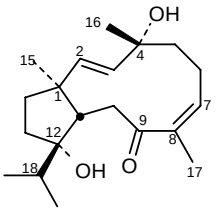

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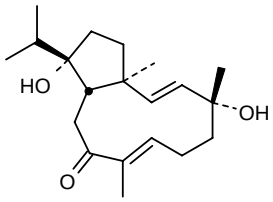

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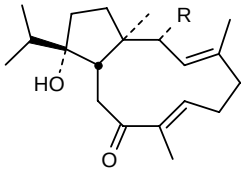
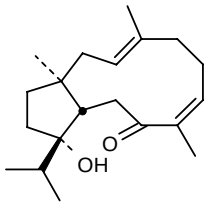


56 R=H
62 R=OAc



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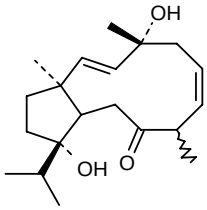
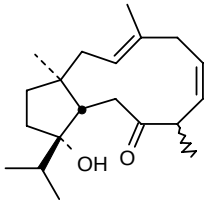


58, 59



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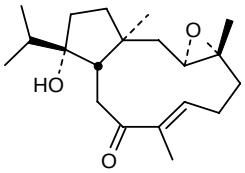

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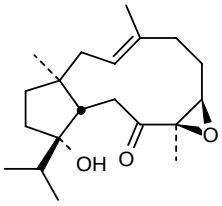

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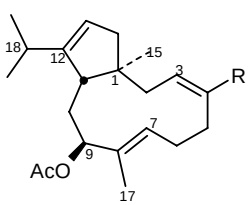
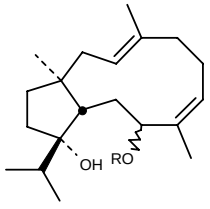
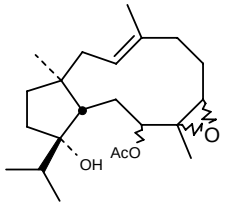


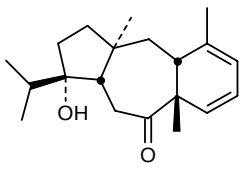
65 R=CHO
66 R=COOH



67 R=Ac



68



69

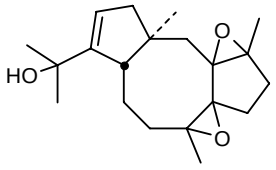
Cope rearrangement, in contrast to other dolastanes that appear to arise by a carbonium ion initiated cyclization of the dolabellane carbon skeleton. The name dolabellane for the diterpene class being isolated from brown algae is from the opisthobranch mollusk, the sea hare *Dolabella californica*, which was first found to contain the diterpenes, having derived them from the (brown) algal diet, comprising *Dictyota dichotoma*[31].

The presence of compounds of mixed origin in the single algal species points to the cosmopolitan nature of the alga. *Dictyota dichotoma* is known to be a cosmopolitan species, and occur in several chemotypes as to why compounds isolated from the alga should be of complex origin involving (i) the xenicane skeleton cyclization between C-2 and C-6, (ii) formation of 2-7 bond followed by migration of 7-8 bond to C-6, etc[32]. Like dolabellanes, the name 'xenicane' was derived from the fact that the compound was first encountered in a soft coral of the genus *Xenia*.

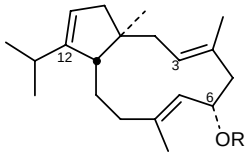
Dictyota divaricata: This alga, collected from the Andaman and Nicobar islands yielded[33] one known **70** and eleven new **71--81** diterpenes. Four of the new compounds **71-74** are dolabellanes, six dolastanes **75-78**, **80**, **81**, and one an aromatic isodolastane **79**. The known compound also was dolabellane **70**, that was previously reported as a new compound from *Dictyota paradalis* from the Great Barrier Reef[34]. The extract also contained sterol mixture, whose characterisation is not published.

***Dictyota bartayresiana*:** This algal species collected from the Gulf of Mannar yielded[35] a known dolastane **82**, five known dolabellanes **83-87** and five new compounds, of which three are dolabellanes **88-90** and two dolastanes **91, 92**.

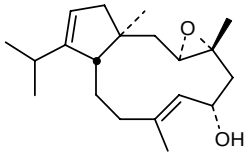
Padina tetrastromatica: Rao and his co-workers[36] examined this species collected off Visakhapatnam. They isolated *trans* phytol **6** and its reaction product the C-18 ketone **16**, which they also encountered in *Caulerpa taxifolia* (see above). In addition, they had isolated loliolide (digiprolactone; **93**), for the first



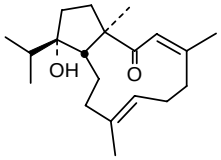
70



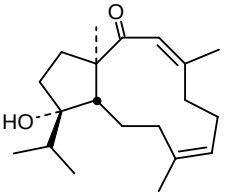
71 R=H



72



73



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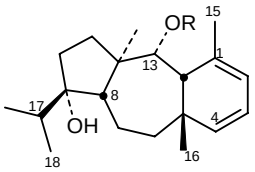
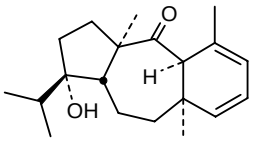


75 R=H**; 76** R=Ac



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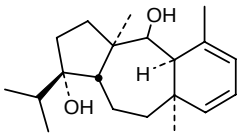

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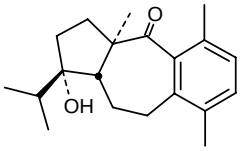

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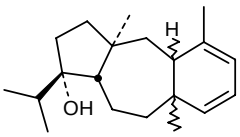


80, 81

time from a marine source and the sterol (24E)-stigmasta-5,24(28)-dien-3-ol **94**.

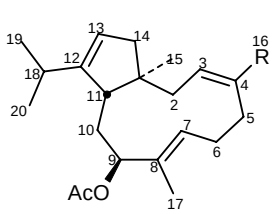
The NIO group also studied the chemical constituents of this alga, having earlier reported[3] spasmogenic, antifertility, hypotensive and antiamoebic activities for its methanolic extract. They isolated three halogenated norsesquiterpenoids, 2-chloro-2,6,10-trimethylundecanoic acid **95**, 2-bromo-2,6,10-trimethylundecanoic acid **96** and 2-chloro-2-carboxy-6,10-dimethylundecanoic acid methyl ester **97** (ref. 37), three non-halogenated terpenoids **98**, **99** and loliolide **93** (ref. 38) and the reduced sugar dulcitol **100**.

Stoechospermum marginatum: This alga was studied by the three major research groups at the AU, IICT and NIO.

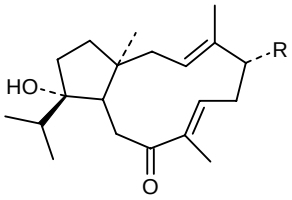
Phthalate esters isolated from this alga[39] are perhaps not natural products but derived from the plastic containers. Methanolic extract of this alga exhibited spasmolytic activity[3] and inhibited the growth of the bacterium *Staphylococcus aureus*[40]. The non-phthalate compounds isolated from the alga[41] were ethyl palmitate **101**, and fucosterol **102** which was trace contaminated with dihydrofucosterol and 24-ketocholesterol **103**.

The NIO group had earlier reported a new spatane diterpene, named stoechospermol, to which an incorrect structure was given by the authors[42]. The compound was found identical to **104**, which was isolated along with nine other new spatane diterpenes from the Sri Lankan collection of the alga[43]. The major metabolites were (in order of abundance) the tetrol **105**, the corresponding monoacetate **106**, and the alcohol **104**. The remaining diterpenes, viz., **107-112** were relatively minor constituents. The tetrol **105** and the acetate **106** were both diastereoisomeric mixtures at C-18, raising the possibility that the metabolite could be artifact formed by 1,4-addition of water to an unsaturated epoxide[43]. The monoacetate **106** has antimicrobial properties[44].

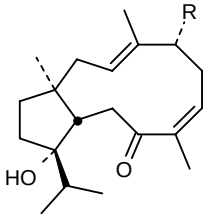
Rao and his co-workers[45], working on the alga collected from the Gulf of Mannar reported five spatane diterpenes, two of them present as mixtures of R and S conformers. Thus, they came across all diterpenes except **112** and **105**, instead reporting the epoxide **113** as the new metabolite. Subsequently, the IICT group who took up the investigation of the alga



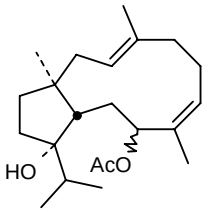
82 R=CHO
83 R=COOH



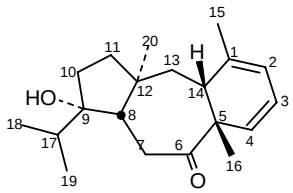
84 R=H
88 R=OAc



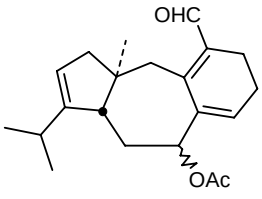
85 R=H
89 R=OAc



86



87



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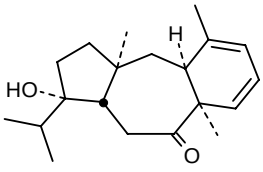

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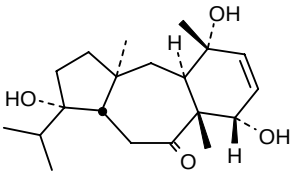
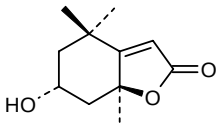


92



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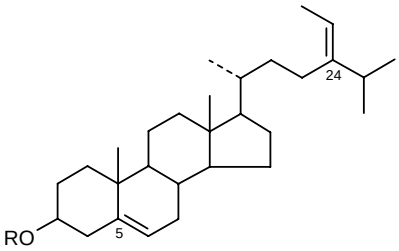
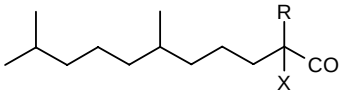
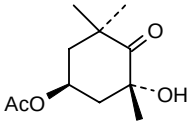


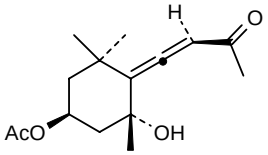
94 R=Ac
102 R=H



95 R=Me, X=Cl
96 R=Me, X=Br
97 R=COOMe, X=Cl



98



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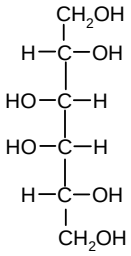
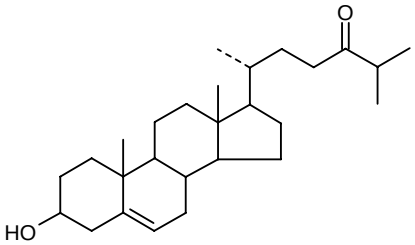


100

$C_{15}H_{29}COOC_2H_5$

101



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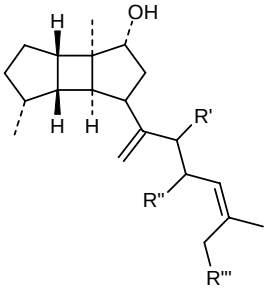
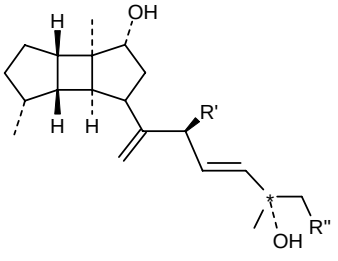
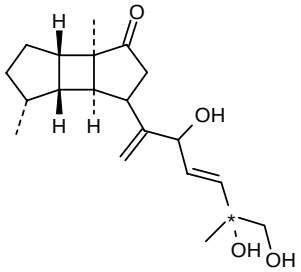
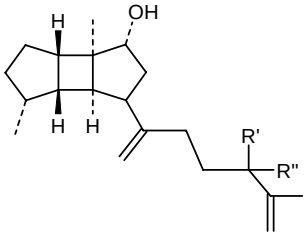




104 R′=R″=R‴=H
107 R′=R″=OH, R‴=OAc

105 R′=R″=OH
106 R′=OH, R″=OAc
110 R′=R″=H





collected from the same region also did not come across **111** and **112**; and they reported the isomeric epoxide **114** as the new compound.

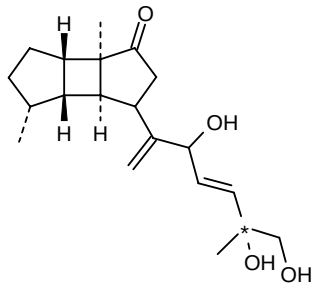
Red Algae

The red algal species not only constitute the bulk of the algal species occurring but also the species subjected to chemical examination.

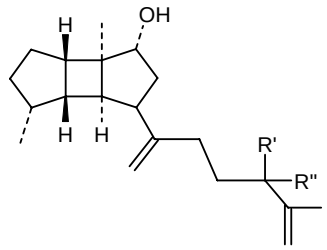
Halymenia durivilliae: The contribution of Andhra University is limited to two species, *Halymenia durivilliae* and *Laurencia obtusa*. From the former collected from the Andaman and Nicobar islands, Rao and Satyanarayana reported[46] a new sphingosine derivative **115**. Hyalamine **116** is an unusual ceramide that was earlier reported from another species of the genus viz., *H. porphyroides* [47].

Laurencia obtusa: From this alga collected from the Minicoy island of the Lakshadweep group of islands, Sarma and his co-workers[48] reported an unprecedented 3,4-dinor cholestane ring A lactol steroid, identified as 2a-oxa-5α-hydroxy-3,4-dinorcholestane **117**, a compound that was previously known as a synthetic product, having been synthesized from 2-hydroxymethylene cholestane **118**. Surprisingly, a steroid of identical ring structure, but differing in the side chain, viz., **119** has recently been reported from a brown algal species *Stypopodium carpophyllum* from the South China Sea[49]. The sterol induced morphological abnormality in the plant pathogenic fungus *Pyricularia oryzae*. Another sterol containing the usual 3β-Δ^5-sterol system, viz., **120** that accompanied the ring A rearranged sterol in the alga, indicates the unique biosynthetic sequence of reactions involving oxidation and cyclisation that the alga is able to perform.

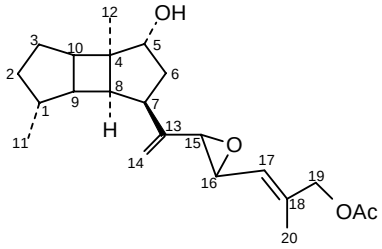
Ecdysones are moulting hormones of crustaceans that are an unique group of steroids. Quite early in



108, **109**
Epimers at *



111 R′=H, R″=OH
112 R′=OH, R″=H



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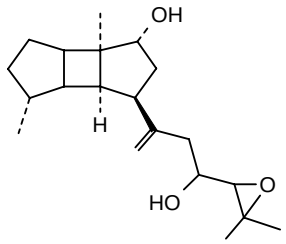
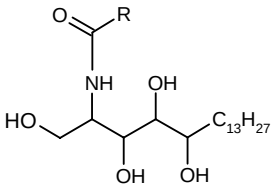
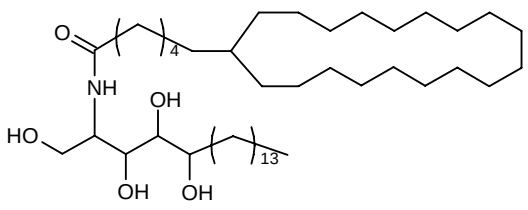


114



115 R=$C_{23}H_{47}$



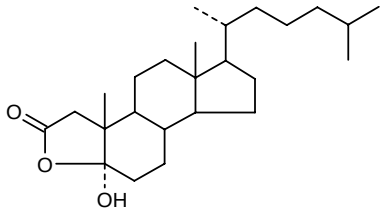
116

time, the ecdysone derivative viz., pinnasterol **121** together with its 2-acetate (pinnasterol acetate, **122**) was isolated from the red alga *Laurencia pinnata*[50]. Pinnasterol indeed has ecdysone activity and was believed to protect the alga from crustacean predators.

Chondria armata: The red algal genus *Chondria* belongs to the same family (Rhodomelaceae, Ceramiales) as *Laurencia*, the most prolific and most widely studied genus among all algae, and whose chemical examination had resulted in innumerable secondary metabolites, in particular the halogen containing terpenes vested with useful biological activities. The NIO group took up the examination of *Chondria armata* as the preliminary screening of the lipid extract showed antiviral, antibacterial and antifungal activities[3] and reported the fatty acids, *n*-pentadecanoic, *n*-octadecanoic, hexadec-4-enoic, hexadec-5-enoic and octadec-9-enoic, and dominantly the palmitic (C_{16}; ~75% of the fatty acid methyl ester mixture) and oleic (C_{18}; ~17%) acids from GC-MS study of their methyl ester mixture[51]. The red algae in general are known for the dominating presence of these fatty acids[52]. More importantly, from the alga are reported[53] new bromotriterpene polyethers named as armatols A-F (**123-128**) that represent a new class of rearranged bromotriterpenes. The precursor 6*S*, 7*S*, 10*R*, 11*R*, 14*R*, 15*R*, 18*S*, 19*S*-squalene tetraepoxide (II), itself from sqalene–I was postulated as the common precursor that could lead to armatols A-F on one hand and the *Laurencia* metabolites on the other.

Acanthophora spicifera: The NIO group also took up a detailed chemical examination of this alga since its hexane and chloroform solubles showed antifertility activity, and the crude MeOH extract, antiviral activity against SFV (Semliki Forest Virus)[3]. Elsewhere[54], the alga is also reported to possess *in vitro* antimicrobial activity against *Staphylococcus aureus*, *Candida albicans* and *Mycobacterium smegmatis*. From this alga, apart from the simple aliphatic stearic and palmitic acids and an unresolved mixture of the latter with arachidic and behenic acids[55] and lauric acid and a phthalate, cholesterol and its related sterols **129** and **130** were also reported[56]. Cholest-4-en-3-one **129** is known, but cholest-4-en-3α, 6β-diol **130** is unique. The sterol fraction of this alga also contained[57] 5α-cholestan-3,6-dione **131** and the novel 11α-hydroxycholestan-3,6-dione **132** (ref. 58). The polar fraction of the alga contained[59] the known but rare dipeptide diaurantiamide acetate **133** along with its diastereo isomer **134**, which is new. The former compound was earlier found in a few land plant families.

Hypnea musciformis: This alga from India also gave the 3,6-diketo-5α-steroids, e.g., **135** whose structure was determined by X-ray crystallography[60], and the diketone **136** with the extra 11α-OH in the sterol ring system. These are accompanied in the alga by the 7-keto-5β-compounds **137** (ref. 61) and **138** (ref. 62), both functionalized at C-11. The uniqueness



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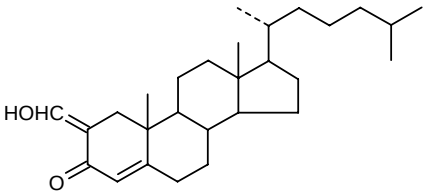

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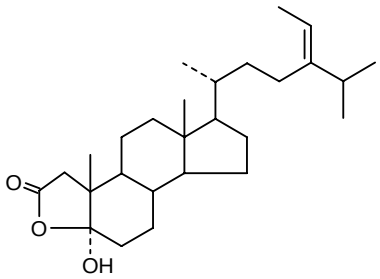

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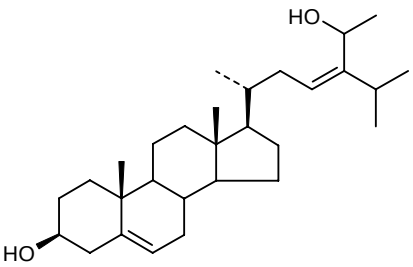

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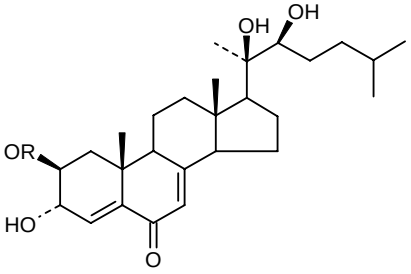
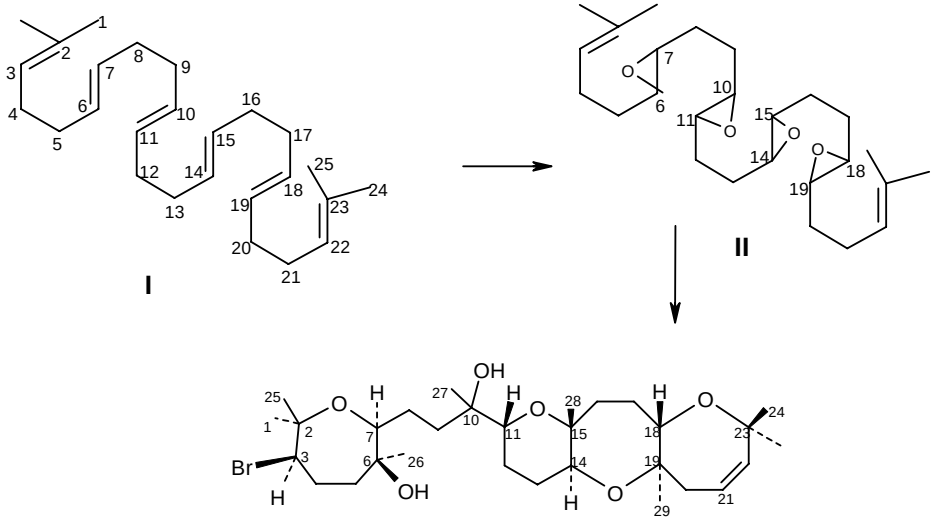


121 R=H
122 R=Ac



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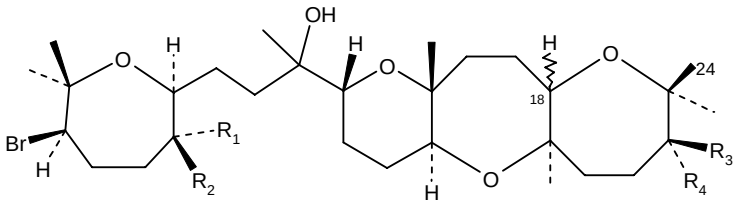
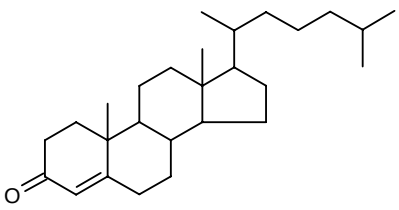


	R_1	R_2	R_3	R_4	18-H
124	Me	OH	H	Br	β
125	OH	Me	H	Br	β
126	Me	OH	Br	H	β
127	OH	Me	Br	H	β
128	Me	OH	H	Br	α



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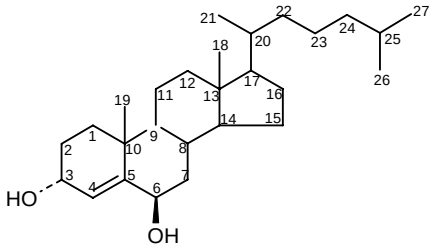


130

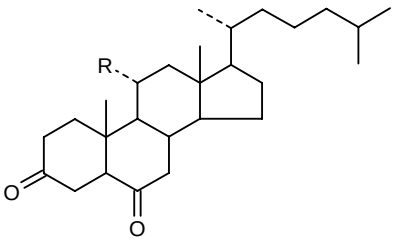
of these structures is, however, the Δ^3 in the former and the complete absence of C-3 functionalisation in the latter, a feature not so far found in marine sterols, and points to a biogenetic migration of Δ^3 to the Δ^2 position within the alga.

Recently, the alga collected from the Atlantic coast of Morocco yielded[63] the 3,6-diketosteroid **139** containing C-20 hydroxylation and an inseparable mixture of **140** and its 22,23-dihydro analogue **141**. The steroid **139** exhibited antielastase activity against

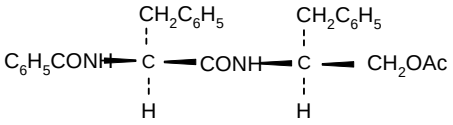
porcine pancreas elastase (PPE). A related steroid **142**, a Δ^5-3,7-dione has recently been reported[64] from the Arabian Sea red algal species of *Melanothamus somalensis*. A group of related sterols is reported recently from *Galaxaura marginata* from Taiwan. The C-24 and C-25 hydroperoxides **143-146** (ref. 65) and **147, 148** and the 24-25 epoxide **149** (ref. 66) indicate that the side chain elaboration in these sterols proceeds through activation from the Δ^{24}.

Amphiroa fragilissima: The crude extract of this alga exhibited oxytocic and spasmogenic activity[3], attributed[67] to the presence of histamine **150**.

Nitophyllum marginatum: This alga collected from the Gulf of Mannar (Mandapam coast) afforded[68] four known compounds, *p*-hydroxybenzaldehyde **151**, 1-methyl-2,3,5-tribromoindole **152**, *p*-methoxybenzyl alcohol **153**, and methylenebisphenol **154**; of these, compound **151** is known



131 R=H
132 R=OH



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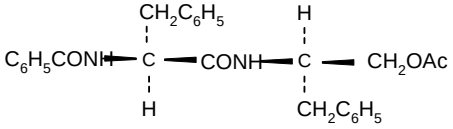

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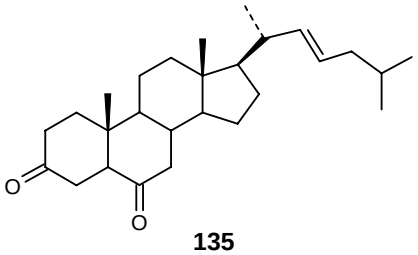
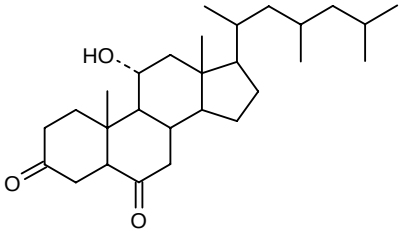


135



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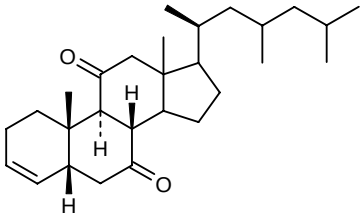

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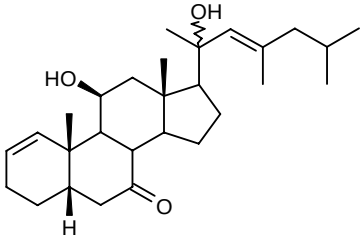

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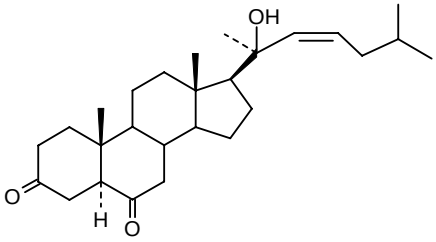

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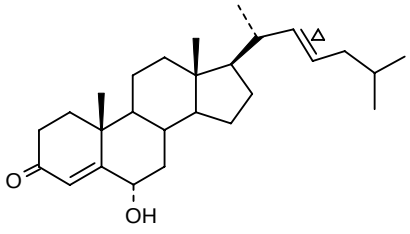
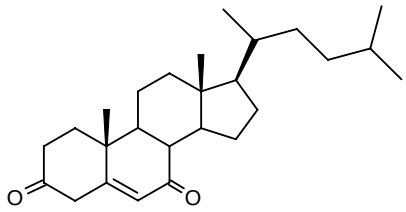


140, 141

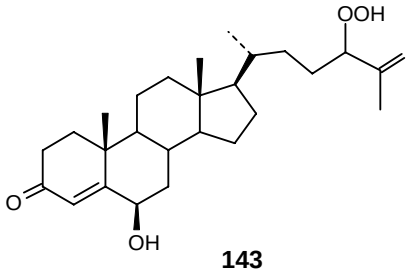
from *Pseudomonas*[69] and *Chromobacter*[70] bacteria, and **152** and **153** from the red alga *Laurencia brongniati*[71].

Gracilaria edulis*:* This alga, of prolific occurrence in the Gulf of Mannar waters is the mainstay of the Indian agar industry operating principally from the Tamil Nadu state. In a series of papers, the IICT group reported[72,73,74] minor C_{29} sterols of the poriferasterol group, viz., clinosterol **155**, its unique $\Delta^{9(11)}$ analogue **156** and five other sterols **157-161** with changing A/B ring oxidation pattern. Oxidation at C-11 was earlier noticed in the sterol **135** isolated from another red algal species *Hypnea muciformis*[61]. This species is also reported as *Polycavernosa asudii* in literature. A Japanese group reported[75] a new class of bioactive triterpenic polyethers named as cavernosides.

Aplysia dactylomela **(Sea hare)**: The mollusks feeding on algae are known to concentrate their metabolites in the gut, perhaps as chemical defence mechanism. Working on the sea hare collected from the Bahamas coast, the Schmitz research group had



142



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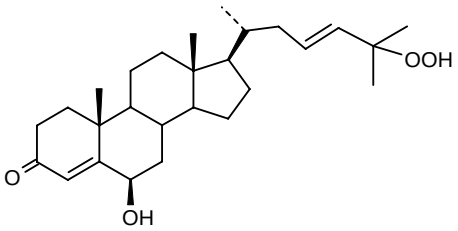

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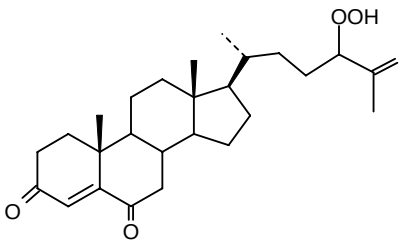

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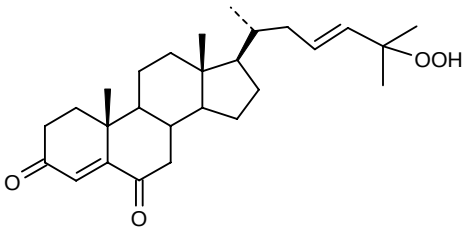

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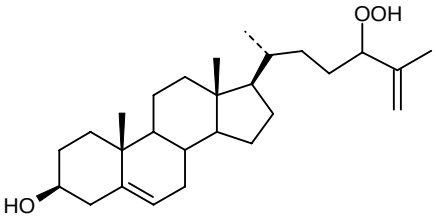

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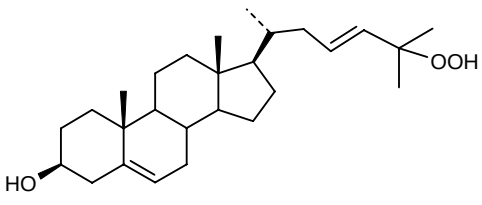

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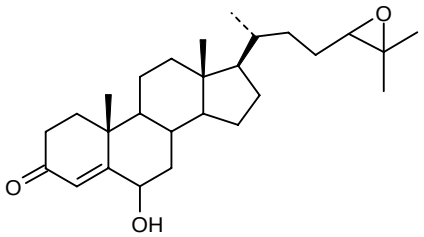

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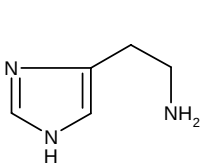

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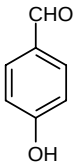

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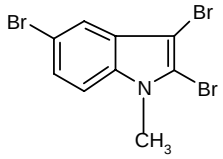

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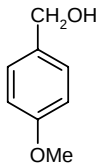

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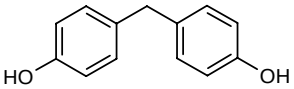

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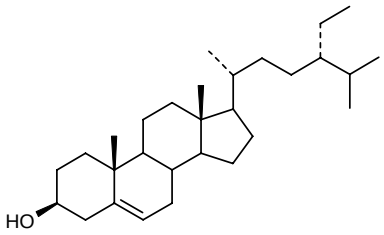

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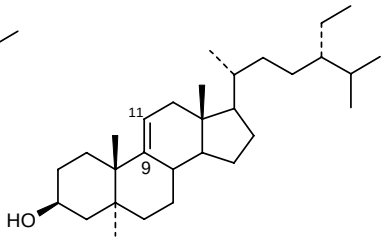

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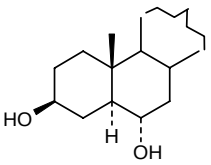

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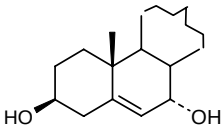

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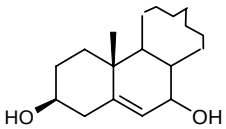

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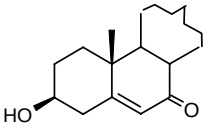

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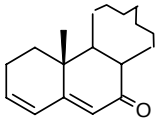
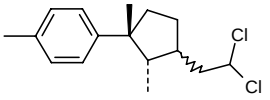
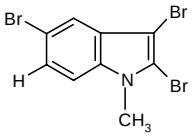


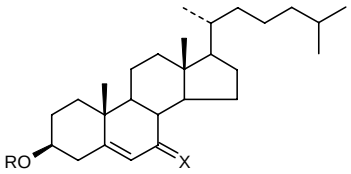
161



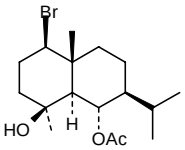
162



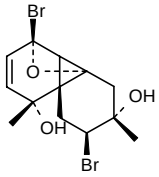
163



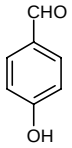
164 R=H; X=2H
166 R=H; X=O



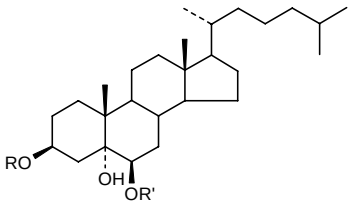
165



167



168



169 R=Ac; R'=H
170 R=R'=H

reported extensively on its halogenated metabolites, some of which have pharmacological activity[76]. The organism, collected from the Gulf of Mannar by Rao's group gave nine compounds **162-170** (ref. 77), two of which **163** and **165** were new. The known compounds were *p*-hydroxy benzaldehyde **168**, 2,3,5-tribromo-N-methyl indole **163**, a chamigrene **165** and cholesterol and three other cholesterol related steroids **166**, **170** and **169**. Of the two new compounds, **165** which is a selinane is the stereoisomer of austradiol aceate. The other, 16,16-dichlorohomolaurane **162**, as indicated by the authors themselves, raises the question of whether it is a bonafide metabolite or an artifact, formed possibly by substitution of bromide ion by the $CHCl_2$ group or a simple addition of the solvent CH_2Cl_2 across a terminal methylene group during the isolation procedure.

Future Research

The marine algae have yielded, in India, several classes of compounds most notably sesquiterpenes, diterpenes and sterols. Even so, the investigations so far done should be rated as meagre, considering the extensive marine algal resource India enjoys in terms of the biomass, species diversity, and unique ecological niches along its long coastline. *Chondria armata* is unique for its triterpene polyethers[53]. A genus closely related to *Chondria* is *Laurencia*, both of which belong to the Rhodomelianaceae family of the Order, Ceramiales (Red Algae). The *Laurencia* species have been prolific sources of unique secondary metabolites. From *L. viridis*, *L. obtusa*, *L. thysifera*, and *L. omaezakiana*, at the global level, have been reported biologically active triterpene polyethers. A unique lanostanoid lactone is reported from *Hypnea cerricornis* from the South China Sea. Hence, chemical examination of these and related Indian species should be expected to be rewarding.

Triterpenes of the cycloartenol class are unique to the green algae, as they are so far known confined to the terrestrial plants notably of the jack fruit plant family. The cycloartenol triterpenes of the green algae are sulfate esters and inhibit protein tyrosine kinase pp 60 enzyme. They were found in *Tricleocarpa fragilis* of Hawaii islands, and *Tydemania expeditionis*. Another green algal species, *Monostroma nitidum* yielded a friedelin triterpene, so far confined to land plants (cork of the European oak). Hence, the chemical examination of *Tydemania expeditionis* occurring on the Andaman and Nicobar island coast, and *Monostroma* sp. occurring on major part of the Indian west coast should also be expected to be interesting.

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