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Terpenoid and Steroid Constituents of the Indian Ocean Soft Coral *Sinularia maxima*

Ammanamanchi S.R. Anjaneyulu,* Kadali S. Sagar and Mukku J.R.V. Venugopal

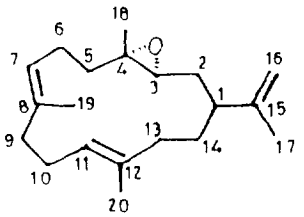
Department of Organic Chemistry, School of Chemistry, Andhra University
Visakhapatnam 530 003, India.

Abstract : The Indian Ocean soft coral *Sinularia maxima* furnished nine terpenoids (**A** to **D**, **G** to **I**) and steroids (**E** and **F**) which include two new sesquiterpenes (**B** and **C**), two 5α,8α-epidioxysterols (**E** and **F**) and a novel tetracyclic diterpenoid, isomandapamate (**D**).

The soft corals (Coelenterata) are a rich source of terpenoids, polyhydroxysterols and others. Soft corals of *Sinularia* genus are of prolific occurrence with 90 species known of which about 35 species have been chemically examined[1-6].

In our continuing interest on the bioactive secondary metabolites of the soft coral species of Indian Ocean[6-11], we have taken up the chemical examination of *Sinularia maxima* collected from Andaman and Nicobar group of Islands from which the isolation and structure elucidation of two new 3β-hydroxy-5α,8α-epidioxysterols, with cyclopropane ring at the carbons 22 and 23 of the side chain has been recently reported[11]. A further detailed chromatographic separation of the residue from the ethyl acetate extract of the soft coral over a column of silica gel resulted in the isolation altogether nine (**A** to **I**) pure compounds in addition to a mixture of monohydroxysterols.

Four (**B**, **C**, **G** & **I**) of the seven compounds happened to be sesquiterpenoids of which two (**G** and **I**) were characterised as the known aromadendranediol (**7**) and alloaromadendranediol (**9**) while the other two have been characterised as the corresponding new monomethyl ethers (**B**,



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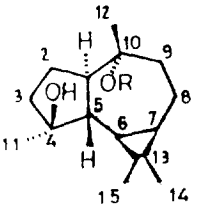

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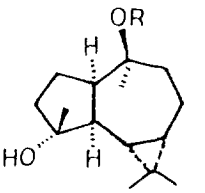
7 R = H



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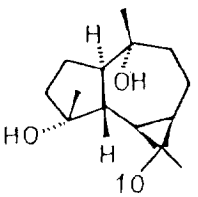
9 R = H



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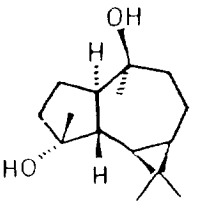

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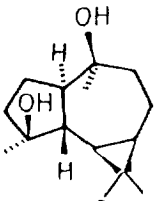

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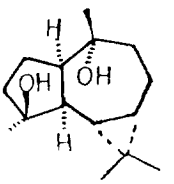

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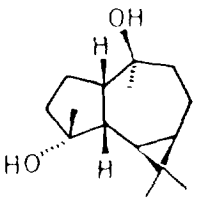

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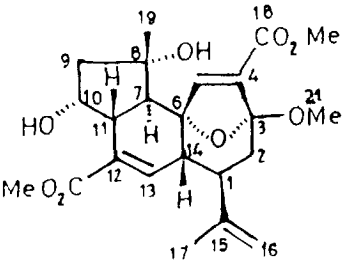

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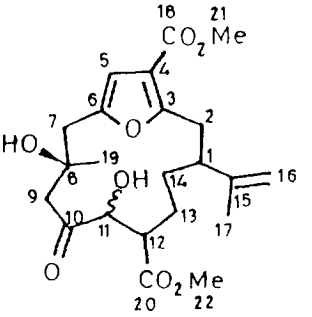

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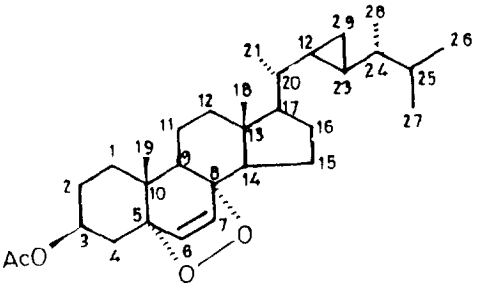

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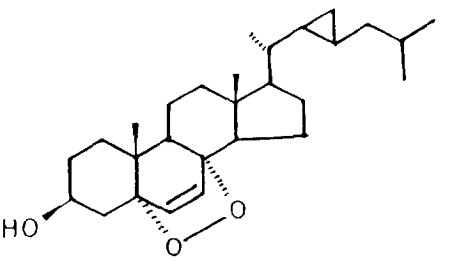

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2) and (**C, 3**). Three are diterpenoids of which two are 3,4-epoxycembrene-A (**A, 1**) and a furanocembranoid methyldiester (**H, 8**) while the third has been characterised as a new tetracyclic diterpenoid designated as, isomandapamate (**D, 4**). Compounds (**E** and **F**) have been recognised as the new 5α,8α-epidioxysterols, namely 5α,8α-epidioxy-23-demethylgorgost-6-ene-3β-yl acetate (**5**) and 5α,8α-epidioxy-23,24-didemethylgorgost-6-ene-3β-ol (**6**) respectively.

Compound **A**, colourless oil, $[\alpha]_D^{27}$ + 50.9°, $C_{20}H_{32}O$, M^+ 288 was characterised as (1R,3S,4S,7E,11E)-3,4-epoxycembra-7,11,15-triene (**1**) by comparing its physical and spectral data (see experimental) with those reported in literature[12].

Compound **G** (**7**) colourless needles from hexane-acetone, m.p. 135-37°C, $[\alpha]_D^{27}$ -22.6° $C_{15}H_{26}O_2$, m/z 220 ($M^+ - H_2O$) and compound **B** (**2**) colourless oil $[\alpha]_D^{27}$ -18.2°, $C_{16}H_{28}O_2$, m/z 252 were recognised as aromadendrane derivatives, the former being a diol and latter its new monomethyl ether which exhibited similar spectral characteristics. Both showed hydroxylic absorption (3380 and 3360 cm^{-1} respectively) in their IR spectrum but no UV absorption above 210 nm.

Their ^1H NMR spectra (Table I) are reminiscent of aromadendrane skeleton[13] showing both the cyclopropyl protons characteristically between δ 0.42 to 0.61, two tertiary methyls around at δ1.05 and two tertiary methyls connected to oxygenated carbons between δ 1.11 to 1.24. Compound **B**, in addition, exhibited a methoxyl at δ 3.19. In conformity the ^{13}C NMR spectra (Table **II**) showed two oxygenated carbons at δ 74.9 (s) and 80.2 (s) in compound **G** and three in **B** at δ 52.2 (q), 78.9 (s) and 80.2 (s).

A search in literature revealed that four isomers (**7, 10, 11 & 12**) of 4,10-aromadendranediols with trans ring junction at C_1 and C_5 have been reported[13]. While all these four compounds have been synthetically derived, two were isolated from the soft coral *Sinularia mayi*[13] the major compound being the enantiomer of (**7**) and the minor compound being (**10**). A third minor diol (**13**) isolated along with the above two (**7 & 10**) was tentatively assigned to have alloaromadendranediol with 1,5-cis junction. An enantiomer of this diol (**14**) was reported from the Jamaican aromatic herb *Ambrosia paruviana*[14] whose structure and stereochemistry were established by a study of its spectral data.

The ^1H (Table **I**) and ^{13}C NMR (Table **II**) spectral data of compound **G** agreed perfectly with those of 4β,10α-aromadendranediol (**7**) showing their identity. With respect to the structure of compound **B**, the position of methoxyl, either at C_4 or C_{10} need to be located. The

Table I. ^{1}H NMR Data of Compounds **B, C, G, I, 7, 13 and 14** in $CDCl_3$, TMS as reference, Chemical shift (δ), J in brackets in Hz

Assignment	B[a]	C[a]	G[a]	I[a]	7[b]	13[b]	14[c]
6-H	0.42 (dd, 11,8)	0.02 (dd, 12, 8)	0.42 (dd) 11, 8)	0.02 (dd, 11, 7.5)	0.30 - 1.0 (Cyclopropyl protons)	0.02 (dd, 10, 6)	0.00 (dd, 11, 9.7)
7-H	0.61 (ddd, 13, 8, 5)	0.62 (ddd, 13, 8, 5)	0.55 (ddd, 12, 8, 5)	0.62 (ddd, 13, 8, 5)		0.63 (m)	0.62 (ddd, 11, 9, 6)
11-H_3	1.13 (s)	1.08 (s)	1.19 (s)	1.21 (s)	1.17 (s)	1.22 (s)	1.19 (s)
12-H_3	1.24 (s)	1.34 (s)	1.24 (s)	1.35 (s)	1.25 (s)	1.36 (s)	1.33 (s)
14-H_3	1.04 (s)	1.04 (s)	1.05 (s)	1.05 (s)	1.04 (s)	1.06 (s)	1.02 (s)
15-H_3	1.06 (s)	1.06 (s)		1.06 (s)			1.03 (s)
1-H		2.61 (m)		2.50 (m)			2.47 (m)
-OMe	3.14 (s)	3.12 (s)					

a : Spectra were recorded at 400 MHz, b from ref. 13, c from ref. 14.

Table II. ^{13}C NMR Data of Compounds **B, C, G, I, 7, 13 and 14** in $CDCl_3$ in ppm

Carbon No.	B[a]	C[a]	G[a]	I[a]	7[b]	13[b]	14[c]	Multiplicity*
1	48.2	48.1	56.3	53.9	53.9	54.0	53.8	d
2	24.1	25.6	23.7	25.5	25.5	25.1	25.4	t
3	41.1	37.1	41.1	37.5	37.5	37.4	37.6	t
4	80.2	82.0	80.2	82.1	82.4	82.1	81.9	s
5	48.2	47.9	48.3	47.7	48.0	47.8	47.5	d
6	28.2	24.7	28.3	25.2	25.2	25.3	25.1	d
7	26.7	28.5	26.6	28.8	28.5	28.8	28.8	t
8	19.7	18.1	20.1	18.8	18.7	18.9	18.7	t
9	41.1	37.1	44.4	38.0	38.0	37.9	38.0	t
10	78.9	78.2	74.9	74.4	74.4	74.3	74.1	s
11	24.4	25.5	25.4	25.4	25.4	25.6	25.1	q
12	23.6	33.7	20.2	32.1	32.1	32.2	32.0	q
13	19.6	18.8	19.5	18.8	18.8	18.6	18.6	s
14	16.4	16.2	16.3	16.2	16.2	16.4	16.1	q
15	28.5	28.9	28.6	28.6	28.8	28.5	28.5	q
OMe	52.2	50.6	--	--	--	--	--	q

a : Spectra were recorded at 100 MHz, b from ref. 13, c from ref. 14, * : Multiplicities are assigned by DEPT spectrum

carbon resonances of compound **B** (Table **II**) agreed closely with those of **G**, but for the variation in the α or β carbons to the hydroxyl or methoxyl functionalities. The effect of C_{10} methoxyl was noticed on C_1 (-8.1), C_9 (-3.3), C_{10} (+4) and C_{12} (+3.4), while the values of C_3, C_4, C_5 and C_{11} remained same in both the compounds, having hydroxyl in both at C_4. The structure and stereochemistry of new monomethylether could thus be established as 4β,10α-aromadendranediol-10-methylether (**2**).

Compound **I** (**9**) colourless needles from hexane - acetone, m.p. 114-15°C, $[\alpha]_D^{27}$ -10°, $C_{15}H_{26}O_2$, m/z 220 ($M^+ - H_2O$) compound **G** (**3**) colourless oil, $[\alpha]_D^{27}$ -27°, $C_{16}H_{28}O_2$, M^+ 252 were recognised as alloaromadendrane derivatives[13,14], the former being a diol and the latter its new monomethylether. Both showed hydroxylic absorption (3380 and 3360 cm^{-1} respectively) in their IR spectra but no absorption above 210 nm in their UV spectra.

The ^1H NMR spectra (Table **I**) of both the compounds exhibited the two cyclopropyl protons, one at higher field around δ 0.02 and the other at lower field δ 0.63 characteristic of 1,5 cis alloaromadendrane skeleton[13,14]. Both exhibited two tertiary methyls between δ 1.04 to 1.06 and two more tertiary methyls connected to oxygenated carbons between δ 1.08 to 1.35. Compound **C** exhibited a methoxyl at δ3.12 (s). The ^{13}C NMR spectra (Table **II**) showed two oxygenated carbons at δ 74.4 (s) and 82.1 (s) in compound **I** and three such carbons at δ 50.6 (q), 78.2 (s) and 82.0 (s) in compound **C** in support of the above functionalities. The ^1H and ^{13}C NMR data (Table **I** and **II**) of compound **I** agreed very well with the alloaromadendranediols (**13** & **14**) showing their identity. It may be pointed out that the resonance of C_{12} appeared at δ 32.1 in compound **I** while the same in compound **G** appeared at δ 20.2 indicating that the C_{12} -H_3 is α-equatorial in compound **I** and β-axial in compound **G**[13,14].

The ^1H and ^{13}C NMR spectral data (Table **I** and **II**) of the new monomethylether (**C**) agreed closely with those of compound **I** except for the difference in the α,β-carbons to the methoxyl as found in compound **B** compared to compound **G**. The change in the chemical shifts of carbons C_1 (-5,8), C_9 (-0.9), C_{10} (+3.8), and C_{12} (+1.6) noticed between compounds **I** and **C** located the methoxyl at C_{10} in compound **C** and the resonances of C_3, C_4, C_5 and C_{11} remained more or less same, with a hydroxyl in both at C_4. The structure and stereochemistry of the new monomethylether could thus be established as 4α, 10β-alloaromadendranediol-10 monomethylether (**3**).

Compound **H** (**8**) colourless needles from hexane - acetone, m.p.

171-72°C, $[\alpha]_D^{27}$ -8.5°, $C_{22}H_{28}O_8$, m/z 402 ($M^+ - H_2O$) was recognised as a furanocembranoid diterpene from its spectral characteristics. Its IR spectrum showed hydroxylic absorption (3460 cm^{-1}), strong and broad carbonyl absorption (1715 cm^{-1}), olefinic unsaturation (1640 and 900 cm^{-1}) besides strong bands at 1608 and 1560 cm^{-1} characteristic of an aromatic or heteroaromatic system in the molecule.[20] the strong absorption between 1000 to 1100 cm^{-1} suggested ether linkage in the molecule. It exhibited UV absorption at 216 and 245 nm indicating the presence of conjugation. It formed a monoacetate $C_{24}H_{30}O_9$, M^+ 462, $[\alpha]_D^{27}$ -11.6° which still showed hydroxylic absorption at 3460 cm^{-1} indicating the presence of at least two hydroxyls, one acylable and the other nonacylable.

The functional groups of this polyoxygenated molecule could be derived from its ^1H NMR spectrum (Table III) which showed the presence of two methyl esters accounting for four oxygens of the molecule. One carbinolic methine proton over a secondary hydroxyl could be noticed at δ 4.60 (s) (which shifted down field to 5.35 in its acetate) suggesting the presence of only one secondary hydroxyl in the molecule and its appearance as a singlet indicated the absence of any neighbouring protons in its vicinity. The ^1H NMR spectrum also showed an isopropenyl group (δ 1.80, 3H, s, and 4.89 and 4.94 each 1H, s) as noticed in cembranoid derivatives[15-18] and a tertiary methoxyl at δ 1.25 connected to an oxygenated carbon bearing possibly a tertiary hydroxyl. Six of the eight oxygens of the molecule thus accounted for, four in carbomethoxyls and two in hydroxyls, at least one of the remaining oxygenes might be locked up in a furan ring which could also account for the IR, UV data. The proton that appeared at δ 6.55 as singlet could be taken a β-proton of trisubstituted furan ring[15-18]. Another proton at 6.98 as triplet could be taken for the β-proton of an α,β-unsaturated carbonyl function[15].

Evidence for the remaining oxygen as well as other functionalities of the molecule could be derived from its ^{13}C NMR spectrum (Table III). Besides the two ester carbonyls at δ 163.9 (s) and 167.1 (s), there appeared a keto carbonyl at δ 209.2 (s) with which all the oxygens of the molecule were accounted for. Of the six oxygenated carbons noticed in the molecule, two at δ 51.4 (q) and 51.9 (q) were assigned to the ester methyl carbons, two at δ 74.1 (s) and 73.5 (d) for the carbons bearing tertiary and secondary hydroxyls and two more at δ 160.1 (s) and 151.4 (s) accounted for the carbons of the furan ring. There appeared eight signals for olefinic carbons, four 160.1 (s), 114.6 (s), 108.9 (d) and

Table III. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) Data of the Compound H and 8 [Chemical shift δ (ppm), Multiplicity, J in brackets in Hz] in $CDCl_3$

Assignment	δ_C		δ_H	
	H	8	H	8
1	43.5, d	43.3, d	2.55 (m)	2.55 (m)
2	30.7. t	30.7, t	3.32 (dd, 15, 2)	3.32 (dd, 15, 2)
			2.84 (dd, 15, 10)	2.85 (dd, 15, 11)
3	160.1, s	160.1, s		
4	114.6, s	114.8, s		
5	108.9, d	108.8, d	6.55 (s)	6.6 (s)
6	151.4, s	151.2, s		
7	30.6, t	30.6, t	3.14 (d, 18)	3.16 (d, 18)
			2.4 (d, 18)	2.55 (d, 18)
8	74.1, s	74.2, s		
9	46.3, t	46.4, t	3.5 (d, 18)	3.5 (d, 17.5)
			3.4 (d, 18)	3.4 (d, 17.5)
10	209.2, s	209.7, s		
11	73.5, d	73.5, d	4.6 (s)	4.6 (s)
12	125.3, s	125.4, s		
13	143.5, d	143.6, d	6.98 (t, 7)	6.98 (t, 7)
14	42.0, t	42.2, t	2.30 (m)	2.36 (m)
15	145.5, s	145.5, s		
16	111.7, t	111.9, t	4.94 (s)	4.97 (s)
			4.89 (s)	4.89 (s)
17	20.7, q	20.9, q	1.80 (s)	1.83 (s)
18	163.9, s	163.9, s		
19	24.9, q	24.4, q	1.25 (s)	1.24 (s)
20	167.1, s	167.2, s		
21	51.4, q	51.4, q	3.75 (s)	3.80 (s)
22	51.9, q	52.1, q	3.70 (s)	3.75 (s)

151.4 (s) of the furan ring, two 145.5 (s) and 111.7 (t) of the isopropenyl group and the remaining two 125.3 (s) and 143.5 (d) of another double bond revealing thus all the functional groups. The compound was therefore, considered to be a bicyclic polyoxygenated cembranoid diterpene with a furan skeleton very much related to that of the furanocembranoid, pukalide which was first reported from *Sinularia abrupta*[16] in 1975. Since that time several related compounds such as 11,12-epoxypukalide[17], 13-acetoxypukalide[18] and 13-acetoxy-11,12-epoxypukalide[18], lophotoxin and others have been reported. When the structure of this furnaocembranoid derivative was almost finalised, a diterpene (8) having similar physical and spectral characteristics has been very recently reported from the soft coral *Sinularia dissecta*[15] along with mandapamate (15), the first member of novel tetracyclic diterpenoids. The physical and spectral characteristics (Table III) of compound H

matched perfectly with those of (8) suggesting their identity which was further conformed by comparison with an authentic smple[15].

Compound D **(4)** colourless viscous oil, $[\alpha]_D^{27}$ + 84.7°, $C_{23}H_{30}O_8$, M^+ 434 was recognised as a new tetracyclic diterpene isomeric with mandapamate (15) recently isolated from *S. dissecta*[19] and thus named as isomandapamate (D).

Its IR spectrum showed strong band for hydroxyl (3480 cm^{-1}), an α,β-unsaturated ester (1715 cm^{-1}) besides olefinic unsaturation at 1640 and 900 cm^{-1}. It exhibited absorption in UV at 216 nm indicating the presence of conjugation. Like compound **H (8)**, it was also found to be a highly oxygenated compound requiring nine degrees of unsaturation.

Its ^1H NMR spectrum (Table **IV**) showed two methyl esters at δ 3.78 (s) and 3.8 (s) besides an aliphatic methoxyl at δ 3.40 (s). Five of the eight oxygens could thus be accounted for in the above functional groups. Its ^1H NMR spectrum further showed an isopropenyl group [δ 1.68 (3H, s) and 4.80 and 4.89 (each 1H, s)] and a tertiary methyl connected to an oxygenated carbon at δ 1.60 as noticed in compound **H**. One carbinolic methine proton was noticed at δ 4.64 accounting for a secondary hydroxyl (moving down field to 5.32 in its monoacetate, oil, $C_{25}H_{32}O_9$, $[\alpha]_D^{27}$ + 75.5°). Two more olefinic protons were noticed at δ 6.72 (s) and 6.71 (d, J = 2 Hz) accounting for the protons of two $\alpha\beta$-unsaturated ester functionalities. In the ^{13}C NMR spectrum (Table **IV**) it exhibited two ester carbonyls [δ 162.0 (s) and 166.8 (s)] six olefinic carbons [135.0 (s), 150.5 (d), 133.6 (s), 143.2 (d), 113.6 (t) and 144.5 (s)] accounting together for 5° of unsaturation suggesting the molecule to be tetracyclic to account for the remaining 4° of unsaturation. The molecule showed seven oxygenated carbons, three at δ 51.8 (q), 51.9 (q) and 51.1 (q) for 2 x COOMe and OMe carbons and two at δ 67.5 (d) and 77.5 (s) for the carbons connected to the secondary and tertiary hydroxyls. The signals at δ 84.8 (s) and 111.2 (s) both indicated linkages to the tertiary carbons, the one at lower field accounting for a doubly oxygenated carbon.

As has been mentioned above, the recently isolated mandapamate **(15)** was the first tetracyclic diterpenoid to be isolated from this source. The proton NMR spectral data of compound **D** and mandapamate **(15)** have been found to be indistinguishable. Their ^{13}C NMR spectral data (Table **IV**) also agreed very well except for the value of one olefinic carbon C_5 appearing at δ 150.5 in compound **D** and at δ 154.4 in mandapamate **(15)**. This subtle difference in the carbon chemical shift of C_5 which might be normally attributed to E, Z configurational change in a double bond

Table IV. ^{13}C [100 MHz : δ in ppm (mult.)] and ^{1}H [400 MHz : δ in ppm (mult. J in brackets in Hz)] NMR Data. 2D NMR (^{1}H-^{1}H, ^{1}H-^{13}C COSY & NOESY, 90 MHz) Correlation Data of Isomandapamate (**4**) and Mandapamate (**15**) in $CDCl_3$

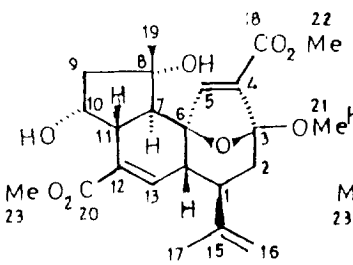
Assignment	δ C		δ H		^{1}H-^{1}H COSY	^{1}H-^{13}C COSY	NOESY	
	4[a]	15	4	15	4	4	4	15
1	43.4	43.2, d	2.20 (m)	2.16 (ddd, 11.6, 11, 6.2)	$2H_2$, 14H	1H - C_1	2 βH, 13H,14H	2 βH, 5H,13H, 14H
2	33.5	33.4, t	1.94 (dd, 13, 5, Hα)	1.94 (dd, 13.1, 11, Hα)	1H, 2β H	2αH - C_2	2 βH,	2β H
			1.65 (dd, 13, 5.2, Hβ)	1.65 (dd, 13.1, 5.2, Hβ)	1H, 2α H	2βH - C_2	2α H, 14H	2α H, 14H
3	111.2	111.1, s						
4	135.0	134.8, s						
5	150.5	154.4, d	6.72 (s)	6.68 (s)	$2Z$-H_3	5H - C_5	--	1H, 7H
6	84.8	84.7, s						
7	52.8	52.6, d	2.73 (d, 13)	2.72 (d, 13.1)	11H	7H - C_7	9 αH	5H, 9 αH
8	77.5	77.5, s						
9	51.5	51.3, t	2.01 (br d, 15, Hα)	2.01 (br d, 14.9, Hα)	10H, 9β H	9α H - C_9	7H, 9β H	7H, 9 βH
			2.22 (dd, 15, 6, Hβ)	2.22 (dd, 14.9, 6, H β)	10H, 9 α H	9β H - C_9	10H, 9α H	10H, 9α H
10	67.5	67.6, d	4.64 (ddd, 6, 3.5, 1.2)	4.62 (ddd, 6, 3.4, 1.1)	$9H_2$, 11H	10H - C_{10}	9β H, 11H	9 βH, 11H
11	47.2	46.9, d	2.52 (m)	2.49 (m)	7H, 10H, 13H	11H - C_{11}	10H, 14H, $19H_3$	10H, 14H, $19H_3$
12	133.6	133.5, s						
13	143.2	143.2, d	6.71 (dd, 3)	6.67 (dd, 3.4, 3)	11H, 14H	13H - C_{13}	1H, 14H, 16a	1H, 14H, 16a
14	43.4	43.2, d	2.28 (m)	2.23 (ddd, 11.6, 3.4, 1.6)	13H, 1H	14H - C_{14}	2 βH, 11H, 16a	2 βH, 11H, 16a
15	144.5	144.2, s						
16	113.6	113.4, t	4.80 (br s, Ha)	4.76 (br s, Ha)	$17H_3$, Hb	16Ha - C_{16}	1H, 14H, 16Hb	1H, 14H, 16Hb
			4.89 (br s, Hb)	4.85 (br s, Hb)	$17H_3$, Ha	16Hb - C_{16}	16Ha, $17H_3$	16Ha, $17H_3$
17	19.8	19.6, q	1.68 (br s)	1.66 (br s)	$16H_2$	$17H_3$ - C_{17}	16Hb	16Hb
18	162.0	162.5, s						
19	27.0	26.8, q	1.60 (s)	1.56 (s)	9β H, 11H	$19H_3$ - C_{19}	9 βH	9β H
20	166.8	166.6, s						
21	51.1	51.8, q	3.40 (s)	3.37 (s)		$21H_3$ - C_{21}		
22	51.9	52.3, q	3.80 (s)	3.78 (s)		$22H_3$ - C_{22}		
23	51.8	52.0, q	3.78 (s)	3.74 (s)		$23H_3$ - C_{23}		

a : From reference 19.

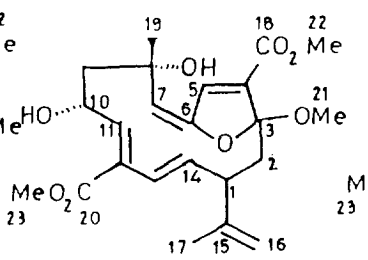
finds no relevance here as both have the same E configuration in the 2,5-dihydrofuran system. As expected, the 2D NMR spectra (^{1}H-^{1}H and ^{1}H-^{13}C COSY) of compound **D** showed the same connectivities as noticed in mandapamate (Table **IV**) except for the difference in ^{1}H-^{13}C COSY that the carbon appearing at δ 150.5 showed connectivity with the proton appearing at δ 6.72 in compound **D** while the corresponding carbon in mandapamate (**15**) at δ 154.4 showed connectivity to the proton at δ 6.68.

A NOESY spectrum of compound D, however, showed the crucial difference from that of mandapamate (**15**). The couplings noticed between the C_5-H and C_1-H and C_5-H and C_7-H in mandapamate were found to be absent in compound D suggesting the possible stereochemical difference at C_3 and C_6 between the two to recognise mandapamate (**15**) and isomandapamate (**4**) (compound D) as diastereomers.

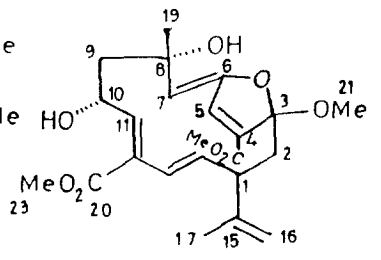
While arriving at the structure of mandapamate (**15**) Venkateswarlu et al[19] suggested that it might have been formed by an intramolecular Diels-Alder cyclisation of the possible hypothetical intermediate (**16**) with 'E' configuration at 6, 7 double bond. It might now be possible that compound D, designated as isomandapamate (**4**) might be considered as a diastereoisomer of mandapamate (**15**) differing at C_3 and C_6 and might have been derived from the hypothetical intermediate (**17**) with 'Z' configuration at 6, 7 double bond by the stereospecific Diels-Alder cyclisation.



15



16



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Compound **E** (**5**) m.p. 148-51°C, $[\alpha]_D^{27}$ + 25.7°, $C_{31}H_{48}O_4$, M^+ 484 and compound **F** (**6**), m.p. 156-58°C, $[\alpha]_D^{27}$ + 16.5°, $C_{28}H_{44}O_3$, M^+ 428, have already been recognised as the new 5 ,8 epidioxysterols, namely 5α,8α-epidioxy-23-demethylgorgost-6-en-3β-yl-acetate (**5**) and 5α,8α-epidioxy-23,24-didemethylgorgost-6-en-3β-ol (**6**) respectively[11].

EXPERIMENTAL

Elemental analyses were determined on a Carlo Erba - 1108 instrument.

IR spectra were recorded on a Perkin-Elmer 841 spectrophotometer. ^{1}H NMR spectra were measured on a Bruker 400 MHz and JEOL JNM Ex-90 spectrometers. ^{13}C NMR spectra were measured on a Bruker 400 MHz spectrometer at 100 MHz and JEOL JNM Ex-90 spectrometer at 22.5 MHz using $CDCl_3$ as solvent and tetramethylsilane as internal reference. Mass spectra were obtained on a JEOL JMS-300 spectrometer. Melting points were determined on VEB-analytic Dreder HMK hot plate and are uncorrected. Optical rotations were determined on a Perkin-Elmer model 141 polarimeter.

Extraction and Isolation. The soft coral *Sinularia maxima* was collected in April 1992 at the Havelock island of the Andaman and Nicobar group of islands in the Indian Ocean. Slices of the soft coral (Ca. 10 kg wet wright) were soaked in ethanol (10 l) at room temperature and the extract was decanted carefully. This process was repeated eight times. The concentrated extract was re extracted into ethyl acetate. The ethyl acetate extract (30 g) was dried over anhydrous $MgSO_4$ and chromatographed over a silica gel column (300 g; 100-200 mesh) using solvents of increasing polarity from hexane through benzene to ethyl acetate. The selected fractions were further purified by passing over a silica gel column or recrystallisation to yield seven pure compounds.

Compound A ***(1R,3S,4S,7E,11E)-3,4-Epoxycembra-7,11,15-triene (1).*** Colourless oil; 500 mg (0.0025%); $[\alpha]_D^{27}$ + 50.9° (C 1.39, $CHCl_3$); Found : C, 83.24; H, 11.01. Calc. for $C_{20}H_{32}O$: C, 83.34; H, 11.12%; IR ($CHCl_3$) : 2980, 1610, 1450, 1370, 1200, 1180, 1090 and 870 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) : δ 1.22 (s, 18-H_3), 1.61 (br s, 17, 19 & 20-H_3), 2.84 (dd, 3-H), 4.65 (br s, 16-H_2) and 5.12 (m, 7 & 11-H) : ^{13}C NMR (22.5 MHz, $CDCl_3$) : 40.4 (d) ppm, 34.6 (t), 63.1 (d), 60.5 (s), 33.7 (t), 23.7 (t), 124.0 (d), 133.2 (s), 39.5 (t), 24.5 (t), 124.2 (d), 135.0 (s), 38.3 (t), 29.8 (t), 148.4 (s), 110.6 (t), 18.4 (q), 17.1 (q), 16.9 (q) and 15.7 (q), (C_1 to C_{20} respectively); EIMS : M^+ 288 (12%), 273 (M^+-CH_3, 24.1%), 247 (M^+ -C_3H_5, 46%), 151 (25.1%), 135 (40%), 107 (45%) and 41 (76%).

Compound B ***4β,10α-Aromadendranediol-10-methylether (2).*** Colourless oil; 20 mg (0.001%); $[\alpha]_D^{27}$ -18.2° (C 0.50, $CHCl_3$) ; Found : C, 76.12; H, 11.0. Calc. for $C_{16}H_{28}O_2$: C, 76.19; H, 11.11%; IR ($CHCl_3$) : 3360 (OH), 1450, 1370, 1160 and 900 cm^{-1}; ^{1}H and ^{13}C NMR data (see Table I and II); EIMS : M^+ 252 (7.1%), 221 (M^+ -OCH_3, 30.6%), 206 (221-CH_3, 24.1%), 203 (221-H_2O, 33.3%), 188 (10.2%), 178 (13.6%), 148 (3.6%), 93 (30.2%) and 41 (93%).

Compound C ***4α,10β-Alloaromadendranediol-10-methylether (3).*** Colourless oil; 25 mg (0.00125%); $[\alpha]_D^{27}$ -27° (C, 0.58, $CHCl_3$); Found : C, 76.01; H,

11.01. Calc. for $C_{16}H_{28}O_2$: C, 76.19; H, 11.11%; IR ($CHCl_3$) : 3360 (OH), 1450, 1370, 1160 and 900 cm^{-1}; ^1H and ^{13}C NMR data (see Tables I and II); EIMS : M^+ 252 (7.2%), 221 (M^+ $-OCH_3$, 39.6%), 206 (221 $-CH_3$, 24.1%), 203 (221-H_2O, 33.3%), 188 (19.2%), 178 (13.6%), 148 (36%), 93 (30.2%), 85 (40.5%) and 41 (100%).

Compound D ***Isomandapamate (4).*** Colourless oil; 40 mg (0.002%); $[\alpha]_D^{27}$ +84.7° (C 0.25, $CHCl_3$); Found C, 63.58; H, 6.82. Calc. for $C_{23}H_{30}O_8$: C, 63.59; H, 6.91%; UV ($CHCl_3$) : 216 nm ; IR ($CHCl_3$) : 3480 (OH), 1715 ($COOCH_3$), 1640, 1430, 1330, 1200 and 900 cm^{-1}; ^1H and ^{13}C NMR and 2D NMR data (see Table IV); EIMS : M^+ 434 (4%), 403 (M^+ $-OCH_3$, 11.9%), 385 (403-H_2O, 14.2%), 370 (7.4%), 316 (12.3%), 149 (15.9%), 139 (11.1%), 71 (70.5%) and 41 (100%).

Acetylation of the compound D. To the compound (10 mg) in dry pyridine (1 ml) was added 1 ml of acetic anhydride and the mixture was allowed at room temperature for 12 hours. After usual workup it yielded a monoacetyl derivative which was purified on silica gel column afforded as colourless oil (8 mg); $[\alpha]_D^{27}$ +68.2° (C, 0.35, $CHCl_3$); $C_{25}H_{32}O_9$; UV ($CHCl_3$) : 216 nm; IR ($CHCl_3$) : 3480 (OH), 1725 and 1760 cm^{-1} (OAc); ^1H NMR (90 MHz, $CDCl_3$) : δ 1.60, 1.68, 2.01, 3.40, 3.78 and 3.80 (each 3H, s), 4.80 and 4.89 (each 1H, s), 5.32 (m), 6.71 (d, J = 2 Hz) and 6.72 (s).

Compound E ***5α,8α-Epidioxy-23-demethylgorgost-6-ene-3β-yl acetate (5).*** Colourless needles from methanol; 25 mg (0.00125%); m.p. 148-51°C; $[\alpha]_D^{27}$ + 25.7° (C 0.28, $CHCl_3$); Found : C, 76.83; H, 9.78. Calc. for $C_{31}H_{48}O_4$: C, 76.85; H, 9.91%; IR ($CHCl_3$) : 1720 and 1280 cm^{-1} (OAc); ^1H NMR (400 MHz, $CDCl_3$) : δ 0.13 (m, 29-H_2), 0.31 (m, 22-H), 0.54 (m, 23-H), 0.79 (s, 18-H_3), 0.86 (d, J = 7 Hz, 28-H_3), 0.89 and 0.92 (each d, J = 7 Hz, 26 & 27-H_3), 0.91 (s, 19-H_3), 0.92 (d, J = 7 Hz, 21-H_3), 5.0 (m, 3-H), 6.25 (d, J = 8 Hz, 6-H) and 6.51 (d, J = 8 Hz, 7-H); ^{13}C NMR (22.5 MHz, $CDCl_3$) : 39.4 (t) ppm, 30.0 (t), 69.5 (d), 51.1 (t), 79.4 (s), 130.9 (d), 135.0 (d), 81.7 (s), 34.3 (d), 36.9 (s), 20.8 (d), 39.5 (t), 44.9 (s), 51.3 (d), 28.7 (t), 23.4 (t), 57.3 (d), 12.5 (q), 18.0 (q), 39.9 (d), 19.0 (q), 25.1 (d), 24.1 (d), 45.0 (d), 33.2 (d), 18.5 (q), 20.6 (q), 16.1 (q), 10.5 (t), 170.0 (s) and 21.2 (q), (C_1 to C_{31} respectively); EIMS : M^+ 484 (0%), 424 (M^+ -AcOH, 39.6%), 392 (424 $-O_2$, 51.2%), 253 (393 $-C_{10}H_{19}$, 20.3%) and 251 (253-H_2, 18.4%).

Compound F ***5α,8α-Epidioxy-23,24-didemethylgorgost-6-ene-3β-ol (6).*** Colourless needles from methanol; 20 mg (0.001%); m.p. 156-58°C; $[\alpha]_D^{27}$ -16.5° (C 0.29, $CHCl_3$); Found : C, 77.5; H, 10.2. Calc. for $C_{28}H_{44}O_3$: C, 78.5; H, 10.28%; IR ($CHCl_3$) : 3380 cm^{-1} (OH); ^1H NMR (400 MHz, $CDCl_3$)

: δ 0.12 (m, 28-H_2), 0.30 (m, 22-H), 0.54 (m, 23-H), 0.78 (s, 18-H_3), 0.89 (d, J = 7 Hz, 27-H_3), 0.91 (s, 19-H_3), 0.91 (d, J = 7 Hz, 26-H_3), 0.92 (d, J = 7 Hz, 21-H_3, 3.98 (m, 3-H), 6.25 (d, J = 8 Hz, 6-H) and 6.51 (d, J = 8 Hz, 7-H); ^{13}C NMR (22.5 MHz, $CDCl_3$) : 39.4 (t) ppm, 30.1 (t), 66.4 (d), 51.1 (t), 79.5 (s), 130.8 (d), 135.4 (d), 82.1 (s), 34.7 (d), 37.0 (s), 20.9 (t), 39.5 (t), 44.9 (s), 51.4 (d), 28.5 (t), 23.4 (t), 57.3 (d), 12.5 (q), 18.5 (q), 39.9 (d), 19.1 (q), 25.1 (d), 24.1 (d), 45.0 (d), 32.8 (d), 18.1 (q), 20.6 (q) and 10.5 (t), (C_1 to C_{28} respectively); EIMS : M^+ 428 (0%), 410 (M^+ -H_2O, 44.1%), 378 (410 -O_2, 25.6%), 253 (378 -C_9H_{17}, 26.5%) and 251 (253-H_2, 15.2%).

Compound G ***4β,10α-Aromadendranediol (7).*** Colourless needles from hexane-acetone; 60 mg (0.003%); m.p. 135-37°C; $[\alpha]_D^{27}$ -22.6° (C 1.5, $CHCl_3$); Found : C, 75.32; H, 10.5. Calc. for $C_{15}H_{26}O_2$: C, 75.63; H, 10.92%; IR ($CHCl_3$) : 3380 (OH), 1450, 1400, 1370, 1095 and 900 cm^{-1}; ^1H and ^{13}C NMR data (see Tables I and II); EIMS : M^+ 238 (0%), 220 (M^+ -H_2O, 17.4%), 205 (220 -CH_3, 26.3%), 202 (220 -H_2O, 28.2%), 187 (17.5%), 162 (64.2%), 147 (43.3%), 121 (50.9%), 107 (66.7%), 93 (70.2%) and 41 (100%).

Compound H ***Furanocembrane diester (8).*** Colourless needles from hexane-acetone; 150 mg (0.0075%); m.p 171-72°C; $[\alpha]_D^{27}$ -8.5° (C 0.15, $CHCl_3$); Found : C, 62.9; H, 6.76. Calc. for $C_{22}H_{28}O_8$: C, 62.8; H, 6.72%; UV ($CHCl_3$) : 216 and 245 nm; IR ($CHCl_3$) : 3460 (OH), 1715 ($COOCH_3$ >C=O, br), 1640, 1608, 1560, 1435, 1207, 1088 and 900 cm^{-1}; ^1H and ^{13}C NMR data (see Table III); EIMS : M^+ 420 (0%), 402 (M^+ -H_2O, 10%), 370 (16.1%), 253 (26.6%), 208 (50.5%), 168 (60%), 148 (30%), 93 (70.5%) and 41 (100%).

Compound I ***4α,10β-Alloaromadendranediol (9).*** Colourless needles from hexane-acetone; 30 mg (0.00015%); m.p. 114-15°C; $[\alpha]_D^{27}$ -10° (C 1.0, $CHCl_3$); Found : C, 75.35; H, 10.52. Calc. for $C_{15}H_{26}O_2$: C, 75.63; H, 10.92%; IR ($CHCl_3$) : 3380 (OH), 1480, 1450, 1370, 1095 and 900 cm^{-1}; ^1H and ^{13}C NMR data (see Table I and II); EIMS : M^+ 238 (0%), 220 (M^+ -H_2O, 23.7%), 205 (220 -CH_3, 24.1%), 202 (220 -H_2O, 25.5%), 177 (14.0%), 162 (61.0%), 147 (16.3%), 121 (15.5%), 83 (100%) and 41 (80.5%).

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