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Bishomoisomandapamate, a New Tetracyclic Diterpenoid from a New Species of the *Sinularia* Genus of the Indian Ocean

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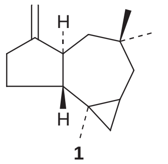
Bishomoisomandapamate, a bishomologue of isomandapamate, has been isolated from a new species of *Sinularia* genus of the Indian Ocean and its structure elucidated.

As part of our continuing interest in the bioactive secondary metabolites of the soft corals of the Indian Ocean,[4–7] we have chemically examined a new species of *Sinularia* genus,[3] collected at Kurshide island of the Mandapam coast (09°18′N, 70°08′E).

The animals were sliced into pieces and repeatedly percolated with methanol. The aqueous methanolic concentrate was fractionated into ethyl acetate. The residue from the ethyl acetate extract, upon chromatography over a silica-gel column, furnished a new tetracyclic diterpenoid **4** along with $\Delta^{9(15)}$-africanene[6,8] (**1**), (24*S*)-24-methylcholest-5-en-3*β*,25-diol (**3**), (24*S*)-24-methylcholestane-3*β*,5*α*,6*β*,23-tetrol-25-monoacetate[6,8] (**5**) and (24*S*)-24-methylcholestane-3*β*,5*α*,6*β*,25-tetrol[6] (**6**) and a mixture of monohydroxy sterols **2** which was found to consist of three monohydroxy sterols, 4*α*,24(*S*)-dimethylcholestan-3*β*-ol[9] (**7**), 4*α*-methyl-3*β*-hydroxy-5*α*-pregnan-20-one (**8**) and 4*α*,23(*E*),24(*S*)-trimethylcholestane-3*β*-ol[10] (**9**) by GC-MS analysis of the acetate mixture **2a**. One of the sterol acetates **8a**, $C_{24}H_{38}O_3$, *m/z* 314 ($M^+ - AcOH$) appears to be a new pregnane derivative, the tentative structure of which has been deduced solely from the mass spectrum, details of which will appear elsewhere.



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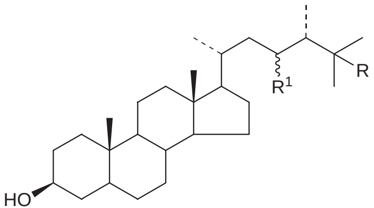
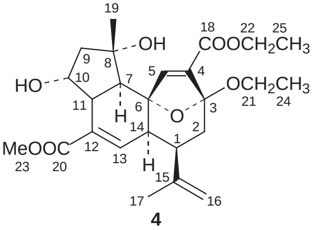


3 R = OH, R^1 = H, Δ^5
5 R = OAc, R^1 = OH, 5α-OH, 6β-OH
6 R = OH, R^1 = H, 5α-OH, 6β-OH
7 R = R^1 = H, 4α-Me
9 R = H, R^1 = Me, 4α-Me



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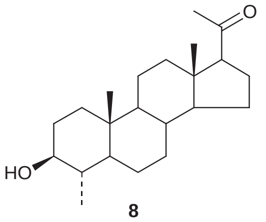

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Table 1 Comparative ^1H and ^{13}C NMR spectral data of **4** and **11**[a] ($CDCl_3$, TMS standard)

	δ_H			δ_C	
Assignment	**4** (200 MHz)	**11** (400 MHz)	Carbon no.	**4** (22.5 MHz)	**11** (22.5 MHz)
1-H	2.15 (m)	2.20 (m)	1	43.4 (d)	43.4 (d)
2α-H	1.96 (dd, $J = 12.9$, 5.0 Hz)	1.94 (dd, $J = 13.1$, 5.2 Hz)	2	33.8 (t)	33.5 (t)
			3	110.9 (s)	111.2 (s)
2β-H	1.61 (m)*	1.65 (m)	4	135.5 (s)	135.0 (s)
5-H	6.66 (s)	6.72 (s)	5	150.1 (d)	150.5 (d)
7-H	2.7 (d, $J = 13.2$ Hz)	2.73 (d, $J = 13.0$ Hz)	6	84.7 (s)	84.8 (s)
9β-H	2.01 (brd, $J = 14.8$ Hz)	2.01 (brd, $J = 15.0$ Hz)	7	52.8 (d)	52.8 (d)
			8	77.5 (s)	77.5 (s)
9α-H	2.2 m*	2.22 (m)*	9	51.5 (t)	51.5 (t)
10-H	4.6 (m)	4.64 (m)	10	67.8 (d)	67.6 (d)
11-H	2.45 (m)	2.52 (m)	11	47.2 (d)	47.2 (d)
13-H	6.65 (d, $J = 2$ Hz)	6.71 (d, $J = 2$ Hz)	12	133.9 (s)	133.6 (s)
14-H	2.39 (m)	2.38 (m)	13	143.4 (d)	143.2 (d)
16-H_2	4.75 (brs)	4.80 (brs)	14	43.4 (d)	43.4 (d)
	4.88 (brs)	4.89 (brs)	15	144.5 (s)	144.5 (s)
17-H_3	1.68 (3H, s)	1.68 (3H, s)	16	113.5 (t)	113.6 (t)
19-H_3	1.56 (3H, s)	1.60 (3H, s)	17	19.8 (q)	19.8 (q)
21-H_2/H_3	3.45 (2H, q)	3.40 (3H, s)	18	162.8 (s)	162.0 (s)
22-H_2/H_3	4.20 (2H, q)	3.80 (3H, s)	19	27.1 (q)	27.0 (q)
23-H_3	3.80 (3H, s)	3.78 (3H, s)	20	166.5 (s)	166.8 (s)
24-H_3	1.25(3H, t)		21	60.1 (t)	51.1 (q)
25-H_3	1.30 (3H, t)		22	61.3 (t)	51.9 (q)
			23	51.8 (q)	51.8 (q)
			24	14.1 (q)	
			25	15.4 (q)	

[a] From ref. 7.

Compound **4** was recognised as a new tetracyclic diterpenoid related to isomandapamate[7] (**11**) and hence

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* To receive any correspondence.

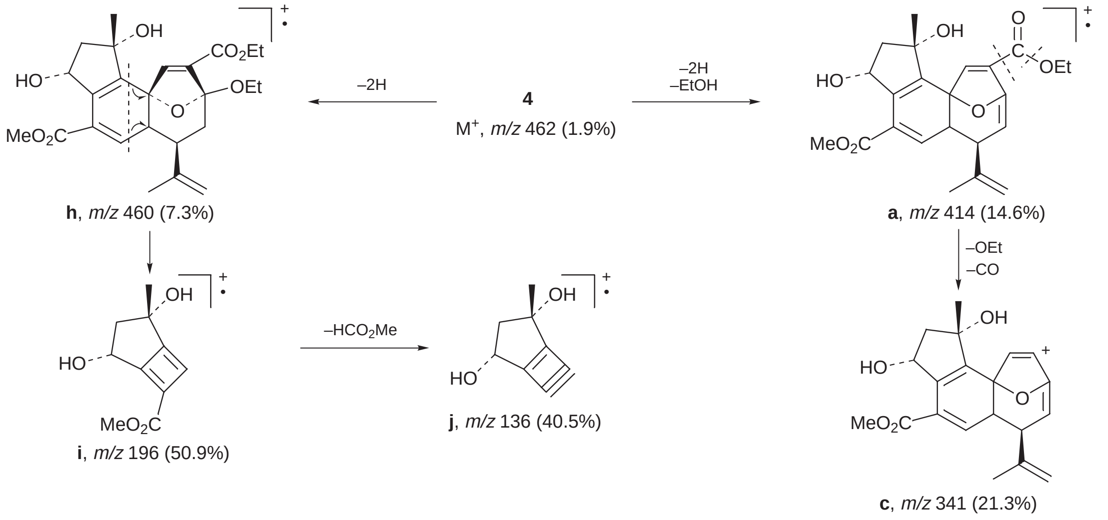
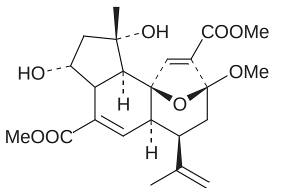


Chart I

designated as bishomoisomandapamate and its structure established by a study of its physical and spectral (UV, IR, ^{1}H and ^{13}C NMR, DEPT, 2D NMR and EI-MS) characteristics.

Mandapamate (**10**) and isomandapamate (**11**) are diastereomers with respect to C3 and C6 chiral carbons. Their ^{1}H and ^{13}C NMR data were identical except for the diagnostic chemical shift difference (≈ 4 ppm) of the C5 carbon (δ 154.4 in **10** and 150.5 in **11**). Another significant difference between them is the NOESY connectivities between C5-H, C7-αH and C14-αH in **10** and their absence in **11**, as demanded by their respective stereochemistry. The appearance of the C5 carbon at δ 150.1 and the absence of NOESY connectivities suggested that **4** has same relative stereochemistry as that of isomandapamate (**11**), being its bishomologue.



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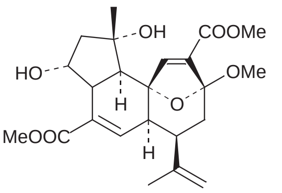

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The ^{1}H and ^{13}C NMR spectral data of **4** are compared with those of isomandapamate (**11**) in Table 1. There are two methoxycarbonyl and one methoxy groups in **11**, while **4** has one methoxycarbonyl, one ethoxycarbonyl and an ethoxy group. If the hemiketalic oxygen is involved in an ethoxy group, the two dissimilar ester functionalities have to be located at C4 and C12; if C4-bears ethoxycarbonyl, C12-bears methoxycarbonyl or *vice versa*. It is difficult to differentiate the two alternatives by the normal spectroscopic evidence. Although a 2D spectrum (HMBC or COLOC) could distinguish them through the respective long-range J_{CH} couplings at 18-CO and 20-CO, unfortunately, such data could not be obtained due to lack of sufficient material. However, a careful study of the ions in mass fragmentation (Chart I) favoured structure **4** with a ethoxycarbonyl at C4 and methoxycarbonyl at C12.

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Techniques used: UV, IR, ^{1}H and ^{13}C NMR, DEPT, 2D NMR and EI-MS

References: 12

Table: 1

Chart: 1

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