

## Rameswaralide, A Novel Diterpenoid from the Soft Coral Sinularia dissecta\*

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Abstract: Rameswaralide (4), a novel diterpene having a 5-7-6 tricyclic skeleton has been isolated along with known terpenes, africanene, 4,5-seco-african-4,5-dione, β-elemene and isomandapamate (3) from the soft coral Sinularia dissecta from the Mandapam coast, South India. The structure and stereochemistry of rameswaralide (4) were determined using spectroscopic methods and confirmed by selective reduction of the unusually stable enol group of 4 to form dihydrorameswaralide (5). 
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Soft corals are a rich source of terpenoids with diverse structures and various biological activities. <sup>1,2</sup> Prior studies have shown that members of the genus *Sinularia* produce unusual sesquiterpenes, cembrane diterpenes and sterols. <sup>3</sup> We have previously reported two new diterpenes, furanocembrane diester (1) and mandapamate (2) from a 1991 collection of the soft coral *Sinularia dissecta*. <sup>4,5</sup> We now report the structural elucidation of rameswaralide (4), a diterpene with an unusual carbon skeleton, along with some known compounds,  $\Delta^{9(15)}$ -africanene, <sup>6</sup> 4,5-*seco*-african-4,5-dione, <sup>7</sup>  $\beta$ -elemene, <sup>8</sup> and isomandapamate <sup>9</sup> (3) from a 1996 collection.

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Table 1. ¹H (300 MHz, CDCl<sub>3</sub>) and ¹¹C (100 MHz, CDCl<sub>3</sub>) NMR data for rameswaralide (4) and dihydrorameswaralide (5).<sup>a</sup>

C#         δc         δh         mult. J (Hz)         HMBC         NOESY         δc         δh         mult. J (Hz)         NOESY           1         41.7         2.58         m         C2 C14 C15, C16, C17         H2, H3, H16a, H17         39.1         2.38         dt, 13.3.5         H2, H14, H16a, H17           3         17.38         m         C2 C14, C15, C16, C17         H1, H14, H16a, H17         39.7         1.68         dd, 14.3.5         H2, H14, H14, H16a, H17           4         95.5         2.45         dd, 18.5, 6.5         C1, C3, C4, C14, C15         H1, H14, H16a, H17         47.7         41.9         P14, H14, H14, H14, H16a, H17           4         95.5         4.35         d, 6         C1, C3, C4, C14, C15         H7, H11, H14         47.7         41.9         P14, H14, H16a, H17           5         4.60         4.35         d, 6         C1, C3, C4, C14, C15         H7, H11, H14         47.7         41.9         P14, H14, H14, H14, H14, H14, H14, H14, H				ram	rameswaralide (4)			•	dihydrorameswaralide (5)	varalide (5)
417         2.58         m         C2, C14, C15, C16, C17         H2, H13, H16a, H17         39.1         2.38         dt, 18, 3.5           34.2         2.39         dd, 18.5, 62         C1, C3, C4, C14, C15         H1, H14, H16a, H17         39.7         1.68         dd, 14, 3.5           173         46.0         dd, 18.5, 65         C1, C3, C4, C14, C15         H1, H14, H16a, H17         47.7         1.68         dd, 14, 3.5           210.5         4.35         d, 6         C1, C3, C4, C6, C14, C18         H7, H11, H14         47.4         47.4         47.9         M6, 55, 4.5           210.5         4.35         d, 6         C1, C3, C4, C6, C14, C18         H7, H11, H14         47.4         4.7         4.9         M6, 55, 4.5           210.5         4.35         d, 6         C1, C3, C4, C1, C12, C19         H7, H9a, H11, H19         68.9         3.75         d, 9           78.3         3.32         d, 9         C6, C8, C11, C12, C19         H7, H9a, H11, H19         68.9         3.75         d, 9           78.3         4, 15.5         C6, C7, C8, C12, C13         H7, H9a, H10, H19         79.4         5.10         t, 7           4.18         4.21         m         C7, C8, C9, C12, C13, C13         H7, H14, H16a, H17         42.1	#3	<b>δ</b> <sub>C</sub>	$\delta_{\mathrm{H}}$	mult., J (Hz)	НМВС	NOESY	ာ်ဝွ	δ <sub>H</sub>	mult, J (Hz)	NOESY
34.2         2.39         dd, 18.5, 10         C1, C3, C4, C14, C15         H1, H14, H16a, H17         39.7         1.68         dd, 14.3.5           173.8         2.45         dd, 18.5, 6.5         C1, C3, C4, C14, C15         H1, H14, H16a, H17         6.7         2.07         dt, 14.3.5           46.0         4.35         d, 6         C1, C3, C4, C6, C14, C18         H7, H11, H14         47.4         4.19         brt, 6           210.5         4.35         d, 6         C1, C3, C4, C6, C14, C18         H7, H11, H14         47.4         4.19         brt, 6           210.5         2.28         d, 15.5         C6, C3, C11, C12, C19         H7, H90, H10, H19         46.5         1.7         d)           46.2         1.84         dd, 15.5, 7         C19         H7, H90, H10, H19         46.5         1.7         d)           79.3         5.05         t, 7         C3, C3, C12, C13, C20         H9a, H9b, H11         42.2         42.2         41.5	_	41.7	2.58	E	C2, C14, C15, C16, C17	H2, H13, H16a, H17	39.1	2.38	dt, 13, 3.5	H2, H13, H16a, H17
13.8         4.6         18.5,6.5         C1, C3, C4, C14, C15         H1, H14, H16a, H17         65.1         4.45         m           95.5         4.0         C1, C3, C4, C6, C14, C18         H7, H11, H14         47.4         4.19         brt, 6           210.5         4.3         d, 6         C1, C3, C4, C6, C14, C18         H7, H11, H14         47.4         4.19         brt, 6           210.5         4.3         d, 6         C1, C3, C4, C6, C14, C18         H7, H11, H14         47.4         4.19         brt, 6           210.5         4.3         d, 9         C6, C8, C11, C12, C19         H7, H96, H10, H19         69.0         3.75         d, 9           78.3         4.6         1.8         4, 15.5         C19         H7, H96, H10, H19         46.5         1.91         dd, 15.5, 7           46.2         2.28         d, 15.5         C6, C7, C8, C10, C11         H9a, H96, H11         42.2         42.2         m         1.15.5         41.55         1.10         dd, 15.5, 7         1.10         1.15.5         1.10         dd, 15.5         1.10         dd, 15.5         1.10         1.15.5         1.10         dd, 15.5         1.10         dd, 15.5         1.10         1.15.5         1.10         1.15.5         1.10	7	34.2	2.39	dd, 18.5, 10	C1, C3, C4, C14, C15	H1, H14, H16a, H17	39.7	1.68	dd, 14, 3.5	H1, H4, H14, H16a, H17
173.8         65.1         445         m           95.5         4.5         4.5         4.45         m           95.5         4.5         4.5         4.7         3.01         dd, 55.4.5           46.0         4.35         d, 6         C1, C3, C4, C6, C14, C18         H7, H11, H14         47.4         4.19         brt.6           210.5         4.9         C6, C8, C11, C12, C19         H7, H9b, H10, H19         69.0         3.75         d, 9           78.3         4.15.5         C6, C7, C8, C10, C11         H9a, H10, H19         46.5         1.91         dd, 15.5, 7           4.6.2         1.84         dd, 15.5, 7         C19         H7, H9b, H10, H19         46.5         1.91         dd, 15.5, 7           4.1.         6.24         dd, 15.5         C6, C7, C8, C12, C13, C20         H7, H10         42.2         42.2         m           135.2         6.54         brs         C1, C5, C9, C12, C13, C20         H1, H14, H16a, H17         42.1         2.86         m           143.0         rs         C1, C5, C6, C12, C13, C13         H2, H5, H13, H16a, H16b, H17         42.1         2.86         m           115.6         s, 34         C1, C15, C17         H1, H2, H13, H14, H16b, H16b, H17         <			2.45	dd, 18.5, 6.5	C1, C3, C4, C14, C15	H1, H14, H16a, H17		2.07	dt, 14, 3.5	H1, H16a, H17
95.5 46.0 4.35 d, 6 C1, C3, C4, C6, C14, C18 H7, H11, H14 49.7 49.7 49.7 49.7 49.7 49.9 49.7 49.7	т	173.8					65.1	4.45	E	H2a, H2b, H4
46.0         4.35         d, 6         C1, C3, C4, C6, C14, C18         H7, H11, H14         47.4         4.19         brt, 6           210.5         68.3         3.32         d, 9         C6, C8, C11, C12, C19         H5, H9a, H11, H19         69.0         3.75         d, 9           78.3         1.84         dd, 15.5, 7         C19         H7, H9b, H10, H19         46.5         1.91         dd, 15.5, 7         d, 9           46.2         1.84         dd, 15.5, 7         C19         H7, H9b, H10, H19         46.5         1.91         d, 15.5         4, 9         46.15.5, 7         4, 9         46.15.5, 7         4, 9         46.15.5, 7         4, 9         46.15.5, 7         4, 9         46.15.5, 7         4, 9         46.15.5, 7         4, 15.5 </td <td>4</td> <td>95.5</td> <td></td> <td></td> <td></td> <td></td> <td>49.7</td> <td>3.01</td> <td>dd, 5.5, 4.5</td> <td>H2a, H3, H14</td>	4	95.5					49.7	3.01	dd, 5.5, 4.5	H2a, H3, H14
210.5         211.0         211.0           68.3         3.32         d, 9         C6, C8, C11, C12, C19         H5, H9a, H11, H19         69.0         3.75         d, 9           78.3         4, 9         C6, C7, C8, C10, C11         H7, H9b, H10, H19         46.5         1.91         dd, 15.5, 7           46.2         1.84         dd, 15.5, 7         C19         H7, H9b, H10, H19         46.5         1.91         dd, 15.5, 7           41.8         4.21         m         C7, C8, C20         H7, H10         42.2         4.2         5.10         t, 7           41.8         4.21         m         C7, C8, C9, C12, C13, C14         H1, H14, H16a, H17         131.5         6.3         brs         4.15.5         m           40.1         2.89         m         C1, C5, C6, C12, C13         H1, H2, H13, H16a, H17         42.1         2.86         m           115.6         4.86         brs         C1, C15, C17         H1, H2, H13, H14, H16b, H114         42.1         48.9         brs           115.6         5.3 H         C1, C15, C17         H1, H2, H13, H14, H16b, H114         48.9         brs           115.6         5.3 H         C1, C15, C15         H1, H2, H13, H14, H16b, H14, H16b, H14, H14, H14, H14, H14, H14, H14, H14	5	46.0	4.35	<b>d</b> , 6	C1, C3, C4, C6, C14, C18	H7, H11, H14	47.4	4.19	br t, 6	H4, H7, H11, H14
68.3         3.32         d,9         C6, C8, C11, C12, C19         H5, H9a, H11, H19         69.0         3.75         d,9           78.3         46.2         1.84         dd, 15.5,7         C19         H7, H9b, H10, H19         78.7         1.91         dd, 15.5,7         49.0         15.5         49.6         1.91         dd, 15.5,7         49.1         46.5         1.91         dd, 15.5,7         49.1         46.5         1.91         dd, 15.5,7         49.1         41.5         2.39         d, 15.5         41.5         2.39         d, 15.5         41.5         42.1         2.86         m         41.5         42.1         2.86         m         41.5         42.1         2.86         m         41.5         42.1         2.86         m         41.5         41.5	9	210.5					211.0			
78.3         78.7         78.7           46.2         1.84         dd, 15.5, 7         C19         H7, H9b, H10, H19         46.5         1.91         dd, 15.5, 7           46.2         1.84         dd, 15.5         C6, C7, C8, C10, C11         H9a, H10, H19         46.5         1.91         dd, 15.5, 7           79.3         5.05         t, 7         C7, C8, C20         H7, H10         12.2         42.2         m           131.8         4.21         m         C7, C8, C9, C12, C13, C20         H1, H14, H16a, H17         135.8         6.63         brs           40.1         2.89         m         C1, C5, C6, C12, C13         H2, H5, H13, H16a, H17         42.1         2.86         m           143.0         4.86         brs         C1, C15, C17         H1, H2, H13, H144         114.7         4.89         brs           115.6         s, 3 H         C1, C15, C17         H1, H2, H13, H144         114.7         4.89         brs           170.8         brs         C1, C15, C17         H1, H2, H13, H144         114.7         4.89         brs           170.8         1.45         s, 3 H         C1, C15, C17         H1, H2, H13, H144         116.7         s, 3 H           169.8         1.4	7	68.3	3.32	d, 9		H5, H9a, H11, H19	0.69	3.75	d, 9	H5, H9a, H11, H19
46.2         1.84         dd, 15.5, 7         C19         H7, H9b, H10, H19         46.5         1.91         dd, 15.5, 7           2.28         d, 15.5         C6, C7, C8, C10, C11         H9a, H10, H19         79.4         5.10         t, 7           79.3         5.05         t, 7         C7, C8, C20         H7, H10         42.2         4.22         m           41.8         4.21         m         C7, C8, C9, C12, C13, C20         H1, H14, H16a, H17         135.8         6.63         brs           135.2         6.54         brs         C1, C5, C6, C12, C13         H2, H5, H13, H16a, H17         42.1         2.86         m           40.1         2.89         m         C1, C5, C6, C12, C13         H2, H5, H13, H16a, H17         42.1         2.86         m           40.1         2.89         m         C1, C5, C6, C12, C13         H1, H2, H13, H14         114.7         4.89         brs           115.6         4.86         brs         C1, C15, C17         H1, H2, H13, H14         114.7         4.89         brs           18.1         1.66         s, 3 H         C1, C15, C16         H1, H2, H13, H14, H16b         19.0         1.73         s, 3 H           18.2         4.85         brs <t< td=""><td>∞</td><td>78.3</td><td></td><td></td><td></td><td></td><td>78.7</td><td></td><td></td><td></td></t<>	∞	78.3					78.7			
2.28       d, 15.5       C6, C7, C8, C10, C11       H9a, H10, H19       79.4       5.10       t, 7         4.18       4.21       m       C7, C8, C20       H7, H10       42.2       4.22       m         4.18       4.21       m       C7, C8, C9, C12, C13, C20       H1, H14, H16a, H17       135.8       6.63       brs         135.2       6.54       brs       C1, C5, C6, C12, C13       H2, H5, H13, H16a, H17       42.1       2.86       m         40.1       2.89       m       C1, C5, C6, C12, C13       H2, H5, H13, H16a, H17       42.1       2.86       m         143.0       4.86       brs       C1, C15, C17       H1, H2, H13, H14       114.7       4.89       brs         115.6       4.86       brs       C1, C15, C17       H1, H2, H13, H14, H16b       19.0       1.73       s, 3 H         170.8       1.66       s, 3 H       C1, C15, C17       H1, H2, H13, H14, H16b       19.0       1.73       s, 3 H         170.8       1.42       s, 3 H       C7, C8, C9       H7, H9a, H9b       26.6       1.57       s, 3 H         169.8       1.215       brs       C18       S, 3 H       S, 3 H         169.8       1.215       brs <td< td=""><td>6</td><td>46.2</td><td>1.84</td><td>dd, 15.5, 7</td><td>C19</td><td></td><td>46.5</td><td></td><td>dd, 15.5, 7</td><td>Н7, Н9b, Н10, Н19</td></td<>	6	46.2	1.84	dd, 15.5, 7	C19		46.5		dd, 15.5, 7	Н7, Н9b, Н10, Н19
79.3         5.05         t,7         C7, C8, C20         H9a, H9b, H11         79.4         5.10         t,7           41.8         4.21         m         C7, C8, C9, C12, C13, C20         H7, H10         42.2         4.22         m           131.8         4.21         m         C1, C5, C20         H1, H14, H16a, H17         135.8         6.63         brs           40.1         2.89         m         C1, C5, C6, C12, C13         H2, H5, H13, H16a, H17         42.1         2.86         m           143.0         145.0         H1, H2, H13, H16a, H17         4.89         brs         145.2         m           115.6         4.86         brs         C1, C15, C17         H1, H2, H13, H14         14.7         4.89         brs           18.1         1.66         s, 3 H         C1, C15, C17         H1, H2, H13, H14, H16b         19.0         1.73         s, 3 H           170.8         1.70         H1, H2, H13, H14, H16b         19.0         1.73         s, 3 H           169.8         1.42         s, 3 H         C7, C8, C9         H7, H9a, H9b         26.6         1.57         s, 3 H           169.8         1.21.5         brs         3.78         s, 3 H           12.15			2.28	d, 15.5	C6, C7, C8, C10, C11				d, 15.5	H9a, H10, H19
41.8       4.21       m       C7, C8, C9, C12, C13, C20       H7, H10       42.2       4.22       m         131.8       6.54       br s       C1, C5, C20       H1, H14, H16a, H17       135.8       6.63       br s         40.1       2.89       m       C1, C5, C6, C12, C13       H2, H5, H13, H16a, H17       42.1       2.86       m         40.1       2.89       m       C1, C15, C17       H1, H2, H13, H14       4.89       brs         115.6       4.86       br s       C1, C15, C17       H1, H2, H13, H14       4.89       brs         115.6       5.3 H       C1, C15, C17       H1, H2, H13, H14, H16b       19.0       1.73       s, 3 H         170.8       1.42       s, 3 H       C1, C15, C16       H7, H9a, H9b       26.6       1.57       s, 3 H         169.8       1.42       s, 3 H       C7, C8, C9       H7, H9a, H9b       52.6       1.57       s, 3 H         169.8       51.2       3.71       s, 3 H       52.6       3.78       s, 3 H         12.15       brs       52.6       3.78       s, 3 H         12.15       brs       53.8       brd, 11	01	79.3	5.05	t, 7	C7, C8, C20		79.4		t, 7	H9a, H11
131.8       131.5         135.2       6.54       brs       C1, C5, C6, C12, C13       H1, H14, H16a, H17       135.8       6.63       brs         40.1       2.89       m       C1, C5, C6, C12, C13       H2, H5, H13, H16a, H17       42.1       2.86       m         143.0       4.86       brs       C1, C15, C17       H1, H2, H13, H14       114.7       4.89       brs         115.6       brs       C1, C15, C17       H1, H2, H13, H14       114.7       4.89       brs         18.1       1.66       s, 3 H       C1, C15, C16       H1, H2, H13, H14, H16b       19.0       1.73       s, 3 H         170.8       1.42       s, 3 H       C7, C8, C9       H7, H9a, H9b       26.6       1.57       s, 3 H         169.8       1.51       s, 3 H       C18       s, 3 H       52.6       3.78       s, 3 H         12.15       brs	=	41.8	4.21	E	C7, C8, C9, C12, C13, C20		42.2		E	H7, H10
135.2       6.54       brs       C1, C5, C20       H1, H14, H16a, H17       135.8       6.63       brs         40.1       2.89       m       C1, C5, C6, C12, C13       H2, H5, H13, H16a, H17       42.1       2.86       m         143.0       4.86       brs       C1, C15, C17       H1, H2, H13, H14       114.7       4.89       brs         115.6       brs       C1, C15, C17       H17       4.89       brs         18.1       1.66       s, 3 H       C1, C15, C16       H1, H2, H13, H14, H16b       19.0       1.73       s, 3 H         170.8       1.70.8       C7, C8, C9       H7, H9a, H9b       26.6       1.57       s, 3 H         169.8       1.51       s, 3 H       C18       s, 3 H         51.2       3.71       s, 3 H       52.6       3.78       s, 3 H         12.15       brs       53.8       brd, 11	12	131.8					131.5			
40.1       2.89       m       C1, C5, C6, C12, C13       H2, H5, H13, H16a, H17       42.1       2.86       m         143.0       115.6       4.86       brs       C1, C15, C17       H1, H2, H13, H14       114.7       4.89       brs         115.6       5.3 H       C1, C15, C17       H1, H2, H13, H14, H16b       19.0       1.73       s, 3 H         170.8       170.8       177.0       177.0       177.0         169.8       12.1       s, 3 H       C18       s, 3 H       52.6       1.57       s, 3 H         12.15       brs       brs       53.6       3.78       s, 3 H	13	135.2	6.54	br s	C1, C5, C20	H1, H14, H16a, H17	135.8	6.63	br s	H1, H4, H14, H16a, H17
143.0         115.6       4.86       brs       C1, C15, C17       H1, H2, H13, H14       114.7       4.89       brs         18.1       4.95       brs       C1, C15, C17       H1, H2, H13, H14, H16b       19.0       1.73       s, 3 H         170.8       170.8       177.0       177.0       177.0       177.0       177.0         26.6       1.42       s, 3 H       C7, C8, C9       H7, H9a, H9b       26.6       1.57       s, 3 H         169.8       12.15       brs       52.6       3.78       s, 3 H         51.2       3.71       s, 3 H       52.6       3.78       s, 3 H	14	40.1	2.89	E	C1, C5, C6, C12, C13	H2, H5, H13, H16a, H17	42.1	2.86	ш	H2a, H5, H13, H16a, H17
115.6       4.86 brs       C1, C15, C17       H1, H2, H13, H14       114.7       4.89 brs         4.95 brs       C1, C15, C17       H17       5.00 brs         18.1       1.66 s, 3 H       C1, C15, C16       H1, H2, H13, H14, H16b       19.0       1.73 s, 3 H         170.8       170.0       177.0       26.6       1.57 s, 3 H         169.8       12.15 s, 3 H       C18       52.6       3.78 s, 3 H         12.15 brs       5.3 H       5.3 H       5.3 H	15	143.0					145.2			
4.95       br s       C1, C15, C17       H17       5.00       br s         18.1       1.66       s, 3 H       C1, C15, C16       H1, H2, H13, H14, H16b       19.0       1.73       s, 3 H         170.8       26.6       1.42       s, 3 H       26.6       1.57       s, 3 H         169.8       169.8       169.5       169.5         51.2       3.71       s, 3 H       52.6       3.78       s, 3 H         12.15       br s	16	115.6	4.86	br s	C1, C15, C17	H1, H2, H13, H14	114.7	4.89	brs	H1, H2, H13, H14
18.1     1.66     s, 3 H     C1, C15, C16     H1, H2, H13, H14, H16b     19.0     1.73     s, 3 H       170.8     170.0     170.0     170.0       26.6     1.42     s, 3 H     26.6     1.57     s, 3 H       169.8     169.5       51.2     3.71     s, 3 H     52.6     3.78     s, 3 H       12.15     brs			4.95	br s	C1, C15, C17	H17		5.00	brs	H17
170.8 26.6 1.42 s, 3 H	17	18.1	1.66	s, 3 H	C1, C15, C16	H1, H2, H13, H14, H16b	19.0	1.73	s, 3 H	H1, H2, H13, H14, H16b
26.6       1.42       s, 3 H       C7, C8, C9       H7, H9a, H9b       26.6       1.57       s, 3 H         169.8       169.5         51.2       3.71       s, 3 H       52.6       3.78       s, 3 H         12.15       brs	18	170.8					170.0			
169.8 51.2 3.71 s, 3 H C18 52.6 3.78 s, 3 H 12.15 brs 5.38 brd, 11	19	26.6	1.42	s, 3 H	C7, C8, C9	Н7, Н9а, Н9ь	56.6	1.57	s, 3 H	Н7, Н9а, Н9ь
51.2 3.71 s, 3 H C18 52.6 3.78 s, 3 H 12.15 brs 5.38 brd, 11	20	169.8					169.5			
12.15 brs 5.38 brd, 11	21		3.71	s, 3 H	C18		52.6	3.78	s, 3 H	
	3-OF	_	12.15	br s				5.38	br d, 11	H1, H3

<sup>a</sup> <sup>1</sup>H<sup>-13</sup>C correlations were determined by HMQC.

The 1:1 dichloromethane-methanol extract of the soft coral *Sinularia dissecta* was chromatographed on Sephadex LH-20 using 1:1 dichloromethane-methanol as eluant, followed by silica gel chromatography to afford  $\Delta^{9(15)}$ -africanene (0.05 % dry wt.), 4,5-seco-african-4,5-dione (0.0005 % dry wt),  $\beta$ -elemene (0.0005 % dry wt.), isomandapamate (3, 0.0025 % dry wt.) and a novel cembrane diterpene, rameswaralide (4, 0.003 % dry wt.), which was purified by HPLC on silica gel using 1:3 hexane/ethylacetate as eluant. The known compounds were identified from literature data.<sup>6-9</sup> The structure of the novel compound, rameswaralide (4) was determined by extensive 1D and 2D NMR experiments and confirmed by selective reduction of the enolic group with sodium borohydride to form dihydrorameswaralide (5).

Rameswaralide (4)<sup>10</sup> was obtained as a white solid, m.p. 169-171 °C,  $[\alpha]_D$  -20.5 (c = 0.22, CHCl<sub>3</sub>). The molecular formula  $C_{21}H_{24}O_7$ , which was derived from HREIMS (m/z 388.1523) and <sup>13</sup>C NMR data, requires 10 degrees of unsaturation. The IR spectrum contained bands at 3500, 1752, 1715, 1670 cm<sup>-1</sup>, from which the presence of a hydroxyl and three different carbonyl groups was inferred. The UV spectrum showed absorptions at 250 nm (sh,  $\epsilon$ 11, 700), 229 (sh, 15,500), 222 (15,700), 205 (14,700), which underwent reversible bathochromic shifts on addition of base, indicating the presence of an enolisable  $\beta$ -keto ester as well as an  $\alpha,\beta$ -unsaturated carboxylic ester in the molecule. The <sup>13</sup>C NMR spectrum (Table 1) contained 21 signals that include a ketone signal at  $\delta$  210.5, methyl ester signals at 170.8 and 51.2,  $\gamma$ -lactone carbonyl signals at 169.8 and 79.3 and six olefinic carbon signals at 173.8, 143.0, 135.2, 131.8, 115.6 and 95.5. The carbonyl and olefinic carbons account for six degrees of unsaturation; hence the compound is tetracyclic. The <sup>1</sup>H NMR spectrum contained signals corresponding to an isopropylidene group at  $\delta$  1.66 (s, 3 H), 4.86 (br s, 1 H), 4.95 (br s, 1 H), a conjugated trisubstituted olefinic proton at 6.54 (br s, 1 H), a methine proton bearing oxygen at 5.05 (t, 1 H, J = 7 Hz), four low field methine protons at 4.35 (d, 1 H, J = 6 Hz), 4.21 (m, 1 H), 3.32 (d, 1 H, J = 9 Hz), 2.89 (m, 1H), a quaternary methyl at 1.42 (s, 3 H) and an exchangeable proton at 12.15 ppm. The COSY spectrum revealed some similarities with mandapamate (2), which was obtained from the same specimen.<sup>5</sup> The spectral data for ring A and ring C were assigned from COSY and HMBC data and the presence of allylic coupling between H-11 and H-13 established the connection between rings A and C. The chemical shifts of H-7 and H-5 and their HMBC correlations to the ketone signal at δ 210.5 completed the 7-membered ring B. An HMBC correlation between H-10 and C-20 established the presence of the γ-lactone and a correlation between Me-17 and C-1 indicated that the isopropyl group was located at

C-1, as expected. The fully enolised  $\beta$ -keto ester moiety that completes ring C was defined by the HMBC correlations from H-5 to the three carbon signals at 173.8 (C-3), 95.5 (C-4) and 170.8 (C-18) and from H-2 to C-3 and C-4. The structure of rameswaralide (4) was further confirmed by selective reduction of enolic group with NaBH<sub>4</sub> to form exclusively single isomer, dihydrorameswaralide (5).

The stereochemistry of rameswaralide (4) was determined by analysis of  ${}^{1}H$  NMR coupling constants and NOESY correlations. The coupling constants  $J_{5,14} = 6$  Hz and  $J_{7,11} = 9$  Hz and a NOESY correlation between H-5, H-7 and H-11 suggested that rings A and C are *cis* fused to ring B. The NOESY correlations between H-10 and H-11 and Me-19 and H-7, together with  $J_{10,11} = 7$  Hz, showed that Me-19, H-10, H-7 and H-11 were all on the same side of ring A. The NOESY data (Table 1) for dihydrorameswaralide (5) showed that the H-14, H-4 and H-2a are axial and that H-5, H-3 and the isopropylidene group are equatorial with respect to ring C and also showed that rings A and B were the same as in rameswaralide (4).

The carbon skeleton of rameswaralide (4) is related to that of isomandapamate (3) by opening of the furan ring with a concommitant migration of the C-14 bond from C-6 to C-5.<sup>11</sup>

## References and Notes

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- 10. The soft coral was collected on the Mandapam coast near Rameswaram, which is one of the mythological and historical sites in India.
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