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Isolation and Structure Elucidation of a New Glycolipid from the Soft Coral *Lobophytum microlobulatum* Collected from Havellock Island of Andaman and Nicobar Group of Islands

Ammanamanchi S. R. Anjaneyulu*, Nidasanametla S. Kameswara Rao, H. S. Garg[1]

Department of Organic Chemistry, Andhra University, Visakhapatnam-530 003, India.
[1]Central Drug Research Institute, Lucknow-226 001, India.

Abstract – A new glycolipid, 2-hydroxy-3 (octadecyloxy)-propyl-α-D-arabinopyranoside (**1**) has been isolated from *Lobophytum microlobulatum* and its structure has been elucidated by physical and spectral (UV, IR, ^1H, ^{13}C NMR, FABMS) data.

Key words – Glycolipid, *Lobophytum microlobulatum.*

Introduction

We have recently undertaken the chemical examination of the soft coral *Lobophytum microlobulatum* and reported the isolation of four new and five known lobane diterpenoids along with three polyhydroxysteroids (Anjaneyulu, 1996). The isolation of a new glycolipid has also been briefly reported and its structure elucidation is now presented here.

Results and Discussion

More polar fractions (EtOAc: MeOH 19:1) from the column chromatography of the ethyl acetate extract of the soft coral left a residue which on crystallization from chloroform-methanol gave colorless needles, 140 mg, m.p. 125-27 °, $[\alpha]_D^{25}$+15.0 ° (c 1.4, MeOH). Its molecular formula was fixed as $C_{26}H_{52}O_7$ by elemental analysis and FABMS (+ve mode) m/z 499 (M^++Na). It is sparingly soluble in common organic solvents indicating its polyhydroxy nature and gave positive Molish test for glycosides. Its IR spectrum showed strong broad bands for hydroxyls (3400 cm^{-1}) and strong bands for ether linkage (1160 cm^{-1}). No conjugation was noticed in its UV spectrum. On acetylation with acetic anhydride and pyridine it gave a tetraacetyl derivative (**1a**) ($C_{34}H_{60}O_{11}$) as a colorless oil, indicating the presence of four acylable hydroxyls. The acetate showed acetyl groups in its IR spectrum (1735, 1260 cm^{-1}) but no further hydroxylic absorption. The three remaining oxygens of the molecule might be present as ether linkages in the absence of any carbonyl functionality.

The compound on treatment with 3N HCl in methanol on steam bath for 6 hrs. gave an aglycone which was found to be identical in every respect with batyl alcohol (**3**). The aqueous solution remained after removal of the aglycone was evaporated to dryness in vacuum to obtain the sugar unit which was identified as D-arabinose by its specific rotation $[\alpha]_D^{25}$ -110.0 ° and co-paper chromatography with an authentic sample. Thus the compound was regarded as arabinopyrano-

*Author for correspondence.

side of batyl alcohol. While batyl alcohol has been found to be more or less an ubiquitous constituent of soft corals, it has not been reported as glycoside so far except for an isolated reference where it was reported as a hexapyranoside from an unidentified species of *Sinularia* (Long, 1988). Neither identification of the hexapyranose nor its spectral details were reported. The present glycolipid has been considered to be new and its spectral details therefore presented.

Its ^{1}H and ^{13}C NMR spectral data could be obtained in pyridine-d_5 at 400 and 22.5 MHz respectively (Table I). Its ^{13}C NMR spectrum showed all the 26 carbons whose substitution pattern could be obtained by the DEPT spectrum. Its ^{13}C showed four oxymethylene carbons, one of which being the methylene carbon of the sugar unit (δ 64.1) and four oxymethine carbons (δ 70.9, 70.1, 69.8, and 73.2) of which the first three belong to the arabinose unit. The anomeric carbon noticed at 103.3 (d) indicated its α-glycosidic linkage (Agrawal, 1985). The α-glycosidic linkage was also evident from the cou-

Table I. ^{1}H and ^{13}C NMR Spectral Data of Compound **1**

^{1}H NMR (400 MHz) (pyridine-d_5)		^{13}C NMR* (22.5 MHz) (pyridine-d_5)	
Assignment	Chemical shift	Carbon No.	Chemical shitf
1'-H	5.45 (d,4)	1'	103.3(d)
2'-H	4.69 (dd,4,8)	2'	70.9(d)
3'-H	4.56 (dd,4,8)	3'	70.1(d)
4'-H	4,40 (br s)	4'	69.8(d)
5'-H	4.22 (dd,4,8)	5'	64.1(t)
5'-H	3.98 (dd,4,8)	1	71.6(t)
1-H	4.30 (d,12)	2	73.2(d)
2-H	4.08 (dd,2,12)	3	70.6(t)
3-H_2	4.44 (q)	1"	64.2(t)
1"-H_2	3.85 (m)	2"	32.0(t)
2"-H_2	3.49 (t,5)	3"	30.1(t)
Aliphatic chain	1.51 (t,5)	4"-17""	29.9(t)
Terminal methyl	1.25 (br s)		29.7(t)
	0.85 (t,7)		29.5(t)
			26.4(t)
			22.8(t)
			14.2(q)
		18"	

*^{13}C assignments are confirmed by DEPT experiments.

Table II. Comparative ^{1}H and ^{13}C NMR Spectral Data of Compounds **1** and **2**

	^{1}H NMR			^{13}C NMR	
Assignment	Sugar part in Compound **1** (py-d_5, 400 MHz)	Sugar part in Compound **2** ($CDCl_3$, 360 MHz)	Carbon No.	Sugar part in Compound **1** (py-d_5, 22.5 MHz)	Sugar part in Compound **2** ($CDCl_3$, 50 MHz)
1'-H	5.45(d, 4)	5.12 (d, 2.7)	1'	103.3(d)	104.1
2'-H	4.69 (dd, 4, 8)	4.14 (br d)	2'	70.9(d)	69.7
3'-H	4.56 (dd, 4. 8)	4.13 (br d)	3'	70.1(d)	69.6
4'-H	4.40 (br s)	4.07 (br s)	4'	69.8(d)	69.5
5'-H	4.22 (dd, 4, 8)	4.33 (br d, 12.3)	5'	64.1(d)	69.3
5'-H	3.98 (dd, 4, 8)	3.83 (br d, 12.3)			
	Aglycone part in **1**	Batyl alcohol (py-d_5, 90 MHz)		Aglycone part in **1**	Batyl alcohol (py-d_5, 22.5 MHz)
1-H	4.30 (d, 12)	4.10 (2H, m)	1	71.6(t)	71.9(t)
1-H	4.08 (dd, 2, 12)	-	2	73.2(d)	73.5(d)
2-H	4.44 (q)	4.30 (q)	3	70.6(t)	71.7(t)
3-H_2	3.85 (m)	3.82 (m)	1"	64.2(t)	64.6(t)
1"-H_2	3.49 (t, 5)	3.55 (t, 5)	2"	32.0(t)	32.1(t)
2"-H_2	1.51 (t, 5)	1.55 (t, 5)	3"	30.1(t)	30.2(t)
Aliphatic chain	1.25 (br s)	1.25 (br s)	4"-17"	29.9(t)	29.9(t)
Terminal methyl	0.85 (t, 7)	0.90 (t, 7)		29.7(t)	29.8(t)
				29.5(t)	29.6(t)
				26.4(t)	26.5(t)
				22.8(t)	22.9(t)
			18"	14.2(q)	14.2(q)

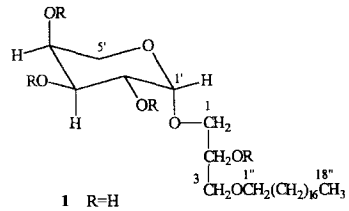
pling constant of the anomeric proton (δ 5.45, d, J=4 Hz). Since the secondary alcoholic group of batyl alcohol was found to exist free, the end primary alcoholic group must have been involved in the glycosidic linkage. The ^1H and ^{13}C NMR spectral data of the glycoside could be compared with the ^1H and ^{13}C NMR data of batyl alcohol, all taken in pyridine-d_5 (Table II). For a comparision of the spectral data of the sugar part with the corresponding protons in the glycoside, a neat spectrum of arabinose could not be obtained in d_5-pyridine. However, the ^1H and ^{13}C NMR spectral data of a phenolic arabinoside, seco-pseudoperosine A (**2**) taken in $CDCl_3$ was reported in literature (Look, 1987) and the same values have beenz utilized in the table for the comparison. The comparative study of ^1H and ^{13}C NMR (Table II) spectral data of compound (**1**) with those reported for its aglycone and sugar parts strongly supported the proposed structure 2-hydroxy-3(octadecyloxy)-propyl-α-arabonopyranoside for it.

Experimental

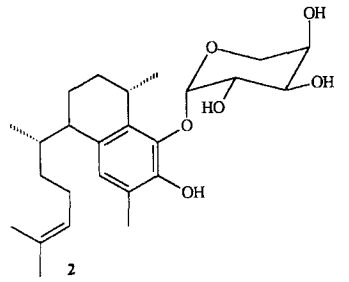
General experimental conditions, collection & extraction of the organism, and isolation procedure of compound (**1**) were given in detail in reference 2 (Anjaneyulu, 1996).

2-hydroxy-3(octadecyloxy)-propyl-α-arabonopyranoside (1) – colorless needles, 140 mg, m.p. 125-27, $[\alpha]_D^{25}$+15.0° (c 1.4, MeOH). Found: C, 65.31, H, 11.22; $C_{26}H_{52}O_7$ requires: C, 65.55, H, 10.92%. R_f:0.43 (Hexane: EtOAc 19:1); IR (KBr): 3400, 2900, 2850, 1140, 1080, 1040, 1000 cm^{-1}. FABMS (+ve mode): m/z 499 (M^++Na), 350, 334, 301, 287.

Acetylation of compound (1) – To the compound (20 mg) in pyridine (2 ml) was added acetic anhydride (2 ml) and the mixture was kept aside at room temperature for 10 hours. After usual workup, it gave tetra-acetyl derivative as a colourless oil, 10 mg. Found: C, 62.50, H, 9.99; $C_{34}H_{60}O_{11}$ requires:



1 R=H
1a R=Ac



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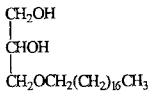

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C, 63.35, H, 10.92%; IR ($CHCl_3$): 2900, 2850, 1735, 1260, 1140, 1080 and 1040 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ: 5.34 (1H, br s), 5.31 (1H, br d, J=4Hz), 5.17 (1H, br d, J=4Hz), 5.14 (1H, br d, J=4Hz), 5.11 (1H, br d, J=4 Hz), 3.96 (1H, d, J=10 Hz), 3.82 (1H, dd, J=4, 10 Hz), 3.65 (2H, m), 3.43 (2H, m), 3.55 (2H, m), 2.15 (3H, s), 2.09 (6H, s), 2.01 (3H, s), 1.6 (2H, m), 1.25 (30H, br s) and 0.89 (3H, t, J=7 Hz).

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