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Two oligosaccharides from *Marsdenia roylei*

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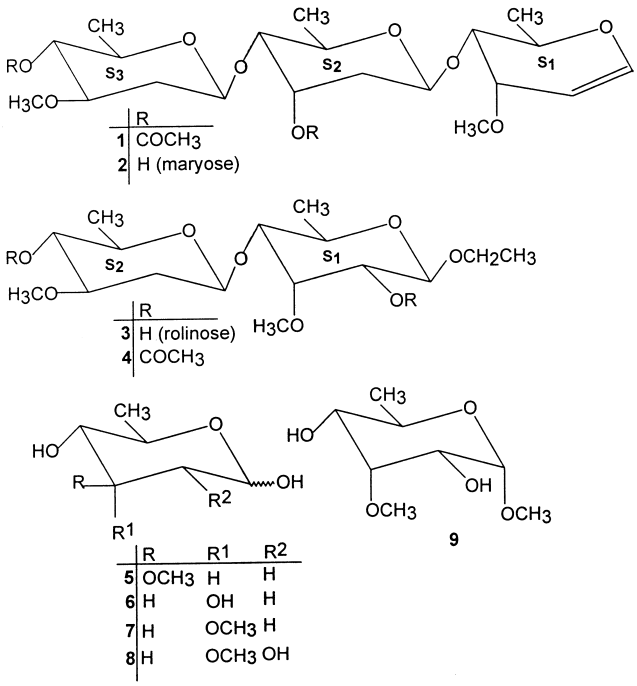
Abstract

Phytochemical analysis of dried twigs of *Marsdenia roylei* (family Asclepiadaceae) has resulted in the isolation of a trisaccharide, maryal, and a diglycoside, rolinose. Their structures were determined as *O*-*β*-D-oleandropyranosyl-(1→4)-*O*-*β*-D-digitoxopyranosyl-(1→4)-D-cymaral and ethyl *O*-*β*-D-oleandropyranosyl-(1→4)-*O*-3-*O*-methyl-6-deoxy-*β*-D-allopyranoside, respectively, by chemical degradation and spectroscopic methods.

Keywords: Marsdenia roylei; Asclepiadaceae; Oligosaccharides; Glycal; Maryal; Ethyl diglycoside; Rolinose

1. Introduction

Oligosaccharides (Tiwari, Khare, & Khare, 1984; Tiwari, Khare, Khare, & Khare, 1984) and oligoglycosides (Mitsuhashi & Hayashi, 1985; Jijun, Zhuaugxin, & Jun, 1990) of 2-deoxy sugars have been reported from plants of the family Asclepiadaceae and shown to possess immunomodulating, anticomplementary, antitumor and anticancer activities (Srivastava & Kulshrestha, 1989; Weymouth-Wilson, 1997). Many oligosaccharides of 2-deoxy hexoses are known to occur in nature as the glycone part of the biologically active pregnanes (Deepak, Srivastava, & Khare, 1997) and cardiac (Deepak, Srivastava, Khare, & Khare, 1996) oligoglycosides. We now report on the isolation from the chloroform-soluble extract of *Marsdenia roylei* of two novel oligosaccharides: a 1,2 glycal, maryal (**2**), and an ethyl diglycoside, rolinose (**3**). Compound **2** was isolated as its acetyl derivative (**1**) after acetylating the fraction containing **2**.



2. Results and discussion

Compound **1**, $C_{24}H_{38}O_{11}$ (FABMS *m*/*z* 503[M+H]$^+$), on alkaline hydrolysis gave maryal (**2**), $C_{20}H_{34}O_9$. The difference of $2\times CoCH_2$ in the molecular formula of **1** and **2** indicated **1** to be the di-*O*-acetyl derivative of **2**. Compound **2** gave positive color tests in the xanthydrol (Khare, Khare, & Khare, 1984) and Keller–Kiliani (Khare et al., 1984) reactions indicating the presence of rare, 2,6-dideoxy hexose(s). It also gave positive tetranitromethane (Fieser & Fieser, 1967) reaction indicative of the presence of double bonds in **2**. Compound **2** was hydrolyzed with mild acid (0.05 N H_2SO_4), affording three chromatographically pure sugars: D-oleandrose (**5**) (Mitsuhasi, Hayashi, & Nomura, 1966), D-digitoxose (**6**) (Iselin & Reichstein, 1944) and D-cymarose (**7**) (Krasso, Weiss, & Reichstein, 1963). Further characterization of the sugars was achieved by preparing their respective

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known phenylhydrazides. The results of hydrolysis indicated that **2** was a trisaccharide of D-oleandrose(S_3), D-digitoxose(S_2) and D-cymarose(S_1) and contained a double bond.

The ^1H and ^{13}C NMR spectra of **1** showed signals at δ 6.36 (d, $J=5.5$ Hz), 4.77 (dd, $J=9$ and 2 Hz) and 4.50 (dd, $J=9$ and 2 Hz) for three H-1 protons and signals at δ 146.01, 99.78 and 98.97 for three C-1 carbons, respectively. The presence of one unusually downfield shifted H-1 and C-1 signals at δ 6.36 and 146.01 along with a triplet at δ 4.93 ($J=5.5$ Hz) of H-2 and a signal of C-2 at δ 100.49 suggested that the double bond was present between C-1 and C-2 of the sugar at the nonterminal end (Bock & Pedersen, 1983; Danishefsky & Bilodeau, 1996). The presence of three free sugars i.e. D-oleandrose, D-digitoxose and D-cymarose in the acid hydrolysate of **2** also supported the position of the double bond between C-1 and C-2 of the sugar at the reducing end (Feather & Harris, 1973). The ^1H NMR spectrum of **1** contained two singlets of three protons each for two methoxy groups (δ 3.48 and 3.32) confirming the presence of only two methylated sugars i.e. D-oleandrose and D-cymarose in the trisaccharide **2**.

The sequence of sugar units in **1** and **2** was determined by their ^1H NMR spectra in conjunction with the 2-D ^1H–^1H HOMOCOSY spectrum of **1**. The downfield shift of the H-4 of D-oleandrose methine proton triplet ($J=9$ Hz) from δ 3.34 in **2** to δ 4.60 in **1** confirmed the presence of D-oleandrose at the terminal end. The 2-D spectrum of **1** showed the connectivity of the H-1 of the nonterminal sugar at δ 6.36 (d, $J=5.5$ Hz) with H-2 (t, $J=5.5$ Hz) at δ 4.93, H-2 showed connectivity with H-3 (dd, $J=5.5$ Hz and 2.5 Hz) at δ 3.81, H-3 showed connectivity with H-4 at δ 3.52 (dd, $J=10$ and 2.5 Hz) which connected with H-5 at δ 4.14–4.09 (m) and H-5 finally coupled with the secondary methyl doublet at δ 1.28. All these resonances were assigned to the second methylated sugar, derivatized from D-cymarose(S_1), which on comparison with the ^1H NMR spectrum of **2** did not show downfield shifting of any proton and was attributed to the absence of an acylated hydroxyl group in S_1 in **1**. These observations confirmed the sugar sequence in **1** and **2** as D-oleandrose, D-digitoxose, D-cymaral derived from D-cymarose starting from the terminal end.

The configuration of the glycosidic linkages were assigned by the ^1H NMR spectrum of **1**. Two double doublets ($J=9$ and 2 Hz) of one proton each at δ 4.77 and 4.50 were attributed to anomeric protons of S_2 and S_3, respectively which suggested the presence of D-digitoxose and D-oleandrose moieties in $^4C_1$(D) conformation joined through β-glycosidic linkages (Allgeier, 1973). The small coupling constant (5.5 Hz) of the H-1 of the sugar at the nonterminal end at δ 6.36 (d) confirmed the *cis* orientation of H-1 and H-2 in S_1. The stucture of **1** was further supported by the ^{13}C NMR spectrum of **1**. The chemical shifts of ^{13}C NMR signals are given in the table.

The FABMS of **1** contained a $[M]^+$ peak at m/z 502 and a $[M+H]^+$ peak at m/z 503. The $[M+H]^+$ ion peak showed the loss of methanol, acetic acid, acetaldehyde, ketene and acetylene (see Section 3). The loss of two molecules each of acetic acid and methanol confirmed the presence of two acylated hydroxyl groups and two methoxy groups in the molecule (Khare & Khare, 1987). The spectrum also contained the significant fragment ions of di- and mono-saccharide units of **1**. The mass spectrum thus fully supported the derived structure of **2**.

In the light of the foregoing evidences, the structure of **2** was established as *O*-β-D-oleandropyranosyl-(1→4)-*O*-β-D-digitoxopyranosyl-(1→4)-D-cymaral.

Rolinose (**3**), $C_{16}H_{30}O_8$ (FABMS m/z 350) gave positive color tests in the xanthydrol (Khare et al., 1984), Keller–Kiliani (Khare et al., 1984) and Feigl (1975) reactions and showed no activity towards Fehling solution. This suggested it to be a glycoside of the rare 2,6-dideoxy and a normal sugar. The presence of two anomeric carbon signals at δ 101.96 and 97.69 in the ^{13}C NMR spectrum and two anomeric proton signals at δ 4.78(1H) and 4.60 (1H) in the ^1H NMR spectrum of **3** showed it to be a diglycoside. The presence of carbon signals at δ 15.17 and 64.43 in conjunction with a triplet (3H, $J=7$ Hz) at δ 1.20 and a quartet ($J=7$ Hz) at δ 3.95 (2H) suggested that these signals were due to a -OCH_2CH_3 group present at the anomeric position as earlier indicated by the non-reducing property of **3**.

Mannich and Siewert (1942) acid hydrolysis of **3**, after four days, afforded D-oleandrose (**5**) (Fieser & Fieser, 1967) and 3-*O*-methyl-6-deoxy-D-allose (**8**) (Mannich & Siewert, 1942). Further identification of sugar **5** was obtained by preparing its known D-oleandronic acid phenylhydrazide (Fieser & Fieser, 1967) while sugar **8** was identified by preparing its known methyl glycoside **9** (Saner, Zerlentis, Stocklin, & Reichstein, 1970). More direct chemical support for **3** being a diglycoside and the sequence of the sugars in it was provided by the results of its very mild acid (Rangaswami & Reichstein, 1949) (0.005 N H_2SO_4) hydrolysis. After 24 h the hydrolysate afforded three spots on TLC having identical mobilities with those of D-oleandrose, starting material **3** and a third spot of intermediate mobility. The hydrolysis was complete in 20 days when only two spots, identified as D-oleandrose and 3-*O*-methyl-6-deoxy-D-allose, were present; thus confirming the presence of D-oleandrose at the terminal end. The large coupling constants of the anomeric protons present at δ 4.78 (dd, $J=9$ and 2 Hz) and δ 4.60 (d, $J=8$ Hz) in the ^1H NMR spectrum of **3** indicated that both sugars were present in the $^4C_1$ (D) conformation joined through β-glycosidic linkages (Allgeier, 1973). The ^1H NMR spectrum of **3** also showed the signals for other ring protons of the sugar moieties (see Section 3).

Acetylation of **3** yielded a di-*O*-acetyl derivative **4**, $C_{20}H_{34}O_{10}$. The ^1H NMR spectrum of **4** showed downfield

shifting of H-4 of D-oleandrose from δ 3.24 to δ 4.30 (*t*, $J=9$ Hz), showing it to be the terminal sugar and H-2 of the normal sugar from δ 3.60–3.50 to δ 4.75. It also showed two singlets of three protons each at δ 2.12 and 2.10 for two acetoxy methyls.

The ^{13}C NMR data of **3** also confirmed the derived structure (see Table 1). The FAB mass spectrum of **3** showed the $[M]^+$ peak at *m/z* 350 and $[M+H]^+$ peak at *m/z* 351. The $[M]^+$ sequentially lost one OCH_2CH_3 and two molecules of CH_3OH giving fragment ion peaks at *m/z* 305, 273 and 241 showing the ethyl glycosidic nature and presence of two methoxy groups in **3**. The fragment ion at *m/z* 273 loses two water molecules to give to fragment ion at *m/z* 237 showing the presence of only two free hydroxyl groups in **3**. The $[M+H]^+$ loses the terminal sugar by hydrogen transfer to give the mass ion fragment at *m/z* 207 which was substantiated by the peak for the monosaccharide fragment at *m/z* 145 (Khare & Khare, 1987). The lower mass region contained the common 2,6-dideoxymonomethoxy hexose fragments at *m/z* 145, 113 and 95 (Khare & Khare, 1987).

In the light of foregoing evidence the structure of rolinose (**3**) was thus established as ethyl *O*-*β*-D-oleandropyranosyl-(1→4)-*O*-3-*O*-methyl-6-deoxy-*β*-D-allopyranoside.

Table 1
^{13}C NMR spectral data for compounds **1** and **3**

	C	**1**		C	**3**
Cym(S_1)	1	146.01	All(S_1)	1	101.96
	2	100.49		2	76.62[a]
	3	70.19		3	80.65[b]
	4	75.28[a]		4	82.43[b]
	5	69.55[b]		5	70.66
	6	18.26[c]		6	18.43[c]
	-OCH_3	57.32[d]		-OCH_3	62.04
Dig(S_2)	1	98.97	Ole(S_1)	1	97.69
	2	29.62		2	34.76
	3	68.99		3	76.69
	4	81.05		4	73.06[a]
	5	71.77[b]		5	66.75
	6	17.38[c]		6	17.01[c]
				-OCH_3	57.63
Ole(S_3)	1	99.78		-OCH_2CH_3	64.43
	2	35.94		-OCH_2CH_3	15.17
	3	79.56			
	4	77.77[a]			
	5	69.55[b]			
	6	18.20[c]			
	-OCH_3	56.42[d]			
	-$OCOCH_3$	21.12			
	-$OCOCH_3$	20.92			
	-$OCOCH_3$	169.98			

Value (ppm) from internal TMS in $CDCl_3$.

Cym = D-cymarose; dig = D-digitoxose; ole = D-oleandrose; all = 3-O-methyl-6-deoxy-D-allose.

[a–d] The assignments in each column may be interchangeable.

3. Experimental

General procedures were the same as reported earlier (Deepak, Srivastava, & Khare, 1997). The aerial part of the plant was collected from Dehradun, India. The identity of the plant was confirmed by Dr. S.C. Saini, Botanist, Birbal Sahini Institute of Palaeobotany, Lucknow, India, where a voucher specimen No. BSIP11870 was deposited. *M. roylei* (10 kg) was extracted as reported earlier (Deepak et al., 1997) yielding hexane (0.81 g), $CHCl_3$ (9.80 g), $CHCl_3$–EtOH (4:1) (4.40 g) and $CHCl_3$–EtOH (3:2) (5.84 g) soluble extracts. Compound **1** (70 mg), as a viscous mass, was isolated by CC of the acetylated simplified fraction of the $CHCl_3$-soluble extract due to poor resolution of the fraction containing **2** on TLC.

3.1. Compound *1*

$[\alpha]_D+216^\circ$ (*c*, 0.37, $CHCl_3$), found: C 57.32; H 7.60 $C_{24}H_{38}O_{11}$ requires C 57.36; H 7.56. Blue coloration with vanillin–perchloric acid spray reagent and positive tests in the xanthydrol and Keller–Kiliani reactions. Positive reaction with tetranitromethane. ^{1}H NMR (400 MHz): δ 6.36 (d, 1H, $J_{1,2}=5.5$ Hz, H-1, S_1), 5.38–5.34 (m, 1H, H-3, S_2), 4.93 (t, 1H, $J_{1,2,3}=5.5$ Hz, H-2, S_1), 4.77 (dd, 1H, $J_{1,2}=9$ and 2 Hz, H-1, S_2), 4.60 (t, 1H, $J_{3,4,5}=9$ Hz, H-4, S_3), 4.50 (dd, 1H, $J_{1,2}=9$ and 2 Hz, H-1, S_3), 4.14–4.09 (m, 1H, H-5, S_1), 3.90–3.85 (m, 1H, H-5, S_2), 3.81 (dd, 1H, $J_{2,3,4}=5.5$ Hz and 2.5 Hz, H-3, S_1), 3.52 (dd, 1H, $J_{3,4,5}=10$ and 2.5 Hz, H-4, S_1), 3.48 (s, 3H, -OCH_3), 3.32 (bs, 6H, -OCH_3, H-4, S_2, H-5 and H-3, S_3), 234-2.28 (m, 1H, H-2eq, S_3), 2.19–2.14 (m, 1H, H-2eq, S_2), 2.12, 2.06 (2s, 6H, $2\times OCOCH_3$), 1.88–1.80 (m, 1H, H-2ax, S_2), 1.62–1.54 (m, 1H, H-2ax, S_3), 1.28, 1.24, 1.13 (3d, 9H, $J=6$ Hz, $3\times CH_3$): FABMS *m/z*: 503 $[M+H]^+$, 502 $[M]^+$, 471 [503-CH_3OH]$^+$, 443 [503-CH_3COOH]$^+$, 439 [471-CH_3OH]$^+$, 429 [471-$CH_2{=}C{=}O$)]$^+$, 411 [443-CH_3OH]$^+$, 369 [429-CH_3COOH]$^+$, 359 $[C_6H_{11}O_3]^+$, 357 [443-CH_3COOH, -CH≡CH]$^+$, 345 [471-$CH_3CH{=}CHOCOCH_3$, -CH≡CH]$^+$, 316 [502-S_3]$^+$, 307 [411-CH_3CHO, -CH_3COOH]$^+$, 299 [359-CH_3COOH]$^+$, 289 [359-CH_3CHO, CH≡CH]$^+$, 285 [345-CH_3COOH]$^+$, 273 [299-CH≡CH]$^+$, 257 [299-$CH_2{=}C{=}O$]$^+$, 226 [273-CH_3, -CH_3OH]$^+$, 207 [299-H_3C–HCO, -CH_3OH]$^+$, 190 [316-S_2]$^+$, 187 [S_3]$^+$, 173 [190-OH]$^+$, 155 [187-CH_3OH]$^+$, 154 [190-$2H_2O$]$^+$, 137 [207-CH_3CHO, -CH≡CH]$^+$, 127 [187-CH_3COOH]$^+$, 113 [173-CH_3COOH]$^+$, 111 [155-CH_3CHO]$^+$, 95 [127-CH_3OH]$^+$, 69 [113-CH_3CHO]$^+$.

3.2. Methanolic KOH hydrolysis of *1*

Compound **1** (55 mg) was dissolved in 1% methanolic KOH (5 ml) and heated under reflux for 1 h which after usual work up yielded maryal (**2**) (41 mg, 89%), $[\alpha]_D$ $+185^\circ$ (*c*, 0.27, $CHCl_3$), found C 57.32; H 8.19, $C_{20}H_{34}O_9$ requires C 57.41; H 8.13, ^{1}H NMR (400 MHz): δ 6.37 (d,

1H, $J_{1,2}=5.5$ Hz, H-1, S_1), 4.95–4.88 (m, 2H, H-2, S_1, H-1, S_2), 4.57 (dd, 1H, $J_{1,2}=9$ and 2 Hz, H-1, S_3), 4.28–4.23 (m, 1H, H-3, S_2), 4.16–4.10 (m, 1H, H-5, S_1), 3.86–3.77 (m, 2H, H-5, S_2, H-3, S_1), 3.55 (dd, 1H, $J_{3,4,5}=10$ and 2.5 Hz, H-4, S_1), 3.46 (s, 3H, -OCH_3), 3.40 (s, 3H, -OCH_3), 3.34 (t, 1H, $J_{,3,4,5}=9$ Hz, H-4, S_3) 3.25 (dd, 1H, $J_{3,4,5}=10$ and 2 Hz, H-4, S_2) 3.20–3.14 (m, 2H, H-5, H-3, S_3) 2.37–2.32 (m, 1 H, H-2eq, S_3) 2.22–2.17 (m, 1H, H-2eq, S_2), 1.86–1.79 (m, 1H, H-2ax, S_2), 1.55–1.48 (m, 1H, H-2ax, S_3), 1.34 (d, 6H, $J=6$ Hz, $2\times CH_3$), 1.28 (d, 3H, $J=6$ Hz, CH_3).

3.3. Mild acid hydrolysis of **2**

To a soln of **2** (30 mg) in 1,4-dioxane (1 ml) 0.1 N H_2SO_4 (1 ml) was added and the soln was warmed for 30 min at 50°. Dioxane was then removed under reduced pressure. The aq. portion was neutralized with freshly prepared $BaCO_3$, filtered and concentrated under reduced pressure followed by CC to afford **5** (9.2 mg, 79%), $[\alpha]_D$ −12° (*c*, 0.76, H_2O), **6** (8.5 mg, 80%), $[\alpha]_D$ +43° (*c*, 0.70, H_2O) and **7** (9.O mg, 77%), $[\alpha]_D$ +54° (*c*, 0.75, MeOH), identified as D-oleandrose, D-digitoxose and D-cymarose by comparison with authentic samples (PC, TLC, $[\alpha]_D$).

3.4. Acid phenylhydrazides

Solns of separated sugars **3**, **4** and **5** (8 mg each) in H_2O (0.4 ml) when oxidized with Br_2 water (6 μl) separately using the usual method to give the respective lactones which on treatment with phenylhydrazine yielded known D-oleandronic acid phenylhydrazide (7.2 mg, 59%), mp 133–136°, D-digitoxonic acid phenylhydrazide (6.9 mg, 56%), mp 121–123°, and D-cymaronic acid phenylhydrazide (8.0 mg, 65%), mp 150–154° (mp, mmp, TLC and PC).

3.5. Rolinose

(107 mg) was isolated by repeated CC of the $CHCl_3$-soluble extract of *M.roylei*. Rolinose, $[\alpha]_D$ +15° (*c*, 0.67, $CHCl_3$), found C 54.92; H 8.52, $C_{16}H_{30}O_8$ requires C 54.85; H 8.57. Blue coloration with vanillin–perchloric acid spray reagent, positive tests in xanthydrol, Keller–Kiliani and Feigl reactions. No reduction of Fehling solution. ^{1}H NMR (400 MHz): δ 4.78 (dd, 1H, $J_{1,2}=9$ and 2 Hz, H-1, S_2), 4.60 (d, 1H, $J_{1,2}=8$ Hz, H-1, S_1), 3.98–3.88 (m, 1H, H-5, S_2), 3.95 (q, 2H, $J_{1,2}=7$ Hz, -OCH_2CH_3), 3.85–3.78 (m, 1H, H-3, S_2), 3.70 (t, 1H, $J_{2,3,4}=3$ Hz, H-3, S_1), 3.68 (s, 3H, -OCH_3, S_1), 3.60–3.50 (m, 2H, H-2, H-5, S_1), 3.45 (s, 3H, -OCH_3, S_2), 3.32 (dd, 1H, $J_{3,4,5}=8$ and 2 Hz, H-4, S_1), 3.24 (t, 1H, $J_{3,4,5}=9$ Hz, H-4, S_2), 2.22–2.12 (m, 1H, H-2eq, S_2), 1.64–1.58 (m, 1H, H-2ax, S_2), 1.30, 1.25 (2d, 6H, $J=6$ Hz, $2\times CH_3$) and 1.20 (t, 3H, $J_{1,2}=7$ Hz, -OCH_2CH_3); FABMS *m/z*: 351 $[M+H]^+$, 350 $[M]^+$, 305 $[M–OCH_2CH_3]^+$, 273 [305-$CH_3OH]^+$, 241 [273-$CH_3OH]^+$, 237 [273-$2H_2O]^+$, 223 [241-$H_2O]^+$, 207 [351-$S_2]^+$, 197 [241-$CH_3CHO]^+$, 175 [207-$CH_3OH]^+$, 145 [S_2l$^+$, 131 [175-$CH_3CHO]^+$, 113 [145-$CH_3OH]^+$ and 95 [113-$H_2O]^+$.

3.6. Mannich hydrolysis of **3**

To a soln of **3** (40 mg) in Me_2CO (5 ml) conc. HCl (0.05 ml) was added. After four days the hydrolysis was complete and after usual workup afforded **5** (15 mg, 80%), $[\alpha]_D$ −11° (*c*, 1.2, H_2O) and **8** (17.0 mg, 83%), $[\alpha]_D$ +9° (*c*, 1.3, H_2O), identified as D-oleandrose and 3-*O*-methyl-6-deoxy-D-allose, respectively, by comparison with authentic samples (TLC, PC, $[\alpha]_D$).

3.7. Very mild acid hydrolysis of **3**

To a soln of **3** (15 mg) in 1,4-dioxane (1.5 ml) 0.01 N H_2SO_4 (1.5 ml) was added and the soln was kept at room temperature. After 24 h, the reaction mixture exhibited three spots on TLC having identical mobility with that of D-oleandrose, unhydrolyzed starting material **3** (TLC, PC) and an unidentified third spot of intermediate mobility. The hydrolysis was complete after 20 days and after usual workup followed by CC afforded **5** (5.5 mg, 88%) and **8** (6.2 mg, 81%) identified as D-oleandrose and 3-*O*-methyl-6-deoxy-D-allose, respectively (TLC, PC, $[\alpha]_D$).

3.8. D-oleandronic acid phenylhydrazide

Solns of sugar **5** (5.0 mg each) in H_2O obtained from the Mannich and very mild acid hydrolysis of **3** when oxidized with Br_2 water (12 μl) separately by the method reported earlier yielded lactone which on treatment with phenylhydrazine yielded known D-oleandronic acid phenylhydrazide (3.5 mg, 46% and 4.2 mg, 55%), mp 133–136° (mp, mmp, TLC and PC).

3.9. *Methyl* 3-O-*methyl-6-deoxy*-α-D-allopyranoside

Sugar **8** (15 mg) obtained from the very mild acid and Mannich hydrolysis of **3** was refluxed with absolute MeOH at 70° for 18 h in the presence of cation exchange IR (120) H^+ resin. The reaction mixture was filtered while hot and filtrate was concentrated. CC of the concentrate gave methyl 3-*O*-methyl-6-deoxy-α-D-allopyranoside (6 mg, 74%), mp 109–111° (mp, mmp, PC, TLC).

3.10. Acetylation of **3**

Amorphous compound **3** (10 mg) was acetylated with Ac_2O (1 ml) in pyridine (1 ml) at 100° which after usual workup gave **4** (11 mg, 80%), $[\alpha]_D$+5° (*c*, 0.43, $CHCl_3$), found *C* 55.23; H 7.87 $C_{20}H_{34}O_{10}$ C 55.29; H 7.83. ^{1}H

NMR (400 MHz): 4.30 (t, 1H, $J_{3,4,5}=9$ Hz, H-4, S_2), 4.75 (dd, 1H, $J_{1,2,3}=9$ and 2 Hz, H-2, S_1), 2.12, 2.10(2s, 6H, $2\times$-OCOCH_3) and other significant peaks.

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