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## Note

# Two new phytoconstituents from *Rumex maritimus*

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A new polyhydroxy ketone derivative and a terpene glycoside have been isolated from the seeds of *Rumex maritimus*. Their structures have been established as 3,7,11,15-tetramethyl-*n*-octadac-13-en-3,4,6,7,8,11-hexol-12-one **1** and 8β-hydroxy-14β-methyl-7-oxopodocarp-5-en-13-(19α-hydroxy-19,22,22-trimethyl-heptyl)-22-O-(β-D-glucopyranosyl)-(4→1) β-D-glucopyranoside **2**, respectively, on the basis of chemical and spectral data analysis.

**Keywords:** *Rumex maritimus*, polyhydroxy ketone, terpene glycoside, 3,7,11,15-tetramethyl-*n*-octadac-13-en-3,4,6,7,8,11-hexol-12-one, 8β-hydroxy-14β-methyl-7-oxopodocarp-5-en-13-(19α-hydroxy-19,22,22-trimethylheptyl)-22-O-(β-D-glucopyranosyl)-(4→1) β-D-glucopyranoside, antipyretic, cathartic, aphrodisiac

*Rumex maritimus* Linn. is a stout erect annual, 30-120 cm high occurring in temperate Himalayas, and on wet ground along riverbanks in the plains of north India. It is found growing in marshes in Assam and Bengal, Western ghats, Nilgiri and Palni hills[1-3]. The plant is an important drug used in Indian systems of medicine as antipyretic, cathartic and aphrodisiac[1-4]. The alcoholic extract is reported to have antifungal activity[5,6]. Presence of anthraquinones, sterols, flavonoids, tannins and carbohydrates has been reported from the plant so far[7-18]. In the present study is reported the isolation and structural elucidation of a new polyhydroxy ketone and a terpene glycoside from the alcoholic extract of the seeds of *Rumex maritimus.*

## Results and Discussion

Compound **1** was obtained as white crystals from chloroform-methanol (9.2:0.8) eluents. Its IR spectrum exhibited absorption bands for carbonyl group (1718 $cm^{-1}$), hydroxyl group (3370 $cm^{-1}$) and unsaturation (1625 $cm^{-1}$). It responded positively to tetranitromethane and decolourized bromine water, indicating unsaturated nature. It formed 2,4-dinitrophenylhydrazone derivative suggesting the presence of carbonyl group. Methylation of the compound produced hexamethoxy derivative, indicating the presence of six-hydroxyl groups. The EIMS of this compound showed a molecular ion peak at *m/z* 418 corresponding to $C_{22}H_{42}O_7$, which was supported by $^1H$,$^{13}C$ and $^{13}C$ DEPT NMR spectra. The important ion peaks 375, 71, 97, 125, 169, 147, 129, 117, 103, 357, 297, 85 and 55 suggested that the compound **1** was a polyhydroxy ketone, possessing a long hydrocarbon chain with carbonyl group at C-12 and unsaturation at C-13, respectively. These observations were fully supported by $^1H$ and $^{13}C$ NMR data. The $^1H$ NMR spectrum of **1** exhibited two downfield one-proton signals at δ 6.14 and 5.62 (*J*=2.1 Hz) corresponding to C-14 and C-13 vinylic protons, respectively. Two one-proton double doublets at δ 4.37 and 4.48 with coupling interaction of 9.32, 4.72 and 8.68, 4.50 Hz were ascribed to α-oriented C-6 and C-8 carbinol protons, respectively and a broad signal at δ 3.76 with half width of 15.5 Hz was associated with α-oriented C-4 carbinol proton. C-19, C-20 and C-21 methyl groups attached to the oxygenated carbons were observed as broad singlets, integrating for three protons each, at δ 1.17, 1.18 and 1.19, respectively. The remaining methyl groups resonated at δ 1.20 ($CH_3$-22), 0.92 ($CH_3$-1) and 0.75 ($CH_3$-18). C-15 methine proton appeared as doublet of doublets at δ 2.20 (*J*=5.8, 6.20 Hz). The methylene protons resonated between δ 1.80-1.22. Further evidence for the structure was provided by $^{13}C$ NMR data. $^{13}C$ NMR spectrum of **1** showed 22 carbon signals. The signals at δ 202.25, 120.41 and 165.18 were assigned to C-12 carbonyl carbon, C-13 and C-14 olefinic carbons, respectively. $^{13}C$ DEPT experiments showed the presence of six methyl, six methylene, four methine, and four quaternary carbons (**Figure 1**). $^1H$-$^{13}C$ HETCOR spectrum showed correlation of H-4 with C-3 and C-5; H-6 with C-7 and C-5; H-8 with C-7 and C-9; H-13 with C-12 and C-4 and H-15 with C-14 and C-16. On the basis of

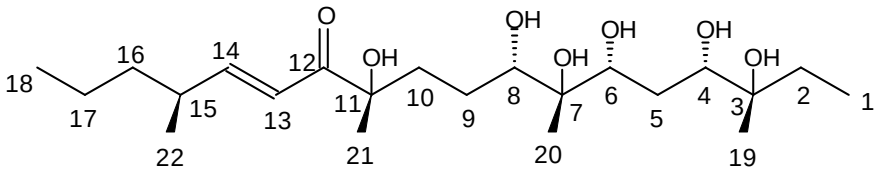


**Figure 1**

these evidences the structure of **1** has been elucidated as 3,7,11,15-tetramethyl-*n*-octadac-13-en-3,4,6,7,8,11-hexol-12-one. This constitutes the first report of the occurrence of a polyhydroxy ketone in *Rumex maritimus*.

Compound **2** responded positively to the Liebermann Burchard reagent and Molish test. Its molecular weight was established as 774 $[M]^+$ corresponding to $C_{40}H_{70}O_{14}$, on the basis of $^{13}C$ NMR and FABMS data. Its IR spectrum showed the presence of hydroxyl group (3400 $cm^{-1}$), carbonyl group (1701 $cm^{-1}$) and unsaturation (1654 $cm^{-1}$). The Mass spectrum displayed prominent ion peak at *m/z* 448 due to the loss of sugar moiety from the aglycone. Significant ions peak at *m/z* 275 suggested that **2** was an analog of podocarpic acid, which was fully supported by $^1H$ and $^{13}C$ NMR and $^{13}C$ DEPT spectra[19]. Other important ion peaks were observed at *m/z* 275, 164, 136, 131, 84 and 59.

The $^1H$ NMR spectrum displayed a one proton broad signal at δ 5.63 assigned to C-6 vinylic proton. Three broad signals at δ 1.18, 0.84 and 0.74, integrating for three protons each, were associated correspondingly with C-27, C-25 and C-28 tertiary methyl groups. A broad signal at δ 1.20 integrating for nine protons was ascribed to C-23, C-24 and C-26 tertiary methyl protons attached to oxygenated carbons. A three-proton doublet at δ 1.17 (*J*=6.5 Hz) indicated the presence of a secondary methyl group at C-14. The presence of methyl resonances between δ 1.12 and 0.74 supported their location on the saturated carbons. A one-proton triplet at δ 2.97 was assigned to C-9 methine proton. C-13 and C-14 methine protons resonated at δ 1.21 as a multiplet. The methylene protons appeared between δ 2.49 and 1.29. Acid hydrolysis of **2** with 2*N* HCl gave a sugar moiety along with the aglycone. The sugar protons appeared in the range of δ 3.10-4.90. The appearance of two anomeric carbon signals at δ 101.00 and 101.04 in $^{13}C$ NMR spectrum and two proton resonances at δ 4.65 (*J*=6.9 Hz) and 4.97 (*J*=7.6 Hz) in the $^1H$ NMR spectrum confirmed the existence of a disaccharide moiety in compound **2**. Further, in the $^{13}C$ NMR spectrum, 10 methine resonances in the range of δ 76-70 and two oxymethylenes at δ 61.68 and 61.08 supported the existence of two hexapyranose residues. The hexapyranose residues were identified as glucopyranose by analysis of COSY and TOCSY spectra. The sugars were also analyzed using PC and HPTLC, by comparing with authentic samples after acid hydrolysis of compound **2**.

The $^1$ H-$^{13}C$ NMR spectrum long-range correlations were observed between the anomeric proton at δ 4.65 and C-22, ascertaining that the sugar moiety was attached at C-22 of the aglycone, which was supported by mass fragmentation data. The interglycosidic linkage and sequence of sugars was established by 2D NOESY and HMBC spectra as β-D-Glu (4→1)-β-D-Glu. The proton resonances at δ 4.65 (*J*=6.9 Hz) and 4.97 (*J*=7.6 Hz) were assigned to anomeric protons of β-D-glucose I and β-D-glucose II, respectively (**Figure 2**).

The $^{13}C$ NMR signals at δ 202.45, 165.44, 120.54, and 68.80 were assigned correspondingly to C-7 carbonyl carbon, C-5 and C-6 vinyl carbons and C-22 of the aglycone, respectively. The $^{13}C$ DEPT experiment of the aglycone supported these assignments. It displayed the presence of seven methyl, ten methylene, four methine, and seven quaternary carbons. In the HMBC spectrum, $^1H$-$^{13}C$ long-range correlations were observed for Me-23 and Me-24 protons with C-21 and C-22. Me-15 protons correlated with C-14, C-13 and C-12. C-25 methyl protons were found to show correlation with C-1, C-9 and C-10. Me-27 and Me-28 protons showed long-range correlations with C-3 and C-4. On the basis of these data, the structure of **2** was elucidated as 8β-hydroxy-14β-methyl-7-oxopodocarp-5-en-13-(19α-hydroxy-19,22,22-trimethylheptyl)-22-O-(β-D-glucopyranosyl)-(4→1) β-D-glucopyranoside **2**.

## Experimental Section

UV-Vis spectra were recorded on a Perkin Elmer Lamda-20 spectrophotometer. IR spectra were

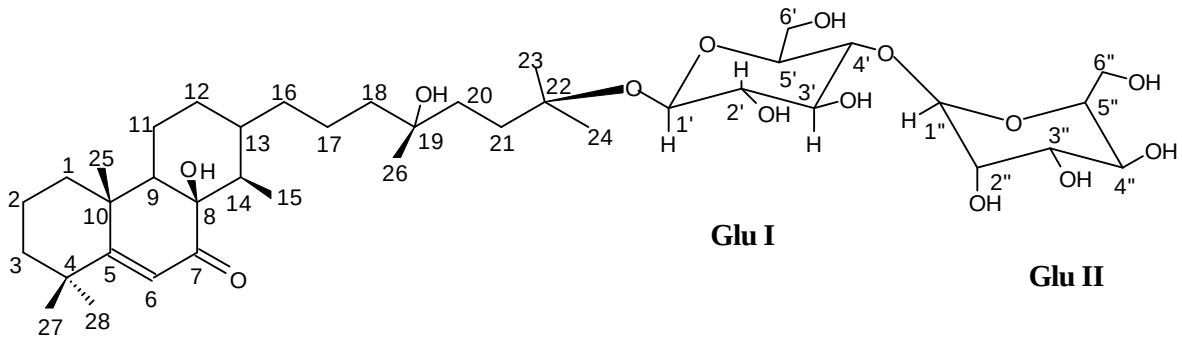


**Figure 2**

recorded in KBr pellets on Win IR FTS 135 instrument. $^{1}$ H, $^{13}$C NMR, $^{1}$ H-$^{1}$ H COSY, HMBC, HMQC, NOESY and TOCSY spectra were recorded on a Bruker 400 MHz spectrometer with TMS as internal standard. FABMS was scanned on JMX-PX 303 mass spectrometer and EIMS was recorded on Joel D-300 mass instrument. HPTLC was carried out on a Camag system using Linomat-5, over silica gel H (5-7 μm) HPTLC plate. The spots were visualized by spraying aniline phthalate reagent and ferric chloride, followed by heating. Column chromatography was carried out over silica gel (60-120 mesh, Merck). TLC was run on silica gel 60 $F_{254}$ (Merck).

**Plant material**: Seeds (1.5 kg) of *Rumex maritimus* were procured from a local market of Delhi and identified by Dr. M. P. Sharma, Department of Botany, Faculty of Science, Jamia Hamdard. A voucher specimen is deposited in Phytochemistry laboratory of this University.

**Extraction and Isolation**: The dried and coarsely ground seeds (1.5 Kg) were extracted successively with petroleum ether, chloroform and ethanol (95%) in a Soxhlet apparatus and the extract concentrated under reduced pressure. The defatted alcoholic extract obtained, as thick dark brown mass, was dried and dissolved in a minimum amount of methanol and adsorbed on silica gel to form slurry. The air-dried slurry was loaded on a silica gel column packed in petroleum ether. The column was eluted successively with petroleum ether-chloroform and chloroform-methanol gradient mixtures to isolate compounds **1** and **2**.

### Acid hydrolysis of compound 2

Compound **2** was hydrolyzed with conc. HCl vapour on the HPTLC precoated plate (85°C, 15 min) followed by developing with solvent system *n*-BuOH-$C_6H_6$-Py-$H_2O$ (5:1:3:3). The comparison was carried out with authentic sugar samples. The brown spots were visualized with aniline phthalate reagent, and the sugar identified as glucose.

### Compound 1

Elution of the column with chloroform-methanol (9.2:0.8) furnished white needle shaped crystals of **1**, which were purified by recrystallization from chloroform-methanol (1:1), 40 mg (0.0037% yield), $R_f$ 0.56 (ethyl acetate-formic acid-water (88:6:6), m.p. 272- 273°C; UV-Vis (MeOH): 225 nm (log ε 4.3); IR (KBr): 3450, 3370, 2963, 1718, 1652, 1467, 1442, 1384, 1229, 1147, 1055, 920 cm$^{-1}$; $^{1}$H NMR ($CDCl_3$): δ 6.14 (1H, brs, H-14), 5.62 (1H, d, *J* = 2.1 Hz, H-13), 4.83 (1H, brs, OH), 4.48 (1H, dd, *J* = 8.68 and 4.50 Hz, H-8), 4.37 (1H, dd, *J* = 9.32 and 4.72 Hz, H-6), 3.76 (1H, brs, $W_{1/2}$ 15.5 Hz, H-4), 2.20 (1H, dd, *J* = 5.80 and 6.20 Hz H-15), 1.80 (2H, m, $H_2$-16), 1.67 (2H, m, $H_2$-10), 1.62 (2H, d, *J* = 6.00 Hz $H_2$-9), 1.52 (2H, m, $H_2$-5), 1.50 (2H, m, $H_2$-17), 1.22 (2H, dd, *J* = 6.50 and 6.00 Hz, $H_2$-2), 1.19 (3H, brs, Me-21), 1.18 (3H, brs, Me-20), 1.17 (6H, brs, Me-19, Me-22), 0.82 (3H, brs, Me-1), 0.75 (3H, brs, Me-18); $^{13}$C NMR ($CDCl_3$): δ 20.21 (C-1), 37.57 (C-2), 83.01 (C-3), 66.54 (C-4), 48.65 (C-5), 66.72 (C-6), 68.75 (C-7), 76.16 (C-8), 46.82 (C-9), 41.31 (C-10), 75.74 (C-11), 202.75 (C-12), 120.41 (C-13), 165.18 (C-14), 50.03 (C-15), 40.67 (C-16), 28.89 (C-17), 17.07 (C-18), 20.90 (C-19), 23.79 (C-20), 26.03 (C-21), 28.94 (C-22); EIMS: *m/z* (%) 418 $[M]^+$ ($C_{22}H_{42}O_7$) (5.3), 375 (11.0), 357 (14.1), 339 (49.3), 321 (10.2), 297 (11.3), 169 (8.7), 142 (11.3), 129 (7.3), 125 (7.6), 123 (10.4), 117 (8.5), 103 (6.7), 97 (48.2), 85 (31.7), 71 (15.6), 55 (36.4), 43 (100).

### Compound 2

Elution of the column with chloroform-methanol furnished white crystals of **2**, which were purified by

recrystallization from chloroform-methanol (1:1), 35 mg (0.0030% yield), $R_f$ 0.34 (ethyl acetate-formic acid-water, 8.8: 0.6: 0.6), m.p. 284-285°C; UV-Vis (MeOH): 240 nm (log ε 4.3); IR (KBr): 3400, 2964, 2877, 1701, 1654, 1450, 1385, 1154, 1077, 1056 $cm^{-1}$; $^1H$ NMR (DMSO-$d_6$): δ 5.63 (1H, brs, H-6), 4.65 (1H, d, *J* = 6.9 Hz, H-1′), 4.97 (1H, d, *J* = 7.6 Hz, H-1″), 3.63 (1H, dd, *J* = 5.5, 5.2 Hz, H-2′), 3.97 (1H, dd, *J* = 5.5, 4.0 Hz, H-2″), 3.99 (1H, m, H-3′), 3.74 (1H, m, H-3″), 4.14 (1H, m, H-4′), 3.62 (1H, m, H-4″), 4.15 (1H, d, *J* = 4.5 Hz, H-5′), 4.08 (1H, d, *J* = 4.50 Hz, H-5″), 3.65 (1H, d, *J* = 9.9 Hz, H-$6_a$′), 3.55 (1H, d, *J* = 9.9 Hz, H-$6_b$′), 3.14 (1H, d, *J* = 6.5 Hz, H-$6_a$″), 3.10 (1H, d, *J* = 6.5 Hz, H-$6_b$″), 2.97 (1H, t, H-9), 2.49 (1H, m, $H_2$-11), 2.26 (1H, d, *J*= 6.3 Hz, H-13), 2.24 (1H, m, $H_2$-1), 2.21 (2H, m, H-13, H-14), 2.00 (1H, m, $H_2$-3), 1.77 (1H, m, $H_2$-12), 1.77 (1H, m, $H_2$-2), 1.64 (1H, m, $H_2$-16), 1.60 (1H, m, $H_2$-17), 1.53 (1H, m, $H_2$-18), 1.38 (1H, m, $H_2$-20), 1.29 (1H, m, $H_2$-21), 1.20 (9H, brs, Me-23 24 and 26), 1.18 (3H, brs, Me-27), 1.17 (3H, d, *J* = 6.5 Hz, Me-15), 0.84 (3H, brs, Me-25), 0.74 (3H, brs, Me-28); $^{13}C$ NMR (DMSO-$d_6$): δ 34.98 (C-1), 30.87 (C-2), 30.36 (C-3), 37.84 (C-4), 165.44 (C-5), 120.34 (C-6), 202.45 (C-7), 83.02 (C-8), 50.13 (C-9), 37.84 (C-10), 26.16 (C-11), 33.15 (C-12), 48.73 (C-13), 46.82 (C-14), 19.91 (C-15), 20.31 (C-16), 20.31 (C-17), 19.91 (C-18), 75.77 (C-19), 26.16 (C-20), 29.05 (C-21), 68.80 (C-22), 29.96 (C-23), 29.05 (C-24), 23.68 (C-25), 23.68 (C-26), 21.02 (C-27), 17.14 (C-28), 101.00 (C-1′), 74.60 (C-2′), 73.69 (C-3′), 70.13 (C-4′), 76.75 (C-5′), 61.08 (C-6′), 101.01 (C-1″), 74.60 (C-2″), 73.69 (C-3″), 63.65 (C-4″), 76.28 (C-5″), 61.08 (C-6″); FABMS: *m/z* (%) 774 $[C_{40}H_{70}O_{14}]^+$(N.O), 448 (65.5), 432 (54.1), 414 (16.8), 375 (11.3), 362 (22.2), 345 (28.3), 319 (18.6), 275 (35.6), 182 (14.1), 164 (9.4), 150 (24.0), 148 (21.5), 136 (12.5), 131 (19.8), 110 (9.1), 104 (51.3), 84 (41.2), 73 (29.6), 59 (30.1), 45 (100).

## Conclusion

Important medicinal properties ascribed to this plant may be partly due to the presence of the phytoconstituents isolated in the present study, as podocarpic acid analogues are associated with a high therapeutic potential[20-22].

## Acknowledgement

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## References

1 Anonymous, *The Wealth of India, Raw Materials* Vol. IX**,** (Publication and Information Directorate, CSIR, New Delhi) **1972**, 90.
2 Chopra R N, Nayar S L & Chopra I C, *Glossary of Indian Medicinal Plants* (National Institute of Science Communication, New Delhi) **1996**, 216.
3 Asima C & Satyesh C P, *The Treatise of Indian Medicinal Plants* Vol. 1, (Publication and Information Directorate, CSIR, New Delhi) **1994**, 66.
4 Ram P R & Melhrotra B N, *The Compendium of Indian Medicinal Plants*, Vol. 3, (Publication and Information Directorate, CSIR, New Delhi) **1984**, 559.
5 Agarwal J S, Rastogi R P & Srivastava O P, *Curr Sci*, 45(17), **1976**, 619.
6 Dhar M L & Agarwal J S, *Indian J Exp Biology*, 11(43), **1973**, 90.
7 Rada K, Hrochora V, Sfarhova H & Brazdova V, *Acta Fac Pharm*, 25, **1974**, 153.
8 Fairbairn J W & El-Muhtadi F J, *Phytochemistry*, 11(1), **1972**, 263.
9 Feliks K & Irena U, *Biul Inst Roslin*, 10(2-3)**, 1964**, 106.
10 Djozan D J & Assadi Y, *Talanta*, 42 (6), **1995**, 816.
11 Temezer A, Omer A N, Orbey M T & Sener B, *J Chem Soc Pakistan*, 10(4), **1988**, 455.
12 Brazdhova V, Krmelova V, Rada K & Starhova H, *Sci Pharm*, 35(2), **1968**, 116.
13 Bagrii A K, Kurmaz B V & Litvinenko V I, *Nauk Uz USSR***,** 2(2), **1966**, 85.
14 Muzychkina R A, Kamzenova V B, Sarsenbaiva K K, Muhkhamed Y M M & Voronova G N, *Alma-Ata*, **1989**, 78.
15 Munirrudin A, Datta B K, Rauf A S S & Ahmad M, *Pharmazie*, 46(7), **1991**, 548.
16 Kusuzum A D & Omer L, *Farm Bilimler Derg*, 22(2), **1997**, 79.
17 Wells J R, Kaufmann P B & Johnes J D, *Aquat Bot*, 9(2), **1980**, 185.
18 Wells J R, Kaufmann P B, Jones J D, Estabrook G F & Ghosheh N S, *J Radioana Chem*, 71(1-2), **1982**, 97.
19 Dethlefs F, Gerhardt K O & Stan J H, *J Mass Spectrometry*, 31(10), **1996**, 1163.
20 Snell N J C, *Antimicrob Chemother*, 47(3), **2001**, 251.
21 Brandt C W & Ross D J, *Nature*, 161**, 1948,** 892.
22 Parish E J & Miles D H, *J Pharm Sci*, 73(5), **1984**, 694.