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NOTE

New triterpenoid glycosides from *Abrus precatorius*

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Abstract : Two new triterpenoid glycosides, 3β,24-dihydroxyurs-12-en-28-oic acid-24-*O*-β-D-xylopyranoside and 3β,24-dihydroxyurs-12-en-28-oic acid-3-*O*-β-D-xylopyranoside were isolated from the aerial parts of *Abrus precatorius* Linn. (Leguminosae). Their structures were elucidated by spectroscopic and chemical methods.

Keywords : *Abrus precatorius*, Leguminosae, triterpenoid glycosides.

Introduction

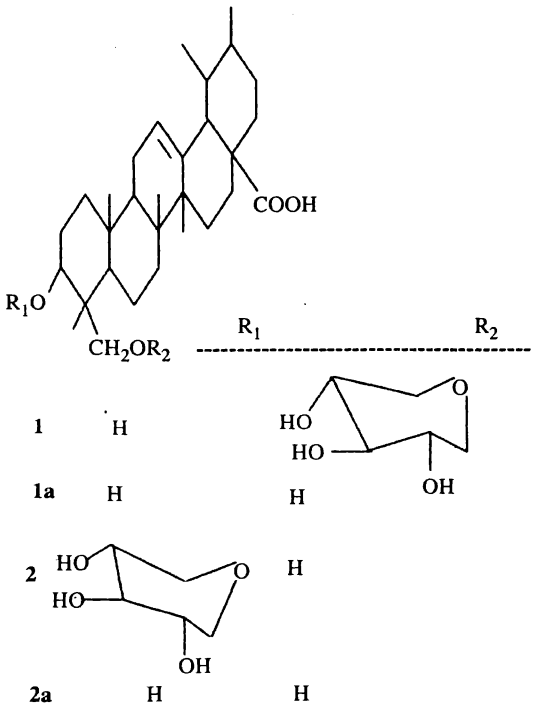
Abrus precatorius Linn. (Papilionaceae, Leguminocae) commonly known Crab's Eye, Ratti, Gunja, Vigrown throughout the holler part and hilly tracts of India. The seed are used as abortifacient, nerve depressant, diuretic, emetic, purgative, sedative and other medical purposes and most are emetic and alexiteric[1,2].

Plants belonging to the genus *Abrus* are well-known drugs in African folk medicine, mainly used due to their expectorant and mucolytic activity. Triterpenoid glycosides from *Abrus precatorius* have been shown to exhibit anti-inflammatory activity[1]. Many compounds of structural significance and medicinal importance have been reported from different species of this genus[2]. As a part of our project on the chemical investigation of medicinal plants, we report herein the isolation and characterization of two new triterpenoid xylopyranosides from the aerial parts of *Abrus precatorius*.

Results and discussion

The water-insoluble portion of the hot ethanolic extract of the air-dried and crushed aerial parts of *Abrus precatorius* was extracted successively with hexane, benzene, chloroform and ethyl acetate in a soxhlet extractor. From hexane fraction on flash column chromatography compounds **1** and **2** were isolated.

Compound **1**, $C_{35}H_{52}O_8$, a glycoside on acid hydrolysis gave D-xylose (^{13}C NMR : δ 106.4, 74.6, 79.4, 71.0, 68.8) and an aglycone **1a**. The aglycone gave colour reactions[3-6] of unsaturated pentacyclic triterpenoid. The IR spectrum of **1a** showed absorption for hydroxyl (3400 cm^{-1}), carboxyl (3200 and 1700 cm^{-1}), trisubstituted olefinic double bond (1630 cm^{-1}). The ^1H NMR spectrum of **1a** showed signals for four tertiary methyl groups at δ 0.92, 0.98, 1.02 and 1.08 (each 3H, s), two secondary methyl groups at δ 0.93 (3H, d, *J* 5.6 Hz) and 1.05 (3H, d, *J* 6.0 Hz) and a vinyl proton at δ 5.45 (1H, t, *J* 3.4 Hz), suggesting it to be an urs-12-ene type of triterpenoid. The mass fragmentation peaks at *m/z* 223 and 248 due to retro Diels-Alder fragmentation of ring C further supported the urs-12-ene structure. Subsequent ion peaks at *m/z* 205 and 203 due to loss of H_2O and -COOH group showed that ring A/B contained hydroxyl group and ring D/E, a carboxyl group. The presence of hydroxyl group, at C-3 was supported by positive Zimmermann test[7] as well as by ^{13}C NMR signal for C-3 at δ 78.0. C-3 hydroxyl was assigned equatorial β-orientation as the ^1H NMR signal for C-3 proton at δ 3.83 (1H, dd, *J* 9.6 Hz) was due to its axial (α) orientation[8,9]. The ion peak at *m/z* 203 (218-COOH) due to ready loss of carboxy group showed the position of -COOH group at C-17 which was also supported by the ^{13}C NMR signal at δ 180.4 for C-28. The ^1H NMR signals at δ 4.35 and 4.52 (each 1H, d, *J* 12.1 Hz) were attributed to the methylene protons of hydroxymethyl group (AB system)[10,11]. Signal at δ 64.5 in ^{13}C NMR spectrum of **1a** for C-24 confirmed the presence of CH_2OH group at C-4. Thus, aglycone **1a** was identified as 3β,24-dihydroxyurs-12-en-28-oic acid.



The ^1H NMR spectrum of **1** showed a signal for an anomeric proton at δ 5.15 (1H, d, *J* 6.5 Hz, H-1, xylose) and sugar protons at δ 3.2–3.8 (br, xylosyl protons) which was consistent with β-configuration of D-xylose. The β-type of glycosidic linkage was also confirmed by hydrolysis of **1** with the enzyme emulsion. The position of attachment of D-xylose at C-24 hydroxyl group was confirmed by down field signal at δ 75.0 in the ^{13}C NMR of **1** for C-24. Thus, the compound **1** was characterised as 3β,24-dihydroxyurs-12-en-28-oic acid-24-*O*-β-D-xylopyranoside.

Compound **2**, $C_{35}H_{52}O_8$, a glycoside, on acid hydrolysis gave D-xylose and an aglycone **2a**. Aglycone **2a** on the basis of colour reactions and spectral evidences was found to be the same as **1a** and was thus, identified as 3β,24-dihydroxyurs-12-en-28-oic acid.

The ^1H NMR spectrum of **2** showed that the sugar was β-D-xylose (δ 5.15, 1H, d, *J* 6.5 Hz, H-1′ xylose and 3.2–3.8, m, xylosyl protons). An easy acid hydrolysis of **2** showed the presence C–O–C glycosidic linkage and hydrolysis with emulsin confirmed β-type of glycosidic linkage. The site of glycosidation at C-3 hydroxy was confirmed by ^{13}C NMR spectrum (δ 80.2, C-3 of compound and 78.0, C-3 of aglycone). Thus, **2** were identified as 3β,24-dihydroxyurs-12-en-28-oic acid-3-*O*-β-D-xylopyranoside.

Experimental

TLC and flash column chromatography were carried out on silica gel G. IR spectra were run in form of KBr pellets. ^1H NMR spectra were recorded at 100 MHz in $CDCl_3$ using TMS as internal standard.

Mass spectra were recorded at 70 eV. Aerial parts of *Abrus precatorious* was collected from Surguja District of Chhattisgarh state.

Table 1. ^{13}C NMR (δ) data of compounds **1**, **1a**, **2** and **2a**

Carbon	1	1a and 2a	2
1	38.7	38.5	38.5
2	27.2	27.0	27.0
3	78.1	78.0	80.2
4	38.8	38.6	8.6
5	55.3	55.3	55.2
6	18.3	18.3	18.2
7	32.7	34.4	32.5
8	39.5	37.6	39.5
9	47.8	47.0	47.8
10	37.4	37.4	37.4
11	23.5	23.5	23.5
12	126.5	126.4	126.5
13	138.0	138.0	138.0
14	42.0	42.0	41.8
15	28.1	28.0	27.8
16	23.6	23.5	23.2
17	48.5	48.3	48.4
18	52.5	52.3	52.3
19	39.1	39.9	38.6
20	38.9	38.3	38.4
21	30.5	30.0	30.2
22	36.8	36.4	36.5
23	28.0	28.0	28.0
24	75.0	64.5	64.4
25	15.7	15.6	15.6
26	16.9	16.8	17.0
27	23.7	23.5	23.8
28	180.6	180.4	180.5
29	16.8	16.8	16.6
30	21.2	21.2	21.5
1′	106.4	-	106.5
2′	74.6	-	74.6
3′	79.4	-	80.0
4′	71.0	-	71.2
5′	68.8	-	68.6

Air-dried and finely crushed aerial parts (3 kg) were extracted with ethanol. The concentrated dark brown alcoholic extract was poured into ice-cold water whereby a coloured residue and water soluble portion was obtained. Water insoluble portion was then extracted with solvents of increasing polarity in a soxhlet extractor. The concentrated hexane fraction was loaded over a flash column and eluted with different solvents of increasing polarity. On elution with benzene : dichloromethane (7 : 3, v/v) compounds **1** (0.7 g) and **2** (0.63 g) were isolated.

Compound **1** : White crystalline solid, m.p. 150 °C; R_f 0.68 (C_6H_6 : EtOAc, 9 : 1, v/v); IR (KBr) : 3400, 3200, 2900, 1630, 1381, 1362, 940 cm^{-1}; ^1H NMR ($CDCl_3$) : δ 3.00 (1H, dd, *J* 9.6 Hz, β-OH at C-3), 2.55 (1H, d, *J* 11.4 Hz, H-18 couples with H-19, ursane type), 4.50 and 4.37 (1H, d, *J* 12.1 Hz, for -CH_2OH group protons), 0.91, 0.96, 1.02, 1.08, (s, 3H ter-Me groups), 0.93 and 1.05 (3H, d, *J* 6.0 Hz for two *sec*-methyl groups), 5.15 (1H, d, *J* 6.5 Hz for β-linkage of glycoside) and 3.2–3.8 (m, for sugar protons); ^{13}C NMR (C_5D_5N) : see Table 1.

Acid hydrolysis of compound **1** : 30 mg of the compound **1** was hydrolysed with 7% H_2SO_4 (50 mL) for 6 h on a water-bath to obtain aglycone **1a** and the hydrolysate was extracted with EtOAc. The EtOAc phase showed the presence of xylose which was identified by paper chromatography.

Enzymatic hydrolysis of **1** : The glycoside (0.1 g) in 50% aqueous ethanol (20 mL) and emulsin solution (10 mL) prepared from almonds were added. The mixture was kept at 40–45 °C for 2 h and then at room temperature for 4 days. The solution was extracted with ethyl acetate and the remaining hydrolysate was concentrated in a rotatory evaporator. The syrup so obtained on paper chromatography gave single spot identical to authentic sample of xylose (R_f 0.18, solvent system reagent B : A : W, spray AHP).

Aglycone **1a** : White crystals, m.p. 200 °C; IR (KBr) : 3400, 3200, 2900, 1700, 1630, 1381, 1362 and 1040 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz) : δ 0.92–1.08 (each 3H, s, four tet-methyl groups), 3.83 (1H, dd, *J* 9.6 Hz), 5.45 (1H, t, *J* 3.4 Hz), 2.55 (1H, d, *J* 11.4 Hz), 4.52 and 4.35 (1H, d, *J* 12.1 Hz), 1.05 and 0.93 (3H, d, *J* 6.0 Hz); ^{13}C NMR : see Table 1; MS (70 eV); *m/z* : 471 $[M+1]^+$, 248, 225, 205, 203, 187, 133.

Compound **2** : White crystalline compound, m.p. 220 °C, yield 630 mg; IR (KBr) : 3400, 3200, 2900, 130, 1381, 1362, 940 cm^{-1}; ^1H NMR ($CDCl_3$) : δ 3.00 (1H, dd, *J* 9.6 Hz), 2.55 (1H, d, *J* 11.4 Hz), 4.50 and 4.37 (1H , d, *J* 12.1 Hz), 5.47 (1H, t, *J* 3.4 Hz), 0.91 (3H, s), 0.96 (3H, s), 1.02 (3H, s), 1.08 (3H, s), 0.93 (3H, d, *J* 6.5 Hz), 1.05 (3H, d *J* 6.0 Hz), 5.15 (1H, d, *J* 6.5 Hz), 3.2–3.8 (m, for sugar protons); ^{13}C NMR : see Table 1.

Acid and enzymatic hydrolysis of compound **2** was done similarly as discussed for compound **1** above.

Aglycone **2a** : Identical with **1a**, in co-TLC and comparison of spectral (IR, NMR and MS) data.

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