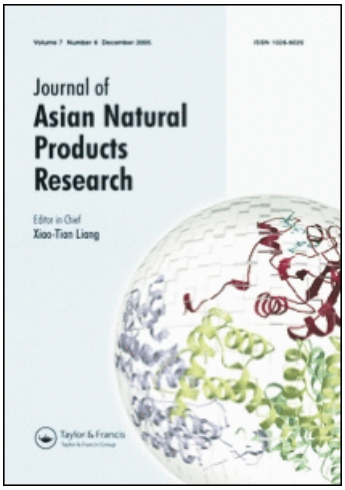

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TRITERPENE GLYCOSIDE FROM *TERMINALIA ARJUNA*

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A new triterpene glycoside, arjunetoside, together with oleanolic and arjunic acids has been isolated from the root bark of *Terminalia arjuna*. The structure of arjunetoside has been established as 3-O-β-D-glucopyranosyl-2α,3β, 19α-trihydroxyolean-12-en-28-oic acid, 28-O-β-D-glucopyranoside by chemical and spectral data.

Keywords: *Terminalia arjuna*; Combretaceae; Triterpenoid-glycoside; Arjunetoside; Arjunic acid; Oleanolic acid

INTRODUCTION

In continuation of our work on *Terminalia arjuna* [1, 2], we report here, the isolation of a new triterpene glycoside designated arjunetoside from the MeOH fraction of the root bark of the plant.

RESULTS AND DISCUSSION

The methanolic extract of the root bark of *T. arjuna* yielded the glycoside, arjunetoside (**1**), mp. 268–70° (dec.), $C_{42}H_{68}O_{15}$. It was recognised as a triterpene glycoside from its colour reaction in the Liebermann-Barchard test. It showed peaks in its IR spectrum at 3330 cm^{-1} (br) for a polyhydroxy

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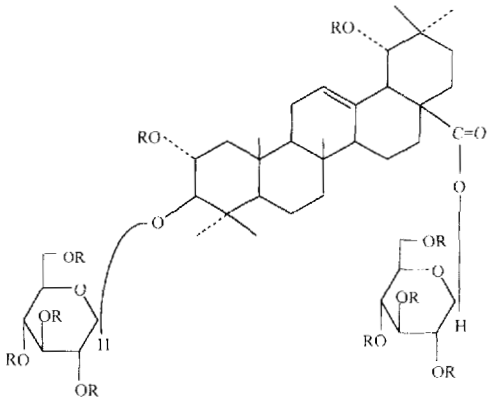
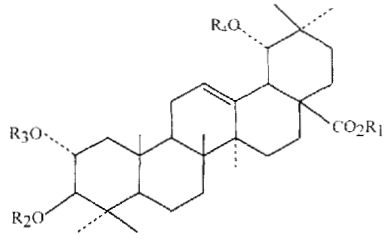
system, at 1715 cm^{-1} for ester carbonyl and at 1650 and 900 cm^{-1} for trisubstituted double bond. On acid hydrolysis, it gave glucose and an aglycone (**2**).

The aglycone (**2**), mp. 333–35°, $C_{30}H_{48}O_5$ (M^+, 488) which was characterised as arjunic acid [3, 4] by spectral data of **2** and its acetate (**3**) and comparison with authentic samples.

The presence of two sugar units in the glycoside **1** was proved from the appearance of two anomeric carbon signals at δ 95.5 (ester glycoside [5]) and 105.5 ppm in its ^{13}CNMR spectrum. Based on this evidence and the fact that the parent glycoside is an ester (ν_{max} = 1715 cm^{-1}) and the aglycone is an acid (ν_{max} = 1700 cm^{-1}, bromothymol blue test), the attachment of one of the glucose units through an ester linkage was



1 : R = H
4 : R = Me



2 : $R_1 = R_2 = R_3 = R_4 = H$
3 : $R_1 = R_4 = H$; $R_2 = R_3 = Ac$
5 : $R_1 = R_3 = R_4 = Me$; $R_2 = Ac$

confirmed [5]. The other glucose unit was considered to be a 3-O-glucoside on biogenetic ground [4].

Methylation of **1** by the Hakomori method [6] yielded a methylated product (**4**) which was methanolysed to give methyl-2,3,4,6-tetra-O-methyl-D-glucopyranoside and the methylated aglycone which on acetylation gave compound (**5**). ^{1}HNMR spectrum of **5** showed signals for the presence of seven methyls, one acetyl, two methoxyl and a carbomethoxy group. A doublet at δ 5.00 ($J = 10$ Hz), one proton multiplet at δ 5.20 and one proton multiplet at δ 5.40 were assignable to H-3α, H-2β and H-12 respectively. It showed a molecular ion peak at m/z 572 and retro-Diels-Alder cleaved mass peaks at m/z 292 and 280. These data favoured the structure of **5** for the aglycone acetate. The formation of **5** favoured structure **1** for the glycoside, which is thus 3-O-β-D-glucopyranosyl-2α,3β,19α-trihydroxyolean-12-en-28-oic acid, 28-O-β-D-glucopyranoside (arjunic acid-3,28-diglucoside).

EXPERIMENTAL SECTION

General Experimental Procedures

Mps. were determined on a Toshniwal apparatus and are uncorrected, IR were recorded on a Perkin-Elmer spectrophotometer model 221 in KBr pellet. ^{1}H and ^{13}C NMR were taken on 100 and 300 MHz NMR on Bruker HX-90 with TMS on internal standard. MS were performed on Kratos MS-50 mass spectrometer operation at 70 eV with evaporation of sample in the ion source at 200° and $[\alpha]_D$ in MeOH at 20° was carried out on Perkin-Elmer polarimeter 141. CC: silica gel columns (BDH, 60–120 mesh); TLC: silica gel G(Merck); PC: Whatman No. 1 paper; solvents for TLC: $CHCl_3$-MeOH (4 : 1) (solvent A), $CHCl_3$-MeOH-H_2O (13 : 7 : 2) (solvent B), $CHCl_3$-MeOH-H_2O (65 : 35 : 10) (solvent C) and for PC: *n*-BnOH-HOAc-H_2O (4 : 1 : 5) (solvent D); paper chromatogram developed with acetonic $AgNO_3$/5% alcoholic NaOH/$Na_2S_2O_3$/H_2O.

Plant Material

Root bark of the plant *T. arjuna* was collected from Banaras Hindu University Campus, Varanasi, India and identified by Dr. N. K. Dubey, the Dept. of Botany, Banaras Hindu University. A specimen sample is kept in the Department.

Extraction and Isolation

Dried root bark (3 kg) was powdered and repeatedly extracted with MeOH by percolation at 25°. The MeOH extract afforded a brown gummy mass (35 g) which was fractionated into C_6H_6, $CHCl_3$ and MeOH fractions by passing through SiO_2 gel column. The $CHCl_3$ fraction was rechromatographed over SiO_2 gel column and the eluants from C_6H_6-$CHCl_3$ (1 : 4) and $CHCl_3$ furnished respectively oleanolic acid (32 mg), mp. 304–306° and arjunic acid (41 mg), mp. 331–34°(dec.). The MeOH fraction was further chromatographed over SiO_2 gel and the eluants from $CHCl_3$-MeOH (1 : 4) yielded arjunetoside (**1**) as colourless granules (52 mg), mp. 268–70° (dec.) (MeOH); $[\alpha]_D^{20}+68$ (*c*, 0.25, MeOH) (Found: C, 62.21, H, 8.30%, $C_{42}H_{68}O_{15}$ requires; C, 62.07, H, 8.40%); FAB-MS : *m/z* 851 $[C_{42}H_{68}O_{15}+K]^+$; IR (KBr) ν_{max} cm^{-1} : 3330, 1715, 1650, 900; ^{13}CNMR (pyridine) δ : 47.5 (C-1), 67.0 (C-2), 88.3 (C-3), 40.0 (C-4), 54.2 (C-5), 18.2 (C-6), 33.0 (C-7), 40.4 (C-8), 48.4 (C-9), 37.6 (C-10), 24.3 (C-11), 123.1 (C-12), 144.2 (C-13), 42.0 (C-14), 29.2 (C-15), 25.8 (C-16), 47.0 (C-17), 44.5 (C-18), 80.6 (C-19), 36.5 (C-20), 31.2 (C-21), 32.2 (C-22), 26.9 (C-23), 16.6 (C-24), 17.4 (C-25), 17.4 (C-26), 29.1 (C-27), 176.5 (C-28), 30.2 (C-29), 24.5 (C-30), 95.5 (C-1′), 73.8 (C-2′), 78.9 (C-3′), 71.1 (C-4′), 78.2 (C-5′), 62.1 (C-6′), 105.4 (C-1″), 75.1 (C-2″), 79.2 (C-3″), 72.4 (C-4″), 78.6 (C-5″), 63.7 (C-6″).

Methanolysis of Arjunetoside (1)

Compound **1** (45 mg) was dissolved in MeOH (10 ml) and H_2O (2 ml) and refluxed with H_2SO_4 (1 ml) for 5 hrs. The reaction mixture was poured into H_2O (15 ml) and the MeOH removed by evaporation on water bath and the remained aqueous solution was extracted with $CHCl_3$. The $CHCl_3$ extract yielded arjunic acid (**2**) (20 mg) as granules, mp. 333–35°, $C_{30}H_{48}O_5$ (M^+, 488), $[\alpha]_D^{20}+20$ (*c*, 0.50, MeOH); IR (KBr) ν_{max} cm^{-1} : 3475 (br) (OH), 1700 (COOH); ^{13}CNMR (pyridine) δ:47.9 (C-1), 68.7 (C-2), 83.3 (C-3), 40.3 (C-4), 54.4 (C-5), 18.6 (C-6), 34.2 (C-7), 39.5 (C-8), 48.1 (C-9), 38.3 (C-10), 24.1 (C-11), 123.7 (C-12), 144.4 (C-13), 42.2 (C-14), 29.2 (C-15), 25.1 (C-16), 47.7 (C-17), 43.5 (C-18), 81.2 (C-19), 35.4 (C-20), 30.7 (C-21), 33.1 (C-22), 27.0 (C-23), 16.7 (C-24), 17.3 (C-25), 17.6 (C-26), 28.9 (C-27), 180.2 (C-28), 29.4 (C-29), 24.6 (C-30); MS : *m/z* 488 (M^+), 264, 246, 224, 201, 190, 189. Acetylation of **2** with Ac_2O-pyridine (1 : 1) at room temperature overnight and usual work up furnished arjunic acid diacetate (**3**), mp. 275–77°; 100 MHz ^{1}HNMR ($CDCl_3$) δ : 0.70 (3H, *s*, H-26), 0.80 (3H, *s*, H-23), 0.88 (3H, *s*, H-24), 0.97 (6H, *s*, H-29, H-30), 1.08 (3H, *s*, H-25), 1.24 (3H, *s*, H-27),

1.99 (3H, *s*, OAc), 2.03 (3H, *s*, OAc), 3.09 (1H, *m*, H-18), 3.33 (1H, *d*, $J = 3$Hz, H-19), 5.05 (1H, *d*, $J = 10$ Hz, H-3α), 5.20 (1H, *m*, H-2β), 5.41 (1H, *m*, H-12). The hydrolysate showed a single spot on PC which corresponded to glucose (co-PC with authentic sample).

Methylation of Arjunetoside (1) by the Hakomori Method

Arjunetoside (**1**) (90 mg) was treated with NaH (320 mg) and MeI (5 ml) in DMSO (30 ml). The reaction mixture was diluted with H_2O and extracted with $CHCl_3$ in the usual way. The methylated product (**4**) on purification by prep. TLC gave a semi solid mass, R_f 0.22 (solvent A), IR (KBr) ν_{max} cm^{-1}: 1715, 1648.

Methanolysis of Permethylated Product (4)

Compound **4** was refluxed with 6% HCl in MeOH for 1 hr. The MeOH was removed from the reaction mixture which was then extracted with $CHCl_3$. The $CHCl_3$ extract on purification with prep. TLC gave an aglycone. The sugar in the hydrolysate was identified as 2,3,4,6-tetra-O-methyl-D-glucose by co-PC with authentic sample available in the laboratory. The aglycone was acetylated with Ac_2O-pyridine at 110° for 4 hr giving compound **5**, mp. 212–14°, $C_{35}H_{56}O_6$ (M^+, 572); 100 MHz ^{1}HNMR ($CDCl_3$) δ : 0.64 (3H, *s*, CH_3), 0.74 (3H, *s*, CH_3), 0.83 (3H, *s*, CH_3), 0.97 (6H, *s*, $2 \times CH_3$), 0.98 (3H, *s*, CH_3), 1.22 (3H, *s*, CH_3), 2.03 (3H, *s*, OAc), 3.23 (3H, *s*, OMe), 3.24 (3H, *s*, OMe), 3.60 (3H, *s*, COOMe), 5.00 (1H, *d*, $J = 10$ Hz, H-3α), 5.20 (1H, *m*, H-2β), 5.40 (1H, *m*, H-12); MS : *m/z* 572 (M^+), 292, 280, 202.

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