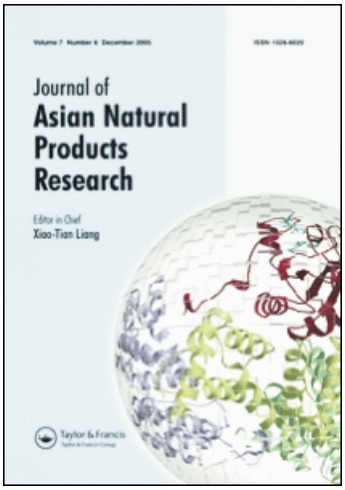

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A NEW CARDENOLIDE FROM THE SEEDS OF *TERMINALIA ARJUNA* (W&A)

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A new cardenolide 14,16 dianhydrogitoxigenin-3-O-β-D-xylopyranosyl (1 → 2)-O-β-D-galactopyranoside was isolated from the ethylacetate soluble fraction of the alcoholic extract of the seeds of *Terminalia arjuna* by various colour reactions, chemical degradations and spectral analysis.

Keywords: Terminalia arjuna (W&A); Combretaceae; Seeds; Cardenolide

INTRODUCTION

Terminalia arjuna [1–3] belongs to the family Combretaceae which is commonly known as "Arjuna" in Hindi. It is cultivated in numerous forms in India. It is used as a tonic. It is used in heart disease as a cardiac tonic, in bilious affections, for sores and as an antidote to poisons. Earlier workers have reported various constituents from this plant. In the present paper we report the isolation and structural elucidation of a new cardenolide 14,16 dianhydrogitoxigenin-3-O-β-D-xylopyranosyl (1 → 2)-O-β-D-galactopyranoside (**1**) from the seeds of this plant by various chemical degradations and spectral analysis.

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RESULTS AND DISCUSSION

The ethyl acetate fraction of the alcoholic extract of the seeds of *Terminalia arjuna* afforded a new compound **1**, molecular formula, $C_{34}H_{48}O_{12}$, m.p. 194–196°C, $[M]^+$ 648. Compound **1** gave a positive response for Kedde test confirming it to be a cardenolide. Its IR spectrum showed the presence of an α,β-unsaturated lactone (1740 cm^{-1}) and a strong hydroxyl absorption (3445 cm^{-1}). Its UV spectrum showed a band at 216 nm with MeOH, which is characteristic of a carbonyl group conjugated with a double bond.

^{1}H-NMR spectrum of **1** showed two singlets at δ 1.09 and δ 1.12 for Me-18 and Me-19 respectively (each for three protons) and were assigned to methyl groups on tertiary carbon atoms. The anomeric proton of the xylose appeared as a doublet at δ 4.58 ($J = 8.0$ Hz) and that of galactose at δ 6.06 (1H, d, $J = 4$ Hz).

In the EIMS of **1**, characteristic ions appeared at m/z 515 and 295, generated by subsequent losses of one galactose and one xylose unit from the molecular ion suggesting that the xylose is the terminal sugar.

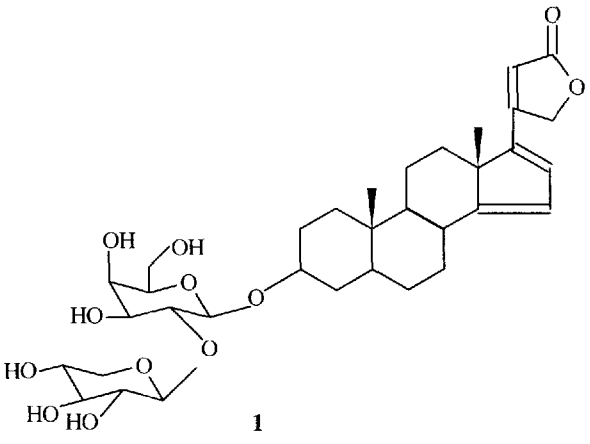
Acid hydrolysis of **1** with 10% H_2SO_4 gave aglycone (**2**), $C_{23}H_{30}O_3$, m.p. 175–176°C [M] 354 (Scheme 1). It responded to the characteristic reactions of cardenolide and identified as 14,16 dehydrogitoxigenin by its spectral analysis (see experimental) [4,5].

The aqueous hydrolysate obtained after acid hydrolysis of the glycoside **1**, was neutralised with $BaCO_3$ and the formed $BaSO_4$ was filtered off, and subjected to Co-paper chromotography. The presence of sugars were identified as D-galactose (R_f 0.15) and D-xylose (R_f 0.27).

Permethylation [6] of **1** followed by acid hydrolysis yielded permethylated aglycone (**3**) and permethylated sugars, which were identified as, 3-4-6-tri-O-methyl-D-galactose and 2,3,4-tri-O-methyl-D-xylose according to Petek [7] showing that the C-1″ of xylose was linked with C-2′ of D-galactose. The inter linkage ($1 \rightarrow 2$) between the sugars were further confirmed by its ^{13}C-NMR spectrum (see experimental). Periodate oxidation [8] of compound **1** confirmed that both the sugars were present in pyranose form.

Enzymatic hydrolysis of compound **1** with equal volume of almond emulsion indicated a β-linkage between D-xylose and D-galactose as well as between D-galactose and aglycone [9].

On the basis of above evidences the structure of compound **1** was established as 14,16 dianhydrogitoxigenin-3-O-β-D-xylopyranosyl ($1 \rightarrow 2$)-O-β-D-galactopyranoside.



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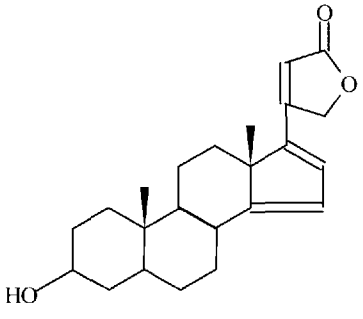

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SCHEME 1

EXPERIMENTAL SECTION

General Experimental Procedures

Melting points are uncorrected. The IR spectra were measured in KBr discs. ^{1}H-NMR spectra were recorded at 400 MHz using TMS as internal standard and $CDCl_3$ as solvent. ^{13}C-NMR spectra were recorded at 100 MHz and DMSO-d_6 as solvent.

Plant Material

The seeds of *Terminalia arjuna* were collected locally in Sagar and taxanomically authenticated by the Department of Botany, Dr. H.S. Gour University,

Sagar. A voucher specimen has been deposited in the Natural Products Laboratory, Department of Chemistry of this University.

Extraction and Isolation

The air-dried and powdered seeds (2 kg) of *Terminalia arjuna* were extracted with 95% EtOH in a Soxhlet extractor. The total ethanolic extract was concentrated under reduced pressure to give a light brown coloured mass and was then successively extracted with petroleum ether (60–80°C), chloroform, benzene, ethyl acetate, acetone and methanol. The ethyl acetate solution fraction was concentrated under reduced pressure to a viscous mass which was subjected to column chromatography over a silica-gel column using $CHCl_3$–MeOH (3:2) to give compound **1**, crystallised from MeOH as white solid, $C_{34}H_{48}O_{12}$, m.p. 194–196°C; $[M]^+$ 648 (elemental analysis: found: C, 62.87%, H, 7.38%, calcd.: C, 62.96%, H, 7.40%); IR ν_{max}^{KBr} 3450, 2940, 1740, 1620 cm^{-1}; UV λ_{max}^{MeOH} 221 and 280 nm. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.09 (3H, s, Me-18), 1.11 (3H, s, Me-19), 5.03 (2H, s, H-21), 4.08 (1H, m, H-3), 6.74 (1H, d, $J = 2.0$ Hz, H-15), 6.06 (1H, dd, $J = 2.1$ Hz, H-16), 5.82 (1H, s, H-22), 6.06 (1H, d, $J = 8$ Hz galactosyl anomeric proton), 4.57 (1H, d, $J = 8$ Hz, H-1″), 4.94 (1H, t, $J = 8$ Hz, H-2″), 5.13 (1H, t, $J = 8$ Hz, H-3″), 4.83–5.19 (2H, m, H-4″) 4.19 (1H, m, H-5″), 1.22–1.29 (complex pattern polymethylene CH_2 and CH). ^{13}C-NMR (100 MHz, $CDCl_3$) 26.6 (C-1), 27.8 (C-2), 64.7 (C-3), 32.3 (C-4), 35.8 (C-5), 25.6 (C-6), 22.7 (C-7), 41.8 (C-8), 34.8 (C-9), 34.8 (C-10), 21.6 (C-11), 39.8 (C-12), 48.5 (C-13), 166.7 (C-14), 127.3 (C-15), 125.0 (C-16), 168.1 (C-17), 21.7 (C-18), 24.2 (C-19), 178.1 (C-20), 74.7 (C-21), 120.4 (C-22), 178.5 (C-23), 101.8 (C-1′), 70.9 (C-2′), 72.5 (C-3′), 68.5 (C-4′), 75.2 (C-5′), 65.8 (C-6′), 94.5 (C-1″), 74.9 (C-2″), 75.0 (C-3″), 64.7-5.1 (C-4″), 64.1 (C-5″).

Acid Hydrolysis of Compound 1

The compound **1** was dissolved in EtOH and treated with 10% H_2SO_4, and refluxed on water bath for 12 h. The contents were concentrated and allowed to cool and the residue was extracted with Et_2O. The aqueous layer was studied separately for the identification of sugars. The ethereal layer was washed with water and evaporated to dryness and the residue was subjected to column chromatography over a silica-gel column using $CHCl_3$: MeOH (4:2) to give aglycone (**2**), $C_{23}H_{30}O_3$; m.p. 175–176°C. $[M]^+$ 354 (elemental analysis found: C, 77.93%, H, 8.45% calcd.: C, 77.96%, H, 8.47%. IR ν_{max}^{KBr} 3445, 2938, 1735, 1620 cm^{-1} UV λ_{max}^{MeOH} 221 and 280 nm.

^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.10, (3H, s, Me-18), 1.14 (3H, s, Me-19), 5.02 (2H, s, H-21), 4.07 (1H, m, H-3), 6.72 (1H, d, $J = 2.0$ Hz, H-15), 6.02 (1H, dd, $J = 2.1$ Hz, H-16), 2.06 (1H, s, 3-OH), 1.21–1.2 (complex pattern polymethylene – CH_2 and CH).

The aqueous hydrolysate was neutralised with $BaCO_3$ and the formed $BaSO_4$ was filtered off. The filtrate was concentrated and subjected to paper chromatography examination (n-BuOH : AcOH : H_2O, 4 : 1 : 5) revealed the presence of D-galactose (R_f 0.15) and D-xylose (R_f 0.27).

Permethylation followed by Hydrolysis of Compound 1

Compound **1** (40 mg) in MeI (5 mg) and Ag_2O (50 mg) in DMF (5 ml) were refluxed for one day. The total reaction mixture was diluted with H_2O and extracted with $CHCl_3$, gave permethylated aglycone (**3**) and methylated sugars which were identified as 3-4-6-tri-O-methyl-D-galactose and 2,3,4-tri-O-methyl-D-xylose (by Co-PC and Co-TLC) according to Petek.

Periodate Oxidation of Compound 1

Compound **1** was dissolved in MeOH and treated with sodium metaperiodate for 40 h. The liberation of formic acid and consumed periodate were estimated by Jone's method.

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