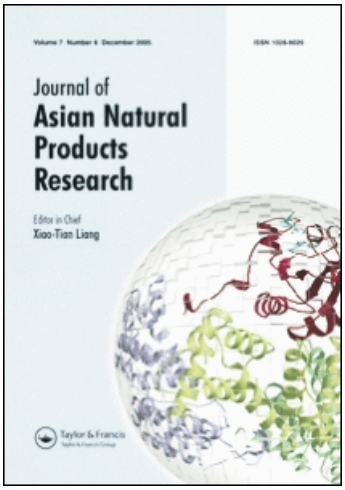

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Note

A NEW CARDENOLIDE UZARIGENIN-3-O-β-D-XYLOPYRANOSYL (1 → 2)-α-L-RHAMNOPYRANOSIDE

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A new cardenolide $C_{34}H_{52}O_{12}$, m.p. 225–226°C, [$M^+ - H$] 651 (EIMS) was isolated from the acetone soluble fraction of the concentrated 90% ethanolic extracts of the seeds of *Tamarindus indica* (Linn.). It was identified as uzarigenin-3-O-β-D-xylopyranosyl (1 → 2)-α-L-rhamnopyranoside (I) by different colour reactions, chemical degradations and spectral analysis.

Keywords: *Tamarindus indica* (Linn.); Leguminosae; Cardenolide

INTRODUCTION

Tamarindus indica (Linn.) [1–3] belongs to Leguminosae family and is commonly known as 'Imali' in Hindi. It is distributed almost throughout India. The plant is used for treatment of skin diseases and to purify blood. Earlier workers have reported the presence of various constituents in this plant [4–6]. The present paper deals with the isolation and structural elucidation of a new cardenolide uzarigenin-3-O-β-D-xylopyranosyl (1 → 2)-α-L-rhamnopyranoside on the basis of various chemical degradation and spectral analysis.

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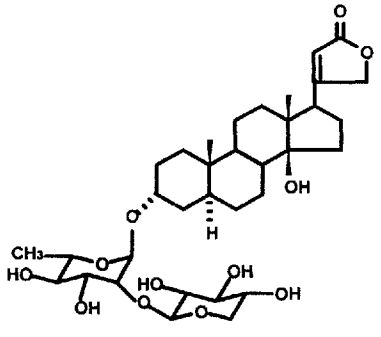
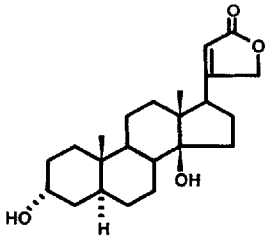
RESULT AND DISCUSSION

The acetone soluble fraction of the seeds of *T. indica* afforded a new compound I (Fig. 1), which has the molecular formula $C_{34}H_{52}O_{12}$, m.p. 225–226°C, $[M^+ - 1]$ 651 (EIMS) and gave all the characteristic reactions of cardenolide [7–9]. Its IR spectrum showed a strong absorption band at 3395–3405 cm^{-1} (–OH groups), 1740–1745 cm^{-1} corresponding to the presence of α,β-unsaturated γ-lactone ring. The ^{1}H-NMR spectrum of I showed two singlets at δ 1.06 and 1.08 which were assigned to two methyl groups at C-18 and C-19 positions, respectively, and another singlet at δ 5.18 assigned to H-22. The anomeric proton signals at δ 5.38 (1H, br, S) and δ 4.34 (1H, d, $J = 7.6$ Hz) were assigned to H-1′ and H-1″ of rhamnose and xylose respectively, and a double signal at δ 1.03 was due to the rhamnosyl methyl group. The mass spectrum of I gave a $M^+ - 1 = m/z$ 651, $M^+ = 652$. The loss of sugar moiety from the molecular ion gave a fragment ion at m/z 357 along with other fragment ion peaks at m/z 339, 203 and 131.



[I]



[II]

FIGURE 1 Structure of compounds I and II.

The position of sugar moiety in compound I was established by permethylation [10] of I followed by acid hydrolysis which afforded methylated sugars identified as 3,4,-di-O-methyl-L-rhamnose and 2,3,4-tri-O-methyl xylose according to Petek [11], suggesting that the C-1″ of xylose was linked with C-2′ of rhamnose and C-1′ of rhamnose was attached to the C-3 of aglycone. The inter linkage ($1 \rightarrow 2$) between both sugars was further confirmed by its ^{13}C-NMR spectrum (see Experimental Section).

Acid hydrolysis of compound I with 7% ethanolic H_2SO_4 yielded aglycone II, $C_{23}H_{34}O_4$, m.p. 235–238°C, $[M]^+$ 374. It responded to all the characteristic reactions of cardenolide and identified as uzarigenin by comparison of its spectral data with authentic sample.

The aqueous hydrolysate obtained after acid hydrolysis of compound I was neutralised with $BaCO_3$, the formed $BaSO_4$ filtered off, and subjected to PC (Co-PC and Co-TLC) and the sugars were identified as rhamnose (R_f 0.36) and xylose (R_f 0.26). Periodate oxidation [12] of compound I confirmed that both sugars were present in pyranose form.

Enzymatic hydrolysis of compound I with β-xylosidase liberated xylose first showing the presence of β-linkage between xylose and rhamnose, while compound I hydrolysed by takadiastase enzyme liberated rhamnose confirming the presence of the α-linkage between aglycone and rhamnose.

On the basis of above evidences the structure of compound I was assigned as a new cardenolide uzarigenin-3-O-β-D-xylopyranosyl ($1 \rightarrow 2$)-α-L-rhamnopyranoside.

EXPERIMENTAL SECTION

General Experimental Procedures

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

Plant Material

The seeds of *Tamarindus indica* (Linn.) were collected locally around Sagar region and was taxonomically authenticated by staff of Botany Department of Dr. H.S. Gour University, and the voucher specimen [12] was deposited in the Natural Products Laboratory of Chemistry Department, Dr. H.S. Gour University, Sagar (M.P.).

Extraction and Isolation

The air dried and powdered seeds (2.5 kg) of *T. indica* were extracted with 90% EtOH in a Soxhlet extractor. The total combined ethanolic extract was concentrated under reduced pressure to give a light brown viscous mass and was then successively extracted with petroleum ether, chloroform, benzene, ethyl acetate, acetone and methanol. The acetone soluble fraction of the ethanolic extract was concentrated under reduced pressure to give compound I as colourless needles, showing a single spot on TLC examination using solvent system ($CHCl_3$–MeOH, 2 : 5) which has the molecular formula $C_{34}H_{52}O_{12}$; m.p. 225–226°C, $[M^+ - 1]$ 651 (EIMS) (elemental analysis; found: C 62.94, H 7.73; calcd. for $C_{34}H_{52}O_{12}$: C 62.60, H 8.00), IR ν_{max}^{KBr}: 3395–3405, 1740–1745, 1615, 1170, 1075, 1020, 890 cm^{-1}. ^{1}H-NMR (400 MHz-$CDCl_3$) at δ 1.06 (3H, s, Me-18); 1.08 (3H, s, Me-19); 5.18 (H, s, H-22); 2.75 (1H, m, H-3); 5.38 (1H, br, s, H-1′); 4.34 (1H, $J = 7.6$ Hz, H-1″); 4.21 (1H, br, d, $J = 3.5$ Hz, H-2′); 3.85 (1H, dd, H-3′); 3.24 (1H, dd, H-4′); 3.66 (1H, d, H-5′); 1.03 (3H, d, $J = 6.0$ Hz Rham-Me); 3.24 (1H, dd, H-2″); 3.31 (1H, dd, H-3″); 3.38 (1H, H-4″); 3.12 (2H, dd, H-5″). ^{13}C-NMR (100 MHz DMSO-d_6) 37.6 (C-1); 28.8 (C-2); 72.9 (C-3); 34.8 (C-4); 45.00 (C-5); 29.00 (C-6); 27.1 (C-7); 41.6 (C-8); 49.5 (C-9); 36.2 (C-10); 20.8 (C-11); 39.8 (C-12); 51.00 (C-13); 85.8 (C-14); 34.00 (C-15); 28.00 (C-16); 51.5 (C-17); 14.8 (C-18); 13.1 (C-19); 173.2 (C-20); 73.5 (C-21); 118.1 (C-22); 174.5 (C-23); 103.2 (C-1′); 82.0 (C-2′); 71.8 (C-3′); 74.1 (C-4′); 72.0 (C-5′); 17.8 (C-6′); 108.1 (C-1″); 74.8 (C-2″); 77.2 (C-3″); 70.2 (C-4″); 67.5 (C-5″). EIMS *m/z* 652 $[M]^+$ 519, 357, 339, 203, 131.

Acid Hydrolysis of Compound I

Compound I (150 mg) was dissolved in EtOH (25 ml) and treated with 20 ml of 7% H_2SO_4 and refluxed on water bath for 10 h. The total reaction mixture was concentrated under reduced pressure and allowed to cool and the residue was extracted with Et_2O. The ethereal layer was washed with water to dryness and the residue was chromatographed over silica-gel using $CHCl_3$–MeOH (3 : 2) to give compound II, $C_{23}H_{34}O_4$, m.p. 235–238°C, $[M]^+$ 374 (EIMS) (elemental analysis; found: C 73.68, H 9.47; calcd. for $C_{23}H_{34}O_4$: C 73.79, H 9.09).

The aqueous hydrolysate was neutralised with $BaCO_3$, the formed $BaSO_4$ filtered off. The filtrate was concentrated and subjected to paper chromatography examination (*n*-BuOH–AcOH–H_2O 4 : 1 : 5) indicating the presence of L-rhamnose (R_f 0.36) and xylose (R_f 0.26).

Permethylation Followed by Acid Hydrolysis of Compound I

Compound I was treated with MeI (5 ml) and Ag_2O (50 mg) in DMF (5 ml) at room temperature for one day and then filtered. The filtrate was dried *in vacuo* and hydrolysed with 15% ethanolic H_2SO_4 for 8 h, after the usual workup yields methylated aglycone and methylated sugars, which were identified as 3,4,-di-O-methyl-L-rhamnose and 2,3,4-tri-O-methyl-xylose according to Petek.

Periodate Oxidation of Compound I

Compound I was dissolved in MeOH and treated with sodium meta periodate for 48 h. The liberation of formic acid and consumed periodate were estimated by Jone's method, which suggests the presence of both the sugars in pyranose form.

Enzymatic Hydrolysis of the Compound I

Compound I was treated with 3 ml of β-xylosidase at 24°C for 34 h then H_2O was added and it was extracted with *n*-BuOH. The *n*-BuOH extract was subjected to column chromatography to give xylose showing the presence of β-linkage between xylose and rhamnose. The compound also hydrolysed with takadiastase enzyme liberated L-rhamnose showing the presence of α-linkage between L-rhamnose and aglycone.

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