Triterpenoidal glycosides from the seeds of
Dendrocalamus strictus

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Received 13 April 1998; accepted (revised) 8 March 1999

Two new triterpenoidal glycosides have been isolated from the seeds of plant Dendrocalamus strictus and are characterised as 3β, 21β, 28-trihydroxyolean-12-en-28-o-β-D-arabinopyranosyl-(1→3)],β-D-arabinopyranose(1→1)-β-D-arabinopyranoside 1 and 3β, 19α-dihydroxy-12-en-28-oate-3-β-D-arabinopyranoside 2 on the basis of chemical and spectral evidence.

Dendrocalamus strictus Roxb. (family Gramineae/Poaceae) is commonly known as Nees or Bamboo. It is deciduous densely tufted plant with strong stems (6-15 m, high by 2.5-7.5 cm diameter) distributed in India, Nepal and Java. The silicious matter of joints is used as a cooling tonic and astringent medicine. The leaves are given to animals during parturition for rapid expulsion of the placenta. We report herein the isolation and structure elucidation of two new triterpenoids 1 and 2 from the seeds of the Dendrocalamus strictus.

Compound 1, C_43H_64O_{15} (M' 854), mp 118°C, non-reducing glycoside showed absorptions in the IR spectra for hydroxyl groups at 3450 cm\(^{-1}\). On hydrolysis with 7% H_2SO_4 it gave aglycone 1a and sugar D-arabinose. An aglycone 1a, C_{30}H_{46}O_{5} (M' 458) positively responded to Liebermann Burchard, TCA and TNNM tests. It formed tricetate on acetylation showing the presence of three hydroxyl groups.

\(^1H\) NMR spectra of 1a showed signals at δ 0.89-1.27 ppm attributed to seven tertiary methyl groups, at δ 3.88 and 4.25 ppm for one CH_{2}OH group (1H, each, a pair of doublets, J_{AB} = 10.0 Hz) and for one olefinic proton at δ 5.25 (t, 1H, J = 3.5 Hz) all of which suggested that the aglycone 1a to be a pentacyclic olean-12-en type of triterpenoid.

The mass spectrum of 1a revealed important peaks at m/z 250, 219, 207, 201, 190 and 189 typical of retro-Diels-Alder fragmentation of ring-C of olean-12-en derivative containing a hydroxyl group in ring A or B. Compound 1a also gave positive Zimmermann test suggesting the C-3 position for this hydroxyl group which was also biogenetically favoured. The aglycone showed signal at δ 3.32 (d, 1H, J = 9.6 Hz) with higher value of coupling constant confirming the β-orientation for hydroxyl group at C-3 (α or axial H). The positions of remaining two hydroxyl groups were confirmed after comparing the \(^13C\) NMR spectral data with those of 3α, 21β, 22α, 28-tetrahydroxyolean-12-ene. All these evidences suggested that out of three hydroxyl groups two –OH groups were present at C-3 and C-21 with β-orientation and one as hydroxymethyl (–CH_{2}OH) function at C-17.

\(^1H\) NMR spectrum of compound showed signals of three anomeric protons at δ 4.77, 4.90 and 5.78 as doublets (J = 5.2 Hz, 7.0 Hz and 7.5 Hz). This confirmed that glycoside was trisaccharide. On permethylation followed by acid hydrolysis permethylated derivative gave 2,4-dimethyl-\(\alpha\)-
arabinose and 2,3,4-trimethyl-O-arabinose. This confirmed that inter sugar linkage was (3→1). The attachment of three sugar moieties were confirmed by comparing the 13C NMR spectral data with 1 and 1a which showed the attachment of sugar to C-28 by higher δ value at C-28 for 1 and lower δ value for 1a. Hydrolysis of 1 with β-glucosidase gave D-arabinose confirming the β-nature of glycosidic linkage.

From the above evidences the structure of compound 1 was determined as 3β, 21β, 28-trihydroxyolean-12-en-28-O-[β-D-arabinopyranosyl (1→3)]-β-D-glucopyranosyl (1→3)-β-D-arabinopyranoside.

Compound 2, C36H56O15 (M+ 619), mp 272°, a non-reducing glycoside gave aglycone 2a and a moiety of sugar arabinose on acid hydrolysis. Compound 2a, C36H56O15 (M' 486), gave colour reactions characteristic of unsaturated pentacyclic triterpenoid. IR spectrum showed absorption peaks at 3400 cm⁻¹ for hydroxyl and at 1722 cm⁻¹ for carbonyl groups. On acetylation 2a formed monohydroxy monoacetate showing that the aglycone contains an acetylable and a tertiary hydroxyl groups.

1H NMR spectrum of aglycone showed signals for six tertiary methyl groups at δ 0.71-1.27 (s, 18H, –CH₃) with one secondary methyl group at δ 0.95 (d, 3H, J = 7.0Hz). It showed characteristic broad signals at δ 2.57 (1H, 18β-H) together with secondary and olefinic proton at δ 5.35 (t, 1H, J = 3.6 Hz, 12-H) suggesting a 19α-hydroxyurs-12-en type of triterpenoid.

The aglycone 2a exhibited molecular ion peaks at m/z 278, 260, 207 and 165 in its mass spectrum via retro-Diels-Alder fragmentation thus showing the presence of an OH group at C-3 with equatorial orientation.

After comparing the 13C NMR values with methyl ester of myrra boric acid it was found that C-28 resonated at δ 178.1 indicating the presence of C-28 as COO-Me at C-17. These results clearly established the structure of 2a as 3β, 19α-di-hydroxyurs-12-en-28-oate. The 1H NMR spectrum of 2 showed a multiplet for anomic protons at δ 3.2-3.8 (m, 1H) and a doublet for arabinose protons at δ 5.15 (d, 1H, J = 7.2 Hz) indicating its β-linkage with aglycone. Hydrolysis with β-glucosidase also confirmed the β-linkage to aglycone. The site of glycosidation was found to be C-3 by comparing its 13C NMR signals with that of its aglycone 2a which was also biogenetically favoured.

From the foregoing evidences the structure of the compound 2 was established as 3β, 19α-di-hydroxyurs-12-en-28-oate-3-O-β-O-arabinopyranoside.

Experimental Section
The plant material used in this study was collected in April 1994 from Jabalpur, M.P., India (a herbarium specimen is in file in Botanical Survey of India, Allahabad sheet no. 35327). All m.ps are uncorrected.
TLC was carried out on silica gel G (Merck 17613) and column chromatography was done on silica gel 60 (Merck 24398). IR spectra were recorded in KBr pellets; $^1$H NMR spectra at 400 MHz in CD$_2$OH+CDCl$_3$ using TMS as internal standard; and $^{13}$C NMR spectra at 25 MHz in CDCl$_3$ solution with TMS as internal standard employing the FT mode.

Extracting and Isolation

The air dried seeds of the plant (3 kg) were extracted with ethanol and the concentrated extract chromatographed over silica gel column. Elution with benzene-CH$_2$Cl$_2$ (4:1, v/v) fraction contained compound 1 and elution with ethyl acetate-methanol (4:1, v/v) yielded compound 2.

Compound 1, C$_{45}$H$_{74}$O$_{15}$, m.p 118$^\circ$ (CHCl$_3$), $R_r$ 0.65 (CHCl$_3$: CH$_3$OH; 3:2) (Found: C, 63.2; H, 8.6. C$_{45}$H$_{74}$O$_{15}$ requires C, 62.8; H, 9.2%). IR (KBr): 3400, 1720 cm$^{-1}$; $^1$H NMR: 0.89 (s, 3H), 0.95 (s, 3H), 0.96 (s, 3H), 1.01 (s, 3H), 1.04 (s, 3H), 1.24 (s, 3H), 1.27 (s, 3H), 2.57 (brs, 1H), 3.28 (t, J = 10.2 Hz), 3.88-4.25 (m, 1H), 5.15 (d, J = 7.2 Hz), 5.38 (t, 1H); MS: m/z 458 (M$^+$), 250, 207, 165; $^{13}$C NMR data are given in Table I.

On hydrolysis with 7% H$_2$SO$_4$ compound 1 gave aglycone 1a and sugar D-arabinose (co-chromatograph with an authentic sample), m.p 298$^\circ$; IR (KBr): 3400, 1722, 1012, 930 cm$^{-1}$; $^{13}$C NMR (cf. Table I).

Acid hydrolysis (7% H$_2$SO$_4$) of compound 2 gave aglycone 2a and sugar D-arabinose (co-chromatograph with an authentic sample), m.p 298$^\circ$; IR (KBr): 3400, 1722, 1012, 930 cm$^{-1}$; $^{13}$C NMR (cf. Table I).

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