Hexahydrocyclopenta[c]pyran-4-carboxylate Iridoid from *Viburnum cylindricum*

**DWARIKA PRASAD¹* and S.P. SATI²**

¹Department of Chemistry  Lovely Professional University. Punjab (India).
²P.G.College Gopeshwar Chamoli Uttrakhand (India).

(Received: September 10, 2011; Accepted: October 22, 2011)

**ABSTRACT**

From ethanolic extract of *Viburnum cylindricum* plant a new iridoid (1S,4aS, 6S, 7R, 7aS)-methyl 6-hydroxy-7-methyl-1-(3,4,5-tri hydroxy-6-(hydroxymethyl) tetrahydro-2H-pyran-2-lyoxy)-1,4a,5,6,7,7a-hexahydrocyclopenta[c]pyran-4-carboxylate have been isolated and characterized with help of ¹H, ¹³C NMR, DEPT and ¹H-¹H COSY studies. These are new studies in chemical analysis of *Viburnum cylindricum*.

**Keywords:** *Viburnum cylindricum*, (1S,4aS, 6S, 7R, 7aS)-methyl 6-hydroxy-7-methyl-1-(3,4,5-tri hydroxy-6-(hydroxymethyl) tetrahydro-2H-pyran-2-lyoxy)-1,4a,5,6,7,7a-hexahydrocyclopenta[c]pyran-4-carboxylate.

**INTRODUCTION**

*Viburnum cylindricum* belong to the family Caprifoliaceae evergreen shrubs with grey bark, leaves oblong lanocelate or ovate glaucous green above occurs in moist shaded oak forest 1200-2500 mt.¹ From leaves of *V. cylindricum* Neochlorogenic acid methyl ester, cryptochlonogenic acid ester and chlorogenic acid methyl ester are isolated². From leaves of *V. pronifolium* 2- acetyldihydropenstemide, 2'- trans-p-caumrayl dihydropenstemide, 2- acetylpatrinoside and patrinoside are isolated³. From leaves of *V. dilatatum* p- hydroxyphenyl-6-0-trans-caffeoyl-β-D-glucoside, p-hydroxyphenyl-6-O-transcaffeoyl- β-D-apiosyble [1-6]- β-D-glucoside are isolated⁴. From leaves of *V. orientale* Acyclic monoterpendiglycosides was isolated⁵. The structure of compounds have been elucidated through mass, ¹H, ¹³C NMR and 2 D-NMR spectra and their biological activities.

**EXPERIMENTAL**

**General**

¹H-NMR at (400 MHz),¹³C-NMR at (75 MHz) TMS as internal standard, using DMSO as solvent column chromatography was carried out on silica-gel 60-120 mesh (Merck). TLC was performed on percolated silica-gel. The eluting solvent was CHCl₃-MeOH spots were visualized by 7% H₂SO₄ followed by heating.

**Plant material**

The whole plant of *Viburnum cylindricum* were collected from Bacchea District. Chamoli
Uttrakhand in the month of October and identified by Department Botany, P.G. College Gopeshwar where vaucher specimen was deposited.

**Extraction and isolation**

The air dried whole plant (3kg) was exhaustively extracted with 90% aqueous EtOH for 72 hours. The ethanol extract was concentrated to dryness. The dry ethanolic extract was chromatographic over silica-gel using methanolchloroform (70:30) as elution solvent which afforded the compound.

**RESULTS**

Compound was refluxed with 5% aqueous HCl (5 ml) at 80°C for 3 h, after cooling the reaction mixture was neutralized with AgNO₃. The aqueous layer after concentration under reduced pressure was subjected to PC using BuOH:AcOH-H₂O (4:1:5) with authentic sugars. The Rf values of sugars were identical with authentic sugars were identical with those of D-glucose.

The elemental analysis of compound found values, C=50.23%, H=6.38% required values for C_{17}H_{26}O_{11}; C=50.25%, H=6.40% corresponded to molecular weight 406. The IR spectrum of compound displayed characteristic absorption maxima at 3500 cm⁻¹ for a chelated OH group at 2900 cm⁻¹ for C-H stretching of saturated carbon atom and at 1700 and 1650 cm⁻¹ for α-β-unsaturated carbonyl function. Its UV-spectrum showed absorption bands characteristic to an iridoid enol showed presence of five double bond equivalence in the molecule.

\[ ^1H-NMR \text{(400MHz, C}_{6}D_{6}N): \delta 6.71 \text{ (1H, d, } J=1.2 \text{ Hz, H-1), 6.53 \text{ (1H, d, } J=6.4 \text{ Hz, H-3), 5.15 \text{ (1H, dd, } J=6.4 \text{, } J=5.2 \text{ Hz, H-4), 4.03 \text{ (1H, dd, } J=11.6 \text{, } J=2.4 \text{ Hz, H-5'}, 2.06 \text{ (1H, dd, } J=14.8 \text{, } J=4.4 \text{ Hz, H-7a}, 2.54 \text{ (1H, d, } J=14.8 \text{ Hz, H-7b), 3.54 \text{ (1H, brs, H-9), 1.59 \text{ (3H, s, H-10), 1.85 (3H, s, OAc), 5.30 (1H, d, } J=8 \text{ Hz, H-1'), 4.00 (1H, dd, } J=8 \text{, } J=8.8 \text{ Hz, H-2'), 3.99 (1H, t, J=8.8 \text{ Hz, H-3'), 4.23 (1H, m, H-4'), 4.26 (1H, dd, } J=11.6 \text{, } J=2.4 \text{ Hz, H-5'), 4.50 (1H, dd, } J=11.6 \text{, } J=2.4 \text{ Hz, H-5'), 4.50 (1H, dd, } J=11.6 \text{, } J=2.4 \text{ Hz, H-6' a), 4.32 (1H, dd, } J=11.6 \text{, } J=5.2 \text{ Hz, H-6' b).} \]

The 1H-NMR spectrum of compound coupled with detailed analysis of 1H-1H COSY indicated presence of two integrated protons signals each for 1H at \( \delta 6.53 \text{ (d, } J=6.4 \text{ Hz, H-3), and 5.15 (dd, } J=6.4 \text{, } J=1.2 \text{ Hz, H-4), two oxygen bearing methine signal at } \delta 6.71 \text{ (d, } J=1.2 \text{ Hz, H-1), methylene protons at } \delta 2.06 \text{ (1H, dd, } J=14.8 \text{, } J=4.4 \text{ Hz, H-7a), and } \delta 2.54 (1H, d, } J=14.8 \text{ Hz, H-7b), one oxygen bearing methine signal at } \delta 4.03 (1H, d, } J=4.4 \text{ Hz, H-6) and methine proton signal at 3.54 (1H, brs, H-9). In addition to this a three protons singlet at } \delta 1.85

\[
(1S,4aS,6S,7R,7aS)-methyl 6-hydroxy-7-methyl-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2H-pyran-2-yloxy)-1,4a,5,6,7,7a-hexahydrocyclopenta[c]pyran-4-carboxylate
\]
assignable for acetoxy group, methoxy protons singlet at $\delta$ 1.59, and seven protons due to the sugar moiety were observed. A methylene proton at $\delta$ 2.06 (dd) showed coupling with another methylene proton at $\delta$ 4.03. A methine proton signal (brs) showed weak coupling with the proton signal appeared at $\delta$ 6.71 which might due to a methine proton bearing two oxygen atoms and is compatible with the H-1 proton signal of most of the iridoids having O-glycosylation at C-1 carbon.

$^{13}$C-NMR (100 MHz, C5D5N): $\delta$ 94.7 (C-1), 142.2 (C-3), 108.1 (C-4), 73.2(C-5), 78.7 (C-6), 45.8 (C-7), 87.2 (C-8), 55.1 (C-9), 22.6 (C-10), 99.1 (C-1’), 74.8 (C-2’), 78.4 (C-3’), 71.6 (C-4’), 76.8 (C-5’), 62.8(C-6’),22.1 (CH$_3$COO), 170.9 (CH$_3$COO). The $^{13}$C- NMR spectrum and distortionless enhancement by polarization transfer (DEPT) spectrum showed 17 carbon signals; three quaternary carbon, 10 methine carbon, two methylene carbon and two methyl carbon.

Acid hydrolysis of compound with 5% HCl gave as a sugar which was identified as D-glucose by paper chromatography. The glycoside nature of the compound was supported by a doublet at $\delta$ 5.30 (J=8.0 Hz) assignable to the anomeric proton of $\beta$-D-glucose. The usual location of sugar moiety at position O-1 of the agycone was shown by the downfield shifted signal of H-1 ($\delta$ 6.71, d, J=1.2 Hz). The $^{13}$C-NMR chemical shift of anomeric carbon atom (C-1’) at $\delta$ 99.1 and the chemical shift of the carbon atom of sugar moiety [$\delta$ 74.8 (C-2’), 78.4(C-3’), 71.6(C-4’), 76.8 (C-5’), 62.8 (C-6’)] are in agreement with the NMR spectrum and thus confirmed the presence of glucose in the molecule. The $^{13}$C-NMR spectrum confirmed the presence of methyl function ($\delta$ 22.6), a methylene carbon [$\delta$ 45.8 (C-7)], two methine carbons [$\delta$ 78.7 (C-6) having oxygen function and 55.1 (C-9)], a secondary carbonyl carbon [$\delta$ 94.7 (C-1)], two quaternary carbons having an oxygen function [$\delta$ 73.2 (C-5) and 87.2 (C-8)], a di-substituted double bond [$\delta$ 142.2 (C-3), 108.1 (C-4)] and an acetate function [$\delta$ 22.1 (CH$_3$COO), 170.9 (-COO-)]. These spectral data was strongly reminiscent of that reported for 8-acetylharpagide. On the basis of above discussed spectral data compound was identified as 8-acetylharpagide. On the basis of above discussed spectral data compound was identified as 8-acetylharpagide that was further confirmed comparison of spectral data with that of reported data.

REFERENCES

6. Takeda, Y., Tsuchida, S. and Fujita, T., Phytochemistry, 26(8), 2303