



A New Tetrahydropyrano[3,4-c]pyran-1(3H)-one Iridoid from *Viburnum cylindricum*

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

ABSTRACT

From ethanolic extract of *Viburnum cylindricum* plant a (4aS, 5R, 6S)-6-(3,4,5-trihydroxy-6(hydroxymethyl) tetrahydro-2H-pyran-2-yloxy)-5-vinyl-4,4a,5,6-tetrahydropyrano[3,4-c]pyran-1(3H)-one Iridoid have been isolated and characterized with help of ¹H, ¹³C NMR, ¹H-¹H COSY, DEPT and HMQC studies. This is new studies in chemical analysis of *Viburnum cylindricum*.

Keywords: *Viburnum cylindricum*, Caprifoliaceae, (4aS,5R,6S)-6-(3,4,5-trihydroxy-6(hydroxymethyl)tetrahydro-2H-pyran-2-yloxy)-5-vinyl-4,4a,5,6-tetrahydropyrano [3,4-c]pyran-1(3H)-one.

INTRODUCTION

Viburnum cylindricum belong to the family Caprifoliaceae evergreen shrubs with grey bark, leaves oblong lanceolate or ovate glaucous green above occurs in moist shaded oak forest 1200-2500 mt. ¹ From leaves of *V. cylindricum* Neochlorogenic acid methyl ester, cryptochlorogenic acid ester and chlorogenic acid methyl ester are isolated². From leaves of *V. Prunifolium* 2- acetyldihydropenstemide, 2'- trans-p-caumrayl dihydropenstemide, 2-acetylpatrinoside and patrinosid are isolated³. From leaves of *V. dilatatum* p- hydroxyphenyl-6-O-trans-caffeoyl-β-D-glucoside, p-hydroxyphenyl-6-O-transcaffeoyl-β-D-apiosyble¹⁻⁶-β-D-glucoside are isolated⁴. From leaves of *V. orientale* Acyclic monoterpendiglycosides was isolated⁵. The structure of compounds have been elucidated through. ¹H, ¹³C NMR and 2 D-NMR spectra and biological activities of plant extract.

RESULTS AND DISCUSSION

It was obtained as yellow amorphous powder from methanol. The elemental analysis of compound found values, C=53.58%, H=6.11%, required values for C₁₆H₂₂O₉; C=53.63%, H=6.14%, Molecular weight 358. UV- spectrum of compound showed characteristic absorption bands at 244 nm for an showed a typical iridoid enol ether system conjugated with a C-4 carbonyl group (6). Compound showed a typical iridoid colour reaction with hydrochloric acid.

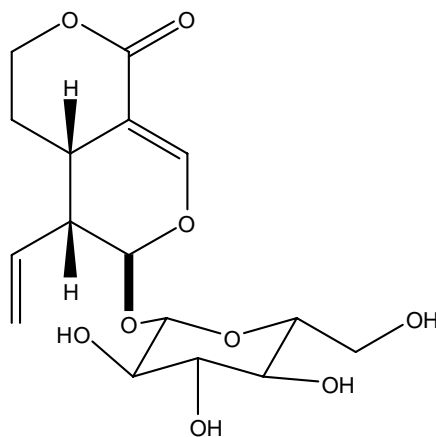
¹H- NMR (400MHz, CD3OD): 5.43 (1H, d, J=1.2Hz, H-1), 7.56(1H,d,J=2.4 Hz, H-3), 3.11 (1H, m, H-5), 1.71(2H, m, H-6), 4.41 (2H, m, H-7), 5.56 (1H, m, H-8), 2.72 (1H, m, H-9), 5.33 (1H,dd, J=2.0, 16.8 Hz, H-10a), 5.25 (1H, dd, J=2.0, 9.0 Hz, H-10b), 4.63 (1H,d, J=8.0 Hz, H-1'), 3.22 (1H, dd, J=80, 8.8 Hz, H-2'), 3.71 (1H, t, J=8.8Hz, H-3'), 3.31 (1H,

m, H-4'), 3.44 (1H, m, H-5'), 3.65 (1H, dd, $J=12.0, 6.0$ Hz, H-6'a), 4.02 (1H, dd, $J=12.0, 6.4$ Hz, H-6'b). The detail analysis of $^1\text{H-NMR}$ spectrum, coupled with of $^1\text{H-}^1\text{H COSY}$ indicated presence of two methylene protons at 1.71 (multiplet for two protons, H-6) which showed coupling with a methylene protons signals (multiplet for two protons) resonated downfield (4.41, H-7) in comparison with H-6 indicated that the later is attached with an oxygen function. The methylene proton signal at 1.71 also showed coupling with a methine proton signal at 3.11 (m, 1H, H-5) which in turn showed coupling with a methine proton signal at 5.43 (d, $J=1.2$ Hz, H-1) and 2.72 (1H, m, H-9). Detailed analysis of $^1\text{H-}^1\text{H COSY}$ showed that the methine proton signal attached to a mono-substituted double bond resonance at 5.56 (1H, m, H-8) showed coupling with a methine proton appeared at 2.72 (H-9), and with two methylene protons appeared at 5.33 (1H, dd, $J=2.0, 16.8$ Hz, H-10a), and 5.25 (1H, dd, $J=2.0, 9.0$ Hz, H-10b). These data indicated presence of a vinyl group in the molecule. An integrated methine proton signal which appeared as a double ($J=2.4$) at 7.56 showed long range coupling in $^1\text{H-}^1\text{H COSY}$ spectrum with the methine proton signal appeared as a multiplet at 3.11 A doublet ($J=1.2$ Hz) appeared at 5.43 was corroborated with the H-1 proton signal of most of the iridoids having O-glycosylation at C-1 carbon (7-9). Beside these protons signals the

$^1\text{H-NMR}$ showed a doublet at 4.63 (1H, d, $J=8.0$ Hz, H-1'), which was corroborate with the presence of a beta-D-glucose moiety in the molecule. The above discussed $^1\text{H-NMR}$ data are strongly reminiscent with those reported for sweroside (10-12). $^{13}\text{C-NMR}$ (100 MHz, CD_3OD); 98.1 (C-1), 154.3 (C-3), 105.3 (C-4), 27.3(C-5), 25.1(C-6), 70.1(C-7), 132.1(C-8), 42.6(C-9), 121.2(C-10), 169.7(C-11), 99.4(C-1'), 73.7 (C-2'), 76.2 (C-3'), 70.2(C-4'), 72.1(C-5'), 61.0 (C-6'). The signals out of which 2 are quaternary, 10 methine and four methylene carbons. The assignment of methylene, methine and quaternary carbon signals readily made by HMQC experiment.

Acid hydrolysis of compound

Hydrolysis of compound was carried out similar to that of compound and the sugar was identified as D-glucose. The glycoside nature of compound was supported by a doublet at 4.63 ($J=8.0$ Hz) assignable to the anomeric proton of beta D-glucose. The $^{13}\text{C-NMR}$ chemical shift of anomeric carbon atom (C-1') at 99.4 and the chemical shift of other carbon atom of sugar moiety (see experimental) are in agreement with the $^1\text{H-NMR}$ spectrum and thus confirmed presence of glucose in molecule. The usual location of sugar moiety at position O-1 of the aglycone was showed by the downfield shifted signal of ^1H (5.43).



(4a*S*,5*R*,6*S*)-6-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yloxy)-5-vinyl-4,4a,5,6-tetrahydropyrano[3,4-*c*]pyran-1(3*H*)-one

The ^{13}C -NMR data of compound are in agreement with the ^1H -NMR data. The presence of a vinyl function as deduced by ^1H -NMR was confirmed by ^{13}C chemical shift of unsaturated carbon atom at 132.1 (C-8) and 121.2 (C-10). The ^{13}C -NMR spectrum also showed presence of two methine carbon bearing an oxygen at 70.1 (C-7), a secondary carbonyl carbon [98.1 (C-1)], a tri-substituted double bond [154.3 (C-3), 105.3(C-4)] and a carbonyl function at 169.7. The location of vinyl group was determined at position C-9 by the ^1H -NMR spectrum in which a methine proton appeared as a multiplet at 2.72(H-9) showed coupling with three methine protons appeared at 5.43 (1H, d, $J=1.2$ Hz, H-1), 3.11 (1H, m, H-5) and 5.56 (1H,m,H-8). The UV absorption coupled with the ^1H and ^{13}C -NMR data established that a carbonyl group is located at C-4 carbon. On the basis of above discussed spectrum data compound was characterized as sweroside which was confirmed by comparison of spectral data with the reported data¹⁰⁻¹².

EXPERIMENTAL

^1H -NMR at (400 MHz), ^{13}C -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 CHCl_3 -MeOH spots were visualized by 7% H_2SO_4 followed by heating.

Plant material

The whole plant of *Viburnum cylindricum* were collected from Bacchehar District. Chamoli Utrakhand 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 (3 kg) 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 Methanol Chloroform (70:30) as elution solvent which afforded the compound.

REFERENCES

1. Gaur; R.D. Flora of District Garhwal" Trans Media, Srinagar Garhwal ,(1999).
2. Zurich-AG, *Helvetica Chemica. Acta* , **88:2**, 339-342 (2005).
3. Tomassiru-L, Cometa-MF, Foddai-S, Nicoletti-M, *Planta Medica* , **65:2**, 195 (1999).
4. Machida-K, Nakona-Y, Kikuchi-M, *Phytochemistry*, **30:6**, 2013-2014 (1991).
5. Calis-I, Yuruker-A, Ruegger-H, Wright-AD, Stricher-U, *Helvetica chemical Acta* , **76 : 1**, 416-424 (1993).
6. Stuppner, H., Muller, E.P., Maller, E.P., Mathuram, V. and Kundu, A. B., *Phytochemistry*. **32(2)**, 375 (1993).
7. Takeda, Y., Tsuchida, S. and Fujita, T., *Phytochemistry*, **26(8)**, 2303 (1987).
8. Stricher, O., *Helv. Chem.Acta.*, **53**, 2010 (1970).
9. Chaudhari, R.K., Afifi-Yazar, F.U. and Stricher, O., *Tetrahedron*,**36**, 2317 (1980).
10. Battersby, A.R. Hali, E.S and Southgate, E., *J. Chem.Sco.*, **5**, 721 (1969).
11. Inouye, H., Ueda,S and Nakamura, Y. *Tetrahedron Letter*, **43** , 5229 (1966).
12. El-naggar, L.J and beal, J.L., *J Nat.peod.*, **43: 649** (1980).