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

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ABSTRACT

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

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

INTRODUCTION

Viburnum cylindricum belong to the family Capriofoliaceae evergreen shrubs with grey bark, leaves oblong lanoceolate 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 isolated[2]. From leaves of *V. pronifolium* 2- acetyldihydropenstemide, 2'- trans-p-caumrayl dihydropenstemide, 2-acetylpatrinoside and patrinosid are isolated[3]. 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 isolated[4]. From leaves of *V. orientale* Acyclic monoterpendiglycosides was isolated[5]. The structure of compounds have been elucidated through mass, ^{1}H, ^{13}C NMR and 2 D-NMR spectra and their biological activities.

EXPERIMENTAL

General

^{1}H-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 *Viburnam cylindricum* were collected from Bacchear 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

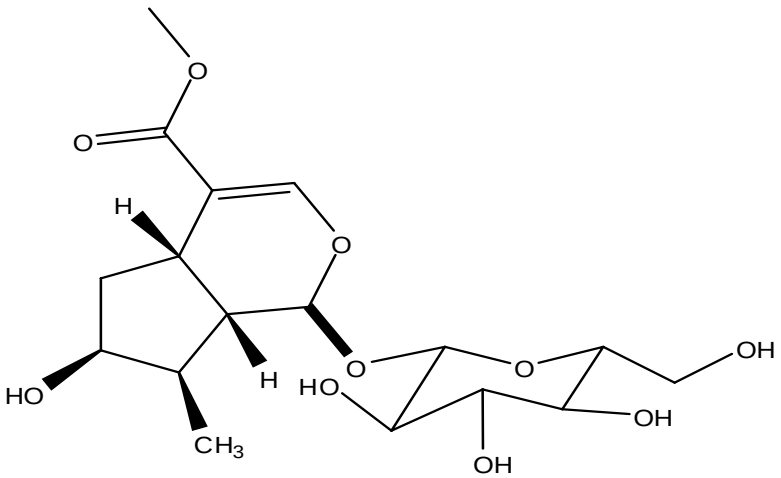
The air dried whole plant (3kg) was exhaustively extracted with 90% aqueous EtOH for 72 hours. The ethanol extract was concentrated to dryness. The dry ethanolic extract was chromatographic over silica-gel using methanol chloroform (70:30) as elution solvent which afforded the compound.

RESULTS

Compound was refluxed with 5% aqueous HCl (5 ml) at 80^{0}C for 3 h, after cooling the reaction mixture was neutralized with $AgNO_3$. The aqueous layer after concentration under reduced pressure was subjected to PC using BuOH:AcOH-H_2O (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.

^{1}H-NMR (400MHz, C_5D_5N): δ 6.71 (1H, d, J=1.2 Hz, H-1), 6.53 (1H, d, J=6.4 Hz, H-3), 5.15(1H, dd, J=6.4, 1.2 Hz, H-4), 4.03 (1H, d, J=4.4Hz, H-6), 2.06 (1H, dd, J=14.8, 4.4Hz, H-7α), 2.54 (1H,d, J=14.8Hz, H-7β), 3.54 (1H, brs, H-9), 1.59 (3H, s, H-10), 1.85(3H, s, OAc), 5.30 (1H,d,J=8Hz, H-1'), 4.00 (1H, dd, J=8.0, 8.8 Hz, H-2'), 3.99 (1H, t, J=8.8Hz, H-3'), 4.23 (1H, m, H-4'), 4.26 (1H, dd, J=11.6, 2.4Hz , H-5'), 4.50 (1H, t, J=11.6, 2.4Hz, H-5'), 4.50 (1H, dd, J=11.6, 2.4 Hz, H-6'a), 4.32 (1H, dd, J=11.6, 5.2Hz, 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 δ 6.53 (d, J=6.4 Hz, H-3), and 5.15 (dd, J=6.4, 1.2Hz, H-4), two oxygen bearing methine signal at δ 6.71 (d, J=1.2 Hz, H-1), methylene protons at δ 2.06 (1H,dd, J=14.8, 4.4 Hz, H-7α), and δ 2.54 (1H, d, J=14.8 Hz, H-7β), one oxygen bearing methine signal at δ 4.03 (1H, d, J=4.4 Hz, H-6) and methine proton signal at 3.54 (1H, brs, H-9). In addition to this a three protons singlet at δ 1.85



(1*S*,4a*S*,6*S*,7*R*,7a*S*)-methyl 6-hydroxy-7-methyl-1-(3,4,5-trihydroxy-6-(hydroxymethyl)tetrahydro-2*H*-pyran-2-yloxy)-1,4a,5,6,7,7a-hexahydrocyclopenta[*c*]pyran-4-carboxylate

assignable for acetoxy group, methoxy protons singlet at δ 1.59. and seven protons due to the sugar moiety were observed. A methylene proton at δ 2.06 (dd) showed coupling with another methylene proton at δ 2.54 and with an oxygen bearing methine proton at δ 4.03. A methine proton signal (brs) showed weak coupling with the proton signal appeared at δ 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[6-8].

^{13}C-NMR (100 MHz, C5D5N): δ 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_3COO). 170.9 (CH_3COO). 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 δ 5.30 (J=8.0 Hz) assignable to the anomeric proton of β-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 (δ 6.71, d, J=1.2 Hz)[6]. The ^{13}C-NMR chemical shift of anomeric carbon atom (C-1') at δ 99.1 and the chemical shift of the carbon atom of sugar moiety [δ 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 (δ 22.6), a methylene carbon [δ 45.8 (C-7)], two methine carbons [(δ 78.7 (C-6) having oxygen function and 55.1 (C-9)], a secondary carbonyl carbon [δ 94.7 (C-1)], two quaternary carbons having an oxygen function [δ 73.2 (C-5) and 87.2 (C-8)], a di-substituted double bond [δ 142.2 (C-3), 108.1 (C-4)] and an acetate function [(δ 22.1 (CH_3COO), 170.9 (-COO-)]. These spectral data was strongly reminiscent of that reported for 8-acetylharpagide[6]. 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[6].

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