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Research Article

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Hexahydrocyclopenta[c]pyran-7-carboxylate iridoid from *Viburnam cylindricum*

Dwarika Prasad

Department of Chemistry(M2), Lovely Professional University, Punjab

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ABSTRACT

From ethanolic extract of Viburnam cylindricum plant a new iridoid (1S, 4aS, 5R, 7S, 7aR)-methyl 4a,5-dihydroxy-7-methyl-1-(3,4,5-trihydroxy-6-(hydroxyl methyl) tetrahydro-2H-pyran-2-yloxy)-1,4a,5,6,7,7a-hexahydrocyclo penta[c]-pyran-7-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,* methyl-dihydroxy-7-methyl-hexahydrocyclopenta[c]-pyran-7-carboxylate, *Capriofoliaceae.*

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.

EXPERIMENTAL SECTION

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 (68:32) as elution solvent which afforded the compound.

RESULTS

It was obtained as amorphous powder from methanol M.P.220-222^{0}C. The elemental analysis of compound was found to have values, C=52.29, H=6.65%, required values for C17H26O10; C=52.31, H=6.67%, Molecular weight 390. It showed a typical iridoid colour reaction by hydrochloric acid and the IR spectrum displayed characteristic absorption maxima for hydroxyl group (at 3450 cm^{-1}), C-H stretching of saturated carbon atom (2900 cm^{-1}) unsaturated ester (1715 cm^{-1}) and enol ether at 1650 cm^{-1}. UV-spectrum of compound showed characteristic absorption band at 224 and 308 nm for an iridoid enol ether system conjugated with a C-4 carbonyl group (12).

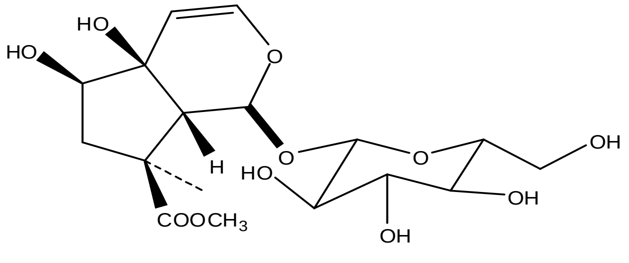
^{1}H-NMR (400 MHz, CD3OD): δ 5.26 (1H, d, J=4.4 Hz, H-1), 7.38 (1H, s, H-3), 3.09 (1H, m, H-5), 1.62 (1H, m, H-6a), 2.03 (1H, m, H-6b), 4.04 (1H, t, J=4.4 Hz, H-7), 1.87 (1H, m, H-8), 2.23 (1H, m, H-9), 1.08 (3H,d, J=6.8 Hz H-10), 3.68 (3H, s, -OCH$_3$), 4.64 (1H, d, J=8.0 Hz H-1'), 3.17-3.39 (4H, m, H-2', H-3', H-4', H-5'), 3.66 (1H, dd, J=11.8, 6.0Hz, H-6'a), 3.89 (1H, dd, J=11.8, 5.2). The ^{1}H-NMR spectrum of compound indicated presence of 26 proton signals, An isolated signal (1H) at δ 7.38 was assigned for a proton attached at tri-substitute double bond. An oxygen bearing methine proton signal at δ 4.04 for 1H appeared as a triplet (J=4.4 Hz, H-7), and three methine proton signal at δ 3.09 (1H, m, H-5), 1.87 (1H, m, Ha-8) and 2.23 (1H, m, H-9) was assignable for H-5, H-8 and H-9 protons of iridoids respectively. Two methylene proton at δ 1.62 and 2.03 each for 1H appeared as a multiple was assigned for h-6b. In addition to this a three protons signal at δ 3.68 assinable for H-6a and H-6b. In addition to this a three protons singlet at δ 1.08 and seven protons due to the sugar moiety were observed. A doublet (J=4.4 Hz) appeared at δ 5.26 was corroborated with the H-1 proton signal of most of the iridoids having O-glycosylation at C-1 carbon(6-8).

13C- NMR (100 MHz, CD$_3$OD): δ 97.7 (C-1), 152.1 (C-3), 114.1 (C-4), 32.2 (C-5), 42.6 (C-6), 74.7 (C-7), 42.2 (C-8), 46.6 (C-9), 13.4 (C-10), 169.6 (-C-OO-), 51.7 (-COOCH$_3$), 99.9 (C-1'), 75.1 (C-2'), 78.3 (C-3'), 71.6 (C-4'), 78.0 (C-5'), 62.1 (C-6'). The ^{13}C- NMR spectrum and distortion less enhancement by polarization transfer (DEPT) spectrum showed 17 carbon signals; two quaternary carbons, 11 methine carbons two methylene carbon and two methyl carbons.

Acidic hydrolysis of compound:
Hydrolysis of compound was carried out similar to that of compound and the sugar was identified as D-sugar.

Acid hydrolysis of compound with 5% HCl gave a sugar, which was identified as D-glucose by paper chromatography. The glycoside nature of the compound was supported by a doublet at δ 4.64 (J= 8.0 Hz) assiggable to the anomeric proton of β-D-glucose. The ^{13}C NMR chemical shift of anomeric carbon atom (C-1') at δ 99.9 and the chemical shifts of other carbon atoms of sugar moiety [δ 75.1 (C-2'), 78.3 (C-3'), 71.6(C-4'), 78.0(C-5'), 62.1 (C-6')] are in agreement with the ^{1}H-NMR spectrum and thus confirmed the presence of glucose in the molecule. The usual location of sugar moiety at the position O-1 of the aglycone was shown by the downfield shifted signal of H-1 (δ 5.26, d, J=4.4 Hz).

The ^{13}C-NMR spectrum confirmed the presence of methyl function (δ 13.6), a methylene carbon [δ 42.6 (C-6)], three methine carbons [(δ 32.2 (C-5), 42.2 (C-8), and 46.6 (C-9)], a methine group having oxygen function at δ 74.7 a secondary carbonyl carbon [δ 97.7 (C-1)], a tri-substituted double bond [δ 152.1 (C-3), 114.1 (C-4)] and an acetate function [(δ 13.6 (-COOCH$_3$), 169.6 (-COO-)]. The location of methyl group was determined at position C-8 by ^{1}H-NMR spectrum in which a methine proton appeared as a multiplet due to coupling with three methyl protons and two methine protons (H-7 and H-9). The downfield chemical shifts of a methine proton at δ 4.04 attributed for H-7 indicated that hydroxyl function was attached at C-7 position. The UV absorption coupled with the ^{1}H and ^{13}C-NMR data established that a carboxyl group is located at C-4 carbon. On the basis of above discussed spectrum data compound was identified as loganin which further confirmed comparison of spectral data with that of reported data(9-11)



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

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