Phytochemical Investigation of EtOH Extract of Flowers of *Senecio Chrysanthemoide*, Asteraceae

[*1]S. C. Sati, [2]Maneesha D. Sati,[3]Shikha Saxena and [4]I. P. Pandey
[*1]Department of Chemistry, H.N.B. Garhwal University (A Central University) Srinagar Garhwal, Uttarakhand, India.246174
[2]Department of Chemistry, Govt. Degree College Devprayag, TehriGarhwal, Uttarakhand, India
[3]Department of Chemistry, D.A.V. (PG) College Dehradun, Uttarakhand, India
[4]Professor Emeritus, Dehradun, Uttarakhand, India
[*]**Email: sati_2009@rediff mail.com**
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Abstract - From the ethanolic extract of flowers of *Seneciochrysanthemoide*one flavone diglycosideonexanthone glycoside have been isolated. The structures of the isolated compounds were identifiedwith the help of chemical and spectral studies.
Key words: *Senecio Chrysanthemoide*, Asteraceae, Flavone Glycosides and Xanthone.

Introduction

*Senecio*species are used in folk medicine for the treatment of cuts, wounds and as antiemetic, anti-inflammatory, antimicro-bialand vasodilator. The parts mostly used are leaves, stem and flowers[1],the pyrroli-zidine alkaloids and the furanosesquiter-penoids are the most important consti-tuents of this genus and thought to be responsible for all of pharmacological activities[2-5].The genus *Senecio*, belongs to the tribe Senecioneae, is the largest and most complex genus in the family of the Asteraceae (Compositae) includes more than 1500 species with a worldwide distribution[6].The chemical constituents of the genus *Senecio*include notably sesquiterpenoids,monoterpenoids[7-8],diter-penoids[9],triterpenoids[10], phenolicand flavonoidcompounds[11-16], essential oils[17]and pyrrolizidine alkaloids[5]. In India the genus *Senecio* comprises 43 species including *S. chrysanthemoide* which grows endemically in all over India[18].The present paper deals with isolation and character-ization of flavone di-glucoside and 3-acetoxyxanthone from the alcoholic extract of the flowers of *S. chrysanthemoide*.

Material and Methods

Mps. Uncorrected, Columnchromato-graphy was carried out on silica gel (60-120) mesh. Merck, eluting solvent ($CHCl_3$MeOH). U.V. was taken in MeOH. ^{1}H-NMR spectra were taken using TMS as internal standard and $CDCl_3$ and CD_3OD as solvents, all the signals are expressed as values downfield from TMS.

Collection of Plant Material

The Flowers of *S. chrysanthemoides*were collected in flowering stage from in Tunganath Chopta, Rudraprayag U.K. India. The plant was identified by expert Taxonomists Department of Botany HNB Garhwal University Srinagar Garhwal. The

voucher specimen (H.N.24446) is available in the herbarium of Plant Identification Laboratory department of Botany HNB Garhwal University Srinagar Garhwal.

Extraction and Isolation

The air-dried and coarsely powered flowers of the plant were defatted with light petroleum in a soxhlet. The defatted mass was exhaustively extracted repeatedly with 90% aqueous EtOH, until the extractive became colorless. All the extracts were mixed and concentrated under reduced pressure using rotatory vacuum evaporator.The concentrated extract was adsorbed on silica gel and fractionated through column chromatography using the solvent system chloroform: methanol (97:3). The polarity of solvent was gradually increased by addition of methanol. Repeated column chromatography afforded compounds 1 and 2 together with β-sitosterol and kaemferol.

Results and Discussion

The ethanolic extract of flowers of *S. chrysanthemoides*on repeated column chromatography over silica gel afforded compounds 1 and compound 2 together with β -sitosteroland kaempferol. The structure of β –sitosterol and kaempferol was confirmed by their comparison with an authentic sample (TLC) and reported data of the compound[19]. The structure of compound 1 was identified as α-L arabinopyranosyl (1→3) β-D glucopyrano-syl (1→3)β–hydroxyoleane-12-ene 28 methyl acetate and compound 2 as xanthone3-Acetoxy-1-hydroxy-6-methoxy8-O-β-Dglucopyranosyl(1→3)α–L rhamnopyr-anosylwith the help of chemical and spectral studies.

Compound 1

It was obtained as crystalline solid from MeOH

Melting Point : 220-222 ^{0} C

Molecular Formula : $C_{30}H_{28}O_{16}$

Molecular Weight : 644

^{1}H-NMR ($CDCl_3$,100MHz,δppm):2.66 (d, J=1.6 Hz), 3.49 (s), 3.25 (s), 7.70 (d, J=8.4 Hz), 6.38 (d, J=7.5 Hz),7.02 (d, J=7.5 Hz), 7.29 (d, J= 1.5 Hz), 5.45 (d, J=6.8 Hz), 5.49 (d, J=7.5 Hz),5.42 (d, J=6.8 Hz,C-1' anomeric proton),4.98 (d, J=5.8 Hz ,C-1"), 3.65-4.72 (sugar multiplets)

^{13}C-NMR($CDCl_3$,150MHz, δ ppm):79.3 (C-2), 43.0 (C-3), 190.1(C-4) 162.8 (C-5), 110 (C-6), 163.5 (C-7), 99.7 (C-8),127.9 (C 9),115.7(C-10), 123.9 (C-11), 113.6 (C-12),141.1 (C-13), 147.0 (C-14)**,** 41(-OCH_3), 40.2 (-OCH_3), 20.9 (-OCH_3)

Arabinopyranosyl: 101.9 (C-1'), 73.1 (C-2'), 76.0 (C-3'), 69.9 (C-4'), 76.0(C-5'), 69.4 (C-6')

Glucopyranosyl: 103.1 (C-1"), 73.1 (C-2"), 75.5 (C-3"), 69.3 (C-4") 75.0 (C-5"), 60.3 (C-6")

The compound 1 was found to be positive for coloration with methanolic $FeCl_3$,Molish test and Shinoda test (Mg/HCl)there by indicating flavonoid nature of compound. IR spectra of compound displayed absorption bands at 3302, 1665, 1622, 1505 showed presence of hydroxyl and carbonyl functions in the compound. The molecular formula of compound was calculated as $C_{30}H_{28}O_{16}$ which corres- pond the molecular weight 644 amu, due to the presence of molecular ion peak at m/z644$[m]^+$,645$[M+H]^+$, 675$[M+CH_3OH]$. Other fragment ion peaks appeared at m/z 452$[(M+H)^+-(OCH_3+162)]$ and 273$[(M+H)^+-(OCH_3+O$

H+2×162)]$^{+}$.The^{1}HNMR spectrum of compound displayed two doublets at δ 6.38 (d, J = 7.5 Hz , C-12) and δ 7.02 (d,J = 7.5Hz, C-13) and one doublet of 1.6 Hz coupling constant appeared at δ 2.66 (C-3) assigned for flavonoid proton. A doublet of 8.4 Hz at δ 7.70 ascribed to C-6 of flavonoid. The position of two, 3H proton singlet at δ 3.49 and δ 3.25 assigned for two OCH3.The ^{1}H signals appeared at δ 3.60-5.4 ascribes the sugar moiety in the molecule. The position of two doublets at δ 5.42 (d, J= 6.8 Hz) and δ 4.98 (J=7.5 Hz) represents two anomeric sugars. The presence of two sugars were further in agreement with the FAB-MS data displayed peaks at m/z 452 and 273 arose by the loss of two sugar molecule from the molecular ion peak.All These values were in agreement with its^{13}C NMR data. The coupling constant value of anomeric sugar showed β configuration in both the sugar molecule. Compound when hydrolyzed with 7% methanolicHCl furnished two glucose molecules (from PC and TLC). Methylation, methanolysis and partial hydrolytic studies revealed the position of both the sugar in different carbon. All these data were in agreement with the reported data of flavonoidal glycoside[20].Hence compound was identified as **Flavon 5, 4'dimethox 8 methyl 7-O-β-D glucopyranoside-5'-βDglucopyranoside. (**Figure-1)

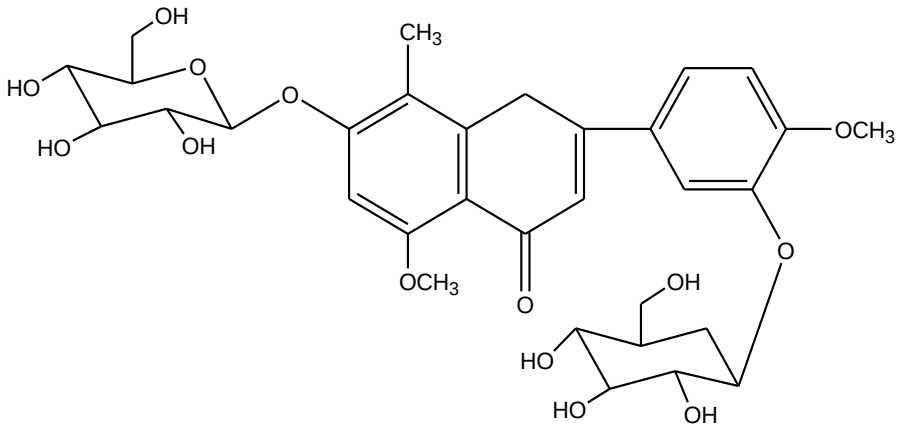

Figure – 1

Compound 2

It was obtainted as colourless crystalline solidfromMeOH

M.P.: 196-198^{0} C
FAB MS (m/z): 606[M]$^{+}$, 607 [M+H]$^{+}$, 460 [M+ H-Rham]$^{+}$298 [MH–(rha+glu)]$^{+}$, 255, 209
^{1}HNMR (CDCl$_3$100MHz,δppm):6.83(d,J=8.4Hz),7.68(s), 7.24(s), 6.62(d, J=8.4Hz), 2.48 (s), 2.65(s),9.06 (s)
Glycone:5.43 (d,J=7.8Hz), 5.2(s), 3.5-4.9 (Sugarproton).
Molecular weight: 606
I.R. (ν_{max}^{KBr}) cm^{-1}: 2995, 3000, 1640

Molecular formula :$C_{28}H_{30}O_{15}$

^{13}CNMR (CDCl$_3$150MHz, δppm):Aglycone163.9 (C- 1), 117.6 (C-2),1473 (C-3),122.21(C-4),125.4(C-5),145(C-6),128.6(C-7),163.3(C-8),191.4(C-9), 18.4(C-10),138.7(C-11), 116.3 (C-12), 115
.7(C-13), 115.4(C-14), 176.0 (C=O), 43.3(CH3),56.3 (OMe)
Glycone:103.0 (C-1'),73.6 (C-2'),79.6 (C-3'), 63.1 (C-4'),76.3 (C-5'), 61.2(C-6').

Glycone:101.9 (C-1''),73.4 (C-2''),77.4(C-3''),69.9(C-4''),60.9(C-5''),18.5(C-6').

It gave green coloration with $FeCl_3$ and also responded positive test with Molishreagent there by indicating phenolic nature of the compound[21]. IR spectrum of compound showed characteristic bands at 2995, 3000 and 1640 cm^{-1} for phenolichydroxy and carbonyl groups. ^1H - NMR spectrum of the compound displayed two 1H proton singlets at δ 7.24 and δ 7.68 for C-5 and C-4 hydrogen, which confirmed the presence of xanthone skeleton in compound. Two doublets of 8.4 Hz coupling constant appeared at δ 6.83 and δ 6.62 showing an ortho-coupling. Two up field sharp singlets at δ 2.48 and δ 2.65 indicated the presence of two methoxy group in compound, whereas a weak singlet at δ 9.06 were assigned for hydroxyl group. Two anomeric proton resonated at δ 5.43 (d, J = 7.8 Hz) and δ 5.2 (s) with other sugar peaks appeared between δ 3.1-4.9 assigned for 10 sugar protons. The molecular weight of compound was deduced as 606 amu which corresponding the molecular formula $C_{28}H_{30}O_{15}$, due to the presence of molecular ion peak at m/z 607 $[M+H]^+$The presence ofthese different groups were in agreement with the mass fragmentation of a compound as shown by its FAB-MS which furnished peaks at m/z 460 $[M+H\text{-}Rham]^+$, 298$[M+H–(Rham+Glu)]^+$, 255 $[M–(2Glu+COCH_3)]$ and 209$[M-(2gly+COCH_3+OCH_3)]$. The structure of glycone was further supported by its hydrolysis studies. Compound was hydrolyzed with 7% methanolicHCl for about 8 hours. It furnished an aglycone identified as 3-Acetoxy 1-hydroxy 6-methoxyxanth- one from its reported data. The neutralized hydrolysate gave two sugars identified as glucose (PC, Rf value 0.18) and rhamnose (PC, Rf value 0.37). Compound 2 on partial hydrolysis yield one rhamnose (PC, Rfvalue 0.37) and one Mono glycosidicaglycone. The prosapogenin on further HOH yield one xanthone as an aglycone (TLC) and glucose (PC, RF) showed the sequential loss of sugars.

The point of glycosidation was established by the^{13}C-NMR data of sugars which was fixed at C-3 of glucose with C-1 of rhamnose.The configuration was found to be β in glucose and α in rhamnose by the J value of anomeric sugar in its ^{1}H-NMR spectrum. These all values were compared with the reported data of xanthone glycosides[20].Thus on the basis of spectral studies compound 2 was identified as **xanthone 3-Acetoxy-1-hydroxy-6-methoxy 8-O–β–D glucopyranosyl (1→3) α–L rhamnopyranoside**. (Figure-2)

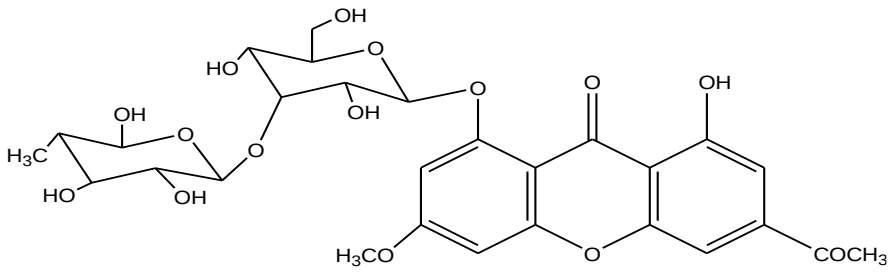

Figure – 2

Acknowledgement

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Disclaimer Statement

Authors declare that no competing interest exists. The products used for this researchare commonly used products in research. There is no conflict of interest

between authors and producers of the product.

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