Indian Journal of Chemistry
Vol. 59B, November 2020, pp. 1745-1748

Note

Composition of a new chemotype of *Senecio chrysanthemoides* DC.

C S Mathela[a] & Balam S Bisht*[b]

[a] Department of Chemistry, Kumaun University, Nainital 263 002, India

[b] Department of Chemistry, Govt. PG College Berinag, Pithoragarh 262 531, India

E-mail: mathelacs@gmail.com; bbbantychem@gmail.com

Received 6 April 2020; accepted (revised) 14 October 2020

1,10β-*epoxy*-6-oxo-furanoeremophilane **1** (21.8%) along with furanoligularenone **2**, germacrene D **3,** selin-11-en-4α-ol **4** and caryophyllene oxide **5** have been identified in *Senecio chrysanthemoides* DC. of the Garhwal region of Himalaya at an altitude of 3600 m. 1,10β-*epoxy*-6-oxo-furanoeremophilane **1** has not been reported in *Senecio chrysanthemoides* DC. but reported in the other species of the genus *Senecio*. Presence of compounds **1-5** and absence of previously reported β-thujone and 6-hydroxy-*p*-menth-4(5)-en-3-one makes it a new chemotype within the genus *Senecio*.

Keywords: *Senecio chrysanthemoides*, Asteraceae, 1,10β-*epoxy*-6-oxo-furanoeremophilane, furanoligularenone

The genus *Senecio* (family *Asteraceae*; tribe *Senecioneae*) consists of more than 1,500 species of aromatic herbs and shrubby plants native to Southern Europe, but now spread all over the world. A few herbaceous species of the genus are grown as ornamental plants[1,2]. Literature reports on the phytochemistry of these species show a large variety of pyrrolizidine alkaloids[3] and sesquiterpenoids[4], diterpenoids[5], triterpenoids[6], Eudesmanolides, shikimic acid and cacalolide derivatives[7,8]. The essential oils of *S. aegyptius* var. *discoideus* Boiss was rich in 1,10β-epoxyfuranoeremophilane[9]. Furthermore, biological activities such as antibacterial[9], molluscicidal[10], antimicrobial[11] and cytotoxic activities[12], and biosynthesis of algal pheromones have been reported for these plants[13]. In traditional medicine, the use of *Senecio* species for wound healing and treatment of coughs, bronchitis, asthma and eczema have been reported[14,15,16].

The leaves of *Senecio* are alternate in arrangement and the flowers are variously coloured (mostly yellow, but blue, purple or white forms are also found). Many species of the genus *Senecio* have been reportedly used as traditional remedies for colds and sore throats, coughs, burns and wounds, enemas in chest complaints, nausea and vomiting, stomach ache, hiccups, purgatives and also for anal protrusion in children, blood purifiers for skin eruptions and treatment of venereal diseases[17,18].

Result and Discussion

From the essential oil of *Senecio chrysanthemoides* five compounds **1-5** were isolated with *1,10β-epoxy*-6-oxo-furanoeremophilane **1** (21.8%, Figure 1) as the major constituents.

Compound **1**, The compound **1** was obtained as white crystals. The EI-MS of compounds showed, molecular ion peak at *m/z* 246, corresponding to molecular formula $C_{15}H_{18}O_3$.The ^{13}C NMR and DEPT of the compound **1** showed 15 signals, which could be attributed to three CH_3, three CH_2, three CH and six quaternary carbon atom. The ^{13}C NMR signal at δ 119.99, 162.28, 119.42 and 140.02 ppm indicated the presence of furan ring. ^{13}C NMR signal at δ 197.6 showed the presence of carbonyl group. The IR stretching at 1672 cm^{-1} indicates that the carbonyl group in conjugation with furan ring. The carbon

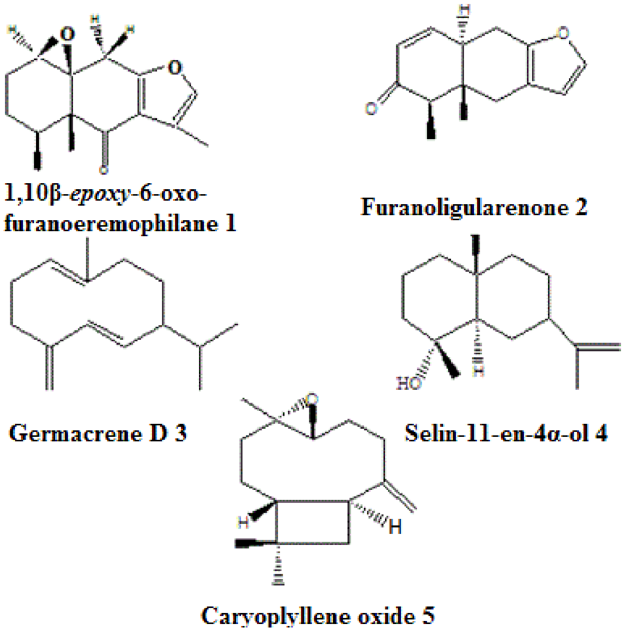

Figure 1

atoms involved in the formation of epoxy ring (C-1 and C-10) showed ^{13}C NMR value at δ 62.85 and 62.71 respectively. The ^{1}H NMR signal at 7.11 ppm indicated the presence of single proton in the furan ring and other carbons of the furan ring must be completely substituted. Three ^{1}H NMR signals at δ 2.21 (3H, s), 1.27 (3H, s) and δ 1.07 (3H, s) showed the presence of three methyl groups also confirmed by the ^{13}C NMR signals appearing at δ 9.04, 18.96 and δ 14.62 . The protons present at C-9 showed different signals bearing same coupling constant. Both the protons were trans coupled and showed ^{1}H NMR signals at δ 2.40 (1H, m) and 3.47 (1H, d). Based on these spectral data, the compound **1** was identified as *1,10β-epoxy*-6-oxo-furanoeremophilane. Finally it was confirmed by comparison of its spectral data with those reported in literature[19].

Compound **2,** The compound **2** is the most abundant component in the extract of the aerial parts and identified as furanoligularenone (Figure 1) on the basis of the spectral data reported in literature[20,21].

Compound **3,** the compound **3** was obtained as viscous liquid .The EI-MS of compounds showed, molecular ion peak at *m/z* 204, corresponding to molecular formula $C_{15}H_{24}$. The ^{1}H NMR spectrum showed a doublet at δ0.89 (6H,d, *J*=6.6Hz) which revealed the presence of an isopropyl groups in the molecule. The signal at δ 1.52 (3H, s) was attributed to a methyl group attached to an olefinic carbon. The ^{13}CMR spectra of compounds represent fifteen carbons which were assigned for three methyl, five metylene, five methine and two quaternary carbons by DEPT experiments. Based on these spectral data, the compound **3** was identified as germacrene D (Figure 1). Finally it was confirmed by comparison of its spectral data with those reported in literature[22,23].

Compound **4,** a crystalline solid, displayed a molecular ion peak at *m/z* 222 [M^{+}] in its EI-MS for $C_{15}H_{26}O$ and fragment peak at 204 due to the loss of H_2O suggesting the compound to be alcohol (IR: 3300 cm^{-1}). Its ^{1}H NMR showed a total of three methyl signals at δ 0.89 for angular methyl at δ 1.12 (s, 3H) attributed to the methyl attached with the carbon bearing hydroxyl group and a downfield signal at δ 1.75 (s, 3H) for methyl attached to exocyclic double bond, two proton multiplet signals at δ 4.70 (m, 2H) due to exocyclic methylene protons. The ^{13}C NMR of the compound showed a total of 15 carbons and their multiplicity assignment marked the presence of three CH_3, seven CH_2, three CH and two quaternary carbon atoms. Compound **4** has thus been identified as selin-11-en-4α-ol (Figure 1) as one of the eight stereoisomer of eudesm-11-en-4α-ol[24,25].

Compound **5,** The compound **5** was obtained as liquid. The EI-MS of the compound displayed a molecular ion peak at *m/z* 220 [M^{+}] corresponding to the molecular formula $C_{15}H_{24}O$. Its ^{1}H NMR showed two singlets at δ 0.98 (3H, *s*) and δ 1.00 (3H, *s*) for gem-dimethyls suggesting that both are attached to a quaternary carbon. The presence of an exocyclic double bond has been confirmed by two doublets at δ 4.85 (1H, *d*, H-12) and 4.97 (1H, *d*, H'-12) which is also supported by the ^{13}C-resonances at δ 151.6 (*s*) and 112.7 (*t*). The ^{13}C NMR of the compound showed total of fifteen carbons and their multiplicity assignment determined through DEPT spectrum marked the presence of three methyl, six methylene, three methine and three quaternary carbons. On the basis of these spectral data compound **5** has been identified as caryophyllene oxide (Figure 1). Its identity was also confirmed by comparison of its spectral data with those reported in literature[26,27].

Experimental Section

The NMR spectra were recorded in $CDCl_3$ on a Bruker DRX-300 MHz, ^{1}H and 75 MHz ^{13}C instrument using TMS as internal standard. The sample was analyzed by using Nucon 5765 gas chromatograph equipped with Rtx-5 non-polar fused silica capillary column (30 m × 0.32 mm, 0.25 µm film coating). The oven temperature (60-210°C) was programmed at 3°C min^{-1} using N_2 as carrier gas at 4 Kg cm^{-2}. The injector temperature was 210°C, detector temperature 210°C and the injection volume 0.5 µL, using a 10% solution of the sample in *n*-hexane. GC-MS was conducted on a Thermo Quest Trace GC 2000 interfaced with a Finnigan MAT PolarisQ ion trap mass spectrometer equipped with Rtx-5 non-polar fused silica capillary column (30 m × 0.25 mm, 0.25 µm film coating). The oven temperature (60-210°C) was programmed at 3°C min^{-1} using helium as carrier gas at 1.0 min^{-1}. The injection, ion source and MS transfer line temperatures were 210°C, 220°C and 275°C, respectively, the injection volume was 0.1 µL, and the split ratio was 1:40. MS were taken at 70 eV with mass range of 40-450 amu.

Plant material

The aerial part of *S. chrysanthemoides* Dc. was collected from Gangi, Tehri garhwal district of

Uttarakhand (3600m). Plant herbarium was identified from the Botanical Survey of India, Dehradun (Acc. No. 113411) and voucher specimen has been deposited in the Phytochemistry Laboratory, Chemistry Department, Kumaun University, Nainital.

Extraction and isolation

The fresh plant material (2 kg) was subjected to steam distillation. The distillates were saturated with NaCl and extracted with *n*-hexane and dichloromethane. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was distilled off. The compounds were isolated by fractionation of the essential oil on silica gel CC (230-400 mesh, Merck, 600 × 25 cm column) packed with hexane, using Et_2O-hexane as mobile phase with gradually increasing the amount of ether (2-15%).

1,10β-*epoxy*-6-oxo-furanoeremophilane 1: Colorless Crystals. IR: 2925, 1672, 1453, 1249, 1058 cm^{-1}; ^1H NMR: δ 1.07 (3H, *d*), 1.27 (3H, *s*), 1.37 (2H, *m*), 1.97 (2H, *m*), 2.21 (3H, *s*), 2.40 (1H, *d*), 2.61 (1H, *ddq*), 3.14 (1H, *d*), 3.47 (1H, *d*), 7.11 (1H, *br,s*); ^{13}C NMR: δ 9.04 (C-13), 14.62 (C-15), 18.96 (C-14), 20.14 (C-3), 25.88 (C-2), 30.25 (C-4), 31.33 (C-9), 49.35 (C-5), 62.71 (C-10), 62.85 (C-1), 119.42 (C-11), 119.99 (C-7), 140.02 (C-12), 162.28 (C-8), 197.63 (C-6); EI-MS: *m/z* 246 [M+], 231, 213, 203, 189, 185, 178, 175, 162, 161, 147, 145, 140, 133, 122, 107, 105, 94, 91, 79, 77, 66, 65, 53.

Furanoligularenone 2: Colorless Crystals. IR: 3130, 3110, 3025, 1685, 1648, 1566, 1539, 1460, 1260, 1213, 1089, 970, 822, 770 cm^{-1}; ^1H NMR: δ 6.60 (*dd* J= 10.0, 1.7 Hz, H-1), 6.06 (*dd*, J= 10.0, 2.9 Hz, H-2), 2.42 (*q*, J= 6.8 Hz, H-4), 2.31 (*m*, H-6), 2.45 (*m*, H-9), 2.81 (*br dd*, J= 14.4, 5.6 Hz, H-9), 2.72 (*dddd*, J= 5.2, 3.0, 2.0 Hz), 7.08 (*br s*, H-12), 1.91 (*d*, J= 1.2 Hz, H-13), 0.68 (*s*, H-14), 1.17 (*d*, J= 6.8 Hz, H-15); ^{13}C NMR: δ 149.5 (C-1), 128.7 (C-2), 201.0 (C-3), 53.6 (C-4), 40.6 (C-5), 25.5 (C-6), 116.6 (C-7), 147.5 (C-8), 33.5 (C-9), 42.8 (C-10), 120.0 (C-11), 137.5 (C-12), 8.0 (C-13), 10.5 (C-14), 7.1 (C-15); EI-MS: *m/z* 230 [M+], 215, 201, 187, 173, 159, 145, 122, 119, 115, 105, 94, 91, 79, 77, 65, 53.

Germacrene D 3: Viscous liquid. ^1H NMR: (300MHz, $CDCl_3$): δ 0.89 (6H, *d*, *J*=6.6Hz, 2 Me 12, 13), 1.52 (3 H, *s*, Me=1), 4.80 (2H, *dd*, *J*=13. 2Hz, H-15), 4.80 (2H, *dd*, *J*=13. 2Hz, H-15), 5.24 (2H, *m*), 5.8 (1H;*s*); ^{13}C NMR (75 MHz,$CDCl_3$): δ 129.8 (*d*,C-1), 29.7 (*t*,C-2), 34.5 (*t*,C-3), 148.8 (*s*,C-4), 135.6 (*d*,C-5) 133.2 (*d*,C-6), 52.9 (*d*,C-7), 26.5 (*t*,C-8), 40.7 (*t*,C-9), 133.7 (*s*,C-10), 32.7 (*d*,C-11), 19.7 (*q*,C-12), 20.9 (*q*,C-13), 15.8 (*q* C-14), 109.9 (*t*,C-15); EI-MS ($C_{15}H_{24}$, 70 eV): *m/z* (rel. int.) 204 [M+], 189, 161(100%), 133, 119, 105, 91, 79, 77, 67, 65 and 43.

Selin-11-en-4α-ol 4: White solid crystals. IR: 3300 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$-TMS): δ 0.89 (3H, *s*, H-14), 1.12 (3H, *s*, H-15), 1.75 (3H, *s*, H-13), 1.81 (1H, *dddd*, H-5), 1.87 (1H, *dquin*, H-13), 1.96 (1H, *dddd*, br., H-7), 4.70, 4.72 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$-TMS): δ 43.3 (t, C-1), 20.1 (t, C-2), 44.6 (t, C-3), 72.2 (s, C-4), 54.9 (d, C-5), 26.0 (t, C-6), 46.3 (d, C-7), 26.8 (t, C-8), 41.0 (t, C-9), 34.6 (s, C-10), 150.7 (s, C-11), 108.1 (t, C-12), 22.7 (q, C-13), 21.0 (q, C-14), 18.6 (q, C-15); EI-MS ($C_{15}H_{26}O$, 70 eV): *m/z* (rel. int) 67 (36.18), 79 (35.81), 81 (53.59), 91 (38.79), 93 (91.14), 95 (32.04), 105 (66.32), 107 (41.96), 119 (39.29), 121 (26.34), 133 (73.00), 134 (25.16), 135 (39.59), 147 (61.09), 148 (30.99), 161 (84.50), 162 (66.05), 175 (31.22), 189 (100.00), 204 (62.30), 222 [M+].

Caryophyllene oxide 5: Liquid. IR (cm^{-1}): 3065, 2925, 1634, 1458, 1386, 1225, 866; ^1H NMR (300 MHz, $CDCl_3$-TMS): δ 0.98 (3H, *s*, Me-14), 1.00 (3H, *s*, Me-13), 1.20 (3H, *s*, Me-15), 2.62 (1H, *dd*, J=9.3 Hz, H-2), 2.87 (1H, *dd*, J=3.6 Hz, 10.5 Hz, H-9), 4.85 (1H, *d*, J=1.5 Hz, H-12) and 4.97 (1H, *d*, J=1.5 Hz, H'-12); ^{13}C NMR (75 MHz, $CDCl_3$-TMS): δ 151.8 (*s*, C-1), 48.7 (*d*, C-2), 39.7 (*t*, C-3), 34.0 (*s*, C-4), 50.7 (*d*, C-5), 27.2 (*t*, C-6), 39.1 (*t*, C-7), 59.8 (*s*, C-8), 63.7 (*d*, C-9), 29.7 (*t*, C-10), 30.2 (*t*, C-11), 112.7 (*t*, C-12), 21.6 (*q*, C-13), 29.8 (*q*, C-14) and 17.0 (*q*, C-15); EI-MS ($C_{15}H_{24}O$, 70 eV): *m/z* (rel. int.): 67 (44.49), 77 (54), 79 (68.20), 91 (100.00), 93 (55.95), 95 (42.85), 105 (65.83), 107 (41.20), 109 (25.31), 119 (40.12), 121 (36.00), 131 (38.30), 133 (21.91), 135 (19.91), 145 (27.09), 159 (28.42), 161 (27.47), 187 (27.14), 205 (10.23), 220 (3.56, M^+).

Acknowledgements

The authors are grateful to the DST, New Delhi for GC and GC-MS grant. One of the authors (BSB) is grateful to UCoST, Dehradun for fellowship and to BSI Dehradun, for plant identification.

References

1 Nordenstam B, 'Senecioneae and Liabeae-Systematic Review', in *The Biology and Chemistry of the Compositae* Vol. 2, (Academic Press, London, UK), p.799-830 (1977).

2 Joffe P, *Creative Gardening with Indigenous Plants*: *A South African Guide* (Briza Publications, Pretoria, South Africa), p.16-32 (2001).

3 Bohlmann F, Zdero C, Jakupovic J, Grenz M, Castro V, King R M, Robinson H & Vincent L P D, *Phytochemistry*, 25 (1986) 1151.

4 Bohlmann F & Ziesche J, *Phytochemistry*, 20 (1981) 469.

5 Rucker G, Manns D, Schenkel E P, Hartmann R & Heinzmann B M, *Phytochemistry*, 52 (1999) 1587.

6 Cheng D, Cao V, Cheng J & Roedei E, *Phytochemistry*, 32 (1993) 151.

7 Ndom J C, Mbafor J T, Azebaze A G B, Vardamides J C, Kakam Z, Kamdem A F W, Deville A, Ngando T M & Fomum Z T, *Phytochemistry*, 67 (2006) 838.

8 Bohlmann F & Bapuji M, *Phytochemistry*, 21 (1982) 681.

9 El-Shazly A, Doral G & Wink M, *Z Naturforsch C Biosci*, 57 (2002) 434.

10 Grace M H & Khattab A M, *J Pharm Sci*, 39 (1998) 253.

11 Perez C, Agnese A M, Cabrera J L, *J Ethnopharmacol*, 66 (1999) 91.

12 Loizzo M R, Tundis R, Statti G A & Menichini F, *Arch Pharm Res*, 30 (2007) 701.

13 Boland W & Mertes K, *Eur J Biochem*, 147 (1985) 83.

14 Hammond G B, Fernandez I D, Villegas L F & Vaisberg A J, *J Ethnopharmacol*, 61 (1998) 17.

15 Uzun E, Sariyar G, Adsersen A, Karakoc B, Otuk G, Oktayoglu E & Pirildar S, *J Ethnopharmacol*, 95 (2004) 287.

16 Mengi N, Garg S N, Agarwal S K & Mathela C S, *J Essent Oil Res*, 7 (1995) 511.

17 Hutchings A, *Bothalia*, 19 (1989) 111.

18 Rose E F, *S Afr Med J*, 1039 (1972).

19 Bohlmann F, & Zdero C, *Chem Ber*, 109 (1976) 819.

20 Patil F, Ourisson G, Tanahashi Y, Wada M & Takahahsi T, *Bull Soc Chim France*, 1047 (1968).

21 Torres P, Ayala J, Grande C, Anaya J & Grande M, *Phytochemistry*, 52 (1999) 1507.

22 Kubeczka K H, *Essential Oil Analysis by Capillary Gas Chromatography and Carbon 13 NMR spectroscopy* (John,Wiley and Sons, England), p.406 (2002).

23 Sleiopoulos P, Wust M & Adam K P, *Phytochemistry*, 60 (2002) 13.

24 Corbet R E & Smith R A J, *Tetrahedron Lett*, 1009 (1967).

25 Kesselmans R P W, Wijnberg J B P A, Groot A D & Van Beek T A, *J Essent Oil Res*, 4 (1992) 201.

26 Cordano G, Merrin M A, Polonsky J, Rabnal R M & Vareume P, *J Indian Chem Soc*, 55 (1978) 1148.

27 Sakar M K, Ercil D, Olmo E D & Feliciano A S, *Fitoterapia*, 70 (1999) 103.