Chemical composition and chiral analysis of β-myrcene rich essential oil from Glossocardia bosvallia (L.f.) DC.

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ABSTRACT

Essential oil from the aerial parts and flowers of Glossocardia bosvallia (L.f.) DC. was analysed using GC, chiral GC, GC-MS and NMR spectroscopy. Chemical composition and identification of compounds in the essential oils were determined by GC and GC-MS analysis respectively. GC analysis depicted β-myrcene as the major compound in both the essential oils, aerial parts containing 61.59% and flowers constitutes 44.86%. Occurrence of β-myrcene was also confirmed using 1H, 13C and DEPT 135° NMR spectroscopy. Chiral GC illustrated the enantiomeric composition of monoterpenol hydrocarbons, in which (1S)-(-)-β-pinene, (-)-sabinene and (4S)-(-)-limonene were the major enantiomers. The present study reports the essential oil composition and enantiomeric composition of β-myrcene rich G. bosvallia essential oil for the first time. G. bosvallia essential oil can be a good source of β-myrcene, a compound with wide range of biological properties.
1. Introduction

Glossocardia bosvallia (L.f.) DC. also mentioned in many reports as Glossocardia bosvallea, is a herb, growing up to 10-15 cm with yellow flowers and needle-like leaves (Fig. S1), found in the waste and cultivated lands in many parts of the Indian sub-continent (Rajopadhye et al., 2016). This plant is native to the region ranging from Sahara through India up to Myanmar. Glossocardia bosvallia is the accepted name for the plant synonyms such as Bidens minuta Miré & H. Gillet, Glossocardia linearifolia Cass., Glossocardia setosa Blatt. & Hallb., Pectis meifolia Wall. [Illegitimate] and Verbesina bosvallia L.f. (Flann et al. 2010; Veldkamp and Kreffer 1991). Essential oil (EO) of G. bosvallia was studied for antimicrobial activity and found that it possesses antibacterial and antifungal activity against different bacteria and fungi (Sharma et al., 1979). Sharma and Garg, 1980 reported phellandrene, p-cymene and β-caryophyllene as the major compounds in the essential oil but no further reports using advanced analytical techniques were found. EO from in-vivo grown plants of G. bosvallia are described with compounds such as limonene and phellandrene/1,8-cineole as the major compound (Reddy et al., 2001). The complete chemical composition of the essential oils and/or the extracts of this plant remain unknown. Thus, in the current study it is intent to investigate the chemical composition of the essential oils by GC, chiral GC, GC-MS and NMR spectroscopy.

2. Results and discussion

Gas chromatographic analysis of G. bosvallia aerial parts and flower essential oils shows β-myrcene as the major compound with 61.59% and 44.86% respectively (Table S1). The other major compounds present as common in both the EOs are limonene (18.2 and 6.30%), n-decanal (5.17 and 3.54%), β-pinene (3.88 and 3.21%), sabinene (1.58 and 1.32%) and α-pinene (1.07 and 0.86%) in aerial parts and flowers respectively. Compounds such as (E)-β-ocimene, 1-undecene, (Z)-myroxide, camphor, citronellol, bornyl acetate, 1-tridecene and patchouli alcohol are present in both essential oils but marked with higher content in flower essential oils. Compounds namely terpinen-4-ol, cryptone, (Z)-myrtilol, undecanal, 7-epi-silphiperfol-5-ene, decanoic acid, α-guaiene, (E)-β-farnesene, linalool isovalerate, γ-gurjunene, caryophyllene oxide, 2-phenylethyl tiglate and γ-eudesmol are found only in the flower EO (Table S1). In general, terpenoids, phenylpropanoid and fatty acid derivative group of compounds are commonly found in essential oils, among this G. bosvallia essential oils are dominated with terpenoid compounds and 2-phenylethyl tiglate is the only phenylpropanoid compound found in flower EO.

Identification of β-myrcene (Fig. S2), the major compound in the G. bosvallia EO, is also confirmed by 1H, 13C and DEPT 135° NMR spectroscopy. Ten prominent signals in 13C NMR spectrum shows the presence of ten carbons correspond to monoterpene compound (Table S2, Fig. S3). The 1H NMR signal at δ 1.70 ppm and δ 1.61 ppm corresponds to both methyl groups at C₈ and C₉ position. Two doublet signals at δ 5.05-5.07 and 5.23-5.26 ppm with J value of 12 Hz and 18 Hz respectively, represent the protons (1a and 1b) at C₁. Two 1H NMR signals in the olefinic region at δ 5.00 and 5.02 ppm corresponds to the proton at C₁₀ and whereas the
signals at $\delta$ 6.36-6.40 ppm and $\delta$ 5.15-5.17 ppm are of the protons at C$_2$ and C$_6$ respectively (Table S2, Fig. S4). The presence of three double bonds in the structure is evidenced by six $^{13}$C signals at $\delta$ 113.03, 138.95, 146.11, 124.11, 131.76, 115.66 among which $\delta$ 115.66 and 113.03 corresponds to the two terminal double bonds in the structure (Fig. S3). Four negative signals at $\delta$ 113.03, 115.66, 31.37 and 26.69 in DEPT 135° spectrum also confirms the four methylene group (C$_1$, C$_{10}$, C$_4$, C$_5$) in the structure and absence of 146.11 and 131.76 shows that C$_3$ and C$_7$ are quaternary carbon (Fig. S5). The NMR signals of the G. bosvallia aerial EO was compared and found matching with the reported NMR signals of $\beta$-myrcene (Rücker et al. 1987; Sahu and Bhowmick 2019).

Enantiomers of $\beta$-pinene, sabinene and limonene in EOs of G. bosvallia were characterized using 6-tert-butyldimethylsilyl-2,3-diethyl-$\beta$-cyclodextrin chiral GC column as reported by Pragadheesh et al. (2015) and found that (1S)-(−)-$\beta$-pinene, (−)-sabinene and (4S)-(−)-limonene were the major enantiomers in both aerial parts and flower EOs (Fig. S6). The enantiomeric excess (ee) values of (1S)-(−)-$\beta$-pinene, (−)-sabinene and (4S)-(−)-limonene is 96.58%, 52.92% and 93.22% in aerial parts EO and 97.69%, 58.15% and 91.56% in flower EO (Table S3). The enantiomeric excess of (1S)-(−)-$\beta$-pinene in EOs of G. bosvallia is also matching with the previous reports on the Asteraceae plants Artemisia pleiocephala, Artemisia annua, Erechtites hieracifolia (Lorenzo et al., 2001; Pragadheesh et al., 2020). Chiral analysis also evidence that (−)-enantiomers are preponderate over (+)-enantiomers in G. bosvallia EOs which is also observed in other Asteraceae plants like A. annua (Holm et al., 1997).

Earlier studies on Asteraceae plants also shows that $\beta$-myrcene as the major compound in its EO; Vernonia polyanthes Less (34.3%) (Moreira et al. 2017), Grindelia integrifolia DC (16.9%) (Nowak et al. 2019), Acritopappus confertus (52.0%) (Lima et al. 2005), whereas G. bosvallia essential oils possess 44.86 to 61.59%. $\beta$-Myrcene is one of the important compounds in both biological studies and chemical synthesis. $\beta$-Myrcene possesses gastric and duodenal ulcers inhibitory activity (Bonamin et al. 2014), antihydatidosis activity (Fabbri et al. 2018) and the structure also aids various applications in synthetic chemistry (Sahu and Bhowmick 2019). The current study describes that the G. bosvallia essential oil can be used as a good source of $\beta$-myrcene. The reported enantiomeric characterization of the chiral terpenoids in G. bosvallia EOs will aid the identification and authentication of the plant species.

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Declaration of conflict of interest

The authors declare no conflict of interest.
References

Bonamin F, Moraes TM, Dos Santos RC, Kushima H, Faria FM, Silva MA, Ivan V, Jr, Nogueira L, Bauab TM, Souza Brito ARM, et al. 2014. The effect of a minor constituent of essential oil from *Citrus aurantium*: The role of β-myrcene in preventing peptic ulcer disease. Chem Biol Interact. 212:11–19.

Fabbri J, Maggiore MA, Pensel PE, Albani CM, Denegri GM, Elissondo MC. 2018. Could beta-myrcene be an alternative to albendazole for the treatment of experimental cystic echinococcosis? Acta Trop. 187:5–12.

Flann C, Greuter W, Nicholas Hind DJ. 2010. Cassini’s *Compositae* genera: A nomenclatural and taxonomic assessment. Taxon. 59(4):1206–1244.

Holm Y, Laakso I, Hiltunen R, Galambosi B. 1997. Variation in the essential oil composition of *Artemisia annua* L. of different origin cultivated in Finland. Flavour Fragr J. 12(4):241–246.

Lima MAS, Barros MCP, Pinheiro SM, Nascimento RF, Matos FJA, Silveira ER. 2005. Volatile compositions of two Asteraceae from the north-east of Brazil: *Ageratum conyzoides* and *Acritopappus confertus* (Eupatorieae). Flavour Fragar J. 20(6):559–561.

Lorenzo D, Saavedra G, Loaya T, DellaCassa E. 2001. Composition of the essential oil of *Erechtites hieracifolia* from Bolivia. Flavour Fragr J. 16(5):353–355.

Moreira RRD, Martins GZ, Varandas R, Cogo J, Perego CH, Roncoli G, Sousa M do C, Nakamura CV, Salgueiro L, Cavaleiro C. 2017. Composition and leishmanicidal activity of the essential oil of *Vernonia polyanthes* Less (Asteraceae). Nat Prod Res. 31(24):2905–2908.

Nowak S, Lisiecki P, Tomaszczak-Nowak A, Grudzinska E, Olszewska MA, Kicel A. 2019. Chemical composition and antimicrobial activity of the essential oils from flowers and leaves of *Grindelia integrifolia* DC. Nat Prod Res. 33(10):1535–1540.

Pragadheesh VS, Yadav A, Chanotiya CS. 2015. Enantiomer differentiation of key volatile constituents from leaves, stems, rhizome and flowers of cultivated *Hedychium coronarium* Koenig from India. J. Essent. Oil Res. 27(2):101–106.

Pragadheesh VS, Bisht D, Chanotiya CS. 2020. Terpenoids from essential oils. Kirk-Othmer Encyclopedia of Chemical Technology. https://doi.org/10.1002/0471238961.koe00056

Rajopadhye AA, Upadhye AS, Taware SP. 2016. Bioactivity of indigenous plant *Glossocardia bosvallia* (L.f.) DC. against insect pests of stored products. Indian J. Tradit. Know. 15(2):260–265.

Reddy U, Reddy K, Acharya BM, Reddy R, Vaidyanath K. 2001. In vitro plantlet regeneration and analysis of oil profiles in *Glossocardia bosvallia* Roxb. Plant Cell Biotechnol Mol Biol. 2(3-4):89–96.

Rücker G, Mayer R, Manns D. 1987. α- and β-Myrcene hydroperoxide from *Artemisia annua*. J Nat Prod. 50(2):287–289.

Sahu P, Bhowmick AK. 2019. Redox emulsion polymerization of terpenes: mapping the effect of the system, structure, and reactivity. Ind Eng Chem Res. 58(46):20946–20960.

Sharma GP, Garg BD. 1980. Chemical examination of the essential oil from *Glossocardia bosvallia* D.C. Journal of Scientific Research. 2(1):37–41.

Sharma GP, Jain NK, Garg BD. 1979. Antimicrobial activity of essential oil from *Glossocardia bosvallia*. Planta Med. 36(2):185–186.

Veldkamp JF, Krefler LA. 1991. Notes on Southeast Asian and Australian Coreopsidinae (Asteraceae). Blumea. 35:459–482.