

Volatile Constituents from the Leaves of *Zanthoxylum armatum* DC., a New Source of 2-Undecanone

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Abstract: The purpose of this study was to evaluate the volatile constituents from the leaves essential oil of *Zanthoxylum armatum*. The essential oil from fresh leaves of *Zanthoxylum armatum* obtained by hydro-distillation was analysed by GC/FID and GC/MS. Twenty three components were identified, representing 99.5% of the oil. The major classes of compounds found in the leaves essential oil were non-terpenic acyclic ketones which represented the main fraction with 2-undecanone (65.6%) as the major constituent, making this plant a new and good source of this substance. The present study suggested that the leaves essential oil of *Z. armatum* collected from Joshimath of the Garhwal region of Uttarakhand Himalaya, India is an outstanding new source of 2-undecanone, a compound highly appreciated in perfumery and flavoring industry as well as due to its strong odor, it is primarily used as insects repellent. Therefore, researchers concluded that leaves essential oil of *Z. armatum* can be used as a commercial source for the isolation of 2-undecanone and can be commercially exploited as valuable perfumery and flavoring ingredient.

Key words: *Zanthoxylum armatum*, Rutaceace, volatile constituents, 2-undecanone, GC/MS

INTRODUCTION

Plants provide a multitude of flavours and fragrances which have found their way into everyday life. According to different researchers, approximately 3000 plants species contain essential oil from which only 300 are commercially important. Essential oils and some of their constituents are used not only in pharmaceutical products for their therapeutic activities but also in agriculture as food preservatives and additives for human or animal use in cosmetic and perfumes and other industrial field. In many cases, they serve as plant defence mechanisms against predation by microorganisms, insects and herbivores (Bakkali *et al.*, 2008).

Zanthoxylum armatum (DC.) of the Rutaceace family is an important aromatic and medicinal evergreen shrub or small tree widely distributed in the hot valleys of the subtropical Himalayas from Jammu to Bhutan at altitudes of 1000-2100 m. The local names of this plant are Tejphal (Hindi), Mukthruhi (Manipur) and Timur (Nepal). In India, 13 species of this genus are recorded in which six species of *Zanthoxylum* occur in Himalayan region (The Wealth of India, 1976; Chopra *et al.*, 1986). The different parts of the *Z. armatum* such as branches, twig,

bark, fruits, seeds and roots are used in fever, dyspepsia, cholera, diabetes, asthma and for piscicidal activity. The twigs are used as tooth brush during gum problems and toothache (Baral and Kurmi, 2006; Abbasi *et al.*, 2010).

The composition of the essential oils of *Z. armatum* whole plant and plant parts have been thoroughly investigated worldwide (Bisht and Chanotiya, 2011; Tiwary *et al.*, 2007; Gupta *et al.*, 2011; Waheed *et al.*, 2011; Mehta *et al.*, 2012). However, the other different types of activities, like antibacterial and antifungal (Chopra *et al.*, 1986), larvicidal (Tiwary *et al.*, 2007), anthelmintic activities (Mehta *et al.*, 2012) and hepatoprotective activity (Ranawat *et al.*, 2010) have been reported. The compound linalool, limonene, methyl cinnamate, β -phellandrene, 1,8 cineole, 2-undecanone (Bisht and Chanotiya, 2011; Tiwary *et al.*, 2007; Gupta *et al.*, 2011), dihydro carveol, 3-borneol, isobornyl acetate, β -elemene and hexadecanoic acid (Waheed *et al.*, 2011) were reported as the major components from the different parts of the essential oils of *Z. armatum*.

In Uttarakhand, *Z. armatum* has been the subject of research in recent years on its phytochemistry, traditional uses and conservational aspects. Up to now, there is only one report (Bisht and Chanotiya, 2011) regarding the

chemical composition of *Z. armatum* leaves oil is available from the Kumaun region of the Uttarakhand but no other report has been published about the leaves of this plant from the Garhwal region of Uttarakhand. Therefore, the aim of the present study is to evaluate the qualitative and quantitative variations in volatile constituents of leaves oil of *Z. armatum* collected from the high altitude of Garhwal region of Uttarakhand Himalaya, India.

MATERIALS AND METHODS

Plant material: The fresh leaves of *Z. armatum* were collected from the Joshimath (altitude 2135 m) of the Garhwal region of Uttarakhand Himalayas (India) in the month of August 2011. Voucher specimen have been duly identified and deposited in the herbarium of Botanical Survey of India (BSI) Northern circle, Dehradun with voucher specimen No. 114147.

Isolation and analysis of essential oil: The essential oils of air-dried leaves were obtained by hydro-distillation using a conventional cleverger-type apparatus for 4 h. The oil was dried over anhydrous sodium sulphate and stored in sealed vial under refrigeration prior to analysis.

Analysis of the oil was carried out by GC/FID and GC/MS using HP-5 capillary column (30 m × 0.32 mm, 0.25 µm film thickness). GC/FID analysis was performed on an Agilent Technology 6890 N instrument, equipped with Chem Station Data Processor Software using the following analytical conditions: carrier gas, nitrogen; flow rate, 1 mL min⁻¹; oven temperature programmed from 60-220°C at 3°C min⁻¹, 220°C (5 min); injector temperature, 210°C; detector temperature 250°C; split ratio 1:50. The essential oil was injected undiluted (0.1 µL). Mass spectra were obtained with a computerized system constituted by a GC Perkin Elmer Clarus 500 coupled to a mass selective detector using the same analytical conditions as above. Mass spectra were taken over m/z 40-500 amu that revealed the Total Ion Current (TIC) using an ionizing voltage of 70 eV.

Identification of constituents was achieved by means of their GC retention indices with GC alkanes standard solution (C₈-C₂₀ Sigma-Aldrich) and by comparison of fragmentation patterns in the mass spectra with those stored in the own library in the GC/MS database and with literature data (Adams, 2009). Quantification of each compound was performed on the basis of their GC peak area using the normalization procedure without corrections for response factor.

RESULTS AND DISCUSSION

The fresh leaves of *Z. armatum* obtained by hydro-distillation yielded 0.4% (v/w) of essential oil.

Table 1: Composition of the essential oil from leaves of *Zanthoxylum armatum*

Components	RI	In oil (%)	Identification method
α-thujene	931	0.1	RI, MS
α-pinene	939	0.3	RI, MS
Sabinene	976	1.2	RI, MS, CoI
β-myrcene	991	0.3	RI, MS
β-phellandrene	1027	0.3	RI, MS
Limonene	1030	3.7	RI, MS, CoI
Trans-sabinene hydrate	1097	0.3	RI, MS
Cis-citral	1253	0.5	RI, MS
Trans-citral	1267	0.3	RI, MS
2-undecanone	1296	65.6	RI, MS, CoI
α-copaene	1377	0.1	RI, MS
β-bourbonene	1417	0.5	RI, MS
Trans-caryophyllene	1420	1.1	RI, MS, CoI
Aromadendrene	1439	0.3	RI, MS
Citronellyl propionate	1444	0.4	RI, MS
α-humulene	1450	0.2	RI, MS
Cis-β-farnesene	1454	0.2	RI, MS
Germacrene D	1481	0.1	RI, MS
α-amorphene	1483	0.1	RI, MS
2-tridecanone	1495	16.6	RI, MS, CoI
Caryophyllene oxide	1581	0.8	RI, MS
Cis-α-santalol	1674	0.2	RI, MS
Cis-farnisol	1698	6.3	RI, MS
Monoterpene hydrocarbons	-	5.9	-
Oxygenated monoterpenoids	-	1.5	-
Sesquiterpene hydrocarbons	-	2.6	-
Oxygenated sesquiterpenoids	-	7.3	-
Non-terpenoids	-	82.2	-
Total identified	-	99.5	-

RI: Retention Indices relative to C₆-C₂₄ n-alkanes on the HP-5 column; MS: Mass Spectrum; CoI: Co-Injection with an authentic standard; components in larger percentage are highlighted in boldface

Qualitative and quantitative analysis of the oil by GC and GC/MS allowed the identification of twenty three components, representing 99.5% of the total oil (Table 1).

The oil was very rich in non-terpenic acyclic ketones (82.2%), especially 2-undecanone (65.6%) and 2-tridecanone (16.6%). Among monoterpenes, limonene (3.7%) was found in the highest percentage. The chemical composition of leaves oil was comparable to that reported (Bisht and Chanotiya, 2011) in terms of its 2-undecanone and 2-tridecanone content. The major constituents in present and that of Bisht's oils were 2-undecanone 65.6 and 48.4-51.8% and 2-tridecanone 16.6 and 5-13.5%, respectively. However, trans-citral (0.3%), β-bourbonene (0.5%), aromadendrene (0.3%), citronellyl propionate (0.4%), β-farnesene (0.2%), cis-α-santalol (0.2%) and β-farnisol (6.3%) occurred in considerable quantities in current study but were absent in Bisht and Chanotiya (2011) oil. The compound β-farnisol was identified for the first time as appreciable amount in leaves essential oil while the menthane monoterpenoids were present in Bisht and Chanotiya (2011) oil but are absent in leaves oil studied.

Thus, the present study showed the qualitative and quantitative differences in the composition of leaves essential oil from the earlier report (Bisht and Chanotiya, 2011) collected from the Kumaun region of Uttarakhand,

India. These variations with other study might occur due to difference in habitat conditions, geographical locations, altitudes or season of sample collection.

CONCLUSION

The leaves essential oil of *Z. armatum* collected from Joshimath of the Garhwal region of Uttarakhand Himalaya is an outstanding new source of 2-undecanone, a compound highly appreciated in perfumery and flavoring industry. In addition, it shows interesting repellent activity against insects which make this essential oil a new and good resource of new product. Therefore, on the basis of above fact, it is concluded that leaves essential oil of *Z. armatum* can be used as a commercial source for the isolation of 2-undecanone and can be commercially exploited as valuable perfumery and flavoring ingredient.

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