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Review article

Phytochemicals from Indian Sandalwood (*Santalum album* L.) and their adulterants: An Overview

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Abstract: Phytochemical investigations of fruit, seed, bark, leaf, stem and root of Indian Sandalwood using various methods, revealed the presence of different groups of phytochemicals like fatty acids (saturated and unsaturated), amino acids (essential and non-essential), sesquiterpene alcohols (*α*- and *β*- santalol etc.), terpenes (squalene), sesquiterpenes hydrocarbons, flavonoids, tannins, esters, aldehydes, vitamin, and minerals. The availability and production of sandalwood have been declined significantly due to overharvesting and poaching of natural resources. The low production and high demand lead to the sky rocketed price of the Sandalwood and its oil. Due to high value, the illegal trade as well as adulteration of Indian Sandalwood and its oil with other similar species and materials, is the major concern of trades and consumers safety. This review paper covers comprehensive information about different classes of phytochemicals found in various parts of Indian Sandalwood and potential adulterants or substitutes of the sandalwood and its oil. To the best of our knowledge this is the first report on the phytochemicals found in different plant parts of the Indian sandalwood being documented.

Keywords: Z-α-santalol - Z-β-santalol - Fatty acid - Ximenynic acid - Adulteration.

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INTRODUCTION

Generally, plants are rich in phytochemicals which they produce for their defence, also known as secondary metabolites. *Santalum album* L. commonly known as Indian Sandalwood, it is one of the precious sources of natural fragrance with high medicinal and commercial values. *Santalum album* has been grown in India for the last more than 25 centuries and esteemed all over the world for its sweet, long-lasting and medicinally valued fragrant oil.

The yellow to brown coloured heartwood is moderately heavy, durable with oily texture (Verghese *et al*. 1990, Arunkumar *et al*. 2012). It is being used worldwide mainly for the high valued fine fragrance, cosmetics and aromatherapy. Sandalwood and oil are extensively revered by three main religions of the world - Hinduism, Buddhism and Islam (Arunkumar *et al*. 2012). The quality and pleasant characteristic scent of the sandalwood and its oil are due to the presence of sesquiterpene alcohols *i.e*., Z-α-santalol and Z-β-santalol along with other minor phytochemical constituents (Verghese *et al*. 1990, Kumar *et al*. 2015, Bisht *et al*., 2020).

Phytochemical analysis of different parts of Indian Sandalwood *i.e*., fruit, seed, bark, leaf, heartwood and root revealed the presence of fatty acids -saturated and unsaturated (Liu *et al*. 1996), amino acids -essential and non-essential, minerals (Shankaranarayana & Parthasarathi 1985), sesquiterpene alcohols, sesquiterpene and other terpenoides (Verghese *et al*. 1990, Zhang *et al*. 2012), flavonoids (Yan *et al*. 2011, 2013), tannins (Shankaranarayana *et al*. 1980a, b), esters, aldehydes, squalene and vitamin E (Zhang *et al*. 2012). It has some specific phytoconstituents such as ximenynic acid (fatty acid), α-santalol and β-santalol (sesquiterpene alcohols). Some other major constituents of *S. album* are depicted in figure 1–3.

FRUIT AND SEED

The seeds of trees from *Santalum* genus mainly contain polyunsaturated fatty oil (seed oil), which is Comprised of acetylenic glycerides-santalbic or ximenynic acid (1) and stearolic acid (2) (Fig. 1). Ximenynic

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acid present in seeds of all members of Santalaceae and it is considered as a characteristic feature of this family (Hatt & Schoemfeld 1956, Liu *et al*. 1996). Seeds of Indian Sandalwood (*Santalum album*) have been found to contain highest amount *i.e.*, 79.0–82.8 % of ximenynic acid (Hopkins & Chisholm 1969, Butaud *et al*. 2008). The oleic (3) and palmitic acid (4) content in *Santalum album* seeds are lesser *i.e*., 12.3–18.0 % and 0.8%, respectively in comparison to ximenynic acid (Fig. 1). While the seeds of other species of *Santalum* genus such as *Santalum acuminatum* A.DC., *Santalum spicatum* (R.Br.) A.DC. and *Santalum murrayanum* C.A.Gardner are richer in oleic acid content in the range of 43.8–58.7% (Hopkins & Chisholm 1969, Rivett *et al*. 1985, Liu *et al*. 1997, Butaud *et al*. 2008).

Pericarps of *Santalum album* also contain ~5% oil, which is composed of fatty acids ~79.5% of the total oil extracted by solvent method. Palmitic acid ~38.8 and oleic acids ~40.3% are the major contributors to the fatty acids present in pericarps. Other constituents of the pericarps oil are- ~5.0% five esters, ~1.2% seven aldehydes, ~1.7% squalene and ~2.5% vitamin E. Apart from the above constituents, minor constituents such as phytosterols, *i.e.* (3β)-cholest-5-en-3-ol (1.3%), fucosterol (1.0%), stigmasterol (0.7%), and (3β)-9,19-cyclolanost-24-en-3-ol (0.6%); sesquiterpenoids, santalol and cedrol are also detected in the *Santalum album* pericarp oil (Zhang *et al*. 2012). *Santalum album* pericarps yields ~2.6% essential oil (EO) obtained by hydro-distillation method. Its EO is a complex mixture of 31 identified constituents, representing about 99.5% of the total oil (Zhang *et al*. 2012) (Table 1). Palmitic acid dominated with 70.4% contribution and many other fragrant components *i.e*., five esters (~13.0) and eight aldehydes (3.8%) are also present in the pericarps EO. Apart from above constituents trace amount (total 0.1–2 %) of four alkanes, three ketones, two heterocyclic compounds, sesquiterpenoids, and alcohols are also present in pericarps (Zhang *et al*. 2012). Presence of betulinic acid (6) in sandal seed coat is also reported by Shankaranarayana & Parthasarathi (1985).

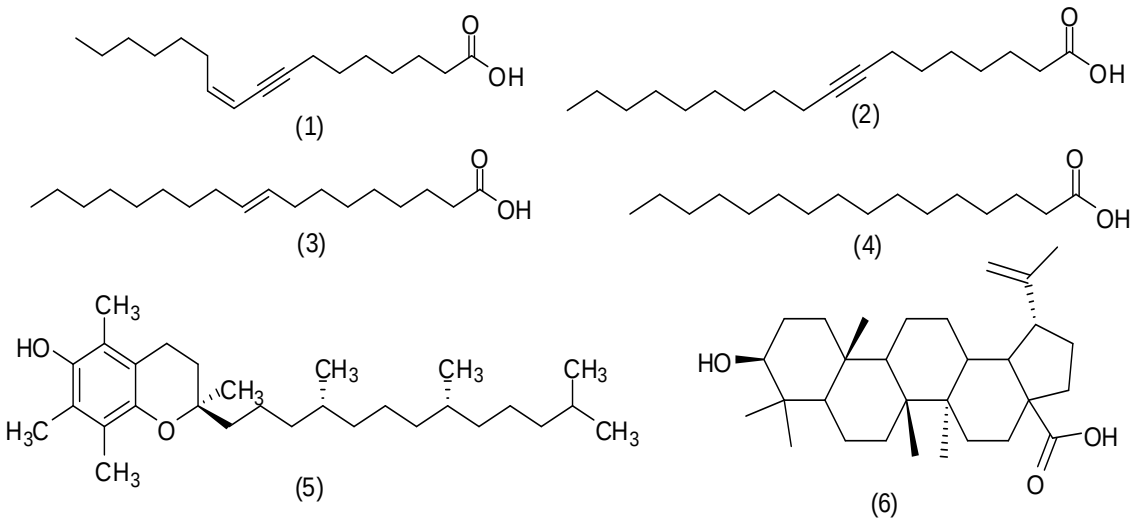

Figure 1. Main compounds present in fruit and seed of Indian Sandalwood (*Santalum album* L.).

Deoiled seed meal prepared from the decoated seeds of sandal contains 52.5% of protein and about 5% mineral constituents (K, Zn, Ca, Mg, Cu, Fe, etc.). The proteins in the deoiled meal were rich particularly in (i) phenylalanine and leucine, essential amino acids and (ii) glycine and glutamic acid, among the non-essential amino acids (Shankaranarayana & Parthasarathi 1985). Further, it was found that nonviable sandal seeds contain slightly larger amounts of fatty oil but less amounts of protein compared to viable seeds (Ananthapadmanabha *et al*. 1989).

BARK AND LEAVES

Sandalwood bark contains major tannins (14%), fatty acids and small amounts of betasitosterol, a triterpene ester (Shankaranarayana *et al*. 1980a, b). A triterpene ester *i.e.*, urs-12-en-3-beta-yl-palmitate (~0.3%) has chemosterilant and an insect growth inhibitory activity (Shankaranarayana *et al*. 1979). Different flavonoids as shown in figure 2 *i.e.*, vitexin (7), isovitexin (8), orientin (9), isoorientin (10), chrysin-8-C-β-D-glucopyranoside, chrysin-6-C-β-D-glucopyranoside and isorhamnetin were isolated and characterized from leaves of *Santalum album* (Yan *et al*. 2011, 2013).

STEM AND ROOT

The heartwood of *Santalum album* is the major source of the costly wood and oil. Oil is mainly accumulated in its heartwood (stem) and root. Matured tree yields upto 6% oil, which depends on the age of the tree,

individual tree, location of the tree and the growth environment of the tree (Shankarnarayana & Parthasarathi 1987, Shankarnarayana & Kamala 1989). Moreover, the compositions of oil obtained from young and mature sandal trees varies while the content and composition of oil varies from heartwood sampled at different levels in the tree (Shankarnarayana & Parthasarathi 1987). The essential oil content in sapwood relatively lowers than that heartwood of Sandalwood (Shankaranarayana *et al*. 1997, Liu *et al*. 2016).

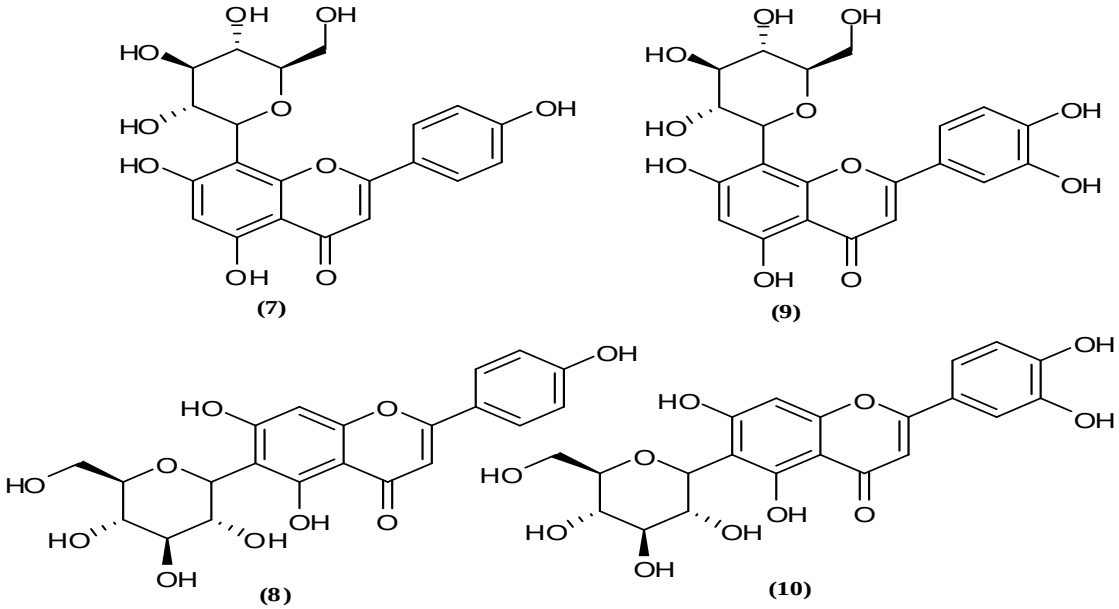

Figure 2. Different flavonoids isolated from leaves of Indian Sandalwood (*Santalum album* L.).

Table 1. List of compounds or class of compounds present in Indian Sandalwood (*Santalum album* L.).

S.N.	Plant part	Class/Name of Major Compound	References
1	Seed	Ximenynic acid, stearolic acid, oleic acid, palmitic acid	Hatt & Schoemfeld (1956), Hopkins & Chisholm (1969), Rivett *et al*. (1985), Liu *et al*. (1996), Liu *et al*. (1997), Butaud *et al*. (2008)
2	Fruit pericarp	Oleic acid, palmitic acid, esters, aldehydes, squalene, vitamin E, 3(β)-cholest-5-en-3-ol, fucosterol, stigmasterol, (3β)-9,19-cyclolanost-24-en-3-ol; sesquiterpenoids, santalol, cedrol, alkanes, ketones, heterocyclic compounds, sesquiterpenoid, alcohol, betulinic acid, mineral constituents (K, Zn, Ca, Mg, Cu, Fe, etc.), phenylalanine, leucine, essential amino acids, glycine, glutamic acid, protein	Zhang *et al*. (2012), Shankaranarayana & Parthasarathi 1985, Ananthapadmanabha *et al*. (1989)
3	Bark	Tannins, fatty acids, triterpene ester (beta-sitosterol and urs-12-en-3-beta-yl-palmitate)	Shankaranarayana *et al*. (1980a, b), Shankaranarayana *et al*. (1979)
4	Leaves	Flavonoids like vitexin, isovitexin, orientin, isoorientin, chrysin-8-C-β-D-glucopyranoside, chrysin-6-C-β-D-glucopyranoside and isorhamnetin	Yan *et al*. (2011, 2013)
5	Stem	*α*-Santalol, β-santalol, α-bergamotenol, epi-cis-β-santalol, cis-lanceol, β-bisabolol, hydrocarbons like α-santalene, β-santalene, epi-β-santalene, α-bergamotene, β-bisabolene, α-curcumene, alcohol, santenol, teresantalol, aldehydes, nor-tricycloekasantalal, isovaleraldehyde, ketones, l-santenone, santalone, teresantalic acid.	Verghese *et al*. (1990), Jones *et al*. (2006)
6	Root heartwood	Sesquiterpenols, sesquiterpenes, a terpenoic acid, 5 sesquiterpenoid isomers.	Zhang *et al*. (2012)

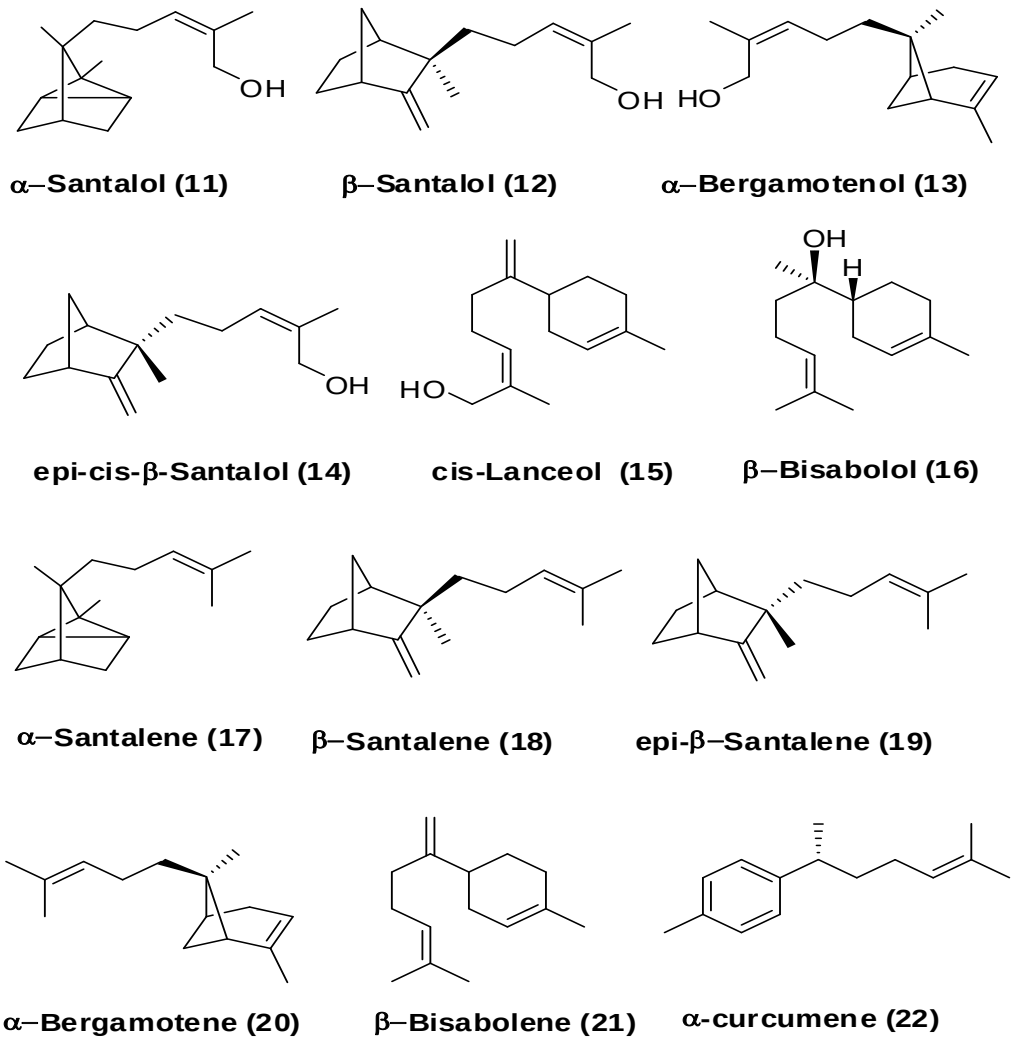

Figure 3. The main volatile metabolites reported from heartwood oil of Indian Sandalwood (*Santalum album* L.).

Sandalwood oil has a long-lasting, pleasant, smooth, and woody scent. It is being used worldwide mainly for the essential oil, cosmetics and aromatherapy industries (Bisht *et al*. 2021). The value of Sandalwood oil mainly depends on its quality. Oil quality can be assessed by oil composition and content of constituents such as sesquiterpene and sesquiterpene alcohols. The sesquiterpene and sesquiterpene alcohols of Indian Sandalwood (*Santalum album*) oil are *α*-santalol (11), β-santalol (12), α-bergamotenol (13), epi-cis-β-santalol (14), cis-lanceol (15) and β-bisabolol (16) (Fig.3). The hydrocarbons α-santalene (17), β-santalene (18), epi-β-santalene (19), α-bergamotene (20), β-bisabolene (21) and α-curcumene (22) were also reported in Sandalwood oil (Fig. 3) (Verghese *et al*. 1990, Jones *et al*. 2006). The other minor constituents reported in the sandalwood oil includes alcohol, santenol and teresantalol; the aldehydes, nor-tricycloekasantalal and isovaleraldehyde; the ketones, l-santenone and santalone and the acids, teresantalic acid occurring partly free and partly in esterified form and α- and β-santalic acids.

Heartwood from the roots of East Indian Sandalwood tree contains a relatively higher amount of oil in compared to the stem. The average recovery of oil from roots is up to ~6–7% extracted by hydro- or steam distillation methods. While the highest recovery of oil recorded is ~10% through the solvent extraction method. Oil extracted from the roots of the tree contains around fifty-three volatile compounds which include 30 sesquiterpenols (78.5%), 9 sesquiterpenes (7.8%), a terpenoic acid (0.4%) and 5 sesquiterpenoid isomers (4.4%) (Zhang *et al*. 2012).

ADULTERATION AND SUBSTITUTION

The availability and production of sandalwood has been declined significantly due to overharvesting and poaching of natural resources (Ananthapadmanabha 2012) and it's also documented as a vulnerable species on the World Conservation Union's Threatened Species Red List (IUCN 2020). Due to high profitable value, the illegal trade as well as adulteration of Indian Sandalwood with other morphologically similar species is a major concern. The common substitutes found in commercial market are the *Santalum spicatum* (Australian

Sandalwood), *Osyris wightiana* Wall. ex Wight ('Nepal Sandalwood', Santalaceae) and *Erythroxylum monogynum* Roxb. ('Indian Bastard Sandal', Erythroxylaceae) (Anupama *et al*. 2012). It is difficult to distinguish among them because the morphological characters are almost similar with 'Indian Sandalwood' (Oyen & Dung 1999, Shyaula 2012). About 25 species, including species in other families *e.g. Amyris balsamifera* L., Rutaceae are traded as 'Sandalwood' (Anonis 1998).

Adulteration or substitution of Sandalwood oil affects its quality which could lead to inconsistency in fragrance, medicinal and aromatherapy properties as well as commercial value (Shankarnarayana & Kamala 1989, Misra & Dey 2013). Adulteration comes in many ways in Sandalwood oil, such as dilution of genuine oil with a cheap carrier oil or solvent, adding synthetic aroma chemicals, or reconstructing oil with natural or synthetic chemicals (Howes *et al*. 2004). Moreover, oil also substituted with the oil from other species for example *Santalum spicatum* which contains 38.7–46.1% total santalol (Naipawer 1988), or the oil can be adulterated with synthetic or semi-synthetic substitutes such as Sandalore (Anonis 1998, Kraft *et al*. 2000). Reported non-synthetic adulterants are castor oil, cedarwood oil and oils from 'Sandalwood' species other than *Santalum album* (Anonis 1998). A variety of synthetic substitutes for sandalwood oil are commercially available, amongst these a number of campholenyl derivatives such as Brahmanol (23), Madrol (24), Sandranol (25), Ebanol (26), Sandalore (27), Firsantol (28), Polysantol (29) and Javanol (30) (Bajgrowicz 1998) (Fig. 4).

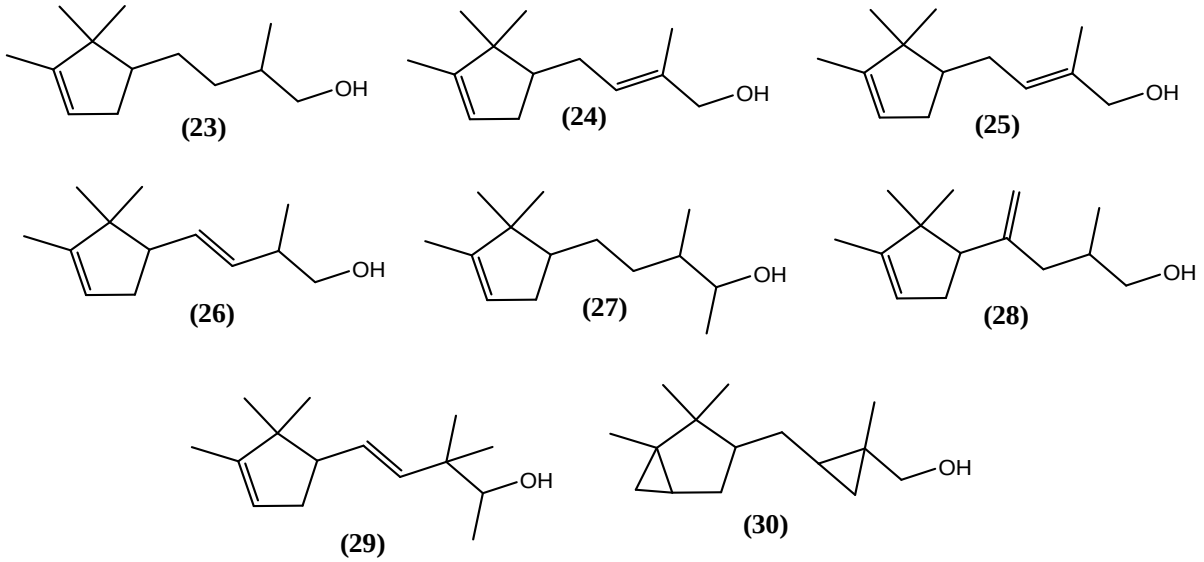

Figure 4. Commercially available sandalwood odorants derived from α-campholenic aldehyde.

Some adulterations are easy to detect; on the other hand, adulteration performed by an expert with the right materials can be very difficult to detect. Adulteration of genuine oil with (semi) synthetic additives influences the physical and chemical properties of the oil. The health issues like allergenic potential, carcinogenicity, damage nervous system and reproductive organs etc. also associated with the use of such additives (Desvergne *et. al.* 2009, McPartland *et. al.* 2014). It is recommended that the essential oil from *Santalum album* should not contain less than 90% w/w of (free) alcohols, calculated as santalols (acetylation method, ISO 3518:1979).

Bisht *et al*. (2020) studies thirty-eight sandalwood (SW) EO samples, including ten samples from the heartwood of *Santalum album* and twenty-eight trade samples of SW EOs, for refractive index (RI), relative density (RD) and α- and β-santalol content. It was observed by GCMS the high content of adulterants such as diethyl phthalate (DEP) and diethylhexyl phthalate (DEHP) present in some of the SW EOs. This study concluded that the quality control and authentication for high valued sandalwood EO should mainly rely on its physical properties (such as RI and RD etc.), as well as chemical analysis (level of α- and β-santalol content) as per Indian Standard (IS 329: 2004) or International Standard (ISO 3518:2002). The ISO has included GC analysis of *Santalum album* oil (ISO 3518:2002) along with other physicochemical parameters for authentic testing of the Indian Sandalwood oil. Thus, it was suggested that Sandalwood oil should be evaluated using gas chromatography (GC) by quantization of the santalol content, with a proposed range of 40–55% for Z-α-santalol and 17–24% for Z-β-santalol (Verghese *et. al*. 1990).

CONCLUSION

Fruit, seed, bark, leaf, stem and root of Indian Sandalwood have different groups of phytochemicals like fatty acids (saturated and unsaturated), amino acids (essential and non-essential), sesquiterpene alcohols *(α*- and

β- santalol etc.), terpenes (squalene), sesquiterpenes hydrocarbons, flavonoids, tannins, esters, aldehydes, vitamin, and minerals which has various therapeutic activities. To overcome the menace of adulterations the quality control measure is highly recommended. Unlike conventional methods, detection and quantification of adulterants in sandalwood oil can be easily conducted by employing the techniques such as GC and GCMS along with other physicochemical methods. One or a combination of these methods can be utilized as a quality control procedure to authenticate oil and ensure a high-quality ingredient. Further, it is suggested that quality control and authentication for high valued Sandalwood oil should be strictly regulated by regulatory bodies or certifying organizations.

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