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Sweet orange (Citrus sinensis) as a source of alkaloids: A review

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ABSTRACT: In this review their alkaloids in sweet orange are discussed since ialkaloids are a large iclass of chemical compoundsi that are iderived from secondary metabolism and have the most significant attribute of any chemical compound in the world: the presencei of basicinitrogen atoms atiany point on the moleculei. Citrus sinensisi(orange) is commonly grownifor its fruit, which is both nutritious andimedicinal. Plants are responsible for producing numerous metabolites that have different physiological properties. The most researchedimetabolites areiphytochemicals, which are primarily secondaryimetabolites generated from plants and are characterized by a variety of structures, quantities, locations and activities, even in the same species. The consumption of citrus fruit has been demonstrated to be beneficial to human health due to the antioxidanti, ianti-inflammatory,icancer-fighting, protective cardiovascular and neurological properties of secondary metabolites in citrus fruit. Citrus fruits can be considered as a source of alkaloids and the most important biologically active constituents of the C.sinensis fruits are phenethylamine alkaloids (i.e. ioctopamine, isynephrine, ityramine, iN-methyltyramine and ihordenine). This review focuses on the alkaloids present in the sweet orange, their chemical structure, biosynthesis, pharmacological activities, and extraction methods.

Keywords: Sweet orange alkaloids, synphrine in sweet orange, phenethylamine alkaloids in orange, alkaloids extraction from orange

1. INTRODUCTION

Plants are responsible for producing numerous metabolites that have different physiological properties. The most researched metabolites are phytochemicalsi, which are primarily isecondary metabolites generated from plants and are characterized by a variety of structures, quantities, locations, and activities. Even between species of theisame plant. Theseimetabolites are typicallyiclassified into three large classes:iPhenolic compounds,iterpenes, and compounds containinginitrogen or sulphur [1]. Alkaloids, which produced from secondary metabolic process, are a wide group of chemicals, their primary criteria is the existence of basic nitrogen atoms in any site other than nitrogen iniamide bonds or peptides. They are typically purified from other plants, but have also been documented in insect, animal,imarine iinvertebrates, and some microorganisms [2]. There are three classes of alkaloids: True Alkaloids (heterocyclics) which are composed of multiple components that are chemicallyicomplex,iphysiologically active compounds and derived from cycliciamino acids. They contain nitrogen within their rings and are native to nature that forms salts with organic acids like .oxalic. acid, ilactic. acid., .maliceacide, tartaric acid, acetic acid and citriceacid. The alkaloids in this group are generated from the amino acids iL-ornithine, iL-tyrosine, iL-phenylalanine, iL-lysine, L-histidinee, L-tryptophane, L-argininei and glycine/aspartic acid. Heterocyclic alkaloids are categorized into ipyrrole, ipyrrolidine, pyrrolizidinei, pyridine, piperidine, tropane, quinolone, iisoquinoline, iaporphine, iquinolizidine, iindole, and iimidazole [3]. The second type are iprotoalkaloids (non-iheterocyclics), chemically, a proto-alkaloid has a nitrogen atom as part of a side chain, but not as portion of a cyclical system. It's able to be derived from either amino acids or ibiogenic amines. Some proto-alkaloids are considered to be imescaline, iephedrine, icolchicine, cathinones, and so on; however, they aren't common in the natural world. Proto-alkaloids can be derived from iL-tyrosine and iL-tryptophan, these molecules are then converted into iphenylethylamines and iterpenoid iindoles, respectively. iMescaline is one of the most prevalent phenylethylamine alkaloids, and can be derived from iLophophora williamsii, the common name of cactus. Conversely, monoterpene iindole ialkaloids iare a ilarge group that includes approximately 3,000 species in families like Apocynaceae, Loganiaceae, and Rubiaceae [4]. The third class of alkaloids are pseudoalkaloids, they are nitrogenous compounds that are not derived from iamino acids. They're typically derived from iacetate, ipyruvic acid, iadenine,

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iguanine or igeraniol. For example, diterpene alkaloids (with 18, 19 and 20 carbon atoms) are cited from different sources like Aconitum, Consolida and Delphinium [5].

2. FAMILY OF SWEET ORANGE

The genus iCitrus (Citrus L.) is part of the ifamily iRutaceae and includes a variety shape like trees, herbs and shrubs that are found around the world [6,7]. Citrus is the most commonly grown and traded plant in the garden category worldwide, it is also ione of the most important crops used for ifruit on all continents of the world [8-10]. Different ispecies of citrus include iC.limoni(lemon), iC.medica (citron), iC.aurantiumi(isour iorange), iC.paradise (grapefruit), iiC.reticulata (imandarin,itangerine), iC. clementina (clementine), and iC.sinensis (isweet orange). Among them, iC.sinensis (orange) is the most commonly cultivated species, its fruit is both nutritious and medicinal [11]. iC.sinensis origin is likely in Southeast Asia, and it's been cultivated in China [12]. It's one of the largely utilized components initraditionaliChinese medicine, with extracts generated from the peel, young ifruit, matureifruit, flowers, and other parts being commonly used. All of these components are converted into food in cChina and are typically used in Chinese recipes because of the existence of significant chemical compounds, such ascflavonoids, ivitamins and phenolic Acids. This demonstrates tthat medicine iand food are derived from the same source [13], (Table 2).

Table 1. - Scientific classification of Citrus sinensis [11]

Kingdom:	plantae
Clade:	tracheophytes
Clade:	angiosperms
Clade:	Eudicots
Clade:	Rosids
Order:	Sapindales
Family:	Rotaceae
Genus:	Citrus
Species:	C. x sinensis

3. BOTANICAL DESCRPIPTION OF SWEET ORANGE

Cystinosis is native to tropical, sub- tropical and moderate regions, and are the most popular citrus trees in the world. The tree's original origin is Asia, and it is now common all over the Pacific region and temperate regions of the world. It's a perennial that typically reaches heights of 7.5 meters, but it can sometimes reach heights of 15 meters. It's made up of a compact crown that is mostly branched, as illustrated in Figure (1). The leaves are soft, dark green, and have a thickness of 3-5 mm and a length of 6.5-15 cm, they are alternated and toothed in various configurations, these configurations are associated with the stem by means of a winged petiole. Because of the leaves rich copious oil content, they emit a strong, distinguishing citrus scent. The flowers are small, greasy white and aromatic. They're axillary and have 6 whorls (5 cm across) with 5 white petals andi20-25 yellow stamens. The fruits have different shapes and sizes (going from spherical to oblong). They're primarily greenish, and when they reach their fullisize, they demonstrate ibrightiyellow to orange instead of green. The fruit is spherical, and has a diameter of 4-12 cm, it is composed of a 6 mm thick leathery shell that is densely adhesive, and it protects the juicy interior of the fruit, which is divided into sections that may or may not have seeds. The variety of the fruit is dependent on the section of the fruit that is consumed. The orange is flavourful, aromatic and juicy [14-16].

FIGURE 1. - Citrus sinensis [14]

The outsideccolouredssurface of thesorange peel is known as the flavedo, swhile the inside whitesspongy layer is known as ialbedo. iFlavedo's essential oil (EO) that is mostly constituted of limonene, whilst albedo's structure is a foamy and high in pectin. The fruit is wrapped by aiskin-like tissue called the endocarp, which is made up of ipulp andijuice, and has thin membranes that divide each part from the other. The peel is full of structuralipolysaccharides and related molecules, includingicellulose (18-20%iw/w, on aidry solid basis) andehemicellulose (14-16% w/w, on a dry solid basis); it contains a lot of free sugars, such as gglucose,gfructose, and sucrose (about 30-36% of the dry solid), as well as other components, like EO (0.3-0.5% of the dry solid) and proteins (up to 8% of the dry solid); it is mostly made up of pectin (max. 42-43% in dry solid) [17].

4. CHEMICAL COMPOSITION OF SWEET ORANGE

Depending on the variety, year of harvest, the storage conditions after harvest, growth region, fruit portion, climate and fruit maturity, C.sinensis's chemical makeup could change. Nonetheless, this fruit has a variety of vital phytoconstituents that are found in the leaves, seeds, blossoms, juice and peel. Many scientists have dedicated their research to describe several types of compounds, including essential oils, Flavonoids, including (polymethoxylated flavones, flavanone glycosides, flavanones), alkanes, alkylamine, carbohydrates, fatty acids, peptides, coumarins, steroids, carotenoids, hydroxy amides, carbamates and vitamins (Table 2, Figure 2) [17-25]. The majority of the bioactive components in citrus fruits are Phenylethylamine alkaloids (e.g., synephrine, octopamine, hordenine, tyramine, and N-methyltyramine). Unripe fruits have multiple different amines that differiin the number and location of theirihydroxyl substituents [26]. Synephrine and octopamine are the primary alkaloids [27-31], Figure (3).

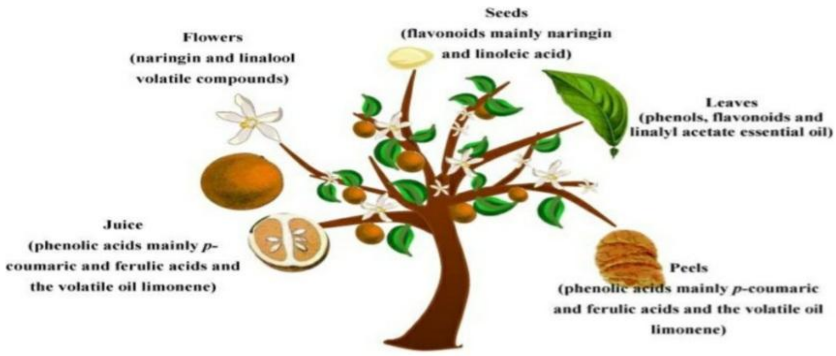

FIGURE 2. - The most abundant active constituent in different parts of C. sinensis [18]

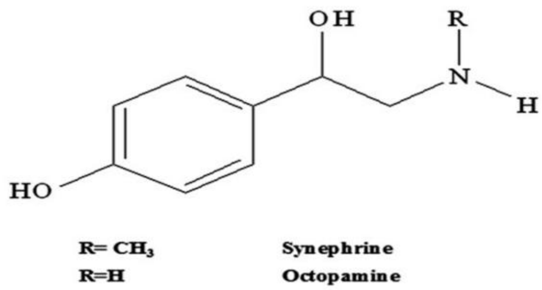

FIGURE 3. - Chemical structure of synephrine and octopamine

Table 2. - Phytochemistry of Citrus sinensis

N0	Class	Compounds	part	Refrences
1	Volatile compounds	Limonene,i α-pinene,Ɣ-Terpinene, α- Terpinene, α-Terpineol, Neral, β-Pinene, Myrcene, Linalool,i (-)-Carvone, Geranyl acetate, Valencene, □-Cadinene,, Vanillin,Guaiacol, Homofuraneol, Sabinene, Cis- β-Ocimene, Geranyl pyrophosphate, (-)−4S-Limonene, Linalyl acetate, (3R)-(-)-Linalool, (3S)-(+)-Linalool, □−3-Carene, and(E)- β-Ocimene	Leaves, flower, peels	16, 17, 18,19
2	Flavonoids	Hesperedin, hesperetin, naringin, naringenin, sakuratin, 3,5,4′-Trihydroxy-7, 3′ -dimethoxy-flavanone-glc, Narirutin i4′-glucoside, Narirutin, Isosakuranetin, Tangeretin, Nobiletin, Chrysoeriol, Limocitrin, Limocitrol, and Quercetagetin,	Peel	20
3	Steroids	β -Sitosterol, β-Sitosterol-3-O- β-d-glucopyranoside	Leaves	21
4	Coumarins	Scoparone, Limetin, Osthol, Xanthotoxin, Bergapten, Isopimpinellin, Bergaptol	Peels, and roots	22
5	Carotinoids	Zeaxanthin, Zeinoxanthin, β-Cryptoxanthin, Lutein, Auroxanthin, α- Carotene	Fruit	23
6	Minerals	Potassium, magnesium, calcium, sodium, iron, magnese, magnesium, zinc	Natural and commercial juices	24
7	Vitamins	A, D, E, K, B1, B2, B3, B5, B6 and C	Fruits, and seeds	25

5. TRADITIONAL USES OF SWEET ORANGE

C.sinensis is a well-known herbal antioxidant that strengthens the body's defenses. It's traditionally used to address a variety of diseases such as constipation, diarrhea, cold, cramps, colic, bronchitis, asthma, fever, vomiting, menstrual issues, anxiety, depression, stress, hypertension and angina, tuberculosis, cough, obesity, and indigestion [32,33]. In traditional Chinese medicine, oranges have a wide application from the ancient time as a form of cooling therapy for colds, coughs, and other respiratory problems. In China, it's traditionally used as a form of good fortune [34], Figure (4).

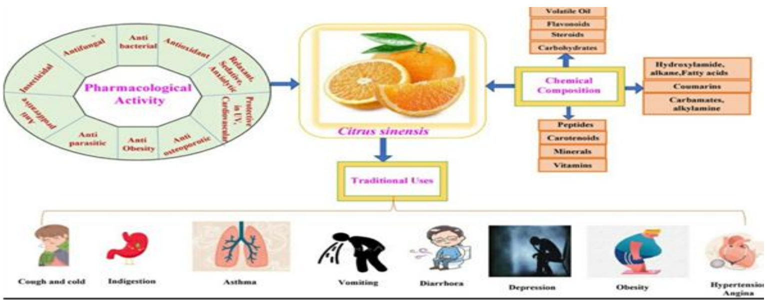

FIGURE 4. - Traditional uses of Citrus sinensis [33]

6. APPLICATIONS OF SWEET ORANGE

C.sinensis is full of numerous nutritious plant components and is frequently utilized for its beneficial effects. Volatile oils in orange composed of sabinene, myrcene, ip-cymene, iterpinene-4-ol, iβ-elemene, ineral, inerol, iα-farnesene, iβ-farnesene, iα-terpineol, igeraniol ,iα-pinene, β-pinene, ithujene, iα-phellandrene, iβ-iphellandrene, ioctanal, ilimonene, idecanal, icitronellal, iheptanal, inonanal, ivalencene, iethyl iheptanoate,igeranyl acetone,ihexyl acetate, iethyl nonanoate, ethylioctanoate, iundecanal, icitronellol, ethanol, istyrene, geranial,ithymol,isativene, iβ-santalene, β-iselinene , α-iterpinene, iterpinolene, ilinalool, neryl acetate, igeranyl acetate and caryophyllene, all these components have different utilization in many fields. In the foodiindustry, the oil is employed as a fungicide to prevent the spoilage of crops and food during transportation. The oil is frequently employed in the cosmetics and cleaning industries because of its aromatic properties. In the chemical industry, the essential oiliderived from orange peels is capable of producing methane. The essential oil is commonly utilized in the manufacturing of isoaps,iperfumes,icosmetics and other hygienic products for the home, as well as in environmental friendly solvents. Since the ancient ages, it has been one of the most popular essential oils in aromatherapy, incorporating massages, baths and inhalations. In the fabric clothes, plastic and paint manufacturing, oil is employed as a means to cover up undesirable smells. Because of its flavor properties, the oil is frequently employed in pharmaceutical shape. Additionally, the oil is employed for its preventative properties, for example. as a cancer inhibitor, diabetes inhibitor, viral infection inhibitor, bacterial infection inhibitor, anti-aging and anti-inflammatory properties [34].

Recently, as consumers have become more concerned with safety of food, this has led to an enhancing in the utilization of oil in food and packaging industries. This is primarily due to its natural properties as an antimicrobial. Some scientists have demonstrated that the regular consuming of Phenolic compounds in oranges can reduce the probability of illness and have a positive impact on human wellness. iPhenolic compounds have a significant role in combating the onset of diseases like liver damage, cancer, neurodegenerative disease and heart disease. They can be employed to remedy multiple other health issues including degenerative arthritis and eye diseases, and estrogenic compound and anti-thyroids. These compounds have a potent ability to scavenge free radicals and have an antioxidant property that is practical to use in the food production through exchanging chemical compounds that contain antioxidants with this natural compound. The flavedo (epicarp), albedo (imesocarp) and the edible part (iendocarp) of the shell are the main components that contain pectin. They are referred to as complex polysaccharide compounds and are mostly located in the cell walls of higher plants. Pectin is manufactured in the industries and commonly utilized as a coating, thickening, and encapsulating materials in jams and confectionery due to its stabilizing, gelling and cohesive properties. Because of its properties associated with the film, pectin can be employed as a packaging material that improves the organoleptic qualities of food products by improving their organoleptic properties and increasing their shelf life [35].

The consumption of citrus fruit has been demonstrated to be beneficial to health because of the anti-iinflammatory, antioxidant, cancer-ifighting, cardiovascular and neurological properties of secondaryimetabolites in citrus fruit [36]. Antioxidants can inhibit, prevent or delay the oxidative process. The process of oxidization produces free radicals, these radicals initiate a chemical reaction series that can directly or indirectly affect cellular components (iDNA,iproteins, etc.). Citrus fruits contain rich endogenous antioxidants like carotenoids, flavonoids, ascorbic acid (also called ivitamin C) and itocopherols (also called ivitamin E) that inhibit the production of oxidative processes. These anti-oxidants can detoxifyi or mitigate the harmful ieffects of reactive oxygen species (ROS), thereby safeguarding cellular constituents from the destruction caused by ROS. Flavonoids with anti-aging properties and other volatile compounds in leaves, juices and phloem sap of farmed citrus species increase dramatically responding to ibiotic stress [37]. Some promising compounds that increase in abundance following abiotic or biotic stress include flavanones (e.g., ihesperidin and inaringenin), iflavanols (e.g., iquercetin) and a few otheriflavanones. These flavonoids have a significant effect on antioxidant and antibacterial properties [38]. Bioactive alkaloids are common in various types of citrus. Some common alkaloids in citrus plants are found to be ityramine,iN-methyltyramine, ioctopamine, iN-methyl nicotine, ihordenine, and synephrine. Synephrine is the most significant chemical found in plants of citrus. iSynephrineialkaloids comprise over 85% of the total amount of proto-alkaloids in citrus fruit. Additionally, the concentration of the compound N-methyltyramine observed in species of citrus is greater than the concentration of hordenine, octopamine, and tyramine. These alkaloids have a significant effect on the antioxidant action of the plants, and have indirect role in the plant developement, ireproduction, and metabolism of citrus plants [39].

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7. ALKALOIDS IN SWEET ORANGE

Phenethylamine alkaloids (i.e. ioctopamine, synephrine, ityramine, N-methyltyramine and hordenine) are the most significant biologically active components of the cC.sinensis fruits. A main synthesis substance, synephrine have ipharmacological properties that include vasoconstriction, blood pressure rise and relaxation of bronchial muscle. Synephrine presents in the peel and the edible portion of Citrus fruit. sSynephrine has been identified as the primary component of citrusifruits andiextracts among the naturally occurring adrenergic amine; the other alkaloids are either nonexistent or only found in trace amount.dSynephrine is an alkaloid sharing similarity in structure toiephedrine (figure 3), the Iprimary active component of plants of the genusiEphedra. To convert ephedrine into ssynphrine, just two substitutions are required: ia side-chain methyl group (CH3) is changed toihydrogen and one of the ring carbon atoms is hydroxylated (OHi replaces H). Instead of theityramine→octopamine→ssynephrine pathway that is thought to be prominent in mammals, the production of synephrine in plants may followithe tyramine→iN-methyltyramine→isynephrine biosynthetic pathway.iTyramine is derived ifrom the aminoiacid tyrosine byidecarboxylation, (figure 5) [40].

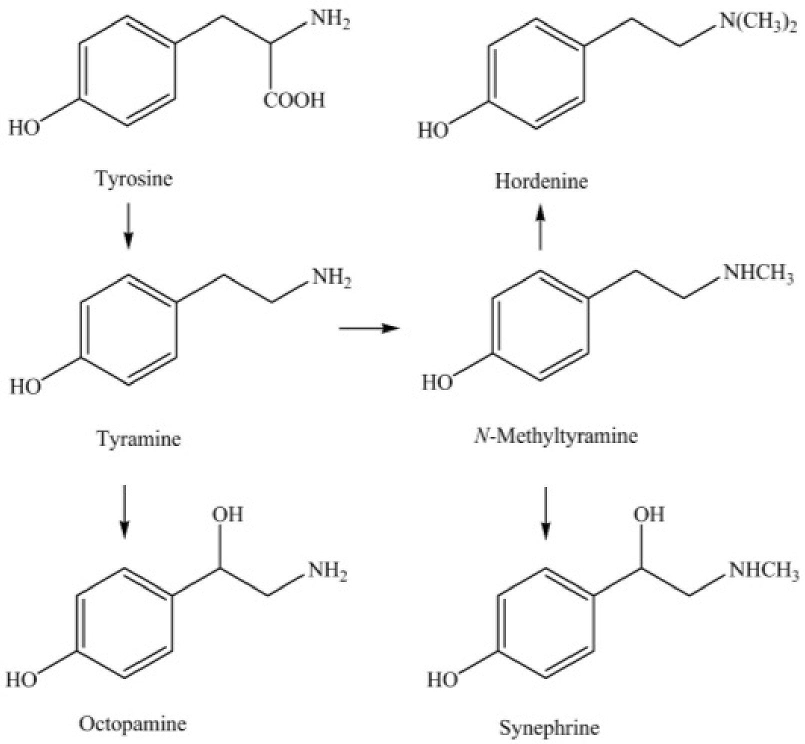

FIGURE 5. - Biosynthetic pathway of phenethylamine alkaloids [40]

Alkaloids facilitate the improvement of intestinal movement, reduce the troublesome effects of digestion, and alter the responses to inflammation, all of which are intended to support the treatment of chronic diseases. Alkaloids can alter neurotransmitters and have the potential to remedy neurological disorders like depression and anxiety. This chemical has garnered significant attention for its unique pharmacological properties. Synephrine have a mild stimulating effect, they promote the metabolism of lipids and increase the temperature of the body, additionally, it has an antimicrobial effect that is effective against a variety of organisms. Synephrine is used as a diabetes treatment by increasing the sensitivity of insulin and improving the uptake of glucose in muscle tissue. It also promotes cardiovascular and neurological health by increasing the activity of catecholamines without causing significant cardiovascular effects, this improves the mood and cognitive attention [41].

A study showed that synephrine has anti-obesity and lipid-lowering properties in a high-fat diet that causes obesity in mice. Synephrine exhibited aidecrease in bodyiweight and fat mass, aidecrease in the accumulation of white adipose tissue and the lipid profile was improved by decreasing the triglyceride and LDL-C levelsiin the serum, and increasing the HDL-C. It was found that synphrine can also increase in the activity of PPAR-α (peroxisomeiproliferator-iactivated receptor α) andiAMPK (AMP-iactivated protein kinase). This indicates that the mice have increased fat metabolism and expenditure, which in turn improves the mice's lipid profile [42]. The molecule is composed of a benzene ring that is substituted with a hydroxyl substitution; this group is lipophilicity and can interact with the adrenergic receptor's pocket as well as participate in aromatic interactions with the receptor's binding site. Additionally, the two carbon chain attached to the amino group facilitates the interaction of this molecule with adrenergic receptors (alike to other catecholamines like norepinephrine and epinephrine). This increases the hydrophilicity of the molecule and increases the specificity of the receptor. It additionally possesses a hydroxyl moiety (-OH) associated with the β-carbon of the side chain (converting it to β-hydroxy Phenylethylamine). This substitution increases the polarity of the group, which facilitates the association of the group with β-adrenergic receptors and the stabilization of the association with β3-adrenergic receptors, these receptors are primarily involved in the process of thermogenesis and the lipolysis [43]. Synephrine is used to reduce appetite, increase energy and metabolism, and has a thermogenic effect. Due to its potential benefits in increasing fat oxidation, this substance is often included in weight loss/body fat reduction supplements. Synephrine is commercially available in 10 mg capsule form [44].

8. EXTRACTION METHODS OF PHENETHYLAMINE ALKALOIDS

The most basic extraction methods based on the utilization of a suitable solvent, typically in conjunction with sonication, given that most majority alkaloids are basicichemicals, matrixipH has a great impact on the extractionnefficiency. Consequently, an initial base treatment could enhance the efficiencyiofiextraction with organicisolvent. The following steps are involved in the typical extraction process: (i) matrix basification with, for example, NH4OH; (ii) extractioniwith a suitable organic solvent; and (iii) evapzoration and re-solubilization in HPLCimobile phase. This method producesian extract with a high yield of alkaloids. A imore selective technigue would be a multistepiacid-ibase extraction. A typical protocoliwould include: (i) making aicrude extract with a suitableisolvent; (ii)iliquid-liquidiextraction with diluteemineral acid; (iii) neutralizing the acid extract and liquid-liquid extraction with a suitable solvent; and (iv)ievaporation and re-solubilization iniHPLC mobile phase. Because the multi-step process may jeopardize recuperation, it is recommended to utilize an internal standard [45]. Phenethylamine alkaloids were isolated from Colchicum crocifolium using the following method: MeOH was used to extract dried plant materials for three hours in a Soxhlet apparatus. A MeOH –was produced by evaporating the solvent at a lower pressure and then fractionating it [46]. The methanolic extract was extracted using light petroleum after being dissolved in 5% acetic acid. Then the resultant aqueous acid residue was extracted 3 times using CH2CL2. Following the adjustment of pH at 12 with 10% NaOH, aqueous residue were extracted 3 times using diethyl ether and CH2CL2, separately. Ephedrine alkaloids were typically separated via a sonification extraction. Ephedrine alkaloids were isolated from Ephedra natural products using sonification and microwave extraction. Using a solvent that includingimethanol or a solution of methanol and hydrochloriciacid (0.8:99.2, v/v) at various ttemperatures (rroomitemperature, 40, or 50 oC) for 15 minutes, sonification was performed. Monomodenmicrowavenapparatus with a closednvesselvsystem was applied to extract 0.25ig of E.vulgarisi grounded aerial parts using 5 mliof solventi(methanol or a mixture ofihydrochloric acidimethanol (0.8:99.2, v/iv)). The sample was then exposed to varying temperature for varying irradiation times (40oC for 15 min,660oC for 4 min, or 80oC for 1 min). Sonification was the most effective technique, enabling the thighest yieldiof all assessed substances in a short amount of time, according to a comparison between sonification and microwave extraction [46].

9. CONCLUSION

Overall, orange peels are rich with substances with therapeutic properties, they are recognized around the world as a rich source of vitamin iC, a powerfulinatural anti-inflammatory that enhancesithe immune system, it also contains flavonoids, tannins, cardiac glycosides, and alkaloids, all of which have a broad range of medicinal properties. Alkaloids present in orange peels are phenylethylamine type (e.g.,ioctopamine, isynephrine, ityramine, iN-methyltyramine, and ihordenine). Synephrine alkaloids comprise over 85% of the total amount of native alkaloids in citrus fruit. It has anti-obesity, antidiabetic and lipid-lowering properties.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest

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