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RESINS FROM HERBAL ORIGIN AND A FOCUS ON THEIR APPLICATIONS

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ABSTRACT

The present article reveals an important role and wide applications played by the resins. Herbal system is considered as a complimentary and alternative system of medicines plays a significant role in India. Resins being the natural products are the secondary metabolites which have therapeutic actions in humans and which can be refined to produce the drugs. Humans have been using plant resins for thousands of years. Because wide use of resins they are collected by artificial injury to plants though they are secreted by plants in response to protect the plant. Resin is a viscous compound hardens over time but softens on melting and does not react with water. This unique property makes the resins as a choice in preparing many excipients in the pharmaceutical dosage forms and even for preparing sustained release medicament formulation. The softer odoriferous oleo-resins and gum resins containing essential oils are more largely used for therapeutic purposes and incense. Thus resins play immense role in today's pharmaceuticals.

INTRODUCTION:

Resins and Resin Combination: Resins are amorphous products of complex nature. These are amorphous mixtures of essential oils, oxygenated products of terpene and carboxylic acids found as exudations from the trunk of various trees. They are transparent or translucent solids, semi-solids or liquid substances containing large number of carbon atoms. Most of the resins are heavier than water. They are insoluble in water, but soluble in alcohol, volatile oils, fixed oils, chloral hydrate and non-polar organic solvents like benzene or ether. They are hard, electrically non-conductive and combustible masses. When heated, they soften and ultimately melt. They are usually formed in schizogenous or schizolysigenous cavities or ducts as end products of metabolism.

Chemically, they contain organic acids, alcohols, esters and neutral resins. Depending upon the type of the constituents of the resin, they are further classified as: acid resin, ester resin and resin alcohols. Resins and oils in homogenous mixtures are called as oleoresins. Oleo-gum resins are the homogenous mixtures of volatile oil, gum and resin. If the resin contains benzoic acid and/ or cinnamic acid, it is called as a balsam [1].

Resin is a hydrocarbon secretion of many plants, particularly coniferous trees. It is valued for its chemical constituents and uses, such as varnishes and adhesives, as an important source of raw materials for organic synthesis, or for incense and perfume. Fossilized resins are the source of amber. Resins are also a material in nail polish. Resins have a very long history and are mentioned by both ancient Greek Theophrastus and ancient Roman Pliny the Elder, especially as the forms known as frankincense and myrrh. They were highly prized substances used for many purposes, especially perfumery and as incense in religious rites. There is no consensus on why plants secrete resins. However, resins consist primarily of secondary metabolites or compounds that apparently play no role in the primary physiology of a plant. While some scientists view resins only as waste products, their protective benefits to the plant are widely documented. Many resinous products are not formed by the plant itself unless and until purposeful and methodical injuries in the shape of incisions are made on them and the secretions or plant exudates are tapped carefully, such as: Balsam of Tolu and Benzoin [2].

The toxic resinous compounds may confine a wide range of herbivores, insects, and pathogens; while the volatile phenolic compounds may attract benefactors such as parasitoids or predators of the herbivores that attack the plant [3].

Distribution of Resins in Plants: The resins and resinous substances are more or less extensively distributed throughout the entire plant kingdom, specifically the Spermatophyta i.e., the seed plants. Notably, their presence is almost rare and practically negligible in the Pteridophyta i.e., the ferns and their allies. However, the resins have not been reported in the Thallophyta i.e. the sea-weeds, fungi etc. Therefore, all these findings and observations lead one to the fact the resins are the overall and net result of metabolism in the higher plants, since majority of them belong to the phylum Angiosperm i.e., seed-enclosed flowering plants, and Gymnosperm i.e., naked-seed non-flowering plants [4].

Occurrence of Resins in plants: In the plants resins usually occur in different secretory zones or structures. A few typical examples of such plant sources along with their specific secretary structures are given below:

i. **Resin Cells:** Ginger
ii. **Schizogenous Ducts or Schizolysogenous Ducts or Cavities:** Pine Wood
iii. **Glandular Hairs:** Cannabis

It has been observed evidently that resins are invariably produced in ducts as well as cavities; sometimes they do not occur in the so called

specialized-secretory structures, but tend to get impregnated in all elements of a tissue, for example: Guaiacum Resin- is obtained from the heartwood of *Guaiacum officinale* Linn. and *G. sanctum* Linn. i.e., it is found in the vessels, fibers, medullary ray cells and wood parenchyma. In this particular instance, the resins occur as tyloses, achieved by chopping off the conduction in these areas so as to enhance the effective usage of root pressure and the capillaries in forcing both the nutritive contents and forcing water to reach the top end of these tall trees.

Chemistry: The resin produced by most plants is a viscous liquid, composed mainly of volatile fluid terpenes, with lesser components of dissolved non-volatile solids which make resin thick and sticky. The most common terpenes in resin are the bicyclic terpenes alpha-pinene, beta-pinene, delta-3 carene and sabinene, the monocyclic terpenes limonene and terpinolene, and smaller amounts of the tricyclic sesquiterpenes, longifolene, caryophyllene and delta-cadinene. Some resins also contain a high proportion of resin acids. The individual components of resin can be separated by fractional distillation.

A few plants produce resins with different compositions, most notably Jeffrey Pine and Gray Pine, the volatile components of which are largely pure n-heptane with little or no terpenes. The exceptional purity of the n-heptane distilled from Jeffrey Pine resin, unmixed with other isomers of heptane, led to its being used as the defining zero point on the octane rating scale of petrol quality. Because heptane is highly flammable, distillation of resins containing it is very dangerous. Some resins when soft are known as 'oleo-resins', and when containing benzoic acid or cinnamic acid they are called balsams. Other resinous products in their natural condition are a mix with gum or mucilaginous substances and known as gum resins.

Many compound resins have distinct and characteristic odors, from their admixture with essential oils. Certain resins are obtained in a fossilized condition, amber being the most notable instance of this class; African copal and the kauri gum of New Zealand are also procured in a semi-fossil condition [4].

Physical properties:

1. Resins are hard, transparent or translucent brittle materials.
2. They are invariably heavier than water having the specific gravity ranging from 0.9-1.25.
3. Resins are more or less amorphous materials but rarely crystallizable in nature.
4. On being heated at a relatively low temperature resins first get softened and ultimately melt down thereby forming either an adhesive or a sticky massive fluid, without undergoing any sort of decomposition or volatilization.
5. On being heated in the air i.e., in the presence of oxygen, resins usually burn readily with a smoky flame by virtue of the presence of a large number of C-atoms in their structure.
6. On being heated in a closed container i.e., in the absence of oxygen, they undergo decomposition and very often give rise to empyreumatic products i.e., products chiefly comprising of hydrocarbons.
7. Resins are bad conductors of electricity, but when rubbed usually become negatively charged,
8. They are practically insoluble in water, but frequently soluble in ethanol, volatile oils, fixed oils, chloral hydrate and non- polar organic solvents e.g., benzene, n-hexane and petroleum ether [5].

Chemical properties:

1. Resins, in general, are enriched with carbon, deprived of nitrogen and contain little oxygen in their respective molecules.
2. Majority of them undergo slow atmospheric oxidation whereby there color gets darkened with impaired solubility.

3. Resins are found to be a mixture of numerous compounds rather than a single pure chemical entity.
4. Their chemical properties are exclusively based upon the functional groups present in these substances.
5. Consequently, the resins are broadly divided into resin alcohols, resin acids, resin esters, glycosidal resins and resene (i.e., inert neutral compounds).
6. Resins are regarded as complex mixtures of a variety of substances, such as: resinotannols, resin acids, resin esters, resin alcohols and resene.
7. Resins are nothing but oxidative products of terpenes.
8. They may also be regarded as the end products of destructive metabolism.
9. The acidic resins when treated with alkaline solutions they yield soaps (or resin-soaps) [6].

Solubility:

1. Majority of resins are water- insoluble and hence they have practically little taste.
2. They are usually insoluble in petroleum ether (a non-polar solvent) but with a few exceptions. Such as: Colophony (freshly powdered) and mastic.
3. Resins mostly got completely dissolved in a number of polar organic solvents, for instance: ethanol, ether and chloroform, there by forming their respective solutions which on evaporation, leaves behind a thin-varnish-like film deposit.
4. They are also freely soluble in many other organic solvents, namely: acetone, carbon disulphide, as well as in fixed oils and volatile oils.
5. Resins dissolve in chloral hydrate solution, normally employed for clarification of certain sections of plant organs [7].

Derivatives: Solidified resin from which the volatile terpene components have been removed by distillation is known as rosin. Typical resin is a transparent or translucent mass, with a vitreous fracture and a faintly yellow or brown color, non-odorous or having only a slight turpentine odor and taste. It is insoluble in water, mostly soluble in alcohol, essential oils, ether and hot fatty oils, and softens and melts under the influence of heat, is not capable of sublimation, and burns with a bright but smoky flame.

This comprises a complex mixture of different substances including organic acids named the resin acids. These are closely related to the terpenes, and derive from them through partial oxidation. Resin acids can be dissolved in alkalis to form resin soaps, from which the purified resin acids are regenerated by treatment with acids. Examples of resin acids are abietic acid (sylvic acid), $C_20H_{30}O_2$, plicatic acid contained in cedar, and pimaric acid, C20H35O2, a constituent of galipot resin. Abietic acid can also be extracted from rosin by means of hot alcohol; it crystallizes in leaflets, and on oxidation yields trimellitic acid, isophthalic acid and terebic acid. Pimaric acid closely resembles abietic acid into which it passes when distilled in a vacuum; it has been supposed to consist of three isomers [8].

Classification of Resins: The resins are broadly classified under three major categories, namely:

Taxonomical Classification: The resins are grouped according to their botanical origin exclusively, such as:

- **Coniferous Resins:** e.g., Colophony, Sandarac;
- **Berderidaceae Resins:** e.g., Podopyllum and
- **Zygophyllaceae Resins:** e.g., Guaiacum

In this particular instance, it has been observed that the resins that usually occur in plants of the same natural order, may exhibit more or less related characteristics features.

Chemical Classification: The resins may also be classified as per the presence of the predominating chemical constituents for instance:

- **Acid Resins:** e.g., Colophony (Abietic acid); Sandarac (Sandracolic acid); Shellac (Alleuritic acid); Myrrh (Commiphoric acid);
- **Ester resins:** e.g., Benzoin (Benzyl benzoate), Storax (Cinnamyl cinnamate);
- **Resin Alcohols:** e.g., Balsam of Peru (Peruresinotannol), Guaiacum resins (Guaicresinol); Gurjun balsam (Gurjuresinol);
- **Resene Resins:** e.g., Dragon's Blood (Dracoresene); Gutta-percha (Fluavil);
- **Glycoresins:** e.g., Jalap resin from jalap i.e, Ipomea purga Haynel; (Family: Conrulvulaceae) Podophylloresin from the dried roots and rhizomesof Podophyllum hexandrum (P.emodi) Royle. (Family Berberidae)

A. Constituents of resin: Invariably, to maintain the simplicity, resins may also be classified according to the major constituents present either in the resin or resin combination e.g., Resins; Oleo-resins; Oleo-gum resins; Balsams.

After having been exposed to the various aspects of resins with regard to their physical and chemical properties, occurrence and distribution, preparation, chemical composition and classification, it would be worthwhile to gain some in-depth knowledge about certain typical examples belonging to resins; Oleo-resins; Oleo-gum-resins; Balsams; and Glycoresins [2].

Uses: The hard transparent resins, such as the copals, dammars, mastic and sandarac, are principally used for varnishes and cement, while the softer odoriferous oleo-resins (frankincense, elemi, turpentine, copaiba) and gum resins containing essential oils (ammoniacum, asafoetida, gamboge, myrrh, and scammony) are more largely used for therapeutic purposes and incense.

B. Isolation of Resins: Pharmaceutical resins are obtained from the plants and animals by one of the following methods [2].

1. By extraction with alcohol and precipitation with water, e.g. Jalap, Podophyllum, Ipomoea, etc.
2. By distillation for separation of oil, e.g. Copaiba, Colophony, etc.
3. By heating the plant part, e.g. Guaiacum.
4. As plant exudates by incisions, e.g. Myrrh, Asafoetida, Balsams, etc.
5. By collecting fossil resins, e.g. copal, kauri, etc.
6. By processing the encrustations i.e. shellac.

Resins: The various resins are as follows:

1. **Colophony:** Colophony is the residue left after the distillation of the oil of turpentine from the crude-oleo-resin obtained from various species of *Pinus* belonging to family Pinaceae. Colophony contains 90% resin acids known as abietic acid. The remaining 10% as resene is an inert substance and is a ester of fatty acids. It also contains a mixture of dihydroabietic acid ($C_{20}H_{30}O_2$) and dehydroabietic acid ($C_{20}H_{28}O_2$). On being heated at 300^{o}C, abietic acid undergoes further molecular rearrangement to produce neo-abietic acid.

Uses:

1. Colophony is a stimulant and diuretic.
2. Colophony is used in pharmacy for the preparation of zinc oxide plasters, ointments and other adhesive plasters.
3. It is widely used in the manufacture of printing inks, rubber, dark varnishes, sealing wax, linoleum and thermoplastic floor tiles.
4. It also finds application as varnish and paint dries, cements, soaps, wood polishes, paper, plastics, fireworks, tree wax, sizes, rosin oil.
5. It is used for waterproofing cardboard, walls etc [6].

2. **Lac:** Stick lac contains 70-80% of resin, sugars, proteins, coloring matter (1-2%), wax (4-6%), extraneous matter (8-10%), and volatile oil in traces. Lac resin consists of hydroxy fatty acid derivatives. Aleuritic acid is the main constituent 35% of resin, while shelloic acid and its isomer along with kerrolic acid and butolic contain laccaic acid which is water soluble.

Uses:

1. It is extensively used for coating tablets and confections.
2. It has also been used for preparing sustained release medicament formulation.
3. It is used chiefly in lacquers and varnishes.
4. It is also employed in the manufacture of buttons, sealing wax, cements, inks, grinding wheels, photograph records, paper.
5. It also finds its use in electrical machines and for stiffening hats. It has also used for finishing leather [9].

3. **Podophyllum:** The composition of resin is made of lignans which contain at least 40% of podophyllotoxin. American podophyllum resin contains only 10% of podophyllotoxin. Podophyllotoxin is teranhydronapthalene derivative with OH and lactone group in trans position which is essential for anti-mitotic activity. In cis position, it possesses only purgative activity. Apart from podophyllotoxin, picropodophyllin, quercetin, astragalin and resinous substances are also found in podophyllin.

Uses:

1. Podophyllotoxin possesses anti-tumor (antineoplastic) properties and may be used in the treatment of cancer.
2. It is used as a drastic but slow-acting purgative.
3. It is invariably prescribed with other purgatives, henbane or belladonna to prevent gripping in infants.

4. **Tar:** Tar contains many chemical constituents in various proportions depending upon the particular species of *Pinus* and its geographic location, such as: hydrocarbons, resin acid, resinous matter, and includes phenols, phenolic ethers, cresols, catechol, methyl cresols, guaiacol, benzene, toluene, xylene and styrene.

Uses:

1. It serves as an expectorant when used in the form of syrup.
2. Pine tar is frequently employed as antipruritic and antibacterial.
3. It is used largely in ointments externally for the treatment of chronic skin diseases and eczema [9].

Oleoresins: A few important oleoresins are as follows,

1. **Capsaicin:**

Chemical Constituents: The capsicum contains 8-12% of an oleoresin capsaicin and a red coloring principle known as capsanthin. The pungency of capsaicin is not affected by dilute alkali, but is destroyed almost completely by subjecting it to oxidation with either $KMnO_4$ or $K_2Cr_2O_7$.

Uses:

1. It is used as a tool in neurobiological research.
2. Pretreatment with capsaicin induces long-lasting desensitization of airway mucosa to various mechanical and chemical irritants [8].

2. **Male Fern:** The main active constituents of male fern are derivatives of phloroglucinol and butyric acid. It has been observed that two or more molecules of simple monocyclic derivatives, such as: aspidinol, filicinic acid and acylfilicinic acid

may get condensed to give rise to bicyclic derivatives.

Uses:

1. Male fern oleoresin is an antihelmentic, specifically a taeniafuge.
2. It is also used as its extract for the expulsion of tapeworms [10].

3. **Ginger:** Ginger contains volatile oil (1-3%), which comprises of zingiberene, α-curcumene, β-sesquiphellandrene and β-bisabolene. Zingiberene has two chiral centers. The acyclic chiral center has been steriochemically related to that in (+)-citronellal, and the cyclic chiral center to that in (-)-zingiberene has the absolute configuration. The oleoresin contains the pungent gingerols and shogaols.

Uses:

1. It is used as flavoring agent, carminative, aromatic and stimulant to gastrointestinal tract.
2. Ginger finds its wide applications in soft drinks, beverages, ginger beer and wine.
3. It is extensively used for culinary purposes in ginger-bread, biscuits, puddings, cakes, soups and pickles [10].

4. **Turpentine:** The gum- turpentine when subjected to steam-distillation yields15-30% of a volatile oil known in the trade as “turpentine oil”. It contains mainly the terpenes, such as: dextra-and laevo-α-pinene, β-pinene and camphene.

Uses:

1. It is employed externally as a counterirritant and rubefacient.
2. It is used as a constituent of stimulating ointments.
3. It is employed industrially as an insecticide.
4. It is used as a solvent for waxes.
5. It is utilized extensively in the production of synthetic camphor.

Oleo-Gum-Resins: The oleo-gum-resins are the naturally occurring mixture of resin, gum, volatile oil, and mostly small quantities of other substances. There are some potent oleo-gum-resins which exhibit remarkable medicinal values. A few drugs containing oleo-gum-resins are as follows.

1. **Asafoetida:** Asafoetida contains volatile oil (8-16^{o}C), gum (25%) and resin (40-60%).The volatile oil essentially consists of some organic sulphides solely responsible for attributing the characteristic garlic-like odor. The resin consists of notannol, asaresinotannol i,e., the resin alcohols, which are present partially in the free state and partially in the combined form with ferulic acid. It also contains umbellic acid and umbelliferone; the latter is found combined with ferulic acid, but it gets generated on being treated with dilute HCl.

Uses:

1. It is abundantly used in India and Iran as a common condiment and flavoring agent in food products.
2. It is also an important ingredient in *Worcestershire Sauce*.
3. It is used as a repellant [2% (w/v) suspension] against dogs, cats, deer, rabbits etc.
4. It is used seldomly as an antispasmodic, carminative, expedorant and laxative.
5. It is still employed in veterinary externally to prevent bandage chewing by dogs.
6. It is also used as a powerful nerve stimulant especially in nervous disorders related to hysteria [11].

2. **Turmeric:** It contains volatile oil (5-6%), resin and substantial quantity of zinzgiberaceous starch grains. The marked and pronounced yellow color in turmeric is due to the presence of curcuminoids which essentially contains curcumin. The volatile oil contains a host of

chemical substances, such as: d-α-phellandene, d-sabinene, cineol, borneol, zingiberene, and sesquiterpenes. Turmeric also contains some other chemical constituents, namely: p,p-dihydroxy dicinnamoylmethane; p-α-dimethyl benzyl alcohol; p-hydroxy-cinnmoylferuloylmethane; 1-methyl-4-acetyl-1-cyclohexene; and caprylic acid.

Uses:

1. It is exclusively used across the globe as a condiment as curry powder.
2. It is employed as coloring agent for ointments.
3. It is used medicinally as a tonic, as a blood purifier, as an anthelmintic and finally as an aid to digestion.
4. It is used medicinally in the form of a facial cream to improve complexion and get rid of pimples.
5. A small quantity of turmeric when boiled with milk and sugar, it helps to cure common cold and cough symptoms [12].

3. **Myrrh:** Myrrh contains volatile oil (7-17 %), resin (20-25 %), gum (57-61 %), and bitter principle (3-4 %). The volatile consists of eugenol, m-cresol and cuminaldehyde. The resin is found to consist of a mixture of α-, β-, and γ- commiphoric acids (resin acids). It also containstwo phenolic resins α- and β- herrabomyrrholic acids which are ether insoluble. The oleo-gum-resin yields alchol-soluble extract not less than 30%. It also contains phenolic compound such as: pyrocatechin and protocatechuic acid. The crude alcohol-insoluble fraction i.e., gum, comprises of protein (18%) and carbohydrate (64%) made up of arabinose, galactose and glucuronic acid. However, the gum is found to be associated with an oxidase enzyme.

Uses:

1. It is used chiefly in perfumes and incense.
2. It is frequently employed as an antiseptic and stimulant.
3. Myrrh acts as an astringent to the mucous membrane and hence it finds its application in oral hygiene formulations, such as: gargles, mouth-washes.
4. It is also used as carminative [13].

4. **Ammoniacum:** Ammoniacum the oleo-gum-resin consists of volatile oil (0.1-1.0%), resin (65-70%), gum (20%), moisture (2-12%), insoluble residue (3.5%) and ash (1%). Ammoresinol, a phenolic substance is the main constituent of the resin, which is a colorless crystal, mp 110^{o}C. It also contains traces of salicylic acid.

Uses:

1. It is an important ingredient of porcelain cements.
2. It is a stimulant, and secreted by the bronchial mucous surface, thereby disinfecting the secretions.
3. It is used in plaster-of-paris (POP) plasters as a stimulant to the skin.
4. It is also used as a disinfectant expectorant in chronic bronchitis amalgamated with excessive discharge (Ashutosh Kar, 2007).

Thus, variety in compositions of resins makes them pharmaceutically useful and its contribution can not be ignored.

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