Olibanum in Focus

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Olibanum, "the frankincense of ancients,"[1] is obtained from the members of the genus *Boswellia* mainly *Boswellia carterii* Birdw and *Boswellia frereana* Birdw and a dozen other species of *Boswellia*[2] such as *Boswellia bhaudarjiana* Birdw, *Boswellia papyrifera* (Del.) Hochst, *Boswellia sacra* Flueckiger.[3] The *Boswellia* species are small trees or shrubs, three to six meters high, which grow in rough and inhospitable arid mountainous regions at an altitude of 1000 to 1800 meters, the favourite areas being northeast Africa and southern Arabia.[2,4]

On the other hand, *Boswellia serrata* Roxb, botanically differentiated into two varieties (viz., var. *serrata* with serrata and pubescent leaves and var. *glabra* with entire, glabrous leaves) is known as the Indian olibanum tree. This belongs to the same genus as the tree which provides the true frankincense or olibanum of commerce.[5,6] *Boswellia serrata* is distributed and constitutes almost pure forests in many places;[5] reliable statisatics as to the exact area of this tree under cultivation is lacking.[7]

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The *Boswellia* tree contains physiological, schizogenous gum-oleoresin pockets on the bark.[8,9] When the bark is incised, a white emulsion exudes which dries into globular, pear or club shaped tears. Depending on the size of the tree, it may be tapped in more than one place. Collection is carried out every fortnight or so. Usually only the exudate that settles on the wood is gathered; what flows down the stem accumulates and is scrapped off only annually; this material is regarded as an inferior or impure form.[2]

Olibanum is harvested in northeast Africa and southern Arabia from December to May except in the rainy season,[9] when its quality deteriorates because the gum-oleoresin is soluble in water.[4]

For *Boswellia serrata*, collections are made from November to June or July with temporary interruption in winter months if a prolonged wet period intervenes.[7] This is because excess of moisture produces a peculiar treacle-like mass; taking up water, the gum swells up, forms a coating on the resin, makes it impervious to solvents and causes difficulties in extraction.[10]

Geographic Origins

Olibanum from Arabia and Somaliland is brought to Aden.[11] The commercial brands, Aden and Eritrea, are usually regarded as derived respectively from *Boswellia carterii* Birdw and *Boswellia frereana* Birdw.[11] On the other hand, *Boswellia carterii* Birdw is cited as the botanical source for both.[12,13] Sudan supplies olibanum tears directly from the country,[4] and its parentage appears to be *Boswellia papyrifera* (Del).[3]

By thin layer chromatographic technique, the botanical origin of Somalian and Ethiopian olibanum has recently been disclosed as, respectively, from *Boswelia carterii* and *Boswellia papyrifera;* the identity of the Indian variety awaits clarification.[14] However, this does not preclude the existence of other species in a particular region.[14]

Olibanum is available as:[1,4]

—Grade I: Tears and most carefully selected, white or white-yellow colour
—Ungraded: A mixed white yellow and reddish angulated masses with particles of bark
—Dust and siftings
—Unassorted olibanum as it comes from the producing regions is regarded as another variety

The raw materials exploited by CMA International are Grade I and Ungraded.[4]

The Indian olibanum, assorted into tears of different size and colour by rubbing with soapstone powder followed by seiving, is available in several forms:[7]

—Stalactitic or club shaped tears: length 3(+) cm, greenish white
—Globular club shaped or stalactitic; length 2-3 cm, green or yellow
—Smaller pieces of Grade I and 2 cm tears
—Small tears; 1 cm diameter, white or yellowish brown

Ungraded brown resinous material, "Salai Guggul," "Gandabiroza" or "Dhup," is also marketed.

Olibanum of northeast Africa-southern Arabia region is composed of 3-8% volatile oil, 60-70% resin and 27-35% gum[2] and is aromatic, balsamic and fragrant.[1,2] *Boswellia serrata* oleo-gumresin contains 6.21% to 9.14% volatile oil, 52.99% to 63.32% resin and 23.86% to 28.28% gum,[7,10] in odour strongly terebinthinous[10] and is rated of "poorer quality as compared to Somalia."[4]

Olibanum for Industry

How are we to judge the olibanum required for industry? Age, appearance, odour and moisture level are factors to be considered. Others are essential oil content, resinoid yield with the chosen solvent, physicochemical and olfactive characteristics of the extractives and their gas liquid chromatographic pattern.[4] Finally, we should seek a fair consistency of the above parameters from lot to lot. More than anything else, olibanum processors know by experience the selection of the right raw material and its source of supply.

Olibanum is one of the pivotal ingredients in the incense and fumigation industry. Its pyrolytic decomposition emancipates fumes with an agreeable aroma. Currently in the United States, the olibanum for incense formulations comes from Eritrea, Somalia and India.[14] However Indian olibanum is questioned as it emits "an odour resembling turpentine or burning rubber" when it is burned.[14] This conflicts with the classical observation that Indian olibanum on burning gives a characteristic aromatic odour[10] and agreeable scent.[2] *Salai guggul* is the common incense and fumigant material.[7] How far the thin layer chromatographic method referred to earlier will aid in the selection of the right olibanum for the incense industry remains to be seen.

Isolated Essential Oil

Let us look at the essential oil isolated by steam distillation of the exudates from various *Boswellia* species other than Indian. Guenther recommends dust and siftings of the exudates as the most suitable quality for oil distillation.[1] Such a substrate, however, furnishes low yield of poorly odouriferous oil.[15] The age of the raw material and distillation parameters, and not its colour, dictate the yield and quality of the oil.[15]

Prior to 1903, the oil distilled displayed laevorotation up to −17° and later ones, dextro-rotation up to +35°; there are also oils with rotation falling outside these limits. This is ascribed to the origin of the gum-oleoresin from different species and geographical regions hitherto untapped or reduction in the time of delivering the material to the selling spot.[1] Happily, CMA International has

Table I. Physicochemical Properties of Olibanum Oils

Property	A	B	C
Specific gravity	0.8770-0.880	0.8830	0.8620-0.8890
Refractive index	1.4760-1.4802	1.470	1.4650-1.4820
Angular rotation	(-)20°4'-(-)10°8'	(-)9°4'	(-)15°-(+)35°
Acid value	-	-	4.0
Ester value	-	-	4-40

Table II. Physicochemical Properties of *Boswellia serrata* Oil

	A Reference 18	B Reference 19	C Reference 20
Density	0.8475(30°)	0.8358(30°)	0.8470(28°)
Refractive index	1.4613(30°)	1.4535(30°)	1.45748(28°)
Optical rotation	+34.35°(30°)	+28.8°(30°)	+24°(28°)
Acid value	-	-	0.76
Saponification value	5.93	4.1	8.5
Saponification value after acetylation	26.4	37.8	42.8

Table III. Properties of Rosin

	A	B	C
Moisture %	0.70	0.70	0.90
Ash %	0.03	0.50	0.40
Melting point °C	68.00	72.00	56.00
Acid value*	55.10	51.50	25.00
Saponification value*	90.20	92.00	66.00

* Milligrams of potassium hydroxide per gram of rosin.

Table IV. Olibanum Resins from *Boswellia serrata* Rosin

Solvent	Resin Yield* %	Resin Appearance
95% ethanol	59	Brown and transparent
Butanol	89	Brown and transparent
Carbon tetrachloride	69	Dark and opaque

* On the basis of rosin

now provided convincing data of the availability of olibanum, Grade I and Ungraded are consistently of excellent quality, which yield oils with physicochemical properties listed in Table I A and B respectively. Food Chemical Codex (FCC) and EOA have opted for the data given in C.[16,17] FCC specifications include the IR spectrum of the oil and botanical origin of the oil as from the trees *Boswellia carterii* Birdw and other *Boswellia* species. EOA restricts the botanical nomenclature to *Boswellia carterii* Birdw.

Olibanum oil, other than Indian, is a mobile liquid, colourless to pale yellow or pale amber green, possessing agreeable balsamic, strongly diffused odour tinged with a faint citrine note, not terebenthinous. It is of the value in the fragrance industry. With this distinguished odour, the oil is an ideal ingredient especially in bouquets having oriental and fancy types to which it imparts unique effect, incorporating soft and velvety notes, the origin of which is difficult to identify.[9] A deterpenised version of olibanum oil, Olibanol, is also in use.[15]

Mainly, resins plus a little water-soluble gum constitute the residue from the steam distillation step.[15] On leaching the residue with a hydrocarbon solvent, we get "olibanum resin." Commercial olibanum resinoid, if diluted with olibanum resin, gains in fixative but loses in odour value.[15]

Boswellia serrata oil is a faintly yellow or slightly greenish yellow mobile liquid with a pleasant ethereal smell[18] and sweet agreeable odour.[10] Its properties are given in Table II.

Work on the recovery of the three constituents of the *Boswellia serrata* exudate (viz., turpentine, rosin and gum) involving solvent extraction followed by steam distillation and steam distillation followed by solvent extraction as well as the design of a plant for this purpose have been described.[10,21]

Indian olibanum oil enjoys a wide and varied use in perfumery;[22] it can well supplant ordinary turpentine in varnish manufacture and is found to be most satisfactory for paint work.[10]

Golden brown, brittle and transparent, the resin from *Boswellia serrata* gum though different in its chemical composition from pine rosin is similar to the latter in physical characteristics and serves as a substitute for pine rosin, e.g., in varnishes and shellac.[10] The rosin dissolves in ethanol as well as in turpentine; unfortunately it is not completely soluble in alkaline solutions and hence unsuitable for soap making.[10] The properties of the rosin are given in Table III.

As in the case of other olibanum rosin, the Indian counterpart yields "olibanum resins" with solvents. The available information is presented in Table IV.[21]

A third product is available from *Boswellia serrata* exudate. Solvent extraction of its rosin leaves a major portion of the ingredients as gum. To refine this product on a large scale is almost impossible. It is, however, found advisable to market it in the same form as other similar gums, namely as flour. This reduction is carried out by grinding and sieving through a fine series of sieves.[10]

A sample of gum, completely free of resin and insoluble woody matter, is analysed as follows:[10]

Moisture, etc. (18.75%)
Ash (3.28%)
Water solubles in 5 parts of water (74.20%)
Water solubles (i.e., the portion dissolved in 60 parts of water by repeated extraction) (74.35%)
Bassorin (7.05%)
Bassorin when using 60 parts of water (6.90%)

The gum is inferior to ordinary gum as a sizing and finishing material in textiles.[10] Under-extracted gum (containing rosin) seems to be useful as a subsidiary sizing material for paper.[10]

Considerable work has been done on the composition of olibanum oils.[1,3,6,11-13,18-21,23,24] Basically the essential oil content depends on the size of the pieces of the resin.[12b] The yield of the oil, therefore, is of little value in identifying a type. Properties such as refractive index, density, saponification value etc. are not trustworthy to differentiate oils.[12b]

Olibanum oils from Aden, Eritrean and Indian brands are structured differently; this is reflected in their olfactive spectra. The essential oil from the Aden brand smells strongly balsamic with a pronounced terpenic note. On the other hand, a dry, woody and strongly balsamic note characterises the oil from the Eritrean brand; the odour is slightly lighter than that of the oil from the Aden variety.[12b] As stated earlier, Indian olibanum oil has a pleasant ethereal smell/sweet agreeable odour. These oils are best differentiated through gas chromatography.[3,12b] Table V lists the percentage concentration of the key ingredients.

From the analytical data in Table V it follows that by measuring the concentration of α-pinene, octyl acetate and α-thujene, we can identify the oil as from the Aden, Eritrean or Indian brand respectively.

Of interest is that CMA International tracks the quality of the gum-oleoresin by the α-pinene content: 37.2-41.7% for the oil from Grade I and 33.4% for the oil from ungraded material, though this constituent does not enjoy any particular character.[4]

Table V. Partial Compositional Data of Olibanum Oils

Compounds	Aden[12] %	Eritrean[12] %	Indian[25] %
α-pinene	43.0	4.6	7.73
α-thujene	-	-	61.36
sabinene	1.0	-	5.07
p-cymene	7.5	-	4.28
o-cymene	0.5	-	-
octanol	-	8.0	-
linalool	-	2.5	0.19
incensole (1)	-	2.4	-
campholenic aldehyde	1.5	-	-
octyl acetate	1.5	52.0	-
methoxytoluol hexyl acetate	-	1.5	-
incensole acetate	-	3.4	-
α-thujone	-	-	1.76
β-thujone	-	-	1.40
verbenone	6.5	-	-

Indian oil wins over the other oils by its richness in α-thujene—a versatile terpene; it is thus the best source of this hydrocarbon. If the oil lacks in "fineness" of odour, it is compensated by this treasure it holds.

While the olibanum oil is rather volatile, the resinoids from the gum-oleoresin are excellent fixatives. They are extracted from the substrate by application of appropriate solvents and contain resins, essential oil, plant pigments, waxes and other soluble matter[8]—"more heavy molecules of fixative value."[4]

Usually ungraded olibanum is the starting point and the reproducibility of the odour is good.[4,15] Useful solvents are benzene,[4,11,15] toluene,[3] hexane,[4,15] ethanol,[4,15] methanol,[29] acetone,[15] ethyl acetate,[3] and methylene dichloride.[15]

A typical industrial recovery of resinoid consists of filtering at low temperature of a concentrated (1:4) solution of olibanum in benzene, hexane or ethanol, cautiously evaporating at slightly reduced pressure.[4] Hot extraction pushes up the yield, but the resulting resinoids emanate slightly different odour from the counterparts of the cold process.[15]

Benzene extracts more of the resinoid with an average yield of approximately 60%: dark red/

orange/reddish brown, fairly solid/plastic/non-pourable, with 5-10% oil.[11,15]

Ethanol is an excellent menstruum for isolating the resinoid. Unlike hydrocarbon and chlorinated solvents, ethanol mingles with the moisture in olibanum, penetrates into it and, in consequence, functions more effectively. By stirring at room temperature, the gum-oleoresin is soluble up to 60-85%,[15,26,27] depending upon its age, quality and mesh size;[15] the insoluble part consists principally of calcium and magnesium arabinate with some bassorin.[27] However, ungraded material frequently gives turbidity in alcoholic solution; sometimes even black specks appear.[4] Coextraction of gummy and other foreign matter seems to be responsible for this behaviour; they tend to coagulate towards the end of desolventisation operation.[4] The isolate from *Boswellia* exudate by this route is termed "resin absolute"—a plastic mass of light amber colour and excellent solubility; this must not be confused with olibanum absolute which is prepared by alcoholic extraction of the resinoid. Marked by soft odour, reminiscent of frankincense, the alcohol soluble resinoid is on a par with true olibanum absolute obtained by a two-step process and has better fixative properties than the oil; in fact it is "one of the best fixatives employed in perfume work."[1]

The resin extracts from the Aden brand have a "warm balsamic odour, with a characteristic incense and somewhat woody note."[12b] On the other hand, the corresponding isolates from the Eritrean type, which are less stable than the Aden counterparts, have a woody, dry, flowery and somewhat metallic odour; a distinct balsamic note develops at the dryout stage. Thin layer chromatograms of these resinoids are exceptionally useful for their differentiation.[12b]

The answer to the solubility problem encountered in the extraction of olibanum with ethanol is to switch to the expensive two-step process which consists in the isolation of the resinoid with a hydrocarbon solvent, e.g., benzene or hexane followed by alcohol purification;[4] this leads, however, to olibanum absolute. It is to be noted that solvents other than benzene and hexane also serve for the initial step. In general, olibanum absolute is a solid/almost plastic mass with pale yellow colour and blessed with a fresh balsamic yet dry resinous odour enriched by a virgin green top note and is the celebrated fixative in the so-called oriental note.[15]

Above we have dealt with the solvent extractives from olibanum other than Indian. Earliest study of the recovery of resinoids of "high grade purity" from *Boswellia serrata* exudate involves extraction with ethanol and petroleum ether.[10] Petroleum ether gives excellent resin of good colour and texture—much paler than that obtained by the use of ethanol.[10,21] For the Soxhlet extraction, the solvent required is thrice the weight of the gum-oleoresin; and for the maceration process, the material is to be treated twice with as much as ten times its weight of solvent.[10]

More recently it has been reported that 90% ethanol dissolves 63% of the resin.[28] Workup of ethanol extract yields a viscous transluscent resinoid having a strong balsamic odour. The resinoid is stated to be similar in properties to one obtained from commercial olibanum of African origin.[22] We have, however, noted that the odour profile of the resinoid from the two sources are dissimilar.

Olibanum "is a representative of the historical conception of the mysterious wealth of the East."[30] No other gum-oleoresin has been the subject of as intensive research as has olibanum. For this, its resinoid, essential oil and various pyrolysates constituted the challenging substrates. Up to 1985, from these materials, 169 components were characterised;[11] later work positively identified 47 and tentatively 41 components.[11] These statistics cover only the findings pertaining to olibanum other than Indian. As it stands, the chemistry of the latter exudate is only partially known.[5-7,10,18,21,28,31]

Biological data on olibanum are available.[32] The oral LD_{50} in rats and the actual LD_{50} in rabbits exceed 5 g/kg.[33]

"Sweet, bitter and hot," *Boswellia serrata* gum-oleoresin is prescribed in indigenous medicine for the treatment of sore throat, cough, bronchitis, mouth sores, fevers, convulsions, diabetes, asthma, jaundice, chronic ulcers, diseased bones, troubles of the testis, menstrual and urinary disorders, gonorrhoea and syphilis.[34,35] In the form of an oily solution it has beneficial effect on the growth of the hair. Alcoholic extract of the defatted gum-oleoresin displays antiarthritic activity.[7]

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