

skillfully employed, oil of opopanax produces peculiar but very attractive tonalities, which harmonize with myrrh, olibanum, sandal, vetiver, and patchouly.

The oil was formerly employed as an antispasmodic and deobstruent, but is now rarely used in pharmacy.

Resinoid of opopanax is a very useful fixative. Its odor is similar to that of the oil, but less pronounced, imparting strength and lasting tonalities to perfume compounds.

### OIL OF OLIBANUM

(Oil of Frankincense)

*Essence d'Oliban*      *Aceite Esencial Olibano*      *Weihrauchöl*  
*Oleum Olibani*

**Botanical Origin.**—Olibanum, the frankincense of the ancients, is derived from *Boswellia carterii* Birdw. and other species of the genus *Boswellia* (fam. *Burseraceae*), small trees growing in Somaliland and southeast Arabia. The regions of production in the order of their importance are: Italian Somaliland, British Somaliland, and French Somaliland, the latter producing only very small quantities of frankincense.

The bark of the tree contains schizogenous gum-oleoresin reservoirs. To collect the gum the natives incise the bark, causing exudation of a white emulsion, which after a time congeals into yellowish tears and drops. The tears can be picked off the bark or from the ground. The gum is collected all year round, except in the rainy, monsoon months (from mid-June to September), when the natives are busy with agricultural work.

**Producing Regions.**—Prior to World War II Italian Somaliland levied an export duty on all frankincense, except that destined for Italy. For this reason Trieste was the leading port for transshipping gum olibanum to other parts of Europe and to the United States. The product of French Somaliland went mostly to Marseilles, while that of British Somaliland and parcels smuggled out of Italian Somaliland were shipped on Arabian dhows to Aden, main port of Arabia.

With the outbreak of the war, Basra, on the Persian Gulf, became a transshipping port of gum olibanum to the United States, and a few parcels seem to have reached ports of the eastern Mediterranean, probably on small coastal steamers or native sailing craft.

**Grading of the Gum.**—In Aden the gum was assorted into three qualities:

1. Grade I (tears): The best and most carefully selected grade, of white color, employed chiefly in church or temple incense.
2. Grade II (reddish): A mixed white and reddish quality, which contains also some particles of bark.
3. Grade III (dust and siftings): Because of its low price, the most suitable quality for oil distillation.

By assorting the crude gum about 33 per cent of each of the three grades is obtained. The unassorted gum, as it comes from the producing regions, might be considered another, or fourth quality.

**Properties of the Gum.**—Gum olibanum consists of yellowish, somewhat translucent, roundish tears, irregular reddish lumps or agglutinated masses. Because of friction the tears are usually covered with a whitish powder; their texture is brittle, the fracture dull and waxy. The odor is aromatic, balsamic, and the taste slightly bitter and acrid. When triturated with water, olibanum forms a milky emulsion; alcohol dissolves about 75 per cent of the gum. The alcoholic solution, after filtration, can be concentrated, preferably *in vacuo*, and yields the so-called resinoid of olibanum. This is a transparent, viscous, almost solid mass, soluble, however, in high-proof alcohol and essential oils.

**Yield of Oil.**—The essential or volatile oil can be extracted from the gum by steam distillation, the yield varying from 5 to 9 per cent. Distilling gum olibanum of own importation in Southern France (Seillans, Var), the author obtained oil yields ranging from 6 to 7 per cent.

**Physicochemical Properties.**—The oil possesses an agreeable, balsamic odor, with a slight lemon-like by-note.

According to Gildemeister and Hoffmann,<sup>1</sup> the properties of olibanum oil vary within the following limits:

Specific Gravity at 15°	0.872 to 0.892
Optical Rotation	The oils distilled prior to 1903 were laevorotatory, up to $-17^{\circ}$ ; since then the oils are dextrorotatory, up to $+35^{\circ}$
Refractive Index at 20°	1.471 to 1.482
Acid Number	Up to 3
Ester Number	5 to 16
Ester Number after Acetylation	28 to 48
Solubility	Soluble in 3.5 to 6 vol. of 90% alcohol, sometimes with slight turbidity

In recent years the properties of olibanum oil have undergone certain changes. The cause is not clear; perhaps the gum is collected from a dif-

<sup>1</sup>"Die Ätherischen Öle," 3d Ed., Vol. III, 158.

ferent plant variety, or in regions which previously had not been exploited, or perhaps it reaches the market faster.

Chris<sup>2</sup> reported on an oil of somewhat abnormal constants. The specific gravity and the alcohol content were very high, the solubility good, the odor fine.

Specific Gravity at 15°.....	0.9404
Optical Rotation at 20°.....	+44° 06'
Refractive Index at 20°.....	1.4849
Acid Number.....	2.52
Ester Number.....	12.63
Ester Number after Formylation....	165.53
Solubility.....	Soluble in 1 vol. of 80% alcohol

In 1939 Schimmel & Co.<sup>3</sup> reported that the constants of olibanum oils (yield 3.3 to 10.4 per cent) had changed, during the previous years, and suggested that the limits, therefore, should be modified as follows:

Specific Gravity at 15°.....	0.8632 to 0.8862
Optical Rotation.....	-26° 3' to +34° 37'
Refractive Index at 20°.....	1.46934 to 1.47740
Acid Number.....	Up to 1.9
Ester Number.....	3.7 to 16.8
Ester Number after Acetylation.....	21 to 47.6
Solubility.....	Soluble in 4 to 6.2 vol. and more of 90% alcohol

Oils distilled within recent years by Fritzsche Brothers, Inc., New York, from imported gum olibanum had the following properties:

Specific Gravity at 15°/15°.....	0.875 to 0.895, in one case 0.917
Optical Rotation.....	+25° 2' to +34° 50'
Refractive Index at 20°.....	1.4710 to 1.4784
Acid Number.....	1.9 to 2.4
Saponification Number.....	4.7 to 30.0
Solubility at 20°.....	Soluble in 0.5 to 5 vol. and more of 90% alcohol

Early in 1950, the same company had occasion to examine several lots of imported gum olibanum, of excellent appearance, which, on distillation, yielded *laevo*-rotatory oils (-6° to -11°). The odor of these oils showed a characteristic phellandrene note. Nothing is known as yet as to the reason for this variation.

<sup>2</sup> *Parfums France* 15 (1937), 147.

<sup>3</sup> *Ber. Schimmel & Co.* (1939), 88.

**Chemical Composition.**—The chemistry of the laevorotatory type of olibanum oil, which used to be produced prior to 1903, has not been thoroughly investigated, except perhaps in regard to the terpenes present in that oil. The following hydrocarbons have been identified:

*l*- $\alpha$ -Pinene. First called "olibene" by Kurbatov,<sup>4</sup> this terpene was identified as *l*- $\alpha$ -pinene by Wallach.<sup>5</sup> It occurs in the fraction b. 157°–160° of the oil and yields a nitrosochloride which, on boiling with alcoholic potassium, is readily converted into nitrosopinene m. 130°.

Dipentene. Wallach<sup>5</sup> identified dipentene in the fraction b. 177°–179° by preparing the tetrabromide m. 124°–125°.

Phellandrene. According to Gildemeister and Hoffmann,<sup>7</sup> laevorotatory oil of olibanum gives the typical phellandrene reaction with sodium nitrite and glacial acetic acid.

Cadinene. Observed by Wallach<sup>5</sup> in the high boiling fractions of laevorotatory olibanum oil.

So far as the dextrorotatory type of olibanum oil (produced since 1903) is concerned, its chemical composition is better known, particularly in regard to the oxygenated components. Years ago, Haensel<sup>8</sup> reported that the oil contains a strongly laevorotatory alcohol  $C_{20}H_{40}O$ , which he named "olibanol." Fromm and Autin,<sup>10</sup> and Fromm and Klein<sup>11</sup> described an  $\alpha$ -,  $\beta$ -, and  $\gamma$ -"olibanol" of the molecular formula  $C_{16}H_{32}O$ , the configuration of which they could not elucidate. More recently Blumann and Schulz<sup>12</sup> arrived at the conclusion that the "olibanol" of Fromm and Autin is in reality a mixture of verbenone, verbenol, and some other terpene alcohols, including most likely *d*-borneol. According to Blumann and Schulz<sup>12</sup> the designation "olibanol" can be maintained only for the alcohol  $C_{20}H_{40}O$  originally described by Haensel (see above).

In the light of these and earlier findings, the dextrorotatory type of olibanum, produced since 1903, contains the following constituents:

*d*l- and *d*- $\alpha$ -Pinene. Identified in the fraction b. 156°–157° of the oil by Schimmel & Co.<sup>10</sup> who prepared the nitrosochloride and the nitropiperidine m. 118°. Oxidation yielded pinonic acid b<sub>7</sub> 170°–175°; the optically active acid melted at 69°–70°, the inactive at 104°.

<sup>4</sup> *Liebigs Ann.* **173** (1874), 1.

<sup>5</sup> *Ibid.* **232** (1889), 100.

<sup>6</sup> *Ibid.*, 101. *Cl. Ber. Schimmel & Co.*, April (1914), 96.

<sup>7</sup> "Die Atherischen Öle," 3d Ed., Vol. III, 159.

<sup>8</sup> *Liebigs Ann.* **271** (1892), 297.

<sup>9</sup> *Chem. Zentr.* (1908), I, 1837; (1908), II, 1437.

<sup>10</sup> *Liebigs Ann.* **401** (1913), 253.

<sup>11</sup> *Ibid.*

<sup>12</sup> *Ibid.* **425** (1921), 215.

<sup>13</sup> *Ber. Schimmel & Co.*, April (1914), 96.

<sup>14</sup> *Ibid.* **478** (1930), 303.

**Chemical Composition.**—The chemistry of the laevorotatory type of olibanum oil, which used to be produced prior to 1903, has not been thoroughly investigated, except perhaps in regard to the terpenes present in that oil. The following hydrocarbons have been identified:

*l*- $\alpha$ -Pinene. First called "olibene" by Kurbatov,<sup>4</sup> this terpene was identified as *l*- $\alpha$ -pinene by Wallach.<sup>5</sup> It occurs in the fraction b. 157°-160° of the oil and yields a nitrosochloride which, on boiling with alcoholic potassium, is readily converted into nitrosopinene m. 130°.

Dipentene. Wallach<sup>6</sup> identified dipentene in the fraction b. 177°-179° by preparing the tetrabromide m. 124°-125°.

Phellandrene. According to Gildemeister and Hoffmann,<sup>7</sup> laevorotatory oil of olibanum gives the typical phellandrene reaction with sodium nitrite and glacial acetic acid.

Cadinene. Observed by Wallach<sup>8</sup> in the high boiling fractions of laevorotatory olibanum oil.

So far as the dextrorotatory type of olibanum oil (produced since 1903) is concerned, its chemical composition is better known, particularly in regard to the oxygenated components. Years ago, Haensel<sup>9</sup> reported that the oil contains a strongly laevorotatory alcohol  $C_{20}H_{44}O$ , which he named "olibanol." Fromm and Autin,<sup>10</sup> and Fromm and Klein<sup>11</sup> described an  $\alpha$ -,  $\beta$ -, and  $\gamma$ -"olibanol" of the molecular formula  $C_{18}H_{34}O$ , the configuration of which they could not elucidate. More recently Blumann and Schulz<sup>12</sup> arrived at the conclusion that the "olibanol" of Fromm and Autin is in reality a mixture of verbenone, verbenol, and some other terpene alcohols, including most likely *d*-borneol. According to Blumann and Schulz<sup>12</sup> the designation "olibanol" can be maintained only for the alcohol  $C_{20}H_{44}O$  originally described by Haensel (see above).

In the light of these and earlier findings, the dextrorotatory type of olibanum, produced since 1903, contains the following constituents:

*dl*- and *d*- $\alpha$ -Pinene. Identified in the fraction b. 156°-157° of the oil by Schimmel & Co.,<sup>14</sup> who prepared the nitrosochloride and the nitropiperidine m. 118°. Oxidation yielded pinonic acid b. 170°-175°; the optically active acid melted at 69°-70°, the inactive at 104°.

<sup>4</sup> *Liebigs Ann.* **173** (1874), 1.

<sup>5</sup> *Ibid.* **252** (1889), 100.

<sup>6</sup> *Ibid.*, 101. *Cl. Ber. Schimmel & Co.*, April (1914), 96.

<sup>7</sup> *Die Ätherischen Öle*, 3d Ed., Vol. III, 159.

<sup>8</sup> *Liebigs Ann.* **271** (1892), 297.

<sup>9</sup> *Chem. Zentr.* (1908), I, 1837; (1908), II, 1437.

<sup>10</sup> *Liebigs Ann.* **401** (1913), 253.

<sup>11</sup> *Ibid.*

<sup>12</sup> *Ibid.* **425** (1921), 213.

<sup>14</sup> *Ber. Schimmel & Co.*, April (1914), 96.

<sup>13</sup> *Ibid.* **478** (1930), 303.