On the Isolation of Oleoresin Black Pepper by Steam Distillation-Cum-Solvent Extraction and Tailoring of Oleoresin

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The manufacture of black pepper oleoresin through homogenization of pepper oil obtained by steam distillation and the solvent extract of the distillation residue is a versatile procedure. Broadly speaking, this "two-step" process may be regarded as a "synthesis" of the oleoresin from its own "ingredients."

Spice/Oleoresin Oil

One of the prerequisites for successful oleoresin production is the availability of pepper oil. By steam distilling coarse, ground or flaked pepper berries, we collect the oil. Depending on the spice, the yield composition and aroma profile of the oil vary. Whereas fresh hulls of pepper[1] and low-priced light pepper[2,3] can be used for distillation materials, data is lacking on the deoiled residues originating therefrom with respect to their solvent extractives, and we do not consider them acceptable as substrates for oleoresin production. What is economically viable for exploitation is the best of "half pepper" (berries of 4½ to 5 months maturity) rich in piperine and essential oil.[4]

It is interesting to compare the oils obtained by steam distillation of the spice with the oil produced by solvent extraction.[5] The distilled spice oil has about twice the amount of low-boiling terpenes and only two-thirds the amount of sesquiterpenes as compared to their amounts in the extracted oil.[5] Steam distillation of the spice, it is stated, takes *ca* 30 hours. Exhaustive distillation is required for isolating the total oil, but this is "commercially uneconomical and impractical."

Fortunately, the total distilled spice oil with high proportion of low-boiling monoterpenes, $C_{10}H_{16}$ fails to entice the "nose" of flavor/perfumery houses. For acceptance of oil, a "topping-off" process—partial elimination of monoterpenes—is necessary. During distillation, the oil may be divided, for example, into three parts: a) initial fraction mainly of $C_{10}H_{16}$ hydrocarbons, b) intermediate cut with minimum amount of sesquiterpenes, and c) heavy oil rich in sesquiterpenes. Certain proportion of the three fractions are pooled in a manner to give an upgraded oil with acceptable aroma profile.

When steam distillation of the spice is not pushed deliberately to the end, a good portion of the heavy oil is retained in the residue from which it is recovered by solvent extraction. A finished oleoresin can be built up from the three distillation fractions, individually or collectively, together with the extracted oil. More than half the quantity of distilled pepper oil produced in India appears to be used for oleoresin preparation.[6]

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Table I. Volatile Oil-Piperine Concentration in Oleoresins from Different Black Pepper*(14)

Entry	Pepper Variety	Oleoresin Percentage in Volatile Oil v/w	Oleoresin Percentage in Piperine w/w
1	Brazilian	29-33	35-46
2	Ceylon (Sri Lanka)	26-31	47-54
3	Lampong	29-34	43-48
4	Malabar	32-44	42-53
5	Saravak	31-37	43-47
6	Tellichery	30-41	39-46

* In runs 1-6, solvent for oleoresin extraction and method of piperine determination are not disclosed.

Table II. Volatile Oil-Piperine Concentration in Oleoresins from Different Black Pepper*(15)

Entry	Pepper Variety	Oleoresin Percentage in Volatile Oil v/w	Oleoresin Percentage in Piperine w/w
7	Malabar black garbled	27.0	43.8(56.4)
8	Malabar black ungarbled	20.1	39.2(50.1)
9	Malabar light	26.3	35.3(42.9)

* In runs 7-9, oleoresin extraction is with EDC; piperine value evaluated spectrophotometrically are given with the Kjeldahl equivalent in brackets.

It is up to the ingenuity and experience of the manufacturer to resort to permutation and combination of black pepper of different origin and maturity and deoiled residue, in order to deliver oleoresins fulfilling customers' wide flavor requirements.

Solvent Extractive

Piperine is in the "solubles" extracted from the residue after distillation. Piperine constitutes the overwhelming proportion of the alkaloid mixture that gives the pungent flavor to black pepper.[7] Piperine is sensitive to heat so that steam distillation provokes its decomposition and additional degradation occurs during desolventization.[8-13]

In our industrial operation, we have noticed an appreciable drop in the piperine level in the distillation residue as compared to its concentration in the parent spice.[11] Viewed from this angle, loss of piperine is more in the "two-step" process than in the "one-step" solvent extraction of oleoresin. Nevertheless, we have exploited the "two-step" process systematically, to fulfill the requirements of volatile oil-piperine ratio. Irrespective of the route

Table III. Volatile Oil-Piperine Concentration in Oleoresins in Commercial Samples and in Independent Standards

Specifications/ Standardized Oleoresins	Volatile Oil Percentage v/w	Piperine Percentage w/w UV Method	Piperine Percentage w/w Kjeldahl Equivalent
EOA (240)	15-35	-	55
EE-S-00645a (ARMY-GL)	15	-	55
FCC	15-35	36	-
IS-5832 (1984)	18-35	40	50
FD 3269*	15-17	50	55
FD 5004*	14.3-15.8	40.4-44.6	44.5-49
FD 5007*	18-20	50-55	55-60
FD 3759	16.5	56	61
Oleoresin Black Pepper FCC Indian**	23-30	39-44	53-57
Fritzbro(R) Black Pepper** Soluble	12-15	18-22	26-29
	25-30	42-44	-
	10	42	-
	10	50	-
Synthite	13	46	-
	20	50	-
	20	55	-

* Standardized Oleoresins, Bush Boake Allen
** The Oleoresin Handbook, Fritzsche D&O, 3rd ed. 1981, p 35

Table IV. Constants of the Volatile Oil from the Oleoresins

Properties	EOA	IS
Optical rotation	-1° to -23°	-1° to -25° (30°C)
Refractive index	1.4790-1.4890	1.473-1.483 (20°C)

adopted for capturing oleoresin, piperine is the pivotal entity and it must be protected since its loss adversely affects the overall economy of the process and quality of the product.

Volatile Oil-Piperine Framework

For a better appreciation of the tailoring of oleoresin, it is instructive to look at the volatile oil-piperine status from different sources (Tables I and II) and disclosed in Specifications and Standardized Oleoresins (Table III).

The quality determinants of the oleoresin are dictated by the equations of the isolation process and "tricks of the trade" and these have led to the emergence of Standardized Oleoresins. As can be seen, the range of the concentration of volatile oil and piperine is very wide. Additionally, EOA 240 and IS 5832 specifications stipulate optical rotation and refractive index for the volatile oil recovered from oleoresin as given in Table IV. These con-

Table V. Analytical Data on Whole Pepper on Oleoresin, Supernatant Fraction *and Piperine Residue*

Material	Percentage	
	Volatile Oil	Piperine
Oleoresin of whole black pepper	33.0	39.0
Supernatant fraction	48.5	13.5
Piperine residue	2.7	90.0

stants are of little intrinsic value in the assessment of the extractive. Strictly speaking of the qualifications for oleoresins, the most important are the volatile oil-piperine level and agreeable organoleptic profile in keeping with the users preference. From these considerations, it is clear that exceptional technical expertise is required to manufacture oleoresin currently in demand.

Tailoring of Oleoresins

Steam distillation-cum-extraction is a versatile route for manufacturing Standardized Oleoresins. This is accomplished by mixing the essential oil and solvent extractive in the required proportion. These isolates do not need to be from the same source.[16] The choice is made to meet specific technical requirements, organoleptical profile and prices, and there is nothing unethical in this as long as deception is not impiled.[17]

Extraction of whole pepper normally yields oleoresin with 15% to 27% essential oil and 35% to 55% piperine,[13,17] though Zieghler[14] quotes 34% volatile oil and 46.5% piperine in oleoresin from Malabar black pepper using boiling acetone. A combination of whole pepper and deoiled substrate produces an extractive with better piperine content but with lower quantum of oil which can be augmented by pepper oil from other sources if necessary. That being the case, how can the oleoresin from solvent extraction of whole pepper be engineered to supplement the two-step process in the preparation of Standardized Oleoresins? The answer to this is partly embodied in the patent granted to Zeighler.[14]

Piperine is not very soluble in oleoresin of whole pepper. By centrifugation, substantially all of the undissolved piperine is retrievable as a dry friable solid residue leaving a dark oil fluid, referred to as supernatant fraction containing some piperine.[14] The liquid oil fraction consists essentially of liquid volatile oil, liquid non-volatile oil and also dissolved piperine. Table V gives a typical analysis of these components.[14]

A slightly different approach to harvesting piperine is to permit the alkaloid to crystallize from the concentrated oleoresin in the presence of the

menstruum and then collect it by centrifugation. If necessary, the crude piperine is upgraded by washing with hexane,[18] and can be purified further by recrystallization, eq., from ethanol.

Moreover, by subjecting the supernatant fraction to fractional distillation at high vacuum and lowest possible temperature, it is upgraded in "high boilers" with concurrent recovery of monocyclic terpenes, $C_{10}H_{16}$.

Using these raw materials—the solvent extractive, supernatant fraction, distilled pepper oil, monocyclic terpenes, piperine factor and diluent—the industry constructs oleoresins of wide variety tailored for many different applications.

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