

Oil from *Pinus Gerardiana*— Chilgoza Oil. Part I.

By S. D. HARDIKAR.

Chilgoza is the fruit of *Pinus Gerardiana*, Wall. It is a moderately sized, ever-green tree belonging to the natural order *Coniferæ* and is indigenous in the dry interior valleys of North-Western Himalaya, generally between 6,000—10,000 ft. from Kunawar westwards and in the territory of Garwhal. This tree is also grown in Afganistan and Persia. In Persia, the tree is called *Sus*, and in Afganistan it is termed as *Chil* and *Zan-ghozeh*, and hence the seed is generally known in India by the name of *Chilgoza*.

The chief product of this tree is the almond-like seed contained in the cones. The cones ripen in October, are plucked before they open, and heated to make the scales expand. The seed—the *Chilgoza*—is irregularly cylindrical about 1 inch in length. The shell is fairly stiff, and can be easily removed from the kernel. The kernels have a very thin upper covering, and are edible.

In Ayurvedic system of medicine, the seeds are considered as an anodyne, stimulant, and are also useful in chronic rheumatic affections. The oil extracted from the seeds is highly esteemed for its stimulating and healing powers when applied as adressing to wounds, ulcers, etc., and is also recommended to be employed as an external application in the diseases of the head. Since no work appears to have been done on the composition of the oil, the author has, therefore, undertaken a detailed chemical study of the seed as well as its oil.

Analysis of the Kernels from the Seed.

The weight of 100 seeds is on an average 30.4 gm. The kernel forms about 67.5 per cent of the seed, the husk on an average being 32.5 per cent. The kernels contain about 50.0 per cent. of the oil,

while the same calculated on the whole seed as such comes to about 33·7 per cent of the oil. The yield of the oil on pressing was found to be only 34·0 per cent.

Table I gives the analysis of the kernels.

TABLE I.

				Observers.	
				Author.	Church.*
Water	...	..		7·51 %	8·7 %
Proteins	.	..		15·87 %	13·6 %
Fat	.	...		49·91 %	51·3 %
Fibre	...	.		2·22 %	0·9 %
Ash	...	..		2·88 %	3·0 %
Carbohydrates		...		21·61 %	22·5 %
Food units	.			186	...
Nutrient ratio	..	...		1 : 8·6	

Analytical Constants of the Oil.

The oil used for examination was obtained by pressing the crushed seeds in a juice extractor made of zinc. The oil is clear, and is of a pale yellowish colour. Grimme (*Agri. Ledger*, 1911-12, No. 5, p. 167) has also determined a few constants of the oil, and the values are given in Table II together with those obtained for the pressed oil examined in our laboratory.

TABLE II

				Observers.	
				Author.	Grimme.
Specific gravity	...	...		0·9144 at 32°C	0·9307 at 15°C
Refractive index	...	...		1·4709 at 32°C	..
Acid value	..	...		3·87	1·6
Saponification value	...	...		192·4	191·3
Acetyl value	...	...		4·07	...
Iodine value	.	..		121·3 (Hubl's)	118·0 (W ₁₁ 's)
Unsaponifiable matter	...	..		0·50	..
Iodine value of the above	...	...		68·4	...
Reichert-Meissl value	..	..		0·33	...
Hebner value (fatty acids)	...	..		95·01	91·46

Table III gives the analytical constants of the fatty acids separated from the oil.

* *Pharmacographia Indica*, 1893, 3, 380

TABLE III.

			Observers.	
			Author.	Grimme.
Specific gravity	..	...	0.8952 at 30°C.	...
Index of refraction	...	...	1.4622 at 30°C.	..
Iodine value	...	...	127.7 (Wij's)	125.0 (Wij's)
Neutralisation value	...	...	200.2	196.7
Mean molecular weight	-	...	280.2	285.2

Composition of the Oil.

The saturated and the unsaturated acids in the fatty acid portion were estimated by (i) the lead-salt-ether method, and (ii) by Twitchell's lead alcohol method (*J. Ind. Eng. Chem.*, 1921, **13**, 806). In the experiment with the latter method 10 gm. of the oil were saponified with alcoholic potash, the dry potassium soap extracted with ether to remove unsaponifiable matter, and then decomposed with hydrochloric acid. From the portion of the fatty acids thus obtained 8 gm. were dissolved in 200 c.c. of 95% alcohol, heated to boiling, and to this was added a boiling solution containing 5 gm. of lead acetate in 100 c.c. of 95% alcohol. The mixture was kept at room temperature overnight. The precipitate was then washed with cold 95% alcohol until the washings were free from lead. The precipitated lead salts were then redissolved in 100 c.c. of boiling 95% alcohol and 0.5 gm. of acetic acid, and the solution cooled overnight. The precipitate was then removed, washed with 95% alcohol, washed from the filter with ether, and decomposed with dilute nitric acid. The ethereal solution containing the solid fatty acids was then washed with distilled water in a 100 c.c. separator until the washings were no longer acid to methyl orange. The ether was then evaporated, the residue dried and weighed.

Table IV gives the percentages of the saturated and the unsaturated acids as estimated by the two methods.

TABLE IV.

	Percentage of saturated acids.	Percentage of unsaturated acids.
Lead salt-ether method	6.57	93.43
Twitchell's method	4.92	95.08

The iodine value of the portion of saturated acids obtained by method (i) was found to be 49.4. This indicates the presence of a

little unsaturated acid being left in the sample. The portion of the saturated acids prepared by the Twitchell's method was pure white, its m.p. being $53^{\circ}5$.

Unsaturated Acids.

The unsaturated acids were examined by means of their bromine additive products as recommended by Jamieson and Baughman (*J. Am. Chem. Soc.*, 1920, **42**, 1198).

The unsaturated acids for this work were prepared according to the method of Eibner and Muggenthalor (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats, and Waxes," 5th edition, Vol. I, p. 573) according to which 2 gm. of the unsaturated acids were dissolved in 50 c. c. of dry ether, cooled in ice to 0° ; bromine was then slowly added, and the mixture allowed to stand for two hours at about -10° . At this stage, no precipitate insoluble in ether was obtained, which indicates that no linolenic acid is present in the unsaturated portion of the acids (the hexabromo-derivative of linolenic acid is insoluble in ether). The excess of bromine was then removed from the ethereal solution by washing it with an aqueous solution of sodium thiosulphate in a separator. All traces of water were then removed from the washed ethereal solution by means of anhydrous sodium sulphate, and the ether was removed by distillation. The residue was then taken up with 100 c. c. of petroleum ether (b. p. $60-80^{\circ}$), and cooled in an ice-box for overnight. A precipitate of linolic tetrabromide was obtained.

From the above, it is clear that in the portion of the unsaturated acids, linolenic acid is absent, while linolic and oleic acids are present. As we were short of bromine in our laboratory to repeat the above quantitatively for ascertaining the percentages of the tetrabromide and the dibromide, the percentages of the linolic and the oleic acids in the unsaturated portion were arrived at from an estimation of the iodine value of the unsaturated acids. The iodine value of the above was estimated both by Hubl's as well as Wij's method. Both the methods gave nearly the same value, the mean being 129.2 .

For the purpose of calculating the percentages of linolic and oleic acids from the iodine value of the unsaturated portion, the following equations have been used.

$$x + y = 100.$$

$$90.07x + 181.42y = 100 I.$$

where x = per cent. of oleic acid in the unsaturated portion;
 y = per cent. of linolic acid in the unsaturated portion;
 and I = Iodine value of the unsaturated portion.

Table V gives the percentages of oleic and linolic acids calculated from the above equations.

TABLE V.

			Percentage in the unsaturated portion.	Percentage in the original oil.
Oleic acid	...	...	57.2	54.4
Linolic acid	...	...	42.8	40.7

Saturated Acids.

The saturated acids for the purpose of the examination were prepared according to Twitchell's method. The percentage of the saturated acid portion in the oil being only about five, more than a kilogram of the oil had to be treated for the preparation of the saturated acids in order to get a sufficient quantity of the material for further analytical work. Thirty-five gm. of saturated acids were obtained from one kg. of the oil.

The saturated acids (35 g.) were converted into methyl esters by the Fischer-Speier process by boiling for four hours with five times its weight of methyl alcohol containing 4 per cent. of dry hydrogen chloride, pouring into water, and then extracting with ether.

Summary and Conclusions.

The oil is a non-volatile fixed oil belonging to the class of semi-drying oils. Nearly 95 per cent. of the oil consists of glycerides of unsaturated fatty acids, namely oleic and linolic, the remaining 5 per cent. being the glycerides of saturated fatty acids. Further investigation on the saturated acid portion is in progress.

In conclusion, I wish to express my gratitude to Mr. Bodhraj Sobti, M.Sc. for the kind interest he took in this investigation.

