# CHEMICAL EXAMINATION OF THE FIXED OIL DERIVED FROM THE SEEDS OF LALLEMANTIA ROYLEANA BENTH. OR TUKHM-I-MALANGA

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LALLEMANTIA ROYLEANA BENTH. commonly known as Tukhm-i-malanga, is an annual herb belonging to the Natural Order of Labiatæ. It is cultivated throughout Northern India for the sake of its highly medicinal and mucilaginous seeds which are widely used as remedial agents in various ailments and also as an added palatable ingredient in cooling drinks and 'sherbets', chiefly by the Muslims.

The seeds are about 1/12 inch in length, 1/16 inch in breadth, dark-brown to black in colour, smooth, three angled and tapering towards the umbellicus which is marked by a tiny white spot. When moistened with water, the seeds become coated with a voluminous and transluscent mucilage. The taste of the moistened seed is bland and somewhat spicy.

According to Day,<sup>1</sup> a poultice of the moistened seeds is found useful in abcesses and inflammations. They are considered to be cephalic, astringent, cardiac tonic and carminative by Dymoch.<sup>2</sup> Kirtikar and Basu<sup>3</sup> describe the seeds as cooling and sedative.

The chemical constitutents of the seeds which impart to it the medicinal properties described above are not known, and the seeds do not seem to have been chemically examined as yet. In the present investigation the seeds have been found to contain 10.8 per cent. of a fixed oil, and one should not be surprised if this oil is responsible for their medicinal properties.

### Experimental

5 Kilos of the crushed seeds were extracted by hot benzene in a large extraction flask, and after removal of the solvent by distillation, the crude fixed oil was left behind as a bottle green and somewhat opalescent liquid. It was purified by treatment with animal charcoal and Fuller's earth and was ultimately obtained as a transparent light green oil. On further examination it was found to be a semi-drying oil having the following physical and chemical constants:

TABLE I

Physical and Chemical Constants of the Oil

Specific gravity at 32° C	• •	0.9162	
Refractive index at 30°	• •	1.4212	
Remactive index at 30	C.	• •	1 7212
Acid value	• •	• •	2.07
Saponification value	• •		191-20
Acetyl value	• •	• •	Nil
Hehner value	• •	••	89-3
Iodine value	• •		108.5
Unsaponifiable matter			0.28%

250 Grams of the oil were saponified in the usual manner with alcoholic caustic potash and the soap thus formed freed from the solvent and dried in the steam oven. It was then extracted exhaustively with ether in order to recover the unsaponifiable matter. After this it was decomposed with dilute hydrochloric acid in presence of petroleum ether and the petroleum ether solution of the fatty acids freed from the solvent by distillation. The fatty acids obtained in this way had the following physical and chemical constants:

TABLE II

Physical and Chemical Constants of the Mixed Fatty Acids

Consistency	li	quid at 20° C.
Specific gravity at 22° C	• •	0.9128
Refractive index at 30° C.	• •	1 · 4102
Neutralisation value	• •	202
Mean molecular weight	• •	277.9
Iodine value	• •	122

The mixture of fatty acids were then separated into saturated and unsaturated acids by Twitchell's<sup>4</sup> lead salt method and the following table gives the percentage, iodine value and the mean molecular weight of the saturated and unsaturated acids:—

TABLE III
Saturated and Unsaturated Acids

Acid	% in mixed acids	I.V.	Neutral- isation	Mean M. W.
Saturated	14.3	10 · 5	211.5	264.8
Unsaturated	85.7	140 · 6	199.7	280.3

Examination of the unsaturated acids.—The constitutents of the unsaturated acids were determined by the method originally suggested by Eibner

and Muggenthaler<sup>5</sup> and later on worked by Jameson and Baughman.<sup>6</sup> According to this method the bromine addition products of the unsaturated acids were prepared and separated as follows: -To a known weight of the unsaturated acids dissolved in dry ether and cooled to  $-10^{\circ}$  C. bromine was added slowly until it was in slight excess. During the process of bromination the temperature was not allowed to rise above -5° C. The mixture was then allowed to stand at  $-10^{\circ}$  C. for two hours. The hexabromide of linolenic acid that was precipitated was filtered off and washed with dry ether, dried and weighed. The melting point of the hexabromide was found to be 176° C. From the weight of the hexabromide and the knowledge of the percentage of bromine in it, the weight of linolenic acid was calculated and its percentage determined. The ethereal solution consisting of the filtrate and washings from the above was treated with an aqueous solution of sodium thiosulphate in a separating funnel and the excess of bromine was thus removed. The ethereal solution was then dehydrated with anhydrous sodium sulphate and the ether removed completely by distillation. The residue was taken up with about 250 c.c. of dry petroleum ether, and the solution kept overnight in a refrigerator. On standing, no precipitate was obtained showing the complete absence of linolenic acid hexabromide. The petroleum ether solution was concentrated to about 50 c.c. by distillation and again kept in the refrigerator, but this time also no precipitate was obtained. The petroleum ether was then completely distilled off, the residue weighed and its bromine content determined by the usual methods. The percentage of bromine was found to be 36.4 thereby showing the complete absence of linolenic acid. In fact the residue was completely oleic acid dibromide. From this the weight of oleic acid was calculated. The following table shows the results of the examination of the bromine addition products:

## TABLE IV Examination of the Unsaturated Acids

Weight of the acids taken		• •	• •	• •		 15·0 gn	n.
Weight of linolenic hexabromide	• •	• •		• •	• •	 12.09 ,	,,
Percentage of bromine in the above	е	• •	••	• •	• •	 63.6 ,,	
Melting point of the hexabromide	• •	• •	• •	• •	• •	 176° C.	
Weight of linolenic acid			• •	• •	• •	 4.56 gm	n.
Weight of residue	• •	• •	••	• •	• •	 16.4 ,,	
Percentage of bromine in the above	В		••	• •	• •	 36•4	
Weight of oleic acid	• •	• •	• •			 10·4 gm	n.
Percentage of linolenic acid in the	unsaturat	ted acids	• •	••	• •	 30.4	
Percentage of linolenic acid in the	mixed ac	cids	• •	• •	• •	 26.1	
Percentage of oleic acid in the unsa	turated a	acids	• •	• •	••	 69.3	
Percentage of oleic acid in the mixe	ed acids	• •	• •	• •	••	 59 • 4	

The proportions of oleic and linolenic acids in the unsaturated acids were also determined from the iodine value of the mixture and they practically coincided with those found from the bromination products.

Examination of the saturated acids.—For the separation of the constituents, the mixed saturated acids were converted into their methyl esters by the usual methods, and the esters distilled under reduced pressure (6.5 mm.). Two main fractions (Nos. 1 and 2) distilling at 170–75° C. and 175–80° C. were obtained and from 17 gm. of the ester taken for distilliation, the weight of the fractions were 11.02 and 5.6 gm. respectively. The following table shows the results obtained at a glance:

TABLE V

Examination of the Saturated Acids

Fract. No.	I.V.	Mean M.W.	Palmitic acid		id Stearic acid		Unsaturated acid	
,			gm.	%	gm.	%	gm.	%
1	3.4	271	10.1	90·4	0.2	1.6	0.3	2.3
2	21.9	292.1	1.1	20.0	3.38	59.6	0.86	15.4
		Total	11.2		3 · 58		1.16	

The percentage of various acids in the mixed saturated acids is given below:

TABLE VI

Acid	}	Percentage in the saturated acids	Percentage in the mixed total acids
Palmitic	••	70.5 .	10.09
Stearic		22.6	3 · 23
Unsaturated	••	7.2	1.03

Examination of the unsaponifiable matter.—The unsaponifiable matter obtained from the soap was found to be ordinary sitosterol, melting at 133-34° C. The acetyl derivative melted at 120° C.

### Summary and Conclusions

The fixed oil from the seeds of Lallemantia royleana Benth. has been isolated in an yield of 10.8 per cent. by extraction with benzene.

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Further examination of the oil revealed the presence of the following fatty acids:

			%
Linolenic acid	• •	• •	26.1
Oleic acid	• •		59 · 4
Palmitic acid		• •	10.1
Stearic acid	• •		3.2
Unsaponifiable n	natter	• •	0.28
(Sitosterol)			

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