UTILISATION OF MYROBALANS.

PART II. MYROBALAN OIL.

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Hooper (*Annual Report, Indian Museum*, 1907–8, p. 13) investigated some of the constants of the myrobalan oil, such as iodine value, saponification value, insoluble acids and unsaponifiable matter, and acid value.

In this work, we have presented additional data on specific gravity, refractive index, acetyl value, optical rotation of the oil and on some physical constants of the mixed fatty acids, the liquid unsaturated fatty acids and solid saturated acids. Owing to the small quantity of the oil available the complete analysis was not undertaken.

The oil used in this investigation was obtained from the seeds of *Terminalia chebula* Retz—myrobalans. The seed kernels were ground to a fine meal and then extracted with petroleum ether having b.p. 30–50° C. in a soxhlet apparatus. The percentage of the oil obtained from seed kernels was 36.4. The whole nuts contained 33% of the seed, and the remaining formed the soft pulp. The seeds contained 5% of the seed kernels which had 36.4% of the oil.

EXPERIMENTAL.

Specific gravity, saponification value, acid value, Hehner value and unsaponifiable matter were determined by the usual standard methods, iodine value by Wij's method, refractive index by direct reading Abbe refractometer. The acetyl value of the oil was calculated from the saponification numbers of the original oil and acetylated oil. Optical rotation of the oil was determined by polarimeter using one decimeter tube.

Separation of the mixed fatty acids.—The oil was saponified as usual, neutralised with acetic acid and the soap solution was evaporated to dryness. After dissolving the soap in water, it was decomposed by dilute hydrochloric acid, the separated fatty acids were extracted with ether, washed with water, dehydrated with anhydrous sodium sulphate and filtered. After distilling off ether, the acids were dried at 98° in an atmosphere of carbon dioxide.

Titer test—solidifying point—was determined by the method given in *Technical Handbook of Oils, Fats and Waxes*, vol. 2, p. 42, by Fryer and Weston.

Separation of saturated and unsaturated fatty acids were effected in the usual manner by lead salt ether method given by Fryer and Weston (*Ibid.*, p. 171). The oil contained 78.8% liquid unsaturated fatty acids and 12.8% solid saturated fatty acids. The constants of the oil, equivalent weights and iodine values are given in the following table.

TABLE I.

Constants of the oil and fatty acids from myrobalan seed kernels.

	Hooper's values	Authors' values			
	Oil	Oil	Mixed fatty acids	Liquid unsaturated acids	Solid saturated acids
Colour	Yellow	Yellow	..	Yellow	White
Sp. Gr. 25°/25°	..	0·9132	..	.	..
Saponification value ..	192·66	190·2	200·5	203·3	218·5
Iodine value	87·5	105·1	109·1	117·5	1·5
Equivalent weights	..	..	279·8	275·5	256·3
Unsaponifiables	..	1·15	..	..	..
Hehner value	96·2	96·0	..	..	..
Refractive Index at 25° ..	..	1·4700	..	1·4642	..
Solidifying point (Titer Test) ..	..	..	27·7	..	m.p. 49–52°
Acid value	8·91	3·4	..	..	..
% of liquid and solid acids in oil	..	..	..	78·77	12·77
Acetyl value of oil	..	5·25	..	..	..
Specific Rotation $[\alpha]_D^{25}$ ..	..	0·1204	..	..	..

Examination of the Liquid Unsaturated Fatty Acids.—The liquid fatty acids were brominated by dissolving the oil in ether, keeping the temperature at 0° and adding bromine slowly, till the solution remained red for four hours. No hexabromide separated. After distilling off ether, the residue was dissolved in petroleum ether b.p. 30–50°. The petrol-insoluble bromide melted at 114° C. (bromine 53%, theoretical 53.3% for linoleic tetrabromide $C_{18}H_{32}O_2Br_4$). The cooled petroleum filtrate on removing petroleum ether yielded a viscous red bromide (bromine 36.9%, theoretical 36.19% calculated from oleic acid dibromide $C_{18}H_{34}O_2Br_2$).

This experiment shows that only two unsaturated fatty acids, namely, oleic and linoleic acids, are present in the myrobalan oil. The percentage composition of the glycerides of the fatty acids contained in the oil was calculated from (1) iodine value of the unsaturated acids, (2) di- and tetrabromide of the unsaturated acids, (3) the formula given by Van Arsdel, Moore and Richter (*Jour. Ind. and Eng. Chem.*, 1917, **9**, 451) depending upon the iodine numbers of the oil and liquid fatty acids, and (4) thiocyanogen and iodine values of the oil.

(1) Knowing that only two acids are present, namely, oleic and linoleic acids, the composition of the oil is calculated from the iodine value of the unsaturated acids as follows:

Quantity of the unsaturated fatty acids taken is 0.1540 grams and the iodine value is 117.5. Supposing x is the quantity of oleic acid and $(0.154 - x)$ that of linoleic acid and their iodine values 89.93 and 181.16 respectively, then,

$$0{\cdot}8993x + (0{\cdot}1540 - x)1{\cdot}8116 = \frac{0{\cdot}1540 \times 117{\cdot}5}{100}.$$

On solving we get $x = 0.1075$ gram oleic acid and 0.0465 gram linoleic acid. Therefore the percentages of oleic and linoleic acids are 69.8 and 30.2 and those of olein and linolein 72.9 and 31.4 respectively. As the oil contained 78.8% unsaturated acids, the percentages of glycerides in the oil are triolein 57.5, trilinolein 24.8 and saturated glycerides 17.7.

(2) The following percentages of the glycerides in the oil are found as calculated from di- and tetrabromides of the unsaturated acids. From 4.448 grams of liquid unsaturated fatty acids taken for bromination, 2.620 grams linoleic tetrabromide and 5.048 grams oleic dibromide are obtained representing 1.220 grams linoleic acid and 3.22 grams oleic acid; therefore the percentages of oleic and linoleic acids are 72.6 and 27.4 and those of triolein and trilinolein 75.8 and 28.5 respectively. As the oil contains 78.8% unsaturated acids, the percentages of the glycerides in the oil are triolein 59.7, trilinolein 22.5 and saturated glycerides 17.8.

(3) Calculation according to the formula:

% saturated glycerides	$= 100 - 104.5\ A/B.$
% olein	$= 207.6\ A/B - 1.144\ A.$
% linolein	$= 100 - (\%$ saturated glycerides $- \%$ olein$).$

in which A is the iodine number of the fat and B that of the liquid unsaturated fatty acids given by Van Arsden, Moore and Richter

gives the following values:—saturated glycerides 6.5%, olein 65.5% and linolein 28%. These values do not agree with those given by the methods (1) and (2).

(4) Thiocyanogen number of the oil was determined according to the instructions given in the report of the Committee on the analysis of commercial fats and oils appointed by the American Chemical Society and published in *Jour. Ind. and Eng. Chem.*, analytical edition, 1936, **8**, 223. The formulæ for the calculation of the composition of the oil, as given in the report, are as follows:—

If I.V. = Iodine number of the oil
T.V. = Thiocyanogen number of the oil
S.G. = % saturated glycerides
O.G. = % oleic glycerides
L.G. = % of linoleic glycerides,
Then L.G. = 1.154 (I.V. − T.V.)
O.G. = 1.162 (I.V. − T.V)
S.G. = 100% − (L.G. + O.G.).

The iodine number of the oil is 105.1 and the thiocyanogen number is 67. The following are the calculated values: linoleic glycerides 44.0%, oleic glycerides 33.6% and saturated glycerides 22.4%.

As the analytical values obtained by this method are widely different from those obtained by the other methods, no reliance can be placed on the data obtained.

The results of the first two methods which vary within 1–2% are given in the following table:

TABLE II.

Composition of the myrobalan oil.

Calculated from	Iodine number	Bromides	Mean
% olein	57·5	59·7	58·6
% linolein	24·8	22·5	23·3
% saturated glycerides ..	17·7	17·8	17·75

The composition of the oil approaches that of peanut oil and the oil is of very little commercial value, owing to the small quantity of the oil in the myrobalan.

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