

# THE OIL FROM THE SEEDS OF *XIMENIA AMERICANA*, LINN. A NEW UNSATURATED FATTY ACID, XIMENIC ACID:

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*Ximenia americana*, Linn. (Syn. *Ximenia Russelliana*, Wall), N. O. *Olacaceae*, Vern., *Kondanakkera* (Telugu), is a shrub found in abundance in the coastal tracks of Tennasserim, the Southern Mabaratta country, Mysore and in many districts of the Madras Presidency. It bears fruit, an ovoid drupe of an orange red colour which when ripe has a pleasant taste. It is used for jam making. The kernels of the seeds taste like filberts and like almonds when roasted. In Southern India these are extracted for the oil which is used as a substitute for *Ghee* (Fischer, *Indian Forester*, 1918, 44, 264).

*Ximenia americana* also occurs in South Africa and in South America and the oil from these sources has been examined mostly for its constants (Grimme, *Chem. Rev.*, 1910, 17, 157; Schröder, *Arbb. d. Kaiserl. Gesundsh.*, 1911, 43, 454; Freise, *Seifens Z.*, 1931, 58, 131; *Bull. Imp. Inst.*, 1935, 33, 277) but a complete chemical examination of this oil or the oil from the *Ximenia* seeds of Indian origin does not appear to have been made so far.

During the separation of the mixed acids of the oil into solid and liquid acids by Twitchell's method it was observed that the solid acids had too high an iodine value (33.9) to be attributed to the small amount of oleic acid which at times accompanies them. The possibility of the presence of an isomeric solid oleic acid (Puntambekar and Krishna, *J. Indian Chem. Soc.*, 1933, 10, 209) was suggested but later ruled out as no dihydroxystearic acid was found among the products of oxidation of the solid acids with cold and dilute potassium permanganate. Instead, however, an oxy-acid very sparingly soluble in petroleum ether and of m.p. 118-19° (M. W. 425), was isolated in pure condition. This high molecular weight and the fact that the main component of the solid acids is cerotic acid made it appear that the oxy-acid might be a dihydroxy derivative of an unsaturated solid acid also of 26 carbon atoms accompanying cerotic acid (C<sub>26</sub>H<sub>52</sub>O<sub>2</sub>). This inference was strengthened by the fact that its M. W. (425) and combustion data (C, 72.4%; H, 11.8%) closely agree with that of dihydroxycerotic acid, C<sub>26</sub>H<sub>52</sub>O<sub>4</sub> (M. W. 428; C, 72.8%; H, 12.2%). An additional proof

that the unsaturated acid in the solid acids is a  $C_{26}$ -acid was supplied by catalytic hydrogenation of the crystallised acids, m. p.  $61-62^{\circ}$ , M. W. 400.5, iodine value 43.7, obtained from the fraction IV of the distilled solid ester when a product (m. p.  $83-84^{\circ}$ , M. W. 398.4, iodine value nil) was obtained and identified as cerotic acid. It is thus evident that this new unsaturated fatty acid belonging to the oleic acid series is a hexacosenic acid. Its separation in pure state, however, has not yet been possible because of its intimate combination with cerotic acid and hence our inability to present complete data on this new acid, which we hope will form the subject matter of a later publication. But at this stage we propose to designate it as *ximenic acid*.

#### EXPERIMENTAL.

The seeds of *X. americana* were obtained from Vizagapatam forest division of the Madras Presidency and consisted of:—air-dried pulp with shell 55%; cream coloured soft kernels 45%; moisture in kernel 3.6%; oil in kernel 49.0%

For determination of its physical and chemical constants, the oil was expressed from the kernels at  $50^{\circ}$  in a hydraulic press. It was very viscous and mucilaginous and the quantity small and therefore for further examination it was extracted from the seeds with petroleum ether. The latter oil was pale yellow and of not unpleasant odour or taste.

#### *Physical and Chemical Constants.*

##### *The Fatty Oil.*

	The authors.	Earlier workers.
	Country of origin : South India.	South and East Africa ; South America.
Specific gravity at $20^{\circ}$	0.9262	0.9165—0.9248 at $15^{\circ}$
Refractive index at $20^{\circ}$	1.4710	1.4737
Iodine value (Hanus)	82.5	80.9—94.5
Saponification value	169.2	155.3—183.1
Acid value	2.3	1—24.6
Hebner value	—	93.9—94.8
Reichert-Meisel value	Nil	—
Unsaponifiable matter	1.7	0.5—2.9

*Mixed Acids.*

	The authors.	Earlier workers
Mean molecular weight	319.8	322.6—326
Iodine value	85.0	71—100.1
Saturated acids	31.0%	—
Unsaturated acids	67.5%	—
Resin acids	1.5%	—

*Composition of the Fatty Acids.*

500 G. of the oil were saponified in the usual manner with alcoholic sodium hydroxide. On distilling off the alcohol and dissolving the resultant soap in water a large amount of rubbery mass, apparently a portion of the unsaponifiable matter, separated out. It was filtered off and then the remaining portion of the unsaponifiable matter in the mixed acids was removed by the usual procedure.

200 G. of the mixed acid, free from the unsaponifiable matter, were separated into solid and liquid acids by performing the Twitchell's operation twice and the separated acids had the following constants.

Acids.	Iodine value.	Mean M. W.	Net weight.
(S) Solid	33.9	381.5	62.0 g.
(L) Liquid	99.2	322.5	135.0
Resin	—	—	3.0

*Solid Acids (S).*

A small portion of the solid acids after three crystallisations from alcohol melted at 83-84°, M. W. 398.3. Further crystallisations did not change these constants indicating thereby the crystalline product to be one homogeneous substance, probably cerotic acid.

The high iodine value of the solid acids indicated their association with some unsaturated acids, very likely with some solid unsaturated acid

(Puntambekar and Krishna, *loc. cit.*). In order to identify this acid 5 g. of the solid acids were oxidised in cold alkaline solution with dilute aqueous permanganate according to the modified method of Hazura (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes", Vol. I, 6th Ed., p. 575). The oxidised product after being extracted with petroleum ether in a soxhlet to remove the unoxidised acids and some of the acids of decomposition, was twice crystallised from 95% alcohol, m.p. 118-119°. (Found: C, 72.4; H, 11.8; M. W., 425.  $C_{26}H_{52}O_4$  requires C, 72.8; H, 12.2 per cent. M. W. 428.4). It appears to be dihydroxycerotic acid. It thus appears that the unsaturated acid occurring in the solid acids is a hexacosenic acid, a  $C_{26}$ -acid belonging to the oleic series.

Of the remaining portion of the solid acids 50 g. were converted into methyl esters by methyl alcoholic hydrochloric acid. After refluxing the mixture for 5 hours and cooling to room temperature, a solid crystalline product (16.3 g.) separated out. It was washed with fresh methyl alcohol and crystallised from acetone, giving a product looking like mother of pearl and melting at 63-64°. The acid liberated from this ester had an iodine value of 1.7 and after three crystallisations from alcohol melted at 83-84°, M. W. 400.5. This appears to be cerotic acid isolated above from solid acids by direct crystallisation, and was confirmed as such by its unchanged mixed melting point with the former acid.

The mother liquor and the washings of the above ester, methyl cerotate (m.p. 63-64°), were combined together and the methyl alcohol was distilled off. The residual esters were taken up in ether, washed with 5% sodium carbonate to remove the unesterified acids and then with water. The ethereal solution was dried and the ether distilled off. The esters (31.5 g.) were then fractionated at 3 mm. into the following fractions.

Fractions.	B.p.	Wt.	Iodine value.	M. W. of the acids.	Component of methyl esters.		
					Stearate.	Ximenate.	Cerotate.
S <sub>1</sub>	180-190°	0.75 g.	13.7	287.6	0.58 g.	0.17 g.	—
S <sub>2</sub>	190-200°	1.40	18.6	—	0.98	0.42	—
S <sub>3</sub>	200-220°	1.70	32.4	341.0	0.82	0.88	—
S <sub>4</sub>	220-270°	16.45	47.9	394.7	—	12.65	3.80 g.
Residue	—	11.00	49.1	—	—	8.67	2.33
Loss	—	0.20	—	—	—	—	—
Total		31.50			2.38	22.79	6.13

Fractions  $S_1$  and  $S_2$  being similar and small in quantity were mixed together and saponified. The resulting mixed acids melted at  $48-49^\circ$ , M. W. 287.6. On crystallisation from dilute alcohol a product, (m.p.  $57-58^\circ$ , M. W. 314.6) was obtained. The acids from mother liquor had a M. W. 282. The amount of material at this stage being too small further fractional study was not possible but from the iodine value of the fractions and of the M. W. of the liberated acids it appears that they mostly consist of stearic and ximenic acids. The presence of the latter acid in total solid acids has already been described above. The presence of a small amount of oleic acid in these fractions, however, is not ruled out but to simplify the calculations the iodine value is assumed to be due to ximenic acid only.

The acids from fraction  $S_3$  had M. W. 341. When crystallised from acetone they gave a product melting at  $60-61^\circ$ , M. W. 381 and a residue with a M. W. of 290. Again in this case the M. W. of the residual acids and the iodine value of the ester fraction suggests that they consist of stearic and ximenic acids. The presence of the cerotic acid is ruled out on the consideration that ximenic acid, as shown by the iodine value, forms a little over 50% of the fraction, the remaining 50% must be made of an acid of lower molecular weight (stearic acid) so as to make the M. W. of the total acids of the fraction 341.

The acids liberated from fraction  $S_4$  had M. W. 394.7. These when crystallised from alcohol gave a product melting at  $61-62^\circ$ , M. W., 400.4; iodine value, 43.7. On hydrogenation of this product (2.5 g. in alcohol) for an hour and half in presence of platinum oxide catalyst (according to Adams), a crystalline product melting at  $83-84^\circ$ , M. W. 398.4 and iodine value nil, was obtained and found to be cerotic acid isolated above. The fraction is, therefore, a mixture of ximenic acid ( $C_{28}H_{50}O_2$ ) and cerotic acid ( $C_{28}H_{52}O_2$ ).

The acids liberated from the residual esters were extracted with petroleum ether ( $60-80^\circ$ ) to remove them from oxidised or resinified matter. After the petroleum ether was driven off on a water-bath and then under vacuum, the extracted acids had a mean M. W. of 417 and iodine value 46.7 and were presumably a mixture of ximenic and cerotic acids. The somewhat high mean molecular weight of the acids is probably due to the fact that the products of oxidation or polymerisation have not been completely removed by petroleum ether.

#### *Liquid Acids (L)*

These were saponified to break up any ethyl ester which might have been formed during the Twitchell separation. The iodine value (99.2) of the

resulting acids indicates them to be a mixture of unsaturated acids consisting of two and more double bonds.

A portion of the liquid acids was converted into potassium soaps and oxidised in cold by a dilute solution of potassium permanganate according to the modified method of Hazura (*loc. cit.*). From the oxidised product only dihydroxystearic acid (m.p. 130-31°, M. W. 316) could be isolated and identified. When, however, it was boiled with a large volume of water and the mixture quickly filtered a small amount of a white crystalline material (m.p. 155-58°) presumably one of the or a mixture of isomeric tetrahydroxystearic acid separated out. No hexahydroxystearic acid was found in the aqueous filtrate from the products of oxidation. The unsaturated acids in the liquid acids, therefore, appear to consist of mainly oleic acid and a small amount of linoleic acids.

Another portion of the liquid acids was converted into methyl esters and 103 g. of them were separated into the following fractions by distillation under 6 mm.

Fraction.	B.p.	Iodine value.	Wt.
L <sub>1</sub>	-165°	59.3	2.44
L <sub>2</sub>	165-85°	76.5	2.19
L <sub>3</sub>	185-95°	86.8	23.63
L <sub>4</sub>	195-97°	94.4	25.37
L <sub>5</sub>	197-203°	98.2	8.15
L <sub>6</sub>	203-10°	100.3	4.97
L <sub>7</sub>	210-30°	86.7	6.74
Residue	—	—	26.67
Loss	—	—	2.84
		Total	103.00

Fractions L<sub>1</sub> and L<sub>2</sub> and L<sub>4</sub>, L<sub>5</sub>, L<sub>6</sub> and L<sub>7</sub> being similar were mixed together. Portions of these mixtures and of L<sub>3</sub> were separately saponified and then oxidised with dilute permanganate in the cold. In the product of oxidation from the first mixture and from L<sub>3</sub> only dihydroxystearic acid could be isolated and identified, whereas both dihydroxy and tetrahydroxystearic acids were found in the oxidised acids from the second mixture. The residue was a very dark viscous mass containing mostly the

methyl oleate and methyl linoleate together with all the colouring matter of the mixed acids.

The above results of the fractional distillation of the methyl esters of the solid and liquid acids on calculation gave the following percentage composition for the fatty acids :—

Stearic (not isolated in pure form), 1.2%; cerotic, 15.2%; ximenic, 14.6%; oleic, 60.8; linoleic, 6.7%; resin, 1.5%.

#### *Unsaponifiable Matter.*

The rubber like product separated from the soap solution after saponification of the oil constituted most of the saponifiable matter. Being insoluble in most of the organic solvents and in dilute mineral acids and alkalis it was not worked up further. The small amount of unsaponifiable matter, isolated from the sodium soaps of the mixed acids in the usual way by extraction with ether, showed the presence of a phytosterol (precipitate with a solution of digitonin in alcohol) but the amount was very small for its identification.

#### S U M M A R Y.

The oil from the seeds of *Ximenia americana*, Linn. consists of the glycerides of stearic, cerotic, ximenic, (hexacosenic), oleic and linoleic acids together with a small amount of a phytosterol and a large amount of a rubber like substance. Arachidic acid reported by Schröder (*loc. cit.*) was not found.

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