

Some Indian Acorn Oils (*Quercus incana*, Roxb., *Q. dilatata*, Lindl., and *Q. ilex*, Linn.).

By S. V. PUNTAMBEKAR AND S. KRISHNA.

Quercus grow all over the hills in Northern India and yield acorns in great abundance. At present these find no commercial application because of the low percentage of oil in the kernel and the poor quantity of the tanning material in the 'acorn cups' ('Valonia' of trade). In view of the absence of any chemical data on the oils (with the exception of *Q. agrifolia*—Blasdale, *J. Amer. Chem. Soc.*, 1895, 17, 935) it is considered desirable to place on record our findings.

Of about thirty species which occur in India, *Q. incana*, Roxb. Vern. *Banj* (Punjab) is probably the most common and the best known and the oil from this was, therefore, investigated in detail. The acorns were sent to us from Waziristan (N. W. F. Prov.).

The kernels (81%) on separation from the shells were dried, powdered and extracted for the oil in a Soxhlet with petroleum ether. In this way 16% of the oil were obtained which after complete removal of the solvent under vacuum was employed for the determination of its constants.

		<i>Q. incana.</i>	<i>Q. dilatata.</i>	<i>Q. ilex.</i>
Consistency	...	Thin	Thin	Thin
Colour	...	Yellow	Orange	Orange
Sp. gr. at 25°	...	0.9081	0.9084	0.9079
Refractive index at 30°	...	1.4576	1.4588	1.4576
Saponification value	...	192.2	188.4	189.9
Iodine value (Hanus)	...	81.5	90.3	83.0
Acetyl value	...	14.8	21.1	17.4
Hehner value	...	96.1	88.2	94.9
Acid value	...	13.0	22.2	8.5
Unsaponifiable matter	...	0.8%	2.3%	0.9%

Composition of the Fatty Acids (incana oil).

After removal of the unsaponifiable matter the mixed fatty acids were separated into solid and liquid acids by the Twitchell's method and both these acids were further divided into their components by the fractional distillation of their methyl esters.

Chemical constants of the mixed fatty acids.

Mean molecular weight	285.2
Iodine value (Hanus)	80.8
Saturated acids	18.0%
Unsaturated acids	82.0%

Saturated acids.—150.7 G. of the mixed acids, from which the unsaponifiable matter had been removed, gave the following fractions after performing the Twitchell's operation twice.

Acids.	Iodine value.	M.W.	Net weight.
S—solid	0	268.1	19.1 g.
SA—solid	43.6	302.0	2.4
L—liquid	85.3	288.0	129.2

Solid acids (S) were converted into their methyl esters and 20.4 g. of the dry neutral esters were fractionated at 3.5 mm. The liberated acids from each fraction were fractionally crystallised for identification of their components.

Fractions.	B.p.	Weight.	M.W. of the acids.	Component of the esters.	
				Methyl palmitate	Methyl lignocerate.
S ₁	168-70°	13.83 g.	254.3	13.83 g.	...
S ₂	170-75	3.30	265.4	3.02	0.28 g.
S ₃	175-85	1.47	275.0	1.22	0.25
Residue	>185°	1.50	282.3	1.15	0.35
Loss	...	0.30			
Total		20.40		19.22	0.88

Fraction S₁ melted at 28-30° and the liberated acids on crystallisation from acetone gave a product (m.p. 61-62° and M.W. 254) which was identified as palmitic acid by its mixed melting point with an authentic sample.

Fraction S₂ melted at 26-28° and the liberated acids had a m. p. of 56-57° and a M.W. of 265·4. Two crystallisations from acetone raised the M.W. to 267 but did not alter the m.p. indicating the fraction to consist mostly of palmitic acid and a small portion of an acid (possibly lignoceric) of higher molecular weight.

Fraction S₃—The acids from this fraction on crystallisation gave a product m. p. 56-58° and M. W. 282·6. Further crystallisation did not appreciably improve the purity of the acids which again appear to be a mixture of palmitic and perhaps lignoceric acids.

The residue on thrice crystallisation gave the following products :

Crystallisation	M.p.	M.W.
1	60-61°	313·2
2	63-64	...
3	68-69	340·6

The amount of acids at this stage being small, further crystallisations were not attempted. The above results show that at no stage do the m.p. and the M.W. agree to those of pure acids (palmitic, stearic, arachidic and behenic). Comparatively high M.W. and the correspondingly low m.p. of the products, however, indicate the residue to be mainly a mixture of acids of high and low molecular weights such as palmitic and and lignoceric but not of two consecutive acids such as palmitic and stearic or stearic and arachidic and so on. Though no lignoceric acid has actually been isolated yet for purposes of calculations its presence has been assumed.

The above results indicate that the solid acids consist mainly of palmitic acid together with a small amount of an acid, such as lignoceric acid, of high molecular weight.

Fraction S₄—The amount of these acids was too small for fuller identification. On dissolving in petroleum ether they produced turbidity. This fact coupled with their appreciable iodine value and high M. W. indicates that besides oleic and palmitic acids they contain a small amount of hydroxylated product such as dihydroxystearic acid.

Unsaturated Acids.

The liquid acids (L) were saponified to break up the esters which might have been formed in the alcoholic treatment. The slightly lower iodine value and the higher M. W., when compared with those for ordinary oleic acid, indicate that the acids contain some saturated acids.

A portion of the acids was converted into its potassium soap and oxidised by a dilute potassium permanganate solution according to the method of Lapworth and Mottram (*J. Chem. Soc.*, 1925, 127, 1628). The oxidised product was identified as dihydroxystearic acid (m. p. varying from 120-132; M. W. 316) and the unoxidised portion (7.0%) was left as a viscous mass of mean M. W. 278.0 and iodine value 7.3. Another portion was oxidised after being converted into potassium soap by a concentrated solution of potassium permanganate according to the modified method of Hilditch and Priestman (*Analyst*, 1931, 56, 354). The unoxidised acids obtained after magnesium salt separation (5.0 %) melted at 53-54° and had a M. W. 280.2 and iodine value zero.

The above oxidation experiments indicate that the unsaturated acids in the liquid acids (L) consist entirely of oleic acid with the possible presence of some of its isomers and that the acids of more than one double bond namely, linoleic etc. are absent. They also prove that the liquid acids still retain a small amount of solid acids probably palmitic acid (a fact is also borne out by the iodine value of the liquid acids). The higher molecular weight is in all probability due to the incomplete removal of the dihydroxystearic acid (Jay, *J. Soc. Chem. Ind.*, 1932, 51, 126 T).

The remaining portion of the liquid acids was converted into methyl esters in the usual way and 110 g. of these were fractionally distilled at 3-5 mm. pressure with the following results.

Fractions.	B. p.	Weight.	Iodine value.	Component of the esters.	
				Methyl palmitate.	Methyl oleate or isomers.
L ₁	50-175°	2.34g.	52.5	0.92	1.42
L ₂	175-180°	41.13	80.2	2.67	38.46
L ₃	180-183°	44.00	85.5	—	44.00
L ₄	183-186°	8.05	78.0	—	8.05
Residue		13.07	57.0	—	13.07
Loss		1.41	—	—	—
Total		110.00	—	3.59	105.00

Fraction L₁.—The acids from this when liberated and dried set to a viscous mass, the dilute alcoholic solution from which on cooling

yielded a small amount of acid, m. p. 55-56°. This appeared to be palmitic acid. The amount being small further purification was not attempted.

Fraction L₂.—The iodine value indicated this fraction to contain a small amount of a saturated substance, evidently methyl palmitate, but it could not be isolated.

Fraction L₃.—This is wholly methyl oleate.

Fraction L₄.—The low iodine value indicates that either the esters must have been polymerised to some extent or that they contain some isomer or isomers of methyl oleate of low iodine value and higher b. p. The varying m. p. of the dihydroxystearic acid obtained in Lapworth's oxidation experiment supports this assumption. It is quite possible that in nature the oleic acid is more often associated with its isomers than is commonly realised. It also appears not unlikely that this fraction contains a small amount of oxidised methyl oleate (Puntambekar and Krishna, *J. Indian Chem. Soc.*, 1933, 10, 210) which, however, was not isolated. The residue was a very dark viscous mass containing mostly the polymerised and degradation products of methyl oleate and almost 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.

Acids.	Weight.	Percentage.
Palmitic	25·9 g.	17·1
Lignoceric (?)	1·2	0·9
Oleic	123·6	82·0

Unsaponifiable matter.—Since the attempts to crystallise the sterols from the alcoholic solution of the unsaponifiable matter, obtained from the mixed fatty acids in the usual manner, was not successful, they were precipitated with 1% solution of digitonin in alcohol. As the amount of the precipitated digitonide was very small it was directly converted to sterol acetate by refluxing it with acetic anhydride. The purified sterol acetate melted at 126-28° and is apparently the acetate of the common phytosterol, sitosterol, found in vegetable oils.

The residue from the mother liquor was taken up in boiling xylene and filtered. The material obtained after the complete removal of the solvent was a viscous mass, iodine value 59.2. It burns with a smoky flame but is soluble in cold concentrated sulphuric acid. These facts indicate it to be an unsaturated hydrocarbon or a mixture of such hydrocarbons. The material being very little further identification was not possible.

SUMMARY.

The oil from the acorn kernels of *Quercus incana* has been found to contain the glycerides of palmitic, lignoceric and oleic acids and a small amount of sitosterol.

FOREST RESEARCH INSTITUTE,
DEHRA DUN.

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