

346. *The Non-saponifiable Matter of Shea Nut Fat. Part I.*

By I. M. HEILBRON, G. L. MOFFET, and F. S. SPRING.

THE acids of shea nut fat have been examined by Hilditch and Saletore (*J. Soc. Chem. Ind.*, 1931, **50**, 468) and by Hopkins and Young (*ibid.*, p. 389). The latter authors also examined the non-saponifiable fraction, the only constituent isolated, however, being a small yield of a hydrocarbon illipene, previously described by Kobayashi (*J. Chem. Ind. Japan*, 1922, **25**, 1188), to which the formula $C_{32}H_{56}$ was ascribed.*

* Since completing this work we have found that Bauer and Umbach (*Ber.*, 1932, **65**, 859) also have isolated from shea nut fat a hydrocarbon $(C_8H_8)_{20-21}$ identical with illipene to which they give the name karitene. In its general chemical properties these authors find that this hydrocarbon closely resembles caoutchouc.

We have commenced a detailed examination of the non-saponifiable matter, the present communication describing a qualitative examination of the principal constituents. A more detailed study of these is now in hand, and will be reported upon at a later date.

Hydrolysis of shea fat was effected by means of alcoholic potash, a latex-like material separating during the reaction, crystallisation of which gave a hydrocarbon which without doubt is the illipene of Kobayashi (*loc. cit.*) and of Hopkins and Young (*loc. cit.*).

The non-saponifiable fraction was obtained as an intractable resinous solid showing no tendency to crystallise from a variety of solvents. Acetylation of the crude material yielded a crystalline mixture, from which a pure acetate, m. p. 235—236°, was readily isolated. The latter we have identified as β -amyrin acetate by its conversion into the free alcohol and the preparation of its benzoate, and by direct comparison of these with the corresponding derivatives of β -amyrin of manilla elemi.

After removal of successive crops of β -amyrin acetate, the acetate mother-liquor on concentration gave a *product*, m. p. 141°, analysis of which indicates the formula $C_{32}H_{52}O_2$ (or $C_{31}H_{50}O_2$). The free *alcohol* and its *benzoate* have been prepared; the constants for these derivatives, which do not appear to have been previously described in the literature, are shown in the table below :

	M. p.	$[\alpha]_D^{20}$ ($CHCl_3$).	Found :		Calc. for $C_{30}H_{50}O$:	
			C.	H.	C.	H.
Alcohol.....	109.5°	-11.9°	84.8	11.4	84.4	11.8
Acetate.....	141	+22.4	81.95	11.25	82.0	11.2
Benzoate	130	—	83.85	10.1	83.7	10.3

The analytical data shown above do not exclude the empirical formula $C_{29}H_{48}O$ for the free alcohol; the relatively low melting points of the alcohol and its derivatives suggest that they are sterolic (tetracyclic) rather than triterpenoid (pentacyclic) in type. This suggestion is supported by a preliminary examination of the action of perbenzoic acid on the acetate, which indicates the presence of two ethenoid linkages and consequently of a tetracyclic system.

Benzoylation of the crude non-saponifiable matter readily yielded the benzoate of lupeol in moderate yield. This has been characterised by the preparation of several derivatives and also by direct comparison of the free alcohol with a specimen of authentic lupeol for which we are indebted to Professor L. Ruzicka. From the mother-liquors obtained after the removal of lupeol benzoate we have isolated β -amyrin benzoate in small amount.

EXPERIMENTAL.

Hydrolysis of Shea Nut Fat.—White shea fat (200 g.) was refluxed for 4 hours with 12% alcoholic potash (500 c.c.). The liquid was decanted from the gum adhering to the sides of the flask, and the latter washed with alcohol and dry benzene and taken up in hot ether. On cooling, a microcrystalline powder separated which after three recrystallisations from the same solvent had m. p. 63—64° (Hopkins and Young, *loc. cit.*, give m. p. 64° for illipene) (Found : C, 87.0; H, 12.7. Calc. for $C_{32}H_{56}$: C, 87.2; H, 12.8%. Calc. for $C_{30}H_{52}$: C, 87.3; H, 12.7%).

The alcoholic solution was poured into a large quantity of water, and the solution extracted with ether. The ethereal extract was washed with water, dried, and the solvent removed; a brown resinous mass remained, m. p. 65—85° (yield, 5% approx.).

Acetylation of the Non-saponifiable Matter.—The powdered non-saponifiable matter (50 g.) was refluxed with acetic anhydride (250 c.c.) for 90 minutes. The solid separating over-night was washed with alcohol and crystallised from the same solvent (600 c.c.). The first crop (10 g.) had m. p. 150°, which was raised to 210° after repeated crystallisation from benzene-alcohol. The final purification of this material was achieved by using ethyl acetate as solvent, a pure constant-melting product being obtained in needles, m. p. 235—236°, $[\alpha]_D^{20}$ * + 76.0° (Found : C, 81.95; H, 10.9. Calc. for $C_{32}H_{52}O_2$: C, 81.95; H, 11.2%), showing no depression in m. p. on admixture with β -amyrin acetate of manilla elemi, m. p. 236° (Vesterberg, *Ber.*, 1890, 23, 3186, gives $[\alpha]_D^{17}$ + 78.6° for β -amyrin acetate). Hydrolysis of this acetate with 5% alcoholic potash gave the free alcohol, crystallising from alcohol in needles, m. p. 193—194°, not depressed on admixture with β -amyrin. The benzoate separated from benzene-alcohol (1 : 4) in plates, m. p. 230°, either alone or in admixture with β -amyrin benzoate.

* The rotations recorded in this communication are for chloroform solution.

Isolation of acetate, m. p. 141°. The mother-liquor obtained after the isolation of crop I was concentrated to 400 c.c. and kept over-night; a second crop then separated (5 g.), which on purification yielded a small amount of β -amyirin acetate. The mother-liquor from crop II was concentrated to 250 c.c. and kept over-night. The separated rosettes of needles (3 g.) were collected, washed, and repeatedly crystallised from alcohol to give clusters of needles, m. p. 141°, not raised by recrystallisation. The acetate is freely soluble in ether, chloroform, and benzene, but only moderately soluble in ethyl acetate and ethyl alcohol. With antimony trichloride-chloroform solution, neither the alcohol nor its acetate gives any coloration; a negative reaction is also obtained with the Salkowski reagent. With the Liebermann-Burchard reagent an immediate yellow coloration is produced, the solution having a very marked green fluorescence, the colour gradually changing to brown and finally to red, the green fluorescence persisting throughout.

Titration of Acetate, m. p. 141°, with Perbenzoic Acid.—The acetate (0.188 g.) in dry chloroform (40 c.c.) was set aside at 0° with a solution of perbenzoic acid in chloroform (10 c.c. of 0.5*N*). From time to time samples of the solution were titrated with *N*/10-sodium thiosulphate, all measurements being standardised against a blank consisting of the same volume of perbenzoic acid solution in chloroform. The following absorptions were observed :

Time (days)	1	3	6	10
Atoms of O absorbed per mole of acetate	1.47	1.75	1.94	2.09

Alcohol, m. p. 109.5°.—The acetate (1 g.), m. p. 141°, was refluxed with alcoholic potash (3%; 50 c.c.) for 4 hours. The solution was precipitated with water, extracted with ether, and the ethereal extract washed and dried over anhydrous sodium sulphate. The product separated from aqueous alcohol (80%) in needles which after two crystallisations from the same solvent had m. p. 109.5°.

Benzoate, m. p. 130°.—The alcohol (0.4 g.), m. p. 109.5°, in benzene (5 c.c.) was treated with benzoyl chloride (3 c.c.) and pyridine (1.5 c.c.), the mixture being maintained at 70° for 6 hours with constant stirring. Removal of the volatile fraction under reduced pressure left an oily residue, which separated from benzene-alcohol (1:4) in plates, m. p. 130° after two crystallisations.

Benzoylation of the Non-saponifiable Matter.—The powdered non-saponifiable matter (150 g.) in benzene (150 c.c.) was treated with benzoyl chloride (95 g.) and pyridine (60 g.), and the mixture heated on the steam-bath for 6 hours with constant stirring. The solvent was then removed under reduced pressure, and the residual brown oil dissolved in a mixture of ethyl acetate and alcohol (1:1, 1000 c.c.). The mixture was gently refluxed, solid commencing to separate after 5 minutes. After 30 minutes' boiling, the copious mass of semi-crystalline solid was filtered off and washed with alcohol (80 g., m. p. 170—194°). Repeated crystallisation of this solid from benzene-alcohol (1:4) and finally from acetone gave prismatic needles, $[\alpha]_D^{20} + 59.9^\circ$, m. p. 261.5°, which could not be raised by repeated crystallisation. Cohen (*Rec. trav. chim.*, 1909, 28, 368) gives m. p. 265—266°, $[\alpha]_D^{20} + 60.4^\circ$ for lupeol benzoate (Found : C, 83.6; H, 10.1. Calc. for $C_{37}H_{54}O_2$: C, 83.7; H, 10.3%).

Lupeol.—The benzoate (10 g.) was refluxed for 3 hours with alcoholic potash (2½%, 750 c.c.), the solution precipitated with water, and the solid dissolved in hot methyl alcohol-acetone (3:1, 25 c.c.), to which water was added until the solution became turbid. On cooling, the alcohol separated in magnificent long needles, m. p. 210—211°, $[\alpha]_D^{20} + 26.4^\circ$, giving no depression in m. p. on admixture with lupeol (Cohen, *loc. cit.*, gives m. p. 211°, $[\alpha]_D + 27.2\%$ for lupeol) (Found : C, 84.9; H, 11.8. Calc. for $C_{30}H_{50}O$: C, 84.4; H, 11.8%).

Lupeol Acetate.—Prepared in the usual manner, the acetate separated from alcohol in clusters of flat needles, m. p. 214°, $[\alpha]_D^{20} + 47.5^\circ$ (Found : C, 82.0; H, 11.25. Calc. for $C_{32}H_{52}O_2$: C, 82.0; H, 11.2%) (Cohen, *loc. cit.*, gives m. p. 214° for lupeol acetate).

β -Amyrin Benzoate.—The mother-liquor from the first recrystallisation of the crude benzoate, m. p. 170—194°, was set aside for 2 weeks. The solid separating had m. p. 235—245° and on purification gave a further quantity of pure lupeol benzoate. The mother-liquor from this crop did not deposit any more solid on standing; on concentration to half bulk and cooling, a small crop of flat plates separated, m. p. 219°. Repeated crystallisation of this solid from benzene-alcohol raised the m. p. to 230.5°, either alone or in admixture with β -amyrin benzoate.