THE FIXED OIL FROM THE SEEDS OF *Amoora rohituka* (W. & A.).

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Amoora rohituka is a middle-sized ever-green tree belonging to the natural order, *Meliaceæ,* and commonly met with in various parts of India and especially in Assam, Oudh and the Western Ghats of India from Konkan to Travancore (*cf.* Kirthikar and Basu, *Indian Medicinal Plants,* 1918, 1, 315).

The vernacular names are:—Sanskrit, Marathi and Telugu—*Rohitaka;* Hindi—*Harinhara;* Bengali—*Raina;* Tamil and Malayalam—*Shem maram;* Assamese—*Amura amari.*

The seeds are oblong with a scarlet arillus and are economically important as they supply an oil which is very much used in North-Eastern India for burning and for medicinal purposes. Beyond a cursory examination of this oil by Crossley and Leseur and Weitz and Lecoq (*J. Soc. Chem. Ind.,* 1898, **17**, 991; *Bull. Imp. Inst.,* 1912, **11**, 561; *Bull. Soc. Pharm.,* 1915, **22**, 75), no detailed investigation of the composition of the oil has been made. In the present work, it is shown that the fatty oil from these seeds belongs to the drying class and can be hydrogenated to a solid fat. The mixed acids are shown to consist of α-linolenic, α-linolic, β-linolic, oleic, stearic, palmitic and myristic acids. On direct bromination, the oil does not yield any ether-insoluble bromides. This fact is in conformity with the poor drying property exhibited by the oil.

EXPERIMENTAL.

The seeds used in this work were procured from near about Noakhali (Bengal) and were identified by Dr. R. L. Dutta, Industrial Chemist, Bengal. The seeds were nearly round and brownish-black with a narrow pale brown hilum and a thin brittle husk closely adhering to the kernel. Each seed weighed, on an average, 0.8 g. The seeds were broken up into shells (22 per cent.) and kernels (78 per cent.). The latter were firm, pale yellow with a noxious, bitter taste. The finely powdered kernels were extracted in a copper soxhlet with petrol (b.p. 50–60°). The oil, amounting to 47 per cent. on the weight of the kernels, was clear, rather viscous and yellowish brown in colour with a bitterish taste and a not very agreeable odour. It had the following analytical characteristics:—sp. gr. 15.5°/ 15.5° = 0.931; n_D^{25} = 1.480; acid value = 13.7; saponification value = 186.0;

iodine value = 134.5; acetyl value = 28.0; unsaponifiable matter = 1.6. About 2 kg. of oil were prepared from about 6 kg. of seeds.

The mixed acids.—These were prepared in the usual way by the saponification of about 200 g. of the oil in two lots. About 180 g. of mixed acids freed from unsaponifiable matter were thus obtained. It analysed as follows:—m.p., 36°; titre, 33·5°; n_D^{60} =1.4590; M.W., 285.2; iodine value, 142.5.

Separation of the mixed acids.—The separation was effected in the usual manner by the lead salt-alcohol method (*J. Ind. Eng. Chem.*, 1921, 13, 806) using 2.5 g. of lead acetate and 9.5 g. of mixed acids in a total volume of 200 c.c. of 95 per cent. alcohol. 2.25 g. of pure white solid acids and 7.27 g. of liquid acids were obtained. About 100 g. of mixed acids were thus separated into 24 g. of solid acids and 76 g. of liquid acids.

Examination of the liquid acids.—n_D^{25} = 1.4775; M.W., 279; iodine value, 178.5. The bromides were prepared essentially by the method adopted in the case of linseed oil (*Lewkowitsch,* 1921, 1, 585). From 8.2 g. of liquid acids, 2.15 g. of ether insoluble hexabromide m.p.181–82° and 15.13 g. of ether soluble bromides with a bromine content of 51.2 per cent. were obtained. 14.06 g. of this latter mixture gave 3.2 g. of petrol insoluble bromide melting at 110–12°. (Br = 53.3 per cent; corresponding to α-linolic-tetra bromide.) A further quantity (4.2 g.) of the same bromide (m.p. 112°) was obtained by cooling the hot petrol solution. The cooled petroleum filtrate, on removal of petrol, yielded 6.66 g. of a viscous bromide with bromine 48 per cent. which was taken to be a mixture of oleic dibromide and isomeric linolic-tetrabromide. About 40 g. of liquid acids were thus brominated and separated. The composition of the liquid acids was calculated as usual from the above data as follows:—α-linolenic acid, 9.6 per cent; α-linolic acid, 45.3 per cent.; isolinolic acid, 30.1 per cent.; oleic acid, 14.6 per cent.

The saturated acids, of which 20 g. were available, were examined by the fractional precipitation of their magnesium salts from a 90 per cent. alcoholic solution of their potassium salts as described below:—10 g. of the acids neutralised with caustic potash in 250 c.c. of 90 per cent. alcohol was heated to boiling and 8 c.c. at a time of a 10 per cent. alcoholic solution of magnesium acetate was added; and after each addition the mixture was cooled, the precipitated magnesium salt filtered and the filtrate treated with a further 8 c.c: of magnesium acetate solution and this process was repeated 4 times. The acids (4 g.) recovered from the first fraction of precipitated magnesium salts melted at 68–69° after one crystallisation from acetone (m.p. unchanged on mixing with pure stearic acid; equivalent = 285). The acids of the second fraction (4 g.) after one crystallisation from methyl alcohol melted at 57–62° corresponding to a mixture of 60 per cent. stearic and 40 per cent. palmitic. The third fraction yielded 1.4 g. of a pure white solid acid melting at 59–60° (equivalent 253, agreeing with that of palmitic acid). The final fraction yielded 0.4 g. of solid acid with an equivalent of 242 by recrystallisation of which from 50 per cent. alcohol 0.2 g. of palmitic acid melting at 57–59° was obtained. Hence this fraction was a mixture of equal proportions of palmitic and possibly myristic acid which, however, was not isolated. The saturated acids, therefore, consist of stearic (64 per cent.), palmitic (33 per cent.) and myristic (3 per cent.) acids.

Unsaponifiable matter.—This was a semi-solid, yellowish brown mass, having a strong, unpleasant smell. On crystallising this twice from 96 per cent. alcohol, a crystalline white sterol melting at 135° was obtained. The acetyl derivative prepared by heating the sterol with an excess of acetic anhydride in presence of a little pyridine gave, after one crystallisation from 90 per cent. alcohol, a sharp melting point of 125°. It was, therefore, sitosterol acetate. By the digitonin method 0.3772 g. of the original unsaponifiable matter gave 0.275 g. of the digitonin compound amounting to 17.8 per cent. sterol.

Drying power of Raina oil.—2 drops of the oil spread over a glass-plate (3″ × 3″) in a thin film became sticky after 2 days, but did not become a tough film even after several days of exposure. A quantitative estimation of the drying power by the method of Liversege and Elsdon (*J. Soc. Chem. Ind.*, 1912, **31**, 207) showed an increase of 1.5 per cent. in 5 days and only 6.5 per cent. in a fortnight, and hence the oil is badly lacking in drying power.

Hydrogenation of Raina oil.—The refined oil was hydrogenated with the aid of a specially prepared nickel catalyst—as detailed below—following the procedure indicated in a previous communication. (Sudborough, Watson and Ayyar, *J. Ind. Inst. Sci.*, 1926, **9A**, 47.) Samples of the heated mixture are withdrawn from time to time, filtered hot and the filtered oil is analysed for iodine value, refractive index and any other properties. The variation of index with iodine value during the course of the hydrogenation has been plotted in Fig. 1 and shows remarkable breaks at points corresponding to iodine values of 105, 85 and 55 respectively, showing selective hydrogenation of linolenic, linolic and oleic acids one after the other.

Refining of the oil.—360 g. of crude Raina oil were treated slowly at 70° with 50 c.c. of 20 per cent. solution of caustic soda, the mixture being well stirred during one hour; and on cooling the separated curdy soap was filtered through a thin muslin cloth. The oil was washed with boiling water till all the soap was removed as tested by phenolphthalein. It was then heated to 100° to drive off all water and, while still warm, about 15 g. of freshly heated and cooled fuller's earth was dusted on the oil while being stirred during one hour. The oil was finally filtered hot through a Buchner and 250 g. of a clear, brownish yellow oil was obtained.

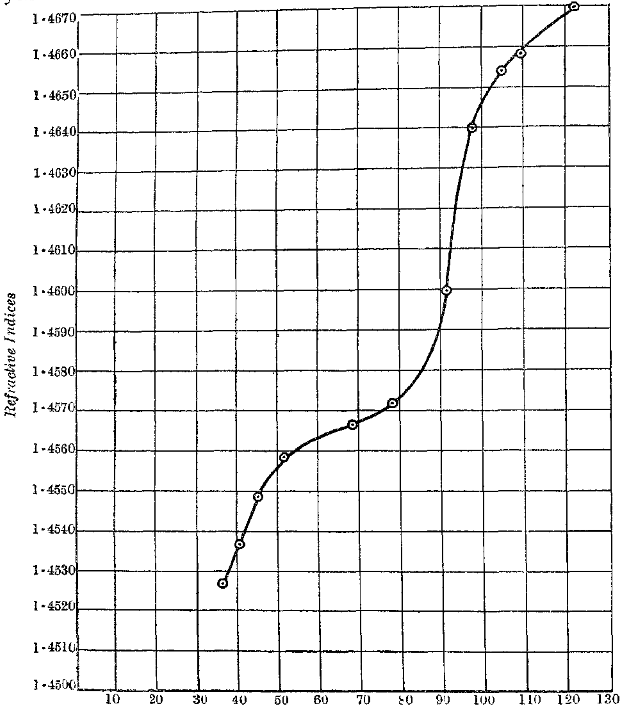

Fig. 1. Hydrogenation of Raina oil.

Preparation of the catalyst.—25 g. of nickel sulphate in 10 per cent. aqueous solution were mixed with 25 g. of kieselguhr and to the boiling solution was added an aqueous solution of 9.5 g. of sodium carbonate (less than that required by theory). The precipitated nickel carbonate was well boiled with water, filtered hot and washed thoroughly with boiling water till the filtrate showed no turbidity with sodium carbonate solution. The precipitate was dried at 100°, powdered and then weighed (30 g.).

Preparation of electrolytic hydrogen.—Electrolytic hydrogen was prepared by the electrolysis of (sp. gr. 1.12) sulphuric acid contained in a battery of 4 wide-mouthed 750 c.c. glass bottles fitted with strips of sheet lead electrodes bent into the form of outer and inner cylinders. The anode was outside and the cathode inside a wide glass tube (0.9″ diam.) which was fitted with a cork carrying the hydrogen delivery tube. The current was supplied from 100 volts mains and was adjusted by means of resistances to give 4–5 amps. The hydrogen dried by concentrated sulphuric acid was passed over a heated copper gauze to remove traces of oxygen and was again dehydrated by calcium chloride and sulphuric acid successively before being led into the hydrogenation flask. About 6 litres of hydrogen were available in one hour.

Hydrogenation.—This was carried out in a 3-necked flask fitted with a mercury-seal stirrer, an inlet tube for hydrogen and an outlet for introducing a thermometer or for pouring oil. 5 g. of the nickel-

TABLE I.

Hydrogenation of Raina oil.

Fraction	I. V.	Ref. Index
Refined Oil	122·5	1·4670
1	109·5	1·4658
2	105·0	1·4654
3	98·0	1·4640
4	91·5	1·4600
5	86·2	1·4580
6	78·0	1·4571
7	68·2	1·4566
8	58·5	1·4562
9	51·5	1·4558
10	45·0	1·4549
11	40·2	1·4537
12	33·5	1·4526

kieselguhr catalyst were introduced into the flask and heated to 300–320° in an air-bath with a current of hydrogen passing through the flask. The greenish catalyst was completely reduced in one hour and became quite black. The flask was then cooled without interrupting the current of hydrogen and 50 g. of the oil were introduced into the flask and the heating restarted and kept at 180° throughout the reduction. At intervals of 1 to 4 hours samples were removed. The first hydrogenation stopped at the iodine value of 50 after 12 hours; hence the hydrogenated oil was filtered and hydrogenation restarted with fresh catalyst, and proceeded to about an iodine value of 30, during a further period of four hours.

The resistance of the partially hydrogenated oil to further hydrogenation is probably due to the position of the double bonds in the unsaturated acids remaining in the reaction product. The iodine values were determined by the bromide-bromate method and the refractive index read on the Abbe refractometer adjusted to 60°. Table I shows the iodine values and refractive indices of 12 samples of partially hydrogenated oil.

SUMMARY.

The mixed acids from the fatty oil of the seeds of *Amoora rohituka* consist of stearic (15.1 per cent.), palmitic (7.8 per cent.), myristic (?) (0.7 per cent.), oleic (11.2 per cent.), α-linolic (34.5 per cent.), isomeric linolic (23.0 per cent.) and α-linolenic (7.8 per cent.) acids respectively. The unsaponifiable matter forming 1.6 per cent. of the oil contains 17.8 per cent. of sitosterol. The oil does not yield ether insoluble bromo-glycerides and is not a good drying oil. The iodine value-refractive index graph showing the course of hydrogenation of the oil reveals remarkable selective absorption of hydrogen by the different types of unsaturated acids present in the oil.

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