## 4. *The Seed Fat of* Parinarium laurinum. *Part I. Component Acids of the Seed Fat.*

By J. P. Riley.

The component acids of the seed oil of *Parinarium laurinum* have been examined and shown to contain besides parinaric acid, reported by earlier workers, substantial amounts of α-elaeostearic and oleic acids, together with minor proportions of palmitic, stearic, linoleic, and conjugated octadecadienoic acids. The identities of the unsaturated acids have been established by oxidation or bromination. Spectrographic values are presented for the determination of parinaric acid in oils, and for its behaviour to alkali isomerisation under the conditions used for the analysis of oils containing α-elaeostearic and linoleic acids. The mean composition of the component mixed fatty acids of two samples of oil from seeds collected in the Fiji Islands has been shown by low temperature crystallisation and spectrographic methods to be: palmitic 4, stearic 1, oleic 7·5, linoleic 2, conjugated octadecadienoic 1·5, α-elaeostearic 30·5, and parinaric acid 53·5% (wt.).

*Parinarium laurinum*, belonging to the family Rosaceæ, is a tree of moderate size, about 3 feet in girth and 30 feet high. It grows in Papua and New Guinea, Java, Borneo, and prolifically on the sea front and river valleys of the Fiji Islands. The tree bears ovoid fruit resembling potatoes and varying considerably in size; these are greatly valued by the natives for medicinal

and other purposes, and are known by a number of native names, the principal of which are Makita (Fiji) and Kusta (New Guinea).

The fruit itself consists of a light-brown, very fibrous shell about ¼" thick, containing a moist, pink kernel. Farmer and Sunderland (*J.*, 1935, 759) found 44% of oil in the kernels. In a private communication Mr. G. Winter writes : " We had obtained a parcel of seeds from New Guinea, which contained seeds which had been collected in various areas of the territory. Examining individual seeds we found the oil content to vary from 3% to 40% of the kernel, the majority being between 20% and 35%. There was also great difference between individual seeds in the shell : kernel ratio. So far, we have not been able to distinguish between high and low oil-bearing seeds according to general appearance, size, or shape. According to Mr. Parham of the Department of Agriculture, Fiji, four varieties of *Parinarium laurinum* are known, all of which bear similar fruit, but differ in the shape of the leaves." The properties of the oil and its actual and possible uses have been discussed in two recent reviews (Anon., *Paint Manuf.*, 1945, **15**, 356; Winter, Nunn, and Ward, *Paint Notes, Austral.*, 1948, **3**, 393).

The chemical composition of the component acids of the oil was first examined by Tsujimoto and Koyanagi (*J. Soc. Chem. Ind. Japan*, 1933, **36**, 110, 673), who crystallised the mixed fatty acids from light petroleum and isolated an acid of melting point 85—86°, which they named parinaric acid but considered to be a geometrical isomer of elaeostearic acid. The same acid was also isolated by Farmer and Sunderland (*loc. cit.*) in 24% yield from the mixed fatty acids of the oil. These workers were able to show that, on hydrogenation, parinaric acid absorbed 4 molecules of hydrogen, yielding stearic acid. Oxidation by alkaline permanganate yielded azelaic, propionic, and oxalic acids, they therefore concluded that parinaric acid is octadeca-9 : 11 : 13 : 15-tetraenoic acid.* These findings were later supported by Kaufmann, Baltes, and Funke (*Fette u. Seifen*, 1938, **45**, 302), who showed that the ultra-violet absorption spectrum of parinaric acid was very similar to that of decatetraene and concluded that the acid contains four conjugated double bonds.

More recently the absorption spectrum of the mixed fatty acids from the oil has been examined by Winter (*Paint Notes, Austral.*, 1948, **3**, 393) who concluded that, besides parinaric acid (46%), there was also present about 34% of a conjugated trienoic acid—probably α-elaeostearic acid.

The present part of this work has as its aims the identification of the component fatty acids present in the oil, and their determination. Three samples of oil have been studied, two of which were extracted in Australia by Winter, and a third which was extracted in Liverpool from seeds collected near Suva. In Table I are given the physical constants of the oils, together with those reported by other workers.

TABLE I.

| Sample. | I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|
| % of oil in dry kernels | 12·9 | 12 | — | — | 17·6 |
| $n^{40}$ | 1·5510 | 1·5527 | 1·5480 | 1·5610 [b] | 1·5610 [c] |
| Free fatty acid (as oleic), % | 18·8 | — | 2·8 | 0·6 | 5·9 |
| I val. | 180·8 [a] | 179·0 [a] | 176·8 [a] | 214·4 | 185 [d] |
| I val. (Toms) | 240·3 | 255·8 | 229·3 | — | — |
| Unsaponifiable matter, % | — | 1·0 | 0·9 | 1·15 | 0·9 |

[a] 20 c.c. of Wijs reagent (200% excess) on 0·1 g. of fat; reaction period, 30 minutes.
[b] At 50°. [c] At 15°. [d] Wijs reagent (200% excess) for 1 hr. at 20°.

I. Seeds collected near Suva and extracted in Liverpool.
II. Oil extracted in Australia from seeds collected near Suva (Fiji).
III. Oil extracted in Australia from seeds collected in Fiji.
IV. Tsujimoto and Koyonagi (*loc. cit.*).
V. Winter's (*loc. cit.*) seed collected near Suva.

There thus seems to be reasonable agreement between the values recorded by the various workers, for all the constants, except the free acidity and iodine values. The free acidity depends greatly on the maturity of the seeds, and their method of collection and storage, and the iodine value varies, when unsaturated acids having conjugated double bonds are present, with the reagent used, its excess, and the time of reaction.

Pure parinaric acid, m. p. 86°, has been isolated by repeated crystallisation of the mixed fatty acids from light petroleum and ether. The acid has been subjected to acetone–permanganate oxidation, yielding azelaic acid as the sole dibasic acid, which confirms the structure for the acid proposed by Farmer and Sunderland (*loc. cit.*). The ultra-violet absorption spectrum of the

* In this paper numbering is according to the Geneva system, the number 1 being assigned to $CO_2H$.

acid (Fig. 1.) agreed fairly well with the observations of Kaufmann *et al.* (*loc. cit.*) and Winter (*loc. cit.*) (see Table II).

TABLE II.

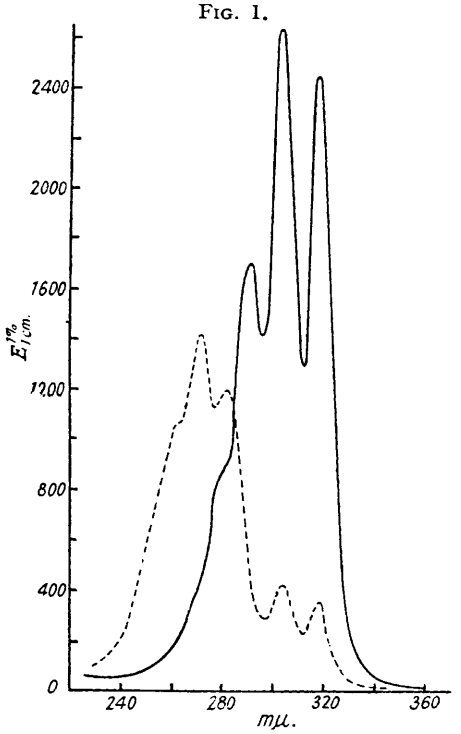
*Absorption spectrum of parinaric acid.*

| | $\lambda_{max.}$ at mμ. | $E^{1\%}_{1\ cm.}$ | $\lambda_{max.}$ at mμ. | $E^{1\%}_{1\ cm.}$ | $\lambda_{max.}$ at mμ. | $E^{1\%}_{1\ cm.}$ |
|---|---|---|---|---|---|---|
| Present work ..... | 291·5 | 1694 | 305 | 2624 | 320 | 2450 |
| Kaufmann *et al.* (*loc. cit.*) ... | — | — | 307 | — | — | — |
| Kaufmann & Keller [1] ..... | 292·5 | 1906 | 306·5 | 2800 | 321·5 | 2400 |
| Winter (*loc. cit.*) ..... | 293 | 1820 | 305 | 2800 | 319 | 2500 |

[1] *Ber.*, 1948, **81**, 152 (in heptane).

The isolation, in a pure state, of the triene acid present in the mixed fatty acids has not proved possible, either by crystallisation or by chromatographic adsorption on silica gel. The

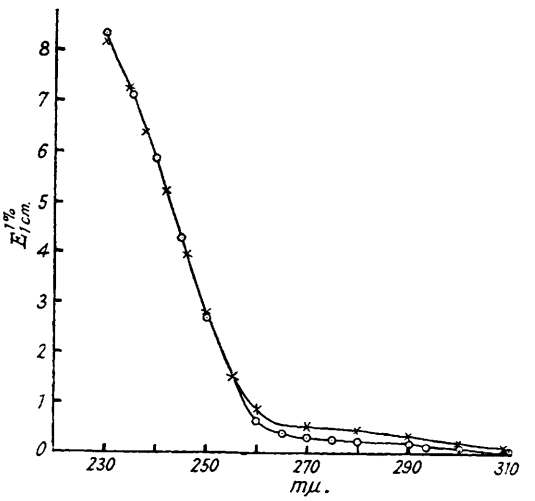
FIG. 1.




*Absorption spectra of pure parinaric acid, continuous line. Concentrate of trienoic acid, broken line.*

FIG. 2.

*Absorption spectra of maleic anhydride adducts.*




⊙ *Triene acid in* P. laurinum *oil.*
× *Authentic α-elaeostearic acid.*

difficulty of separation is largely due to the extremely labile nature of the parinaric and triene acids, and partly to the comparatively small difference in solubility. Nevertheless a concentrate containing 76% of conjugated triene with 16% of parinaric acid has been obtained by crystallisation. This acid shows an absorption spectrum having maxima at the same wavelengths as α-elaeostearic acid (Fig. 1). The methyl ester of the concentrate on oxidation by means of permanganate in acetone yielded azelaic acid as the sole dibasic acid in amount considerably greater than would have been yielded by the parinaric acid present. The triene acid must therefore have its double bonds in the 9 : 11 : 13-positions, and thus be either α-elaeostearic acid or a *cis-trans*-isomer thereof. Its identity as α-elaeostearic acid has been proved by its conversion into its maleic anhydride adduct, which after crystallisation from light petroleum had melting point 62°, and did not depress the melting point (62—63°) of an authentic specimen. The absorption spectra of the two maleic anhydride adducts were identical (Fig. 2). Parinaric acid, when treated with maleic anhydride under the same conditions, yielded only a brownish resin, insoluble in light petroleum.

A small amount of conjugated dienoic acid also occurs in the mixed acids, as shown by a maximum in the absorption curve at 234 mμ. It has not been possible to obtain a sufficiently high concentration of the acid for it to be identified, but by analogy it is probably octadeca-9 : 11-dienoic acid. The spectrum of the mixed acids has been examined without success for the presence of conjugated pentaenoic or more unsaturated acids.

The non-conjugated unsaturated acids present have been shown by conversion into di- and tetra-hydroxystearic acids (by oxidation of concentrates of the acids with dilute alkaline permanganate) to be the normal oleic and linoleic acids occurring in seed oils. On bromination of the concentrate in ether, no insoluble hexabromides were obtained, agreeing with the findings of Hilditch and Riley (*J. Soc. Chem. Ind.*, 1946, **65**, 74T) that linolenic acid does not occur in the presence of α-elaeostearic acid.

The principal saturated acid present in the oil has been shown—after hydrogenation and fractionation of the methyl esters of the mixed acids—to be palmitic acid. Small amounts of lower saturated acids also occur in the oil; these have not been identified, but are probably oxidation products of the parinaric acid.

The compositions of the mixed acids from two of the samples of oil have been determined by a modification of the methods used by Hilditch and Riley (*loc. cit.*) for the examination of oils containing elaeostearic acid. The mixed acids were resolved into fractions by crystallisation from light petroleum and acetone at low temperatures, before spectroscopic examination. The parinaric acid was determined by the absorption of the alcoholic solution at 305 mμ. After allowance has been made for its absorption at 270 mμ. (band-head of α-elaeostearic acid) and at 234 mμ. (band-head of conjugated diene), the elaeostearic and conjugated dienoic acids were determined. Similar corrections were applied to the values obtained by alkali isomerisation for the determination of linoleic and linolenic acid. Values used in the calculations, determined with pure parinaric acid, are given in Table III (values used in the calculation of results are given in bold type).

TABLE III.

*$E^{1\%}_{1\,cm.}$ for pure parinaric acid.*

| $E^{1\%}_{1\,cm.}$ at | 234 mμ. | 270 mμ. | 291·5 mμ. | 305 mμ. | 320 mμ. |
|---|---|---|---|---|---|
| Untreated | **53·6** | **386** | 1694 | **2624** | 2450 |
| Alkali-treated, 170°/15 mins. | 90·6 | **452** | — | — | — |
| Alkali-treated, 180°/60 mins. | **91·0** | — | 681 | 744 | 473 |

Saturated acids were determined in each case by the Bertram method (*Z. deutsch Oel Fett Ind.*, 1925, **45**, 733) and palmitic acid by fractionation of the hydrogenated methyl esters as proposed by Gunstone and Hilditch (*J. Soc. Chem. Ind.*, 1946, **65**, 8T).

From the data obtained the component fatty acids (excluding unsaponifiable matter) of the two oils have been deduced (see Table IV).

TABLE IV.

*Component fatty acids of* Parinarium laurinum *(excluding unsaponifiable matter).*

| | Sample II (from Suva). | Sample III. |
|---|---|---|
| Palmitic + stearic | 4 | 5 |
| Oleic | 6 | 10 |
| Linoleic | 2 | 2 |
| Linolenic | — | — |
| Conjugated octadecadienoic | 1 | 2 |
| α-Elaeostearic | 31 | 30 |
| Parinaric | 56 | 51 |

From these figures it will be seen that there is comparatively little difference between the two oils, although the proportion of parinaric acid is rather variable. The analysis confirms the deduction made from bromination, that linolenic acid is absent. It is thus evident that *P. laurinum* is similar to many other members of the *Parinarium* species in containing α-elaeostearic acid, with lesser amounts of linoleic, oleic, and palmitic acid, but is so far as is known almost unique in also containing the conjugated tetraenoic parinaric acid. Parinaric acid has, however, been reported in the seed fats of *P. glaberrimum* and *P. scabium* (Frahm, *De Ingenieur in Nied-Indie*, 1941, **7**, 42) and of a few members of the Balsaminaceæ, *e.g.*, *Impatiens Roylei Walpers* (Kaufmann and Keller, *loc. cit.*).

Since the completion of this work the following private communication has been received from Mr. Winter: " Some (*P. laurinum*) fats when examined spectrophotometrically were

found to contain more trienoic than tetraenoic acid, in others again there was hardly an inflexion at the 271·5-mμ. band and the spectrum showed only the characteristic maxima for the tetraene acid. The unfortunate part, however, is that there appears to be no correlation whatsoever in these differences with the appearance, size, or shape of the seeds."

## Experimental.

The following data were obtained on the oil extracted by light petroleum (sample III) in Australia, and similar results were obtained for the oil sample from Suva (sample II).

*Characteristics of the Oil.*—Iodine value (Wijs, on a 0·1-g. sample for 30 minutes) 176·8, iodine value (Toms) 229·3, free fatty acid (as oleic) 2·8%, unsaponifiable matter [by Society of Public Analysts' method (*Analyst*, 1933, **58**, 203)] 0·9%, $n^{40}$ 1·5480, total saturated acids (Bertram) 5·2%.

*Hydrolysis of the Oil and Low-temperature Crystallisation of the Mixed Acids.*—The oil (46·9 g.) was neutralised with potassium hydroxide solution, and the neutral oil hydrolysed by boiling it under reflux for an hour with a solution of 25 g. of potassium hydroxide in 250 ml. of alcohol. The acids were liberated from the soaps with sulphuric acid and extracted with ether as rapidly as possible to prevent polymerisation. After removal of the ether the acids were preserved in the dark in a well-corked flask filled with carbon dioxide and stored on solid carbon dioxide until required, to prevent the polymerisation of parinaric acid.

The mixed acids (42·53 g.) from the oil were boiled with 350 ml. of light petroleum, and the solution decanted from the resinous polymerised material $P_1$, the latter was washed twice with 40 ml. of boiling light petroleum, and the washings added to the main solution. The solution of the acids in light petroleum was crystallised at −25°, and the deposited acids (36·52 g.) were recrystallised from light petroleum (50 ml./g.) at 0°, yielding crystallised acids *A* (22·17 g.), polymerised material $P_2$ (0·90 g.) (which was combined with $P_1$; total, 2·62 g.), and soluble acids (13·45 g.). The soluble acids were recrystallised from light petroleum (20 ml./g.) at −35°, giving crystallised acids *B* (12·18 g.) and soluble acids *C* (1·27 g.). The soluble acids (4·29 g.) from the crystallisation from light petroleum (10 ml./g.) at −25° were recrystallised from acetone (10 ml./g.) at −60°, yielding insoluble acids *D* (1·19 g.) and soluble acids *E* (3·10 g.). Data for these fractions are given in Tables V, VI, and VII.

Table V.

*Crystallisation data.*

| Fraction. | Wt., g. | %. | I val. (Toms). |
|---|---|---|---|
| *A* | 22·17 | 52·1 | — |
| *B* | 12·18 | 28·7 | — |
| *C* | 1·27 | 3·0 | 176·2 |
| *D* | 1·19 | 2·8 | — |
| *E* | 3·10 | 7·3 | 196·3 |
| $P_1$ | 1·72 | 4·0 | — |
| $P_2$ | 0·90 | 2·1 | — |
| | 42·53 | | |

Table VI.

*Spectrographic examination of fractions.*

| | Untreated. | | | | Alkali isomerised | |
|---|---|---|---|---|---|---|
| | | | | | at 170° for 15 mins. | at 180° for 60 mins. |
| Fraction. $E^{1\%}_{1\,cm.}$ at | 234 | 270 | 305 | 320 | 270 | 234 mμ. |
| Mixed acids * | 100·5 | 667 | 1267 | 1106 | 687 | 120·8 |
| *A* | 97·0 | 539 | 1945 | 1725 | 569 | 106·8 |
| *B* | 142·2 | 1029 | 612 | 500 | 952 | 151·9 |
| *C* | 155·9 | 749 | 283 | 206 | 699 | 223 |
| *D* | 96·4 | 890 | 123·0 | 95·3 | 835 | 128·9 |
| *E* | 127·0 | 635 | 324 | 245 | 615 | 265 |

* Including polymerised.

Table VII.

*Component acids of fractions* (% wt.).

| | Mixed acids.* | *A*. | *B*. | *C*. | *D*. | *E*. |
|---|---|---|---|---|---|---|
| Saturated<br>Oleic<br>Unsaponifiable ..... | 22·5 | 9·4 | 21·3 | 36·1 | 43·2 | 35·1 |
| Linoleic ..... | 0·7 | — | 0·9 | 7·8 | 3·1 | 15·3 |
| Linolenic ..... | — | — | — | — | — | — |
| Conjugated dienoic ..... | 1·5 | 2·3 | 1·7 | 5·6 | — | 4·3 |
| Conjugated trienoic ..... | 27·0 | 14·2 | 52·8 | 39·7 | 49·0 | 33·0 |
| Parinaric ..... | 48·3 | 74·1 | 23·3 | 10·8 | 4·7 | 12·3 |

* Including polymerised.

*Determination of Palmitic Acid by Hydrogenation.*—The refined oil (53 g.) was hydrogenated at 100° with Raney nickel, and the product [I val. (Wijs), 100·3] was saponified. The acids were converted into the methyl esters, which were rehydrogenated at 100°. The product (I val., 12·1) was fractionated as proposed by Gunstone and Hilditch (*loc. cit.*); 4·2% of palmitic acid were present, together with a quantity of polymerised matter (see Table VIII).

TABLE VIII.

*Fractionation of hydrogenated methyl esters of* Parinarium laurinum *oil.*

| No. | G. | Sap. equiv. | I val. | Palmitic. | $C_{18}$. |
|---|---|---|---|---|---|
| *H*1 ..... | 1·97 | 276·1 | 4·6 | 1·50 | 0·47 |
| *H*2 ..... | 2·80 | 295·5 | 1·7 | 0·23 | 2·57 |
| *H*3—*H*12 ..... | 31·85 | 299·1—326·6 | 1·8—12·9 | — | 31·85 |
| Residue ..... | 4·97 | 376·2 | 66·5 | — | 4·97 |
| Total ..... | 41·59 | | Total ..... | 1·73 | 39·86 |
| | | | Palmitic acid, % | 4·2 | 95·8 |

From the above results, the composition of the mixed acids of the oil was calculated to be as shown in Table IX.

TABLE IX.

*Component acids of* Parinarium laurinum *seed fat* (%, wt.).

| Fraction : | *A*. (52·1%). | *B*. (28·7%). | *C*. (3·0%). | *D*. (2·8%). | *E*. (7·3%). | $P_1+P_2$. (6·1%). | Total. | Acids including unsaponifiable, % (wt.). |
|---|---|---|---|---|---|---|---|---|
| Palmitic ..... | 4·90 | 6·11 | 1·08 | 1·21 | 2·55 | — | 4·20 | 4·2 |
| Stearic ..... | | | | | | | 1·00 | 1·0 |
| Unsaponifiable | | | | | | | 0·90 | — |
| Oleic ..... | | | | | | | 9·75 | 9·9 |
| Linoleic ..... | — | 0·26 | 0·23 | 0·09 | 1·13 | — | 1·71 | 1·7 |
| Conj. dienoic ..... | 1·20 | 0·49 | 0·17 | — | 0·31 | — | 2·17 | 2·2 |
| Conj. trienoic ..... | 7·40 | 15·15 | 1·19 | 1·37 | 2·41 | — | 27·52 | 30·1 |
| Parinaric ..... | 38·60 | 6·69 | 0·33 | 0·13 | 0·90 | — | 46·65 | 50·9 |
| Polymerised * ... | — | — | — | — | — | 6·10 | 6·10 * | — |

* The polymerised acids have been assumed to arise from elaeostearic and parinaric acids in the relative proportions observed for these acids.

*Identification of Acids.—Palmitic acid.* Fraction *H*1 (1·31 g.; Table VIII) was redistilled through a micro-distillation apparatus, yielding a fraction (0·37 g.) of sap. equiv. 272·9, which was converted into its *p*-bromophenacyl derivative; after recrystallisation from alcohol this had m. p. 82—83·5° alone or mixed with *p*-bromophenacyl palmitate (m. p. 83·5—84°).

*Parinaric acid.* (i) Crystallisation fraction *A* (Table V) was recrystallised repeatedly from light petroleum and ether, and yielded parinaric acid, m. p. 86°, $E^{1\%}_{1\,cm.}$ 2624 at 305 mμ.; these values could not be increased by further crystallisation. The above spectrographic value was the mean obtained by triplicate determinations (ranging from 2604 to 2644) on four preparations of parinaric acid.

(ii) *Oxidation of methyl parinarate.* Parinaric acid (7·00 g.) was esterified with methyl alcohol containing 0·5% of hydrogen chloride. The resultant esters (4·91 g.) were oxidised in solution in 100 ml. of acetone with 50 g. of potassium permanganate. There was obtained 1·00 g. of crude dibasic acid, together with a considerable amount of ether-insoluble polymerised material. The acid on recrystallisation from 100 ml. of water yielded 0·31 g. of azelaic acid, m. p. 102—104° alone or mixed with authentic material (m. p. 103—105°). Parinaric acid (17·95 g.) on oxidation under the same conditions yielded 4·63 g. of crude azelaic acid, which on recrystallisation from water had m. p. 103—104°.

(iii) *Combination of parinaric acid with maleic anhydride.* Parinaric acid (2·80 g., 0·01 mol.) was heated to 100° for 5 minutes in an atmosphere of carbon dioxide with maleic anhydride (2·1 g., 0·0215 mol.). The resultant dark viscous fluid, which was insoluble in light petroleum, solidified in 2 days to a hard brittle resin.

*α-Elaeostearic acid.* (i) *Preparation of a concentrate of the trienoic acid.* The mixed acids (133 g.) from the oil were crystallised from 2660 ml. of light petroleum at 0°. The resultant filtrate was then cooled to −15°, and a further crop of crystals (12·8 g.) removed. The volume of the filtrate was reduced to 800 ml., and the solution cooled to −65°. The deposited crystals (34 g.) were recrystallised from light petroleum (900 ml.) at −45° and then from 300 ml. of ether at −20°. The soluble acids (23·2 g.) from the ether crystallisation were twice crystallised from acetone at −15° and then at −75°. The crystalline product (14·5 g.) had $E^{1\%}_{1\,cm.}$ 1409 at 270·5 mμ. and 428 at 305 mμ., corresponding with 76·3% of α-elaeostearic and 16·3% of parinaric acid. This concentrate was used for the characterisation of the triene acid.

(ii) *Oxidation of the concentrate.* The methyl ester (5·14 g.) of the concentrate was oxidised in 50 ml. of acetone with 35 g. of potassium permanganate. The crude dibasic acid (1·50 g.) after recrystallisation from 100 ml. of water yielded 0·553 g. of azelaic acid, m. p. 103—105° (mixed m. p. undepressed).

(iii) *Preparation of the maleic anhydride adduct of the trienoic acid.* The concentrate (3·28 g.) was heated with maleic anhydride (0·72 g.) at 105° for 15 minutes in a current of carbon dioxide. The cooled mixture was boiled twice with light petroleum (100 ml.), and the clear liquid decanted from the

small amount of insoluble oil. On cooling, there separated from the light petroleum 0·5 g. of a white crystalline adduct, which was twice recrystallised from 140 ml. of light petroleum, yielding 0·38 g. of adduct, m. p. 62—63° (undepressed by the maleic anhydride adduct of α-elaeostearic acid, m. p. 62—63°).

(iv) *Preparation of maleic anhydride addition compound of α-elaeostearic acid.* α-Elaeostearic acid (2·78 g., 0·01 mol.), $E^{1\%}_{1\,cm.}$ 1795 at 270·5 mμ., was heated with maleic anhydride (1·0 g., 0·0102 mol.) at 105° for 15 minutes. The adduct was separated and recrystallised as above, yielding 0·31 g. of colourless adduct, m. p. 62—63° (Morrell and Samuels, *J.*, 1932, 2251, record m. p. 62·5°). The ultra-violet absorption spectra of this compound and the adduct from the concentrates of the triene acid were identical.

*Linoleic and oleic acid. Preparation of a concentrate of linoleic and oleic acid.* The mixed acids (210 g.) from the oil were crystallised from 2·5 l. of light petroleum at −70°, and the resultant liquid acids (80·5 g.) were recrystallised from 400 ml. of light petroleum at −60°. The filtrate from this crystallisation [11·9 g.; I val. (Toms), 135·9], which contained linoleic 17·3, parinaric 3·2, α-elaeostearic 15·2, and conjugated dienoic acids 5·5%, was employed for the characterisation of oleic and linoleic acid.

(i) *Bromination (detection of linoleic acid).* The concentrate (3·05 g.) was brominated in 60 ml. of light petroleum at −10° with 0·82 ml. of bromine. The clear liquid was decanted from the deposited oil and set aside overnight at 0°. 0·29 G. of crystalline bromides separated. The latter were recrystallised from 10 ml. of ether at −40°, yielding 0·102 g. of 9 : 10 : 12 : 13-tetrabromostearic acid, m. p. 113·5—114° alone or mixed with authentic tetrabromostearic acid, m. p. 114°. Complete solubility of the bromides in ether indicated the absence of hexabromostearic acid, and hence of linolenic acid from the oil.

(ii) *Oxidation with dilute alkaline permanganate.* The concentrate (7·37 g.) was oxidised by the method of Lapworth and Mottram (*J.*, 1925, **127**, 1628). There were recovered 1·63 g. of hydroxy-acids and 2·23 g. of saturated and unoxidised acids. On recrystallisation of the former from water and ethyl acetate, 0·50 g. of dihydroxystearic acid, m. p. 132°, was obtained (mixed m. p. with 9 : 10-dihydroxystearic acid, m. p. 132°, undepressed). In addition the two 9 : 10 : 12 : 13-tetrahydroxystearic acids, m. p. 153° (0·32 g.) and 173° (0·13 g.), formed by the oxidation of linoleic acid, were also recovered.

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