A STUDY OF THE CONSTITUENTS OF THE SEEDS OF *CROTON SPARSIFLORUS* (MORUNG)—PART II

Chemical Examination of the Components

BY S. V. ANANTAKRISHNAN, S. ARAVAMUTHACHARI
AND
V. S. GOVINDARAJAN
(*From the Chemical Laboratories, Annamalai University, Annamalainagar*)

Received September 1, 1941

IT has been noticed in Part I that the petroleum ether extract contains most of the solvent extractables and this extract has been used for a more thorough investigation as to the component " resins ", unsaponifiables and glycerides.

While the formation of a deep red colour on refluxing with alkali may be indicative of the presence of a resinous component, neither the method of Flaschentrager and Wollffersdorff[6] who isolated the poisonous resinous component or 'Naturstoff' from *Croton tiglium*, nor the more general methods described in text-books gave any appreciable quantity of such a substance in a sufficiently pure state for a complete study. That any such component is present at best in minute amounts only is indicated from the physical and chemical constants of the treated oil which shows no appreciable difference. The method of Cherbuliz[2] also gave a similar result.

The colour with alkali is presumably due to the colouring matter in the seed coat.

As may be expected, the oil contains unsaponifiable matter which could be separated into several components which are still under investigation. A sterol, m.p. 138°, $(\alpha)\ {}^{29.5^{\circ}C}_{5460.7}$. $(C = 0{\cdot}8013) = 56{\cdot}27$ has been isolated. Microscopic examination of the sterol, melting point of the sterol and of the acetyl derivative and the rotation indicate this to be a phytosterol largely consisting of α-sitosterol.

Component Acids.—The chemical examination of the fat may be considered under two heads, the nature of the glycerides and the component acids in the glyceride. Information regarding the latter can be obtained in several ways, and the components definitely established are given in Table I.

TABLE I

Distribution of component acids in the oil (by weight %)

Component acids	Total % in oil	Component acids	Total % in oil
Palmitic	5·49	Linolenic	9·36
Stearic	4·75	Unsaponifiable matter	0·98
Oleic	5·72	Glycerine (by difference) ..	8·02
△9:12-octa-decadienoic ..	65·70		

The Hehner value indicates 91·96% of acids saturated and unsaturated together with unsaponifiable matter in the oil. These components were obtained after saponification under standardised conditions (*vide* experimental part). The separation of solid and liquid components has been effected by Twitchell's lead salt alcohol method,[30] some modification, of the same[10] and by direct crystallization from acetone solution.[25] The results of these different methods are appended in Table III.

Mention should be made here of the relative accuracy of the different methods. Repeated trials have shown that Bertram's oxidation method gives accurate results for saturated acids provided the conditions of temperature are maintained so as to completely eliminate hydroxy acids arising from the unsaturated acids (see also Gay[7] and Hilditch and Priestman.[12])

The modified lead salt-alcohol method[10] has been consistently found to yield more accurate results and a purer solid acid than other methods involving lead salts. Rigid control of temperature at 15–16° C. for twelve hours is absolutely necessary for concordant results.

As the methods of separation do not completely eliminate liquid acids, a correction factor based on the iodine value of the two fractions[16] has to be used for an accurate estimation of solid acids.

With reactive unsaturated compounds and with possibilities of isomerization catalysed by the saponifying reagents, lead salt methods are liable to lead to some uncertainty arising from the greater or different solubilities of some of the lead salts. Physical methods of separation are preferable and in the present case, crystallization of the scids in acetone solution at different temperatures have been adopted.

It will be noticed that the component acids are mostly liquid (90%) and these have a high iodine value (Tables II and III).

TABLE II

Method	Reference	Weight % in acids				Weight % in oil*	
		Solid acids			Liquid acids (by difference)	Solid acids	Liquid acids
		Found %	Iodine value	Corrected %			
Twitchell lead salt alcohol ..	(30)	10·92	15·54	9·92	90·08	9·03	81·95
Modified Twitchell lead salt alcohol	(10)	10·85	6·30	10·45	89·55	9·51	81·47
Ba gman-Jamieson lead salt ether	(16)	16·78§	30·20	13·80	86·20	12·55	78·43
Bertram oxidation (modified)	(16)	11·25‡	..	11·25	88·75	10·24	80·74
Crystallization method ..	(25)	10·90	..	..	..	9·92	81·06

* Calculated for 90·98% of total acids (Hehner value—unsaponifiable %) in oil from corrected values.

§ Calculated from the value 15·27, obtained for per cent. of saturated acid, direct from oil.

‡ Calculated from the value 10·24 for per cent. of saturated acid, direct from fat.

TABLE III

Details of analysis	Total acid	'Solid' acid	'Liquid' acid (by difference)
Weight % on total acids	100	11·25	88·75
Iodine value (Rosenmund-Kuhnhenn) ..	165·7	0·1	169·5
Thiocyanogen value	91·34	..	92·12
Mean molecular weight	289·3	265·5	1233*

* The high molecular weight of the liquid acids may be due to polymerisation by intermolecular addition of the unsaturated acids.

The solid acids obtained are essentially palmitic and stearic acids. Partial separation of the acids was effected by fractional distillation of the methyl esters under reduced pressure, the rich fractions being used for the preparation and identification of the pure acids. The final estimate of the relative proportions were made by the method of thermal analysis and molecular weight determination.

In establishing the relative amounts of the different unsaturated acids present, bromination, partial oxidation, fractional distillation of methyl esters and Kaufmann's method using thiocyanogen-iodine and iodine values have been employed.

The formation of an ether insoluble crystalline hexabromostearic acid (m.p. 182° C.) while indicative of the presence of linolenic acid in the oil cannot always be taken to be quantitatively representative of the triolefinic acid content (Rollet,[23] Erdman and Bedford[5] and McCutcheon[22]). The low hexabromide value combined with the high iodine value indicates a high proportion of linoleic acid with smaller amounts of oleic and linolenic acids. However, bromination of the mixed fatty acids failed to yield any solid tetrabromide characteristic of α-linoleic acid usually found in seed fats. The high bromine content (50·29%) of the oily liquid from the separation of the hexabromide indicates the presence of a peculiar C_{18}-diethenoid acid. This is considered in greater detail in a later section.

Controlled oxidation of the acids may also be expected to give an insight into the component acids. The method of Lapworth and Mottram[20] was found unsatisfactory and that of Hilditch and Jasperson[11] has been adopted. An impure product, m.p. 124–126°, from which only a very small amount of tetrahydroxy-stearic acid (m.p. 172° C.) could be isolated was obtained. After recrystallization only impure dihydroxy-stearic acid could be obtained. This was obtained in a pure state and in sufficient amounts by a slight modification of the process (Experimental). The isolation of this product connotes the presence of oleic acid in the glyceride. No keto-stearic acid was isolable in the process and only small amounts of hexahydroxy acid could be got.

Complete oxidation of the methyl esters of 'liquid' acids in acetone with potassium permanganate (weakly alkaline) gave *n*-hexoic, oxalic and azelaic acids. The formation of these indicate the presence in the original mixture of $\Delta^{9:12}$-linoleic and linolenic acids.

The close boiling points of the methyl esters ruled out the separation of the constituent acids by fractional distillation of the esters under reduced pressure and all attempts failed to separate the constituents.

It has been found[18] since Kaufmann's thiocyanogen-iodine number determination that a combination of this with iodine values can be used for computing the proportions of the unsaturated acids. If a mixture contains S% saturated acids, X% linolenic, Y% linoleic and Z% oleic acids then

$$100 \times (\text{iodine value}) = 273{\cdot}7\,X + 181{\cdot}1\,Y + 89{\cdot}9\,Z$$

$$100 \times (\text{thiocyanogen value}) = 182{\cdot}5\,X + 90{\cdot}5\,Y + 89{\cdot}9\,Z$$

$$100 = X + Y + Z + S.$$

If S is determined by any of the usual methods, X, Y and Z can be calculated. The results of such a computation are given below:

TABLE IV

Distribution of Fatty Acids in Mixed Acids

Acids	Kaufmann method (weight %)	Bromination method (weight %)
Saturated (Bertram)	11·14	11·14
Oleic	6·30	..*
$\Delta^{9:12}$-octa-decadienoic	72·28	..*
Linolenic	10·28	4·04

* The iodine value of the remaining unsaturated acids after allowing for the observed amounts (4·04) of linolenic acid, corresponding to the hexabromostearic acid isolated, was still in excess of that of linoleic acid. This is, in itself, proof that linolenic acid is not completely separated as insoluble hexabromide. It will also be noted that the bromination method records only 39·25% of the linolenic acid content indicated by thiocyanometric analysis.

Though the accuracy of this method has been questioned,[31] it now appears from the work of Hilditch and co-workers[13, 14] that the method is fairly accurate (see however Smith and Chibnall[26])

C_{18} Acids.—It is necessary, at this stage, to consider in greater detail the C_{18} acids, especially the unsaturated acids.

The formation of hexabromostearic acid (m.p. 182°) by bromination and of dihydroxy stearic acid (m.p. 131°) by controlled oxidation clearly indicate the presence of linolenic and oleic acids in the oil. The evidence for an octa-decadienoic acid is however, not so direct. According to Hilditch[13] (see also foot-note to Table IV) the hexabromide value of an oil measures approximately 40% of the actual linolenic acid present and on this basis, the hexabromide value (10·99) corresponds to 10·1% linolenic acid in the mixture of acids from the oil. If the rest of the mixture were to contain only oleic acid (78·76) and saturated (11·14% observed value) acids, the iodine value of the total acids should be 99·26 while the actual value obtained is 165·7. This clearly indicates a higher unsaturation, than one double bond (if remaining unsaturated acid is diolefinic iodine value should be 170·3). The absence of a benzene insoluble bromide (*vide* Experimental) precludes the presence of higher unsaturation than a trieth-enoid type. One must necessarily conclude that a diethenoid compound is present in appreciable amounts to account for the high iodine value. Further, complete oxidation of the methyl esters leads to *n*-hexoic acid, oxalic acid (presumably from malonic acid) and azelaic acid, clearly pointing to the presence of $\Delta^{9:12}$-octa-decadienoic acid (*vide* Haworth[9]).

The presence of mono-, di- and tri-ethenoid C_{18} acids having been established, it is clear that the thiocyanometric method is the best for

estimating the relative proportions. This gives the values tabulated earlier (Table V). It is significant that with such a high percentage of $\Delta^{9:12}$-octadecadienoic acid, bromination of the unsaturated acid fails to give the petroleum ether insoluble, crystalline tetrabromide (m.p. 114°) characteristic of the common or α linoleic acid but yields an oily liquid bromide soluble in petroleum ether (Bromine content 50·28%). Prolonged keeping of the oily bromide gives a small amount of a low melting waxy solid. It must be mentioned that Kass and Burr[17] have obtained a similar waxy solid (m.p. 75·5–78°) from the products of bromination of elaidinised α linoleic acid. The linoleic acid present in the oil under investigation must therefore be an isomeric form. Our observations, however, are enough to show that this is not likely to be either the *cis-cis* or the *trans-trans* forms.

Evidence for conjugated unsaturation is inadequate but the small but definite maleic anhydride value and effect of weight of sample on the iodine value by Wijs and Hanus methods suggest some conjugation.

The configuration of the linoleic acid is under investigation.

Glyceride structure.—The oil does not contain any fully saturated glyceride, the small quantity of solid resulting from acetone permanganate oxidation being only the unsaponifiable matter.

A preliminary study of the mixed unsaturated saturated glycerides has been made by the fractional crystallization of the brominated glycerides and comparing them with those prepared from linseed oil. The glycerides from linseed oil were separated by the method of Tom.[29] The bromoglyceride corresponding to α-linoleo-di-α-linolenic glyceride melted even after several recrystallisations only at 153° C. Another fraction having m.p. 143° was also isolable. Following Eibner[3] this has been taken to be β-linoleo-di-α-linolenic bromoglyceride.

Following Tom's procedure, the oil under study gave 17·8% of the more insoluble glyceride showing the presence of linoleo-di-linolenic glyceride in the oil. The product had a m.p. 143–144° and the m.p. was not depressed by admixture with a similar product from linseed oil. This must therefore be β-linoleo-di-α-linolenic bromoglyceride. The separation by Suzuki and Yokoyama[28] of two isomeric linoleo-di-linolenin from linseed oil, however, leaves this an open question and further investigation is necessary before establishing the identity of this compound. The absence of a product of m.p. 156° corresponding to the α-linoleic-di-α-linolenin indicates that α-linoleic acid is not present in the oil to any appreciable extent.

Another fraction isolated having m.p. 118° probably corresponds to triolein or oleic-linoleic-linolenic glyceride.

It is interesting to compare here the different properties of the three members of this genus.

TABLE V

Comparative Data of the Three Species of the Genus Croton

Characteristics	*Croton tiglium*	*Croton Elliotianus*	*Croton sparsiflorus*
Physiological	A powerful vesicant an irritating purgative	Non-vesicant non-irritating purgative	Non-vesicant no purgative action
Colour	Dark yellow	Yellow	Light yellow
Type of oil	Non-drying	Drying	Drying
% Yields of oil on seeds ..	50	30	32
Iodine value	102–108	143–147·5	164–171

TABLE V—*Contd.*

Component Fatty Acids (Weight %)

Acids	*Croton tiglium*	*Croton Elliotianus*	*Croton sparsiflorus*
Palmitic	1·30*	10·0§	5·97
Stearic	0·50		5·17
Oleic	55·80	10·0	6·30
Linoleic	28·80	80·0	72·28‡
Other unsaturated acids ..	Traces of steam volatile lower acids	..	Linolenic 10·28
Observers	Flaschentrager and Wollffersdorff[6]	Imperial Institute[1a]	Present work

* Also 11·3% myristic and 2·3% arachidic acids.

§ Chiefly palmitic.

‡ The acid is an isomer of usual seed fat linoleic acid.

The constituent acids conform to the general observation that the Euphorbiaceæ seed fats contain about 10% saturated and about 80% unsaturated acids but *Croton tiglium* differs from the other two in the nature of the saturated acids. The oil under investigation is also exceptional in containing linolenic acid and no steam volatile components.

Experimental

Preparation of acids.—The best procedure after several trials was found to be the following: 100 parts of the oil were refluxed on a steam-bath for four hours with a solution of 40 parts of potassium hydroxide in 500 parts of 95% alcohol (by weight). Most of the alcohol was removed by distillation in a current of carbon dioxide, the soaps dissolved in a large volume of water and the unsaponifiable matter removed in a continuous extractor. The

free acids were obtained from this either by acidulation and extraction or by the method of Steele and Washburn,[27] the operations being carried out in an inert atmosphere. Completion of saponification was tested by Geitel's[8] test. For large quantities, the second method works better.

Separation of saturated and unsaturated acids.—The separation of saturated and unsaturated acids was effected by the usual standard lead salt methods and by direct crystallization. The apparatus for this last process can be constructed from common laboratory materials, namely a wide mouthed vacuum jar, a large test-tube and a thistle funnel closed by a filter paper, the arrangement being as in Fig. 1.

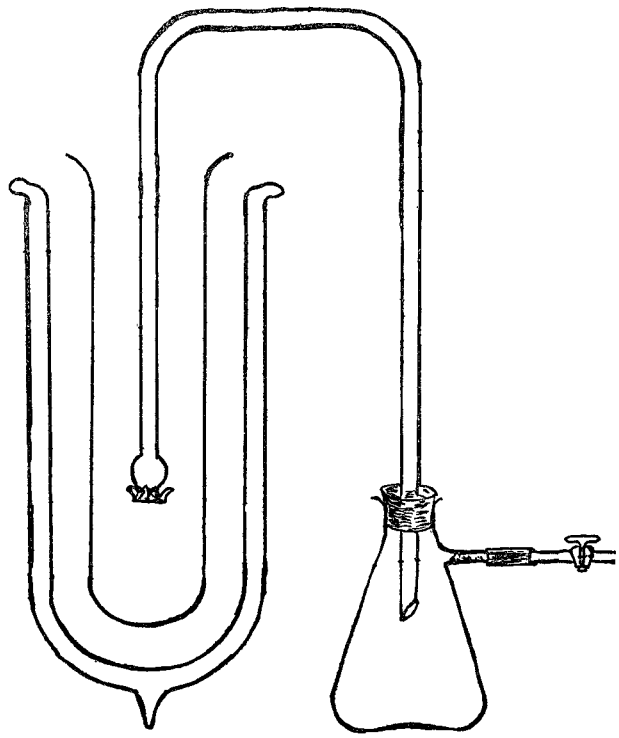

FIG. 1

A solution of the mixed acids in acetone is placed in the test-tube and cooled to different temperatures using appropriate freezing mixtures. After equilibrium at each temperature, the solution was drawn through the filter paper by suction and the residual solid washed with cooled acetone two or three times. The solids thus obtained at each stage indicated a good separation of the components. The advantage of this arrangement over that of Shinowara and co-workers[25] is that all filtrations and washing are carried out at specified low temperatures at which crystallization takes place.

Separation of saturated acids is complete in six hours at $-19°$ to $-22°$ C. From 60 gm. of the total acids 6·54 g. saturated acid were obtained. The same acids were also obtained by Bertram's oxidation method modified by Jamieson[16] correction for adsorbed unsaturated acids being applied by means of the iodine value. Molecular weights of the acids were determined by the usual methods.

Unsaturated acids.—85·73 g. of freshly separated 'liquid' acids (Twitchell's method) were converted into the methyl esters by the usual methods and when purified 73·25 g. of the mixed esters was obtained. 62·5 g. of this mixture was taken in an ordinary Ladenburg flask and distilled under 1 mm. pressure, using a Perkin triangle to collect the fractions. The middle bulb of the flask was two-thirds filled with glass beads supported on a thin strip of copper gauze. The three bulbs and neck were thickly coated with asbestos with slit windows for observation in order to minimise overcondensation of esters. The bottom bulb was completely immersed in an oil-bath whose temperature was maintained 50–60° higher than that indicated by the thermometer at the top of the column. The results of this fractionation are given in the table below.

TABLE VI

Fractional Distillation of the Methyl Esters of the 'Liquid' Acids

(62·47 g.)

No.	Weight in g.	Temperature at head of the column °C.	Iodine value*	No.	Weight in g.	Temperature at head of the column °C.	Iodine value*
1	1·25	140–150§	93·6	5	7·87	158–160	154·0
2	10·95	150–154	129·4	6	14·43	160–162	169·4
3	6·84	154–156	133·7	7	12·88	Residue	..
4	8·25	156–158	148·3				

* Rosenmund-Kuhnhenn method.

§ A few drops collected below 140° C.

All the fractions gave Martins colour test for linolenic acid.[21]

The liquid acid mixture was brominated in chloroform, ether and petroleum ether by adding excess bromine in solution and removing the excess with amylene. In each case after one or two recrystallizations pure hexabromostearic acid, m.p. 181–82° C. was obtained; the identity was established by comparison with an authentic specimen and by analysis. (Br found: 63·6; $C_{18}H_{30}O_2Br_6$ requires Br = 63·3%.) From the residual solutions, no tetrabromostearic acid was isolable in any of the experiments. Prolonged keeping of a petroleum ether solution at or below 0° C. gave rise to a low melting white solid with a bromine content of 50·29%.

Oxidation of liquid acid esters.—The middle fractions from the fractionation of the methyl esters were submitted to oxidation by Haworth's method[9] using potassium permanganate in acetone solution. After oxidation, acetone was distilled off and the residue extracted with a hot dilute solution of sodium hydroxide. The combined extracts were concentrated to 150 c.c. acidified with hydrochloric acid and ether extracted.

The presence of oxalic acid in the aqueous layer was detected by the formation of calcium oxalate, decolourization of potassium permanganate and the formation of urea oxalate. The urea oxalate was compared with an authentic specimen.

The ether extract was washed free of acid, the solvent distilled off and the residue steam distilled. The non-volatile residue was decolourised with animal charcoal in aqueous solution, filtered and allowed to crystallise. White crystals (m.p. 103°) were obtained. On recrystallization, a pure product (m.p. 105·5°, molecular weight 187·5) was got and was identified as azelaic acid.

The volatile distillate was thrice extracted with petroleum ether (50°–60°), dried over anhydrous sodium sulphate and the solvent carefully distilled off. *n*-Hexoic acid was obtained (m.p. Ca −2°) and confirmed by the formation of an anilide (m.p. 92°) (m.p. of *n*-hexoic acid −2°; m.p. of its anilide 95°).

Partial oxidation of liquid acids by Lapworth's method gave only dihydroxy stearic acid as a product. Dioxane was found to be the best solvent for recrystallizing this compound. (Found: m.p. 131°; mol. wt. 316·2.)

The method of Hilditch and Jasperson[11] gave better results. After oxidation with cold very dilute permanganate, the solution was decolourized with sulphur dioxide and acidified with hydrochloric acid. The precipitated crude hydroxy acid was refluxed with petroleum ether (50–60°) after drying at 65–70° C. to remove unoxidized acids. The residue after filtration was refluxed thrice with ethyl acetate (for 0·77 g. of the crude hydroxy acid, 50 c.c. of the ethyl acetate was used each time) and filtered hot. A small quantity of a white substance was left undissolved and on recrystallization from alcohol melted at 169° (one of the tetrahydroxy stearic acids melts at 172°–73° C.).

The ethyl acetate solution on cooling deposited white crystals (m.p. 124–26°) and further purification did not affect the melting point (mixed m.p. with pure dihydroxy stearic acid 128°). Equivalent weight of this compound was 241·8.

Selective oxidation.—The procedure was based on that of Kaufmann and Fiedler for oleic acid.[19] Mixed acids (14·75 g.) were just made alkaline

with alcoholic potassium hydroxide, diluted to two litres with water, cooled to 0° C. and oxidized with two litres of a 1% solution of potassium permanganate with efficient stirring during 30 minutes. The solution was allowed to stand for 10 minutes, acidified with sulphuric acid and decolourized with sodium bisulphite. The solid obtained was collected on the filter, the solution being examined for hexahydroxy acids.

The crude hydroxy acid (0·91 g.) was taken up with a large volume of warm ether. A very small quantity (0·08 g.) of a brownish substance gave on recrystallizations from alcohol a pure white product melting sharply at 172°. This is presumed to be tetrahydroxy stearic acid.

The ether extract gave a white solid which after washing with petroleum ether gave a powdery substance (m.p. 129°; equivalent weight 334·2). Recrystallization from dioxane gave pearl-white flakes (m.p. 130°) confirmed as dihydroxystearic acid by comparison with an authentic specimen.

The filtrate from the original oxidised solution after separation of the crude hydroxy acid was concentrated to small bulk and acidified. The product after recrystallizations from alcohol and water was very small in quantity (m.p. 196°). Being more soluble in water than the tetrahydroxy acid and with a m.p. higher than that of the known tetrahydroxy acids, this is presumed to be hexahydroxy stearic acid. The quantity obtained was too small for definite identification.

Solid acids.—The solid acids from Twitchell's method were converted into neutral methyl esters and distilled under reduced pressure. The results of fractionation are tabulated below.

TABLE VII

Fractionation of Methyl Esters of 'Solid' Acids

Fraction No.	Temperature at head of the column ° C.	Weight of fraction g.	Saponification value	Molecular weight	Acids identified
a	145–54	0·62	204·2	274·9	Palmitic
b	154–57	2·55	203·8	275·4	Palmitic and stearic in small amounts
c	157–60	2·61	203·5	275·7	Palmitic and stearic
d	160–62	1·63	198·2	283·1	Stearic and palmitic
e	162–64	2·23	192·1	292·1	Stearic and palmitic in small amounts
f	163–64	2·14	192·2	292·0	Do.
g	Residue including loss	0·96	192·0	292·2	..

TABLE VIII

Calculated Distribution of 'Solid' Acids

Fraction No.	Palmitic acid (weight in g.) calculated from ester	Stearic acid (weight in g.) calculated from ester	Total acid (weight in g.)
a	0·49	0·10	0·59
b	2.00	0·44	2·44
c	2·00	0·48	2·48
d	0·84	0·70	1·54
e	0·47	1·60	2·07
f	0·47	1·57	2·04
g	0·20	0·71	0·91
Total (weight in g.) ..	6·47	5·60	12·07
% (weight) on solid acids	53·58	46·42	100
Calculated on 11·25% of mixed acids	% (weight) 6·03	5·22	11·25
	% (mole) 6·34	4·91	11·25

Pure palmitic and stearic acids were obtained from the fractions.

Unsaponifiable matter.—The crude unsaponifiable matter was again saponined for one hour. Tne white flakes that separated out on cooling were filtered off and washed with methanol. The product answered the usual colour reactions for sterols. The Rosenheim reaction was negative indicating the absence of conjugation. The sterol was purified by precipitating as the digitonide and decomposing it with pyridine (Schonheimer and Dam[24]). The specific rotation of the sterol was observed in chloroform solution.

TABLE IX

The Constants of the Sterol

Melting point	138° C.
Melting point of acetyl derivative	125° C.
Melting point of digitonide	Softens 206° C.; melts to brown liquid 235° C.
$(\alpha)^{29°.5}_{5460.7}$ (C = 0·8013)	−56·27
$(\alpha)^{29°.5}_{5790.7}$ (C = 0·8013)	−32·64

Small quantities of an alcohol and a low melting solid hydrocarbon were isolated from the filtrate from sterol digitonides but the quantities were inadequate for complete investigations.

Glyceride structure.—Fully saturated glycerides were determined by the oxidation method of Hilditch and Lea.[15]

Reference substances for Tom's method[29] were prepared from pure linseed oil.

The oil under investigation (1 g.) was brominated in ethyl acetate (10 c.c.) at about 0° C. by slow addition of 1 c.c. bromine with efficient stirring. The crude bromoglyceride was separated by filtration, washed with 20 c.c. portions of ethyl acetate and dried at 80°. Further purification with alcohol, ether and tetralin gave a white substance (m.p. 143°) identical with β-linoleo-di-α-linolenin obtained from linseed oil. From the ethyl acetate filtrate a second product unidentified (m.p. 117° C.) was obtained.

The authors thank the Superintendent, Government Test House, for a sample of tested raw linseed oil which was used for comparison.

Summary

The oil from the seeds of *Croton sparsiflorus* has been examined for its composition. Apart from palmeitic, stearic, oleic and linolenic acids, the glyceride contains an unusual isomeric form of the common α-linoleic acid. Complete analysis of the oil has been effected by using Bertram's oxidation method and Kaufmann's thiocyanometric method. Fully saturated glycerides are absent and the oil contains β-linoleo-di-α-linolenin.

The sterol in the unsaponifiable matter is essentially sitosterol.

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