Fatty Acids. Part II. The Nature of the Oxygenated Acid present in* Vernonia anthelmintica *(Willd.) Seed Oil.*

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Vernolic acid, reported to be 11-hydroxyoctadec-9-enoic acid † (Vidyarthi, *Patna Univ. J.*, 1945, **1**, 51) is now shown to be 12 : 13-epoxyoctadec-9-enoic acid. The approximate composition of *V. anthelmintica* seed oil has been determined.

IN Part I,* *Strophanthus sarmentosus* seed oil was shown to contain 9-hydroxyoctadec-12-enoic acid isomeric with the more familiar ricinoleic (12-hydroxyoctadec-9-enoic) acid of castor oil. 9-Hydroxyoctadec-12-enoic acid is now known to occur in other species of the *Strophanthus* genus (Gunstone, *J. Sci. Food Agric.*, 1953, **4**, 129). The isolation of this acid casts some doubt on the structure of similar hydroxy-acids, present in other fats, which have been described as ricinoleic acid merely on the basis of iodine value, equivalent, and acetyl value, and accordingly a number of these fats are being reinvestigated. This paper deals with *Vernonia anthelmintica* seed oil which has been reported to contain 11-hydroxyoctadec-9-enoic acid, another isomer of ricinoleic acid (Vidyarthi, *Patna Univ. J.*, 1945, **1**, 51).

It is further hoped that this study of naturally occurring oxygenated acids may contribute to the solution of the problem of the biogenesis of seed oils, since the hydroxy-acids present in seed fats may be the immediate precursors of the widely occurring unsaturated acids (oleic, linoleic, linolenic), which certain species or genera are unable, wholly or partly, to dehydrate, or alternatively may be examples of structures, not normally produced in plant systems, which, once formed, cannot be further metabolised owing to lack of suitable enzymes.

Vernonia anthelmintica (Willd.), syn. *Serratula anthelmintica* (Roxb.) and *Conyza anthelmintica* (Linn.), also known as the purple flea-bane and belonging to the family *Compositae*, is reported to be a tall robust leafy annual met with throughout India. Parts of the plant are said to have anthelmintic properties (Caius and Mhaskur, *Indian J. Med. Res.*, 1923, **11**, 353; Chopra, Ghosh, and Mukerji, *ibid.*, 1934, **22**, 183; Majumdar, *Indian J. Pharm.*, 1943, **5**, 61) and to be of value in the treatment of leucoderma (Ghosh, *Pharm. J.*, 1928, **121**, 54).

Chemical investigation of this seed oil has been reported by Kesava-Menon (*J. Soc. Chem. Ind.*, 1910, 1431), Vidyarthi and Mallya (*J. Indian Chem. Soc.*, 1939, **16**, 479), Majumdar (*loc. cit.*), and Vidyarthi (*loc. cit.*). These authors have drawn attention to the high acetyl value and optical rotation of this oil and have reported the presence of myristic, palmitic, stearic, oleic, linoleic, and vernolic acids among the component acids. The latter was considered to be 11-hydroxyoctadec-9-enoic acid.

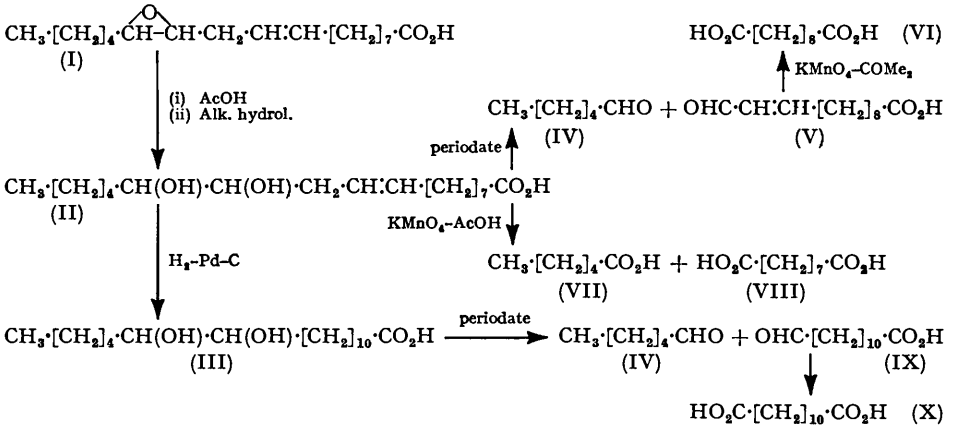
The Oxygenated Acid.—V. anthelmintica seeds were obtained from India (see p. 1616). The small green-brown bullet-shaped seeds yielded a dark green oil (26—27%) when extracted with light petroleum. Preliminary experiments showed that the oil contained an epoxy-acid; thus methanolic hydrogen chloride converted the acids into a product of low equivalent weight owing to the formation of a chloro-hydroxy-ester, whilst methanol containing concentrated sulphuric acid gave the hydroxy-methoxy-ester with a high equivalent weight (cf. Nicolet and Poulter, *J. Amer. Chem. Soc.*, 1930, **52**, 1186; Atherton and Hilditch, *J.*, 1943, 204; Swern, Findley, Billen, and Scanlan, *Analyt. Chem.*, 1947, **19**, 414; King, *Nature*, 1949, **164**, 706, *J.*, 1951, 1980). Quantitative determination of the epoxy-group (King, *loc. cit.*) showed that this was present in high proportions.

Because of the reactivity of the epoxy-compound it was converted into the corresponding dihydroxy-acid by treatment with acetic acid before the usual alkaline hydrolysis. A concentrate of the dihydroxyoctadecenoic acid was then easily prepared by partition of the

* Part I, *J.*, 1952, 1274.

† Geneva numbering, $CO_2H = 1$.

mixed acids between light petroleum and aqueous methanol. This readily gave a pure specimen of dihydroxyoctadecenoic acid which is almost certainly the *cis*-isomer and, after isomerisation of the concentrate, the higher-melting *trans*-isomer was also isolated. Hydrogenation of the mixed acids obtained on hydrolysis of the epoxide gave dihydroxystearic acid. Both the *cis*-unsaturated and the saturated acid showed a small lævorotation. Reinger (*Ber. deut. Pharm. Ges.*, 1922, **32**, 124) has described 12 : 13-dihydroxyoctadec-9-enoic acid as a syrupy liquid, whilst McKay and Bader (*J. Org. Chem.*, 1948, **13**, 75) have described the *cis*- and the *trans*-isomer of 9 : 10-dihydroxyoctadec-12-enoic acid as a liquid and a solid (m. p. 97°) respectively. The two racemic forms of 12 : 13-dihydroxyoctadecanoic acid are well known.



Dihydroxystearic acid (III), treated with periodate (King's procedure, *J.*, 1938, 1826; 1942, 387; cf. Huber, *J. Amer. Chem. Soc.*, 1951, **73**, 2730), gave a volatile aldehyde (not isolated) and a solid aldehydo-acid ($C_{12}H_{22}O_3$) which must be 11-formylundecanoic acid (IX) since oxidation gave dodecanedioic acid (X). The acid (IX) has not previously been described, though its methyl ester is known (Tomecko and Adams, *J. Amer. Chem. Soc.*, 1927, **49**, 529; Lycan and Adams, *ibid.*, 1929, **51**, 627). An attempt to prepare the semicarbazone of (IX) gave a product containing only a little nitrogen, possibly a derivative of a polymer.

The concentrate of the dihydroxyoctadecenoic acid (II), when similarly oxidised, gave a volatile aldehyde, the 2 : 4-dinitrophenylhydrazone of which gave correct analyses and had the same m. p. as that of *n*-hexanal (IV). The other product was an unsaturated aldehydo-acid ($C_{12}H_{20}O_3$) which readily gave a deep orange 2 : 4-dinitrophenylhydrazone. This was formulated as 11-formylundec-10-enoic acid (V) since oxidation gave sebacic acid (VI). The ultra-violet absorption spectrum showed that the double bond was conjugated with the carbonyl or the carboxyl group, and the former was preferred because of the deep colour of the 2 : 4-dinitrophenylhydrazone, and the lack of absorption in the original dihydroxyoctadecenoic acid.

Another portion of the concentrate of the dihydroxyoctadecenoic acid (II) was oxidised with potassium permanganate in acetic acid (Armstrong and Hilditch, *J. Soc. Chem. Ind.*, 1925, **44**, 43T), a method which is known to indicate satsifactorily the position of double bonds (cf. Begemann, Keppler, and Boekenoogen, *Rec. Trav. chim.*, 1950, **69**, 439). This gave *n*-hexanoic acid (VII) and azelaic acid (VIII) in good yield.

These results indicate that the dihydroxy-acid is 12 : 13-dihydroxyoctadec-9-enoic acid. Only one result is at variance with this conclusion, the appearance of 11-formylundec-10-enoic acid (V) as a product of periodate oxidation. Movement of double bonds into conjugation occurs frequently, though more generally in alkaline conditions. The author is unaware of any previous report of a double-bond shift under the very mild conditions of periodate oxidation, but this is what seems to have happened.

The original acid must clearly have been 12 : 13-epoxyoctadec-9-enoic acid, a result somewhat different from the earlier conclusions of Vidyarthi (*loc. cit.*) which were based on the isolation of azelaic acid and " a hydroxy-acid (m. p. 70°, equivalent 172) considered to be hydroxypelargonic " as products of the oxidation of methyl vernolate. Considerable modification of the epoxy-acid must have occurred during the preparation of methyl vernolate, and it is very unlikely that 2-hydroxynonanoic acid would result from oxidation; further degradation would surely occur.

Discussion of Quantitative Data.—12 : 13-*Epoxyoctadec-9-enoic acid.* Determination of the epoxide by King's method (*loc. cit.*) showed the oil to contain 67·1% of epoxyoctadecenoic glyceride.

The mixed acids obtained after acid and alkaline hydrolysis were esterified and the saponification equivalent was determined before and after acetylation. From these values it is possible to calculate the acetyl value (209·1) (cf. Riley, *Analyst*, 1951, **76**, 40; Gupta, Hilditch, and Riley, *J. Sci. Food Agric.*, 1951, **2**, 245). This is equivalent to 72·6% (wt.) of dihydroxyoctadecanoic acid. Before comparing this value with that for epoxyglyceride, allowance must be made for (*a*) a change in molecular weight, and (*b*) the removal of much of the unsaponifiable material (7·0%) before the second determination. Expressed as a molecular percentage of the acids (excluding unsaponifiable) these values correspond to 70·1% of epoxy-acid and 70·7% of dihydroxy-acid. It is proposed to use the mean of these values. The absence of dihydroxystearic acid before hydrogenation has been demonstrated.

The dihydroxyoctadecenoic acid does not show any ultra-violet light absorption after alkali isomerisation (Hilditch, Morton, and Riley, *Analyst*, 1945, **70**, 67). Its iodine value is higher than the calculated value, indicating some interaction between the reagents and the hydroxyl groups (cf. Part I; also McKay and Bader, *loc. cit.*, who report that both *cis*- and *trans*-9 : 10-dihydroxyoctadec-12-enoic acid have the correct iodine value).

Other acids present. Although the component acids present in this seed oil have not been quantitatively determined in the usual manner involving distillation, an approximate analysis has been made in the following way. As already described a concentrate of the dihydroxy-acid was prepared by partition. The light petroleum extracts (18%), containing only minor amounts of the dihydroxy-acid, were esterified, distilled and analysed in the usual way. This does not account for the non-hydroxy-acids in the methanol extracts but, on the assumption that these are similar in composition to those remaining in the petroleum, the composition of the acids (excluding unsaponifiable matter) is given in Table 1 (given to 0·5% because of their approximate nature; palmitic, stearic, and linoleic acids were identified in the usual way).

TABLE 1. *Component acids* (% *wt.*) *of* V. anthelmintica *seed oil.*

	Saturated					Unsaturated		
	C_{12}	C_{14}	C_{16}	C_{18}	C_{20}	Oleic	Linoleic	" Vernolic "
Present work	—	0·5	3·5	1·5	—	6·0	16·5	72·0
Vidyarthi	Trace	7·5	7·3	6·0	Trace	5·8	9·8	63·6

Conclusion.—This investigation has shown clearly that vernolic acid is 12 : 13-epoxyoctadec-9-enoic acid. Now that the structure is known it is suggested that the trivial name be dropped and be replaced by the systematic name or by 12 : 13-epoxyoleic acid. This is the first time that an epoxy-acid has been shown to occur in natural fats, though mono- and di-hydroxy- and keto-acids are known.

Reports of the occurrence of oxygenated acids have to be accepted with reserve for there are several examples where the reported claim was later disproved. Oxygenated acids of the C_{18} series which may be accepted as confirmed are set out in Table 2.

Much more information is obviously required before the structure of these acids can be used as evidence in any theory of the biogenesis of unsaturated acids in seed oils, but it is apparent that with one exception the monohydroxy-acids carry their hydroxyl group on C_9, C_{12}, or C_{18}. If these acids are built up from a three-carbon unit (cf. Hilditch, *Nature*, 1951, **167**, 298) then C_9, C_{12}, and C_{18} along with C_3, C_6, and C_{15} will represent the same carbon

atom of that unit. 12 : 13-Epoxyoleic acid may be related to 12-hydroxyoleic acid (ricinoleic) since stereospecific bio-hydrogenation could convert the former into the latter (cf.

TABLE 2. *Occurrence of oxygenated acids in natural fats.*

Acid	Formula	Species	Family
Ricinoleic	$CH_3\cdot[CH_2]_5\cdot CH(OH)\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$	Several *Ricinus* spp.	Euphorbiaceae [a]
9-Hydroxyoctadec-12-enoic	$CH_3\cdot[CH_2]_4\cdot CH{:}CH\cdot[CH_2]_2\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H$	Several *Strophanthus* spp.	Apocynaceae [b]
18-Hydroxyelæostearic	$HO\cdot[CH_2]_4\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$	*Mallotus philippinensis*	Euphorbiaceae [c]
12 : 13-Epoxyoleic acid	$CH_3\cdot[CH_2]_4\cdot CH(O)CH\cdot CH_2\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$	*Vernonia anthelmintica*	Compositae [d]
Unsaturated derivative of 8-hydroxystearic	$CH_3\cdot[CH_2]_9\cdot CH(OH)\cdot[CH_2]_6\cdot CO_2H$	*Onguekoa Gore*	Olacaceae [e]
9 : 10-Dihydroxystearic	$CH_3\cdot[CH_2]_7\cdot CH(OH)\cdot CH(OH)\cdot[CH_2]_7\cdot CO_2H$	Several *Ricinus* spp.	Euphorbiaceae

[a] Hilditch, "The Chemical Composition of Natural Fats," Chapman and Hall, London, 2nd Edn., p. 170. [b] Gunstone, *locc. cit.* [c] Aggarwal *et al.*, *J. Sci. Ind. Res., India*, 1948, **7**, *B*, 136; 1951, **10**, *B*, 76; 1952, **11**, *B*, 463; Calderwood and Gunstone, *Chem. and Ind.*, 1953, 436. [d] Present work. [e] Riley, *J.*, 1951, 1346. [f] Eibner and Münzing, *Chem. Umschau*, 1925, **32**, 159.

Mack and Bickford, *J. Org. Chem.*, 1953, **18**, 686, who have recently reported the stereospecific catalytic reduction of 9 : 10-epoxystearic acid).

EXPERIMENTAL

V. anthelmintica *Seed Oil.*—The seeds (286 g.; 100 = 0·45 g.) were coarsely ground and extracted (Soxhlet) with light petroleum (b. p. 40—60°). Removal of the solvent left a viscous green liquid (71·4 g.) which solidified at 0°. Regrinding and re-extraction gave a little more oil (5·4 g.; total, 26·9% of the seeds). The oil had sap. equiv. 322·9, I val. 107·6, unsap. 7·9 (S.P.A. Committee, *Analyst*, 1933, **58**, 203), free acid 26·4% (as epoxyoleic), and epoxide 67·1% (as epoxyglyceride).

Attempted Esterification of the Mixed Acids.—The oil (54·0 g.) was hydrolysed, by boiling alcoholic potassium hydroxide, to the mixed acids (52·1 g.; sap. equiv. 314·1, I val., 111·1). When treated with methanol (40 ml.) containing hydrogen chloride at room temp. for 24 hr. then at the b. p. for 45 min., the acids (8·1 g.) gave esters (8·5 g.) of low equivalent weight (255·6), but when refluxed with methanol (50 ml.) and concentrated sulphuric acid (0·5 ml.) the acids (8·6 g.) gave a product (9·3 g.) of high equivalent weight (350·7).

Conversion of Epoxy-glycerides into Dihydroxy-acids.—*V. anthelmintica* seed oil (98·4 g.) was boiled with acetic acid (700 ml.) for 7 hr. After removal of some solvent (500 ml.) the residue was diluted with water and extracted. The product was then hydrolysed by boiling alcoholic potassium hydroxide, and unsaponifiable material (6·81 g., 7·0%) removed by the S.P.A. method (*loc. cit.*; the quantities of solvents and reagent were increased proportionately). Acidification and extraction gave the required acids (91·1 g.; epoxide, nil) in which the material present in the oil as epoxy-glyceride had been converted into the corresponding dihydroxy-acid.

Determination of Dihydroxyoleic Acid.—The foregoing acids (21·8 g.) were esterified (22·1 g.) with methanolic hydrogen chloride at room temperature overnight and some of the esters (11·1 g.) acetylated by boiling with acetic anhydride (35 ml.) for 2 hr. and for a further hour after the addition of water (25 ml.), the acetylated esters (12·5 g.) being isolated by ether-extraction. Quadruplicate determination of the equivalent weight of both ester and acetylated ester gave the following results :

Ester	319·7	320·4	319·4	320·2	(Mean) 319·9
Acetylated ester	157·3	157·2	157·0	157·2	(Mean) 157·2

The acetyl value is given by the equation Ac val. $= (B - A)/(1 - 0{\cdot}00075A)$, where A and B are the sap. values of the ester and the acetylated ester respectively. (This relation is quoted by Riley, *loc. cit.*, for ricinoleic acid but can be shown to hold for a dihydroxy-acid.) These results give an acetyl value of 209·1 and indicate that the esters contain 72·6% (wt.) of methyl dihydroxyoctadecadienoate.

Another sample (4·89 g.) of acids obtained after hydrolysis of epoxides, which did not crystallise from ethyl acetate at 0°, was hydrogenated in presence of palladium–charcoal. Hydrogen, equiv. to 371 ml. at N.T.P., was quickly absorbed; this corresponds to an iodine val. of 86·0, compared with 100·8 measured with Wijs reagent in the usual way. The product (4·87 g.), crystallised from ethyl acetate (50 ml.) at 0°, gave 3·63 g. of insoluble material (74·5% of the dihydroxy-acid without a solubility correction; cf. Riley, *loc. cit.*).

Examination of the Non-hydroxylic Acids.—Light petroleum (b. p. 40—60°; 1 l.), methanol (800 ml.), and water (200 ml.) were equilibrated by shaking. The acids (58·8 g.) obtained after hydrolysis of epoxides were shaken with the petroleum phase (500 ml.) and the aqueous methanol phase (200 ml.), the methanol extract being re-extracted with light petroleum (2 × 100 ml.). Further methanol extracts (3 × 100 ml.) were made, each being re-extracted as above. In this way 7 solutions were obtained, and the solvent was removed from each. Fraction 7 was considered to be a concentrate of the dihydroxy-acid and was used in experiments described below.

	Light petroleum			Aq. methanol			
No.	1	2	3	4	5	6	7
Vol. (ml.)	500	100	100	100	100	100	100
Wt. (g.)	8·62	0·76	1·05	0·14	0·37	1·94	45·19

Fractions 1—3 (10·43 g.) were combined, esterified with methanol and concentrated sulphuric acid, and the resulting esters (10·39 g., iodine val. 113·2) were distilled through an electrically heated and packed column (Towers 117) with the following results:

Fraction no.	1	2	3 *	4	Res †
Wt. (g.)	1·78	1·80	2·28	2·54	1·86
Iodine val.	37·7	137·1	144·6	133·0	99·7
Sap. equiv.	271·7	290·3	292·6	293·4	327·5

* The acids from this fraction after isomerisation (180°/60 mm.) had $E^{1\%}_{1\,cm.}$ 636·4 at 234 mμ; for the unisomerised acids the value was only 5·2.

† 1·4803 g. of this residue contained 0·0984 g. of unsaponifiable material.

The esters thus have the following composition (as acids, % wt.): myristic 2·5, palmitic 11·9, stearic 4·4, oleic 20·4, linoleic 53·3, dihydroxyoleic acid 6·3, and unsaponifiable material 1·2%. Dihydroxyoleic acid has already been shown to account for 70·4% (mol.) of the acids and if it is now assumed that all of the non-hydroxy-acids (29·6% mol.) are present in the same proportion as in the distilled sample, the composition of the hydrolysed acids and hence of the original component acids can be computed to be as in Table 1.

Palmitic (m. p. 62—63°) and stearic (m. p. 68—70·5°) acids were obtained from fractions 1 and 4 respectively, and 9 : 10 : 12 : 13-tetrabromostearic acid (m. p. and mixed m. p. 112—113·5°) was prepared by bromination of the acids from fraction 3. Attempts to identify oleic acid in fraction 4 as dihydroxystearic acid were unsuccessful.

12 : 13-*Dihydroxystearic Acid* (III).—Crystallisation of the hydrogenation product described above from chloroform or ethyl acetate yields 12 : 13-*dihydroxystearic acid*, m. p. 95—96° [mixed m. p. with 9 : 10-dihydroxystearic acid (91—93°) was 83—86°] (Found: C, 68·3; H, 11·0. $C_{18}H_{36}O_4$ requires C, 68·3; H, 11·5%). The following were prepared by standard methods: *methyl ester*, m. p. 67·5—69° (Found: C, 69·1; H, 11·4. $C_{19}H_{38}O_4$ requires C, 69·1; H, 11·6%); *ethyl ester*, m. p. 61—63° (Found: C, 69·6; H, 11·5. $C_{20}H_{40}O_4$ requires C, 69·7; H, 11·7%); p-*bromophenacyl ester*, m. p. 102—106° (Found: C, 60·8; H, 8·0; Br, 15·9. $C_{26}H_{41}O_5Br$ requires C, 60·8; H, 8·0; Br, 15·6%).

Periodate Oxidation of 12 : 13-*Dihydroxystearic Acid.*—A solution of potassium periodate (0·6 g.) in N-sulphuric acid (30 ml.) was added to the dihydroxy-acid (0·8 g.) in ethanol (40 ml.) at 40° and the mixture kept at this temperature for 15 min., water (100 ml.) was then added, and the solution extracted with ether (5 × 70 ml.). The solvent was removed and the product steam-distilled. The residual solution, cooled to 0°, deposited a solid which was filtered off, dried, and extracted with light petroleum (b. p. 40—60°; 40 ml.). The extract, on cooling, gave 11-*formylundecanoic* (IX) which, after repeated crystallisation from the same solvent, melted at 60—62° (Found: C, 67·1; H, 10·5. $C_{12}H_{22}O_3$ requires C, 67·3; H, 10·4%).

Some of the crude compound treated with semicarbazide hydrochloride and sodium acetate gave a crystalline product, m. p. 103·5—107° (Found: C, 66·3; H, 10·1; N, 3·2%).

Another portion of the formyl compound suspended in dilute sulphuric acid was treated with excess of potassium permanganate solution on a steam-bath for 40 min. The solution, when

decolourised (sulphur dioxide) and cooled to 0°, gave crystals of dodecanedioic acid (X), m. p. 124—126° after crystallisation from ethyl acetate; this was raised to 125—127° when mixed with an authentic specimen (lit., 128°).

12 : 13-*Dihydroxyoctadec*-cis-9-*enoic Acid* (II).—A pure sample of 12 : 13-*dihydroxyoctadec*-cis-9-*enoic* acid was readily obtained from the concentrate of this acid (fraction 7 of the aqueous methanol–light petroleum partition) by crystallisation from a mixture (1 : 1) of ether and light petroleum (b. p. 40—60°), m. p. 53—54° (Found : I val., 95·8; C, 68·7; H, 10·6%. $C_{18}H_{34}O_4$ requires I val., 80·8; C, 68·8; H, 10·9%); its p-*bromophenacyl ester* had m. p. 72—74° (Found : C, 61·0; H, 7·8; Br, 15·4. $C_{26}H_{39}O_5Br$ requires C, 61·1; H, 7·7; Br, 15·6%).

When heated at 180° for 1 hr. with a solution (7½%) of potassium hydroxide in ethylene glycol, 12 : 13-dihydroxyoleic acid shows practically no absorption at 234 mμ ($E^{1\%}_{1\,cm.}$ 3·8).

12 : 13-*Dihydroxyoctadec*-trans-9-*enoic Acid*.—The concentrate of dihydroxy-acid (6·5 g.) was suspended in 50% nitric acid (2·6 ml.) at 60° during addition of sodium nitrite solution (0·2 g. in 1·3 ml. of water) and then kept at 55—65° for 10 min. The product was extracted and after prolonged storage in ether–light petroleum (b. p. 40—60°) a small quantity of the *trans*-acid was obtained, m. p. after several crystallisations 67·5—69·5° (Found : C, 68·8; H, 10·8%); its p-*bromophenacyl ester* had m. p. 84·5—86° (Found : C, 61·3; H, 7·6; Br, 15·8%).

Periodate Oxidation of 12 : 13-*Dihydroxyoctadec*-cis-9-*enoic Acid*.—This acid (2·0 g.) was oxidised by the method described above. Extraction of the steam-distillate afforded hexanal [2 : 4-dinitrophenylhydrazone, m. p. 102·5—104° (lit., 104°) (Found : C, 51·7; H, 5·9; N, 19·8. Calc. for $C_{12}H_{16}O_4N_4$: C, 51·4; H, 5·8; N, 20·0%)]. The non-volatile fraction gave 11-*formylundec*-10-*enoic acid* (V), m. p. 65—66°, absorption max. at 224 mμ (log ε 4·02 in EtOH) (Found : C, 68·0; H, 9·5. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%). Its 2 : 4-*dinitrophenylhydrazone*, m. p. 81·5—83·0° (Found : C, 55·3; H, 6·3; N, 14·2. $C_{18}H_{24}O_6N_4$ requires C, 55·1; H, 6·2; N, 14·3%), was obtained from ethanol as deep orange crystals.

Oxidation of (V) by potassium permanganate in aqueous acid or acetone gave sebacic acid, m. p. and mixed m. p. 129·5—131·5°.

Permanganate Oxidation of 12 : 13-*Dihydroxyoctadec*-cis-9-*enoic Acid*.—To the concentrate of dihydroxyoleic acid (3·76 g.), dissolved in acetic acid which had been purified by treatment with potassium permanganate, finely powdered permanganate (10 g.) was added portionwise, the temperature being kept below 50°. When all the reagent had been added and the temperature began to fall the mixture was kept at 40—50° for 3 hr. The solvent was then removed under reduced pressure and the product, suspended in dilute sulphuric acid, decolourised with sulphur dioxide. The resulting mono- and di-basic acids were separated by steam-distillation and extracted from the volatile and the non-volatile portions respectively.

Distillation of the volatile acids (1·89 g.) under reduced pressure gave a small fore-run (63 mg.), probably acetic acid, and a remainder which distilled as a single fraction (531 mg.). This was converted to its *p*-bromophenacyl ester, m. p. 70—71° (undepressed when mixed with the ester of hexanoic acid) (Found : C, 53·5; H, 5·5; Br, 25·6. Calc. for $C_{14}H_{17}O_3Br$: C, 53·7; H, 5·5; Br, 25·5%).

The non-volatile product (2·27 g.) was extracted with boiling water (170 ml. in four portions) and filtered from insoluble oil. The filtrate, reduced to small volume, gave azelaic acid (1·00 g.) when cooled to 0°. After crystallisation from ethyl acetate this had m. p. and mixed m. p. 103—106°.

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