S 18. *The Constitution of Some Minor Unsaturated Fatty Acids of Rape-seed Oils.*

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The small amounts of eicosenoic acid (*ca.* 5%) and docosadienoic acid (*ca.* 1%) present in rape-seed oils have been shown respectively to be eicos-11-enoic and docosa-13 : 16-dienoic acids. All the unsaturated C_{18}, C_{20}, and C_{22} acids of rape-seed oils thus conform with the general structure $\text{R·CH:CH·[CH}_2]_n\text{·CO}_2\text{H}$, where n is either 7, 9, or 11, and R·CH:CH· is a mono-, di-, or tri-ethenoid group. Rape-seed oils also contain up to 1% of hexadec-9-enoic acid, accompanied by small proportions of a polyethenoid C_{16} acid and traces of a lower unsaturated (probably tetradecenoic) acid.

The most prominent fatty acids in the glycerides of rape (*Brassica campestris*) seed oils of the family Cruciferæ are: docos-13-enoic * (erucic, 45—50%), octadeca-9 : 12-dienoic (linoleic, 15—20%), octadec-9-enoic (oleic, 10—15%) and octadeca-9 : 12 : 15-trienoic (linolenic, 7—10%). It has recently been found that these are accompanied by small proportions of an eicosenoic acid (about 5%), of a docosadienoic acid (about 1%) and of unsaturated acids of the C_{16} series (about 1%).

The presence of eicos-11-enoic acid in a Cruciferous seed oil was first observed by Hopkins (*Canadian J. Res.*, 1946, **24**, *B*, 211) in the case of hare's-ear mustard (*Conringia orientalis*). Hopkins suggested that the presence of small proportions of this acid might have been overlooked in other Cruciferæ seed fats, and the present work shows that this has indeed been the case so far as rape-seed oils are concerned. Again, Hilditch, Laurent, and Meara (*J. Soc. Chem. Ind.*, 1947, **66**, 19) observed that ester-fractions of unsaturated C_{22} acids from a rape-seed oil showed somewhat higher unsaturation than that due to methyl erucate alone, and that on treatment with alkali at 180° they gave rise to an absorption band at 234 mμ indicative of conjugated diene unsaturation, thus pointing to the presence of small amounts of a docosadienoic acid in which the system $\text{·CH:CH·CH}_2\text{·CH:CH·}$ is present.

In the course of a recent study (Baliga and Hilditch, *J. Soc. Chem. Ind.*, 1948, **67**, 258) of the component acids of a number of rape-seed oils from different sources, the minor unsaturated acid constituents became concentrated in various fractions (obtained by fractional distillation in a vacuum) of the methyl esters of the rape-oil acids which were left in solution when the latter were crystallised from ether at $-40°$ (or from acetone at $-60°$). By uniting the appropriate ester-concentrates obtained in a number of these analyses, sufficient material was collected to allow us, by further crystallisation from solvents at low temperatures and fractional distillation of the esters, eventually to isolate the unsaturated C_{16} acids, the eicosenoic acid, and a mixture of docosadienoic and erucic acids of which the first-named formed about 70%, in quantities sufficient for their constitutions and characteristics to be determined.

Eicos-11-*enoic Acid.*—In earlier work in this laboratory and again in our recent work (*loc. cit.*) on rape-seed oils, the occurrence of small fractions of distilled esters with equivalents approximating to that of methyl eicosenoate (324) has been invariably noticed; but formerly these had been looked upon as probable intermediate mixtures of esters between the large quantities of unsaturated C_{18} and C_{22} esters in process of separation. Thus, from 540 g. of mixed rape-seed oil acids there were obtained about 30 g. of esters with equivalents of 322·5—322·8 and iodine values of 88·6—92·8. On refractionation these gave 20·5 g. of esters (equivalents 322·8—324·8, iodine values 89·2—86·0), with 7·5 g. of lower-boiling material of higher iodine value (unsaturated C_{18} esters) and 2·7 g. of residual esters (equivalent 337·7) which contained some erucic ester. The acids (iodine value 91·7) from the main fraction (20·5 g.) of esters were crystallised from ether at $-40°$ and $-60°$, and the product melted at 19—20° and had an iodine value of 83·5 (eicosenoic acid $C_{20}H_{38}O_2$, iodine value 81·9).

Oxidation of the methyl esters of these acids in acetone solution with powdered potassium permanganate (Armstrong and Hilditch, *J. Soc. Chem. Ind.*, 1925, **44**, 43T) led to the production of nonane-1 : 9-dicarboxylic acid and nonoic acid, so that the acid was eicos-11-enoic acid. Isomerisation of the eicos-11-enoic acid with selenium at 220° produced a mixture of geometrical isomerides which were separated by crystallisation from ether at $-40°$ into *trans*-eicos-11-enoic acid, m. p. 43—44° (about 66%), and (impure) unchanged *cis*-eicos-11-enoic acid, m. p. 15—16°. Oxidation of the natural *cis*-eicos-11-enoic acid, (*a*) with ice-cold aqueous alkaline permanganate yielded 11 : 12-dihydroxyeicosanic acid, m. p. 128—129° (Hopkins, *loc. cit.*, gives 129—130°),

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* In this paper, following the nomenclature which has long been used for unsaturated long-chain fatty acids and alcohols, the carbon atom of the terminal carboxylic group is numbered 1.

and (*b*) with peracetic acid in acetic acid solution, the isomeric dihydroxy-acid, m. p. 90—92° (Hopkins, *loc. cit.*, gives 94—95°).

It is possible (cf., Experimental, p. S 93) that still smaller proportions of an eicosadienoic acid accompany the eicos-11-enoic acid present in rape-seed oils.

Docosa-13 : 16-*dienoic Acid.*—Distilled methyl ester fractions from rape-seed oil unsaturated acids which consisted almost wholly of unsaturated C_{22} esters (equivalents 348—354, iodine values 73—78) were bulked and crystallised from acetone at −60°; much of the methyl erucate (equivalent 352, iodine value 72·2) was then deposited, leaving in solution about 5—10% of the original weight of esters taken, with an iodine value of 100—110. Refractionation of these esters effected the removal of further small quantities of C_{20} esters and produced esters of the C_{22} series with iodine values of about 113—125. The acids from these were further crystallised from acetone and from ether at −60°, leaving in solution concentrates of eicosadienoic acid which in different experiments had iodine values of 126, 131, 135, corresponding respectively to contents of 67, 75, and 79% of docosadienoic acid (iodine value 151·2) admixed with erucic acid (iodine value 75·2). Further removal of erucic acid from these concentrates was not attained.

A concentrate estimated to contain 67% of docosadienoic acid was converted into methyl esters which were oxidised in acetone solution with powdered potassium permanganate, and yielded 57·0% of their weight of a single dicarboxylic acid which was shown to be undecane-1 : 11-dicarboxylic acid. Quantitative formation of this acid from the 33% of methyl erucate present would have accounted for its production to the extent of only 23% of the weight of mixed esters oxidised, so that the remainder must have been formed by oxidation of the dienoic acid. Although the amount of the corresponding monocarboxylic acid product of oxidation was too small for purification and identification, the fact that the dienoic acid yields a conjugated diene acid on heating with alkali at 180° shows that the system $\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot$ is present. Hence the structure of the acid is established as docosa-13 : 16-dienoic acid.

It unites with bromine to yield a crystalline tetrabromobehenic acid, m. p. 106—107°, sparingly soluble in cold light petroleum (b. p. 40—60°), but soluble in ether.

As remarked elsewhere (Hilditch, *J.*, 1948, 249), these results lead to the disclosure of an interesting structural relationship between the unsaturated fatty acids containing 18, 20, or 22 carbon atoms in rape-seed oils (and probably in most other Crucfieræ seed fats): the unsaturated groups are uniformly situated at the end of the carbon chain remote from the carboxyl group, *i.e.*, they are all structurally derived from the system $CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot$. They may be represented by the general formula $R\cdot CH{:}CH\cdot[CH_2]_n\cdot CO_2H$, in which R is $CH_3\cdot[CH_2]_7\cdot$ (oleic, eicosenoic, erucic), $CH_3\cdot[CH_2]_4\cdot CH{:}CH\cdot CH_2$ (linoleic, docosadienoic), or $CH_3\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot CH_2\cdot$ (linolenic); and n is 7(oleic, linoleic, linolenic), 9(eicosenoic), or 11(erucic, docosadienoic).

Hexadecenoic Acid.—As in other seed-fats which have been intensively investigated (cf. Hilditch and Jasperson, *J. Soc. Chem. Ind.*, 1938, **57**, 84), the presence of traces of unsaturated acids with fewer than 18 carbon atoms in the molecule is shown by the consistent appearance in the lower-boiling methyl ester fractions of rape-seed oil unsaturated acids of small quantities of material with mean equivalents of 240—280 and iodine values of 20—40. A large number of such fractions from rape-seed oil analyses were bulked and refractionated, and esters with equivalents of 263—269 and iodine values of 23—35, and a much smaller amount of esters with mean equivalent about 247 and iodine value 37, were obtained.

The acids from the first-mentioned fractions, when crystallised from ether at −40°, deposited saturated (palmitic) acid of negligible iodine value and left in solution liquid acids with an equivalent of 253·4 and an iodine value of 117·5 (hexadecenoic acid, equivalent 254·0, iodine value 100·0). This indicates the presence in rape oil of a certain proportion of polyethenoid C_{16} acids in addition to hexadecenoic acid, the latter alone having been identified in the other seed fats which have previously been examined in this respect (Hilditch and Jasperson, *loc. cit.*). It is interesting, therefore, to note that Shorland (*Nature*, 1945, **156**, 269) has observed the presence of hexatrienoic acid to the extent of 11—17% in the fatty acids of the lipids of rape leaves.

The methyl esters of the hexadecenoic acid concentrate (iodine value 117·5), when oxidised in acetone solution with powdered potassium permanganate, yielded azelaic and heptoic acids (the latter accompanied by lower monocarboxylic acids), thus identifying the acid as hexadec-9-enoic acid, $CH_3\cdot[CH_2]_5\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$. It will be observed that this is the hexadecenoic acid which has been observed in other seed fats and, indeed, also in those of marine and land animals. It belongs, like oleic acid, to the series $R\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$ and not to the alternative series $CH_3\cdot[CH_2]_7\cdot CH{:}CH\cdot[CH_2]_n\cdot CO_2H$ to which the unsaturated C_{18}, C_{20}, and C_{22} acids of rape oil conform.

As in other seed fats, the unsaturated C_{16} acids of rape-seed oils amount to not more than 1% of the total fatty acids. Unsaturated acids of still lower carbon content are present, but in exceedingly small amount: the lowest boiling fraction of the bulked esters mentioned above yielded acids of which the greater part was soluble in ether at −40°, but this portion only had an iodine value of 47, *i.e.*, more than half of it consisted of lower saturated acids.

EXPERIMENTAL.

Eicos-11-enoic Acid.—Isolation. The example which follows is typical of the procedure employed to separate eicosenoic acid from the other unsaturated acids of rape-seed oil. The mixed acids (539 g.) from 575 g. of rape-seed oil were first crystallised from acetone at −50°; 309 g. of acids (iodine value 72) were then deposited, leaving 230 g. of acids (iodine value 157) in solution; the latter contained most of the unsaturated C_{18} acids of the oil, whilst the deposited acids included most of the erucic and eicosenoic acids, with some oleic and linoleic acids. They were converted into methyl esters (311 g.) which, when fractionally distilled, gave the results summarised in Table I.

TABLE I.

Fract. No.	Wt., g.	Equiv.	Iodine value.	Remarks.
1	4·0	278·7	75·8	Unsaturated C_{16} and C_{18} esters.
2	11·1	285·0	98·4	,, ,, ,, ,,
3—5	41·8	290—293	120·2—133·1	Chiefly unsaturated C_{18} esters.
6—12	131·9	293—294	160·6—164·6	Unsaturated C_{18} esters (linoleate, oleate, linolenate).
13	17·6	296·0	137·9	Chiefly unsaturated C_{18} esters.
14	5·7	307·2	120·2	Unsaturated C_{18} and C_{20} esters.
15	6·6	318·2	93·1	,, ,, ,, ,,
16	15·0	322·5	92·8	Chiefly unsaturated C_{20} esters.
17	15·5	322·8	88·6	,, ,, ,, ,,
18	6·4	336·5	87·3	Unsaturated C_{20} and C_{22} esters.
19	11·8	349·6	85·5	Chiefly unsaturated C_{22} esters.
20—27	43·6	351—358	76·1—85·1	,, ,, ,, ,,

The esters in fractions 16 and 17 (Table I) were combined and refractionated (30 g.) with the results shown in Table II.

TABLE II.

Fract. No.	Wt., g.	Equiv.	Iodine value.
1	2·1	310·4	112·0
2	2·7	318·6	101·3
3	2·7	322·6	93·7
4	3·0	322·8	89·2
5	4·8	322·0	87·7
6	4·0	324·5	87·6
7	3·4	325·0	87·1
8	3·0	324·2	87·4
9	2·3	324·8	86·0
10	2·7	337·7	84·0

Fractions 1 and 2 (Table II) contained some unsaturated C_{18} esters, whilst some C_{22} esters were present in the final residue. Fractions 4—9, however, appeared from equivalents and iodine values to be almost pure esters of C_{20} unsaturated acids, and when the acids therefrom (17·0 g., iodine value 91·7) were combined and crystallised from ether at −40° and −60°, 11·5 g. (iodine value 83·5) were deposited and 5·5 g. (iodine value 106·6) left in solution finally at −60°.

In another experiment 14·1 g. of crude eicosenoic acid isolated in a similar manner from ravison-seed oil fatty acids deposited 1·0 g. of acids (iodine value 63·8) from ether at −40°, this evidently including a small amount of saturated acid. The acids left in solution in ether at −40° deposited 6·9 g. of eicosenoic acid (iodine value 80·8) when the solution was cooled to −60°, and left in solution at −60° 6·2 g. of acids (iodine value 97·2). The eicosenoic acid with iodine values of 80·8 and 83·5 ($C_{20}H_{38}O_2$, iodine value 81·9) solidified on cooling to 0° to a mass of colourless crystals which melted at 19—20°.

The material of high iodine value left in solution in ether at −60° may have been still contaminated with traces of linoleic or linolenic acid, but it seems likely that it consists mainly of an eicosadienoic acid. If this is the case, however, the amount of this diene C_{20} acid present is only about 8—10% of the total unsaturated C_{20} acids, and therefore not more than 0·5% of the total acids of rape-seed oil.

Constitution. The methyl esters (11·2 g.) of the specimen of purified eicosenoic acid of iodine value 83·5 (above) were dissolved in acetone (112 ml.) and oxidised by slow addition of finely powdered potassium permanganate to the boiling solution in the course of about an hour, followed by boiling under reflux for 10 hours. After removal of inorganic salts and of 1·1 g. of unoxidised material, there were recovered 5·6 g. of crude dicarboxylic and 3·1 g. of crude monocarboxylic acid products of oxidation. After repeated crystallisation from water and from chloroform, the dicarboxylic acid melted at 105° (equiv. 106·9). Mixed with synthetic nonane-1 : 9-dicarboxylic acid [m. p. 105—107°, equiv. (calc.) 108], the m. p. remained unchanged. The crude monocarboxylic acids were distilled at atmospheric pressure and yielded about 2·5 g. of acids (equiv. 160—164) which were converted into the silver salt (Found : Ag, 40·9. Calc. for $C_9H_{17}O_2$ Ag : 40·7%). These data establish the structure of the acid as eicos-11-enoic acid.

Derivatives. On treatment with a trace of powdered selenium at 220° (Bertram, *Chem. Weekblad*, 1936, **33**, 3) the natural eicos-11-enoic acid (iodine value 80·8, m. p. 19—20°) yielded a mixture of acids from which 66% of an isomer melting at 43—44° was separated by crystallisation from ether at −40°, the remainder (m. p. 15—16°) being mainly the unchanged original acid. The natural *cis*-eicos-11-enoic acid thus yielded the usual equilibrium of *cis*- and *trans*-isomers (cf. Griffiths and Hilditch, *J.*, 1932, 2315) on elaidinisation with selenium.

Eicosenoic acid (iodine value 83·5, 1·0 g.) was oxidised as potassium salt in aqueous solution (800 ml.) at 0° with excess of alkaline permanganate for a short time (Lapworth and Mottram, *J.*, 1925, **127**, 1628), and from the products of oxidation 0·7 g. of crude dihydroxy-fatty acids were obtained which, after crystallisation from ethyl acetate, gave 0·58 g. of an acid which melted at 128—129°. This m. p. was unchanged after admixture with an authentic specimen of 11 : 12-dihydroxyarachidic acid (m. p. 130—131°), but was depressed to 118° by admixture with 9 : 10-dihydroxystearic acid (m. p. 132°), and to 122—124° by admixture with 13 : 14-dihydroxybehenic acid (m. p. 128—129°).

Eicosenoic acid (iodine value 80·8, 2·0 g.) was also oxidised in glacial acetic acid solution with a dilute solution therein of peracetic acid (Scanlan and Swern, *J. Amer. Chem. Soc.*, 1940, **62**, 2305), and an isomeric 11 : 12-dihydroxyarachidic acid (m. p. 90—92°, 0·9 g.) was obtained after purification and crystallisation from ethyl acetate.

Docosadienoic Acid.—Isolation. Since the diene C_{22} acid is present to the extent of not more than 1% in the mixed fatty acids of rape oil, and so forms barely 2·5% to 3% of the total acids of the C_{22} series, its isolation presents considerable difficulty, and large quantities of rape-seed oil were employed in order to obtain the amount of diene C_{22} acid concentrate necessary for its characterisation. This was effected in the first place by low temperature crystallisation of the methyl esters of rape oil C_{22} acids which had been separated by fractional distillation. The application of this preliminary ester-fractionation to the methyl esters (260 g.) of a batch of rape-seed oil mixed fatty acids is illustrated by the condensed ester-fractionation data in Table III.

TABLE III.

Fract. No.	Wt., g.	Equiv.	Iodine value.	Remarks.
1	2·4	271·5	47·5	Chiefly palmitate and hexadecenoate.
2	5·0	288·8	117·8	Palmitate, unsaturated C_{16} and C_{18} esters.
3	9·2	288·1	126·0	,, ,, ,, ,,
4—8	53·6	290—294	142·0—148·4	Unsaturated C_{18} esters (linolenate, oleate, linoleate).
9—11	54·4	296—310	138·1—136·4	Chiefly unsaturated C_{18} esters (with some C_{20}).
12	9·8	333·7	81·2	C_{20} and C_{22} esters (chiefly unsaturated).
13	7·1	348·2	73·6	C_{22} esters (with some C_{20} esters).
14—23	114·8	349—362	74·3—62·4	Mainly unsaturated C_{22} esters, with small amounts of saturated C_{20}, C_{22} and C_{24} esters.
24	6·1	Residual esters		

The methyl esters (98 g.) of fractions 13—23 (Table III), in which unsaturated esters of the C_{22} series largely predominated, were crystallised from acetone at −60°; the 92·2 g. (iodine value 66·2) which separated consisted practically entirely of methyl erucate accompanied by small proportions of arachidate, behenate and lignocerate. There was left in solution 5·8 g. of iodine value 110·3.

By similar procedure three other preliminary concentrates of unsaturated C_{22} esters from other batches of rape-seed oil fatty acids were prepared, so that a quantity of about 16 g. of esters of iodine value 108·3 was accumulated and, at this point, submitted to a further fractional distillation (Table IV).

TABLE IV.

Fract. No.	Wt., g.	Equiv.	Iodine value.	Remarks.
1	2·2	319·9	95·5	Unsaturated C_{20} and C_{22} esters.
2	2·2	332·0	97·9	,, ,, ,, ,,
3	2·4	348·7	112·0	Unsaturated C_{22} ester concentrate.
4	2·3	352·2	127·9	,, ,, ,, ,,
5	2·8	351·8	112·9	,, ,, ,, ,,
6	2·6	351·7	110·3	,, ,, ,, ,,
7	1·9	360·7	97·0	

The acids from fractions 3—6 (Table IV) were combined (7·0 g., iodine value 114·9) and crystallised from acetone and from ether at −60°; 2·7 g. (iodine value 91·9) separated, leaving in solution 4·3 g. of iodine value 131·5. In the course of two additional repetitions *ab initio* of this lengthy procedure, further small quantities of docosadienoic acid concentrates were prepared, namely, 6·0 g. (iodine value 126·5) and 1·2 g. (iodine value 134·6). Attempts to effect further separation of the erucic and docosadienoic acids in these concentrates were unsuccessful.

The acid concentrate of iodine value 131·5, after isomerisation with alkali at 180° (Hilditch, Morton and Riley, *Analyst*, 1945, **70**, 68), showed absorption in the ultra-violet at 268 mμ to a very small extent, and a pronounced band at 234 mμ ($E^{1\%}_{1\,\text{cm.}}$ 409). Calculated from the iodine value (131·5) as a mixture of erucic acid (iodine value 75·2) and docosadienoic acid (iodine value 151·2), this concentrate contained about 74% of docosadienoic acid.

Constitution. The concentrate of iodine value 126·5 (containing about 67% of diene acid) was converted into methyl esters, 4·4 g. of which were oxidised in acetone solution (88 ml.) with finely powdered potassium permanganate (44 g.). From the acidic products of oxidation there were obtained 2·5 g. of dicarboxylic acid. Repeated crystallisation of this from water and from chloroform indicated that only one acid was present, and, as finally obtained, this melted at 103—104° and had an equiv. of 122·3 ($C_{13}H_{24}O_4$, equiv. 122). This proves that, in the diene acid as well as in the accompanying erucic acid, unsaturation commences in the 13 : 14 position. [The amount of methyl erucate (1·5 g.) present in the ester concentrate oxidised would theoretically have given rise to 1·04 g. of undecane-1 : 13-dicarboxylic acid, so that the greater part of the 2·5 g. of this acid actually isolated must have been derived from the dienoic ester.]

The quantity of monocarboxylic acids produced in the oxidation was too small to permit of purification and identification : but the production of undecane-1 : 13-dicarboxylic acid, coupled with that of a conjugated diene acid on isomerisation with alkali at 180° (indicating the presence of a methylene group between two ethenoid bonds), establishes the structure of the diene C_{22} acid as docosa-13 : 16-dienoic acid.

13 : 14 : 16 : 17-*Tetrabromodocosanic Acid.*—The acid concentrate (1·1 g.) of iodine value 134·6 (above) was dissolved in light petroleum (b. p. 40—60°, 11 ml.), and to the stirred solution at 0° was added bromine until a permanent yellow coloration persisted. After standing overnight at 0° the precipitate formed (0·28 g.) was collected and recrystallised from light petroleum, and 0·20 g. of crystals which melted at 106—107·5° was obtained (Found : Br, 47·0. Calc. for $C_{22}H_{40}O_2Br_4$: Br, 48·8%).

Hexadecenoic, etc., Acids.—A large number of the small lowest-boiling fractions of methyl esters of rape-seed oil unsaturated acids, which had accumulated during our examination of a series of these oils (*loc. cit.*) and which had analytical characteristics similar to those of the fractions 1 in Tables I and III above, were combined together and refractionated with the results shown in Table V.

TABLE V.

Fract. No.	Wt., g.	B.p. (0·2 mm.).	Equiv.	Iodine value.
1	1·8	68—80°	189·2	27·4
2	2·7	80—118	247·0	37·3
3	2·3	118—120	263·4	35·2
4	3·4	120	266·8	30·9
5	4·2	120	269·0	26·8
6	3·5	120	268·4	22·6
7	3·6	120—122	271·8	42·0
8	3·4	122	274·0	135·8
9	5·1	122	290·8	144·7
10	4·3	Residue	282·9	155·8

Unsaturated C_{16} *Acids.*—The acids (11·8 g.) from the ester-fractions 3—6 (Table V) were combined and crystallised from ether at −40°; 8·9 g. of acids of iodine value 1·5 (mainly palmitic acid) were deposited, leaving in solution 2·9 g. of liquid acids (iodine value 117·5, equiv. 253·4; $C_{16}H_{30}O_2$, iodine value 100·0, equiv. 254·0). Thus the hexadecenoic acid from rape-seed oil is accompanied by a certain amount of polyethenoid C_{16} acids.

A small quantity (2·5 g.) of methyl esters from the acids of iodine value 117·5 was oxidised in acetone solution (100 ml.) with powdered potassium permanganate (15 g.); after removal of 0·8 g. of neutral esters there was obtained 0·5 g. of dicarboxylic acid which melted at 102—104° (mixed with an authentic specimen of azelaic acid, m. p. 101—104°). Distillation of the small quantity of monocarboxylic acids also produced gave 0·23 g. (equiv. 108) and 0·17 g. (equiv. 121), suggesting the presence of short-chain monocarboxylic acids from polyethenoid C_{16} acids as well as of heptoic acid (equiv. 130). The yield of azelaic acid obtained suffices, however, to define the structure of the mono-ethenoid acid as hexadec-9-enoic acid.

Lower Unsaturated Acids.—The acids (2·9 g.) from ester-fractions 1 and 2 (Table V) were united and crystallised from ether at −40°; 0·8 g. (iodine value 5·6) was deposited, leaving in solution 2·1 g. of acids (iodine value 46·8, equiv. 195·0). The latter thus still contained saturated acids of lower molecular weight, and it is most likely that the unsaturated component consisted of tetradecenoic acid (equiv. 226, iodine value 112·4); the amount of this was at most about 25—30% of the unsaturated C_{16} acids present in the same mixture, so that the content of unsaturated acids with fewer than 16 carbon atoms in the total rape-seed oil acids is only of the order of 0·2%.

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