85. *Erucic Acid. Preparation of Erucic Acid. General Oxidation Reactions. Oxidation with Gaseous Oxygen.*

By Charles Dorée and Albert C. Pepper.

A method for the preparation of erucic acid, m. p. 33·8°, iodine value 75, from rape seed oil, in yields of 25—30%, is described.

Hydrogen peroxide, without a catalyst, converts erucic acid into 13 : 14-dihydroxybehenic acid, m. p. 101°, and brassidic acid into the isomer, m. p. 132°, but if osmium tetroxide is present erucic acid gives the derivative of m. p. 132° and brassidic acid that of m. p. 101°.

The allocation of the "*cis*"*-relationship to the 13 : 14-dihydroxybehenic acid, m. p. 101°, is supported by measurement of the rates of reaction of the isomers with lead tetra-acetate.

Neutral potassium permanganate with potassium erucate gives 13 : 14-dihydroxybehenic acid, m. p. 132°, and a mixture of isomeric hydroxy-ketobehenic acids. Perbenzoic acid gives oxidoerucic acid, which on hydrolysis yields 13 : 14-dihydroxybehenic acid, m. p. 101°, whereas oxidobrassidic acid yields the isomeric acid, m. p. 132°. Periodic acid, like lead tetra-acetate, converts the 13 : 14-dihydroxybehenic acids into nonaldehyde and brassylic semialdehyde.

Methyl erucate and brassidate are converted by hydrogen peroxide into *methyl dihydroxybehenates*, which give the 13 : 14-dihydroxybehenic acids, m. p. 101° and m. p. 132°, respectively. *Methyl oxidoerucate*, m. p. 28°, and *methyl oxidobrassidate*, m. p. 42·3°, are formed by the action of perbenzoic acid on the respective esters.

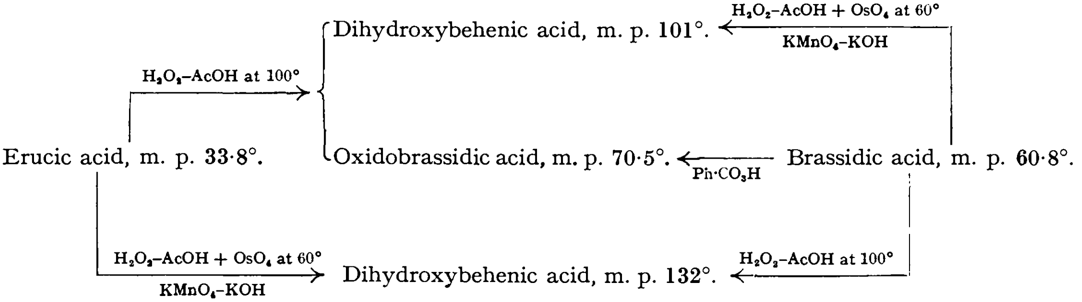
When treated with oxygen at 70° in the presence of a catalyst, erucic acid gives oxidoerucic acid, but at 120°, or at 70° in acetic anhydride solution, oxidobrassidic acid is formed. No free dihydroxy-acids are present, but if the residue is saponified, 13 : 14-dihydroxybehenic acid, m. p. 132°, is obtained in each case. Methyl erucate, treated at 70° with the addition of cobalt erucate, gives methyl oxidobrassidate and a complex which, after saponification, gives 13 : 14-dihydroxybehenic acid, m. p. 132°.

By the methods previously described for the preparation of erucic acid from rape seed oil, the pure acid has never been obtained in satisfactory quantity. The lead and lithium salting process, successfully used by Hilditch (*J. Soc. Chem. Ind.*, 1925, **44**, 43T) with the fatty acids of olive oil, gave less than 20% of erucic acid of low iodine value. The fractionation of the methyl esters (Grün and Janko, *A.*, 1916, i, 789; Holde and Wilke, *A.*, 1922, i, 713), followed by fractional precipitation of the acids obtained with lithium acetate, gave no more than 5% of pure erucic acid, iodine value 75. Direct crystallisation of the mixed fatty acids from alcohol (Reimer and Will, *Ber.*, 1886, **19**, 3320; Noller and Talbot, *Organic Syntheses*, 1930, **10**, 44) gave, however, a crude acid, m. p. 33·3°, iodine value 73, in good yields (30—35%), but fractional distillation of the mixed acids (Caldwell and Dye, *Ind. Eng. Chem.*, 1933, **25**, 338; Lepkovsky, Feskov, and Evans, *J. Amer. Chem. Soc.*, 1936, **58**, 978), stated to yield 40% of erucic acid, gave only 8% of a product of iodine value 72.

Starting from the crude product obtained by the method of Noller and Talbot (*loc. cit.*), we were unable to raise the iodine value above 73·5 by crystallisation from solvents or by distillation in a vacuum either of the mixed acids or of their methyl esters. By the addition of a lead salt to the alcoholic solution in fractions of the total required for complete precipitation (Täufel and Bauschinger, *Z. angew. Chem.*, 1928, **41**, 157) a satisfactory purification was, however, effected and erucic acid, m. p. 33·8°, iodine value 75, was readily obtained in yields of 25% upwards, calculated on the original rape seed oil.

The general and gaseous oxidation of oleic acid has been investigated by a number of workers. Primary products are oxido-oleic acid, the 9 : 10-dihydroxystearic acids, m. p. 95° and 132°, and the 9-hydroxy-10-keto- and 10-hydroxy-9-keto-stearic acids respectively. The *trans*-isomer, elaidic acid, gives similar products, but a reagent which produces one of the dihydroxystearic acids from oleic acid always produces the isomeric form from elaidic acid.

Erucic acid, $C_{22}H_{42}O_2$, Δ^{13} (*cis*), and brassidic acid (*trans*) form a similar pair of isomeric fatty acids. Their general behaviour on oxidation has now been investigated and some of the experimental results are summarised in the following scheme :



Hydrogen peroxide in boiling acetone had no action on erucic or brassidic acid, but in glacial acetic acid at 100° oxidation took place, giving in the absence of a catalyst, 13 : 14-dihydroxybehenic acid, m. p. 101°, and

---

* The terms "*cis*" and "*trans*" applied to these acids are used in accordance with the practice of previous writers (cf. Marsden and Rideal, J., 1928, 1169).

in the presence of osmium tetroxide the isomer, m. p. 132°. The converse is observed with brassidic acid. Oleic and elaidic acids behave similarly in the absence of a catalyst, 9 : 10-dihydroxystearic acids, m. p. 95° and 132°, respectively being formed (Hilditch, J., 1926, 1828). In the presence of osmium tetroxide, we find that oleic acid gives the acid of m. p. 132° and elaidic acid that of m. p. 95°. An inversion apparently due to the catalyst takes place and it is worthy of note that when vanadium pentoxide was substituted for osmium tetroxide, hydrogen peroxide was without action. The oxidative effect of hydrogen peroxide with osmium tetroxide as catalyst resembles that of alkaline permanganate in that only one of the isomeric dihydroxy-acids is formed in each case.

After removal of the dihydroxybehenic acid from the non-catalytic oxidation product of erucic acid, an oil was left which, on distillation, gave some 30% of its weight of a solid, b. p. 220—240°/3 mm., from which oxidobrassidic acid was isolated. The general reactions of the oil indicated that it might consist of a mixture of erucic acid peroxide and of acetylated derivatives of hydroxy-acids which decomposed on distillation, oxidobrassidic acid being one of the products.

Earlier results showing that alkaline potassium permanganate converted erucic acid exclusively into the 13 : 14-dihydroxybehenic acid, m. p. 132°, and brassidic acid into that of m. p. 101° have been confirmed. With the modified technique of Lapworth and Mottram (J., 1925, **127**, 1628) yields of 80—90% of the dihydroxy-acids were obtained.

Neutral potassium permanganate, however, acting on potassium erucate under controlled conditions (King, J., 1936, 1789), gave in addition to dihydroxybehenic acid, m. p. 132°, a mixture of the two hydroxyketobehenic acids, which were isolated as semicarbazones.

The oxido-derivatives of erucic and brassidic acids are probably primary products of oxidation. Albitski (*J. pr. Chem.*, 1900, **61**, 65) attempted to prepare them from the chlorohydrins, but could not isolate definite products. Warmbrunn and Stutzer (*Ber.*, 1903, **36**, 3604), through bromohydroxybehenic acid, $C_{22}H_{43}O_3Br$, obtained an oxidoerucic acid, m. p. 64°. Brassidic acid similarly gave an oxido-acid, m. p. 71°, which was very stable. It required heating with aqueous potassium hydroxide at 170° to give dihydroxybehenic acid, m. p. 132°.

Bauer and Bähr (*J. pr. Chem.*, 1929, **122**, 201) had obtained an oxidoerucic acid, m. p. 67·5°, by the action of perbenzoic acid on erucic acid, which after alkaline hydrolysis at 170° gave the higher-melting (132°) dihydroxybehenic acid. If this is correct, erucic acid (*cis*) through the oxido-acid gives rise to the " *trans* "-dihydroxy-acid, whereas oleic acid (*cis*) through oxido-oleic acid yields the " *cis* "-dihydroxy-acid. We now find that the oxido-derivatives of erucic and brassidic acids are readily obtained by the use of perbenzoic acid. Their properties and reactions are shown below, erucic acid (*cis*) giving rise to the " *cis* "-dihydroxy-derivative :

Erucic acid $\xrightarrow{\text{Ph}\cdot\text{CO}_3\text{H}}$ Oxidoerucic acid, m. p. 63·5° $\xrightarrow{\text{hydrolysis}}$ Dihydroxybehenic acid, m. p. 101°
Brassidic acid $\xrightarrow{\text{Ph}\cdot\text{CO}_3\text{H}}$ Oxidobrassidic acid, m. p. 70·5° $\xrightarrow{\text{hydrolysis}}$ Dihydroxybehenic acid, m. p. 132°

The oxido-acids were difficult to hydrolyse in alkaline solution, but aqueous-alcoholic hydrochloric acid was effective. The oxidoerucic acid of Bauer and Bähr (*loc. cit.*) was impure and the severe hydrolytic treatment probably brought about inversion.

The chlorohydrin synthesis was repeated in the case of erucic acid, but the yield of oxido-acid (about 10%) compared unfavourably with the 60—70% obtained by the use of perbenzoic acid.

A similar series of experiments was carried out on methyl erucate and brassidate. Their reactions with hydrogen peroxide are shown below, the dihydroxy-acid derived from each ester being the same as that obtained directly from the acid :

Methyl erucate, b. p. 183°/0·2 mm. $\xrightarrow{\text{H}_2\text{O}_2\text{–AcOH at }100^\circ}$ Methyl dihydroxybehenate, m. p. 78° $\xrightarrow{\text{hydrolysis}}$
Dihydroxybehenic acid, m. p. 101°
Methyl brassidate, m. p. 33° $\xrightarrow{\text{H}_2\text{O}_2\text{–AcOH at }100^\circ}$ Methyl dihydroxybehenate, m. p. 111° $\xrightarrow{\text{hydrolysis}}$
Dihydroxybehenic acid, m. p. 133°

Methyl oxido-esters were readily obtained by the action of perbenzoic acid. *Methyl oxidoerucate*, m. p. 28°, and *methyl oxidobrassidate*, m. p. 42·3°, when saponified in the cold gave the corresponding oxidoerucic acid, m. p. 63°, and oxidobrassidic acid, m. p. 71°, respectively.

Severe oxidation resolves erucic acid into *n*-nonoic acid and brassylic acid, $[CH_2]_{11}(CO_2H)_2$. Green and Hilditch (J., 1937, 764) found that the 13 : 14-dihydroxybehenic acids were much more difficult to break down than the 9 : 10-dihydroxystearic acids, but that with alkaline permanganate, acids of lower molecular weight were formed. The specific reactions of periodic acid and of lead tetra-acetate with 1 : 2-glycols (Malaprade, *Compt. rend.*, 1928, **186**, 382; Criegee, *Ber.*, 1931, **64**, 260) made it probable that the 13 : 14-dihydroxybehenic acids would be smoothly resolved by these reagents. This proved to be the case. Potassium periodate gave nonaldehyde in quantitative yield together with brassylic semialdehyde, which was isolated from a polymerised product initially formed (cf. King, J., 1938, 1826). Lead tetra-acetate also reacts smoothly with *cis*-1 : 2-glycols, whereas *trans*-1 : 2-glycols are less readily attacked. Both 13 : 14-dihydroxybehenic acids were oxidised by this reagent, giving in each case nonaldehyde and *brassylic semialdehyde.* Comparative oxidation at 40° following the procedure of Criegee (*Ber.*, 1932, **65**, 1770) gave the following results :

Mols. of $Pb(OAc)_4$ consumed per 1 mol. of dihydroxy-acid.

Time (mins.)	5	20	50	80
Acid, m.p. 101°	0·778	0·996	1·370	1·660
Acid, m.p. 132°	0·751	0·890	0·929	0·960

These figures support the opinion that the acid, m. p. 101°, has the "*cis*"-configuration (cf. Hilditch and Jasperson, *Nature*, 1941, **147**, 327).

The action of oxygen on erucic acid does not appear to have been investigated. Skellon (*J. Soc. Chem. Ind.*, 1931, **50**, 382T) found that its action on oleic acid at 120° produced *iso*oleic acid, 9 : 10-dihydroxystearic acid, m. p. 132°, and nonoic acid. With a cobalt catalyst present, azelaic acid, 10-hydroxystearic acid, m. p. 84°, and the isomeric 9 : 10-dihydroxystearic acids, m. p. 95° and 132°, were obtained. Ellis (*Biochem. J.*, 1932, **26**, 791) studied the absorption of oxygen by oleic and elaidic acids when finely dispersed on filter-paper. At 65—75°, with a cobalt catalyst, oleic acid showed an oxygen uptake of 20% in 36 hours and later the same uptake was achieved in 7 hours (*ibid.*, 1936, **30**, 753).

Under such restrained conditions both oleic and elaidic acids gave oxidoelaidic acid, so an oxido-derivative would appear to be an initial product of oxidation. The difference in the results obtained by these authors is probably due to the fact that the former saponified the oxidised material prior to separating its constituents, whereas the latter did not. The action of alkali would hydrolyse the oxido-acid and induce reactions of condensation and polymerisation.

The apparatus employed by us for the gaseous oxidation of erucic acid consisted of a large, electrically heated oil-bath fitted with thermostatic temperature control and a slowly moving stirrer. Purified dry oxygen was passed through a meter into the melted acid, which was contained in large Pyrex test-tubes set in the bath in parallel. The oxygen inlet tubes ended in a bubbler device which produced a fine stream of bubbles, bringing the gas into uniform contact with the liquid under treatment. Volatile products were collected in a cooled trap-bottle, and carbon dioxide absorbed in baryta solution.

Oxidations were carried out at 70° and 120° with and without the addition of cobalt erucate (0·6%). About 25 g. of acid were used in each experiment with an oxygen flow of 5 l. per hour. To ascertain the rate of action under these conditions, samples were withdrawn at intervals, and the constants of the product determined. Typical results for erucic acid at 120° are shown below :

Time in hours	0		4·5		7·8		12·0	
Iodine value	(*a*) 75	(*b*) 75	(*a*) 59	(*b*) 57	(*a*) 48	(*b*) 43·5	(*a*) 37	(*b*) 34·5
Acid value	(*a*) 166	(*b*) 166	(*a*) 150	(*b*) 148	(*a*) 144	(*b*) 142	(*a*) 142	(*b*) 139

(*a*) with and (*b*) without the addition of cobalt erucate.

The iodine value is reduced to about one half in 12 hours at 120° whether a catalyst is present or not; the acid value falls at a much slower rate. When the acid was heated for 12 hours at 120° without oxygen, no change in its constants could be observed. At 70° the rate of oxidation was slower, the iodine value falling to 53 in 12 hours and to 38 in 24 hours, the acid value increasing slightly during that period. The end products were much less coloured at 70° than at 120°.

The resolution of the oxidised material was effected through the observation that oxido-erucic and -brassidic acids crystallised readily from 95% alcohol, whereas the complex oxidation products remained soluble even at 0°. Further separation of the alcohol-soluble fraction was obtained by extraction of the residue with light petroleum. The following is a typical result obtained with the oxidation product of erucic acid formed at 120° in the presence of cobalt erucate.

Product.	Yield, %.
(*a*) Oxidobrassidic acid	12
(*b*) Light petroleum-soluble, giving after saponification 10% of its weight of dihydroxybehenic acid, m. p. 132°	40
(*c*)) Brown residue insoluble in light petroleum, giving on saponification 11% of dihydroxybehenic acid, m. p. 132°	39

No brassylic acid could be obtained from fraction (*b*) and neither fraction (*b*) nor (*c*) gave dihydroxybehenic acid prior to saponification. An attempt to isolate ketol-behenic acids from fraction (*c*) by conversion into the semicarbazones and separation in ethylene dichloride solution was unsuccessful. A product obtained at 120° in the absence of a catalyst gave only 1% of oxidobrassidic acid. From the fractions soluble and insoluble in light petroleum neither brassylic nor dihydroxybehenic acid could be isolated, but after saponification a total yield of 12% of 13 : 14-dihydroxybehenic acid, m. p. 132°, was obtained.

The course of oxidation at 70° was somewhat different. Ellis (*Biochem. J.*, 1936, **30**, 753) had shown that both oleic and elaidic acids, when treated with oxygen at this temperature, gave oxidoelaidic acid, oxido-oleic acid not being formed in appreciable quantity. It was expected that the catalytic gaseous oxidation of erucic acid at 70° would yield oxidobrassidic acid, but instead oxidoerucic acid was obtained, the yield being about 15% (24 hours) and 20% (50 hours).

A typical oxidation of erucic acid (24 hours) with 0·6% of cobalt erucate at 70° gave the following results :

Product.	Yield, %.
(*a*) Oxidoerucic acid, m. p. 63·5°	15
(*b*) Light petroleum-soluble, giving after saponification 6% of its weight of dihydroxybehenic acid, m. p. 132°	48
(*c*) Residue insoluble in light petroleum, giving after saponification 17% of its weight of dihydroxybehenic acid, m. p. 132°	32

Fraction (*b*) gave on distillation in a vacuum a small amount of nonoic acid and from fraction (*c*) by extraction with 50% alcohol a little brassylic acid, m. p. 111°, was obtained. No brassylic semialdehyde could be isolated from fraction (*c*) after boiling with dilute sulphuric acid, a method by which this substance was obtained from the product of oxidation of erucic acid with potassium periodate.

The oxidation of oleic and erucic acids with hydrogen peroxide proceeds most readily in the presence of acetic acid. This was attributed by Böeseken (*Rec. Trav. chim.*, 1926, **45**, 842; 1927, **46**, 622) to the presence of peracetic acid. An experiment was therefore carried out on the catalytic gaseous oxidation of erucic acid dissolved in twice its weight of acetic anhydride at 70°. The reaction was rapid, the iodine value falling to 38 (6 hours), 20 (12 hours) and 16 (after 15 hours), a white solid forming in the tube. This proved, however, to be oxidobrassidic acid (15%) and from the solution a small amount only of dihydroxybehenic acid, m. p. 132°, was obtained. The presence of acetic anhydride therefore brings about the formation of oxidobrassidic acid and its normal hydrolysis product, dihydroxybehenic acid, m. p. 132°, whereas in its absence oxidoerucic acid is the main product of reaction at 70°.

Methyl erucate, when treated with oxygen at 70° in the absence of a catalyst, was hardly affected even after 24 hours. In the presence of cobalt erucate reaction was immediate, the iodine value of 72 becoming 60 (3 hours), 38 (12 hours) and 21·5 (after 24 hours), the acid value increasing slowly from 0 to 50. The free acids were extracted with potassium carbonate solution and from the neutral residue methyl oxidobrassidate was obtained. The following represents a typical analysis :

Product.	Yield, %.
(*a*) Free oxidised fatty acids	18
(*b*) Neutral oxidised ester fraction consisting of	
(i) methyl oxidobrassidate	14·5
(ii) a complex which after saponification gave 12% of dihydroxybehenic acid, m. p. 132°	48·5

An oxidation of methyl erucate in the presence of acetic anhydride and cobalt erucate at 70° gave a similar result. The iodine value fell to 21·9 in 12 hours and methyl oxidobrassidate was the main product.

An oxidation at 120° in the presence of cobalt erucate gave the following :

Product.	Yield, %.
(*a*) Free oxidised acids	15
(*b*) Neutral oxidised ester fraction consisting of	
(i) methyl oxidobrassidate	9
(ii) a complex which after saponification gave 10% of its weight of dihydroxybehenic acid, m. p. 132°	74

No other definite products could be obtained.

The gaseous oxidation of erucic acid therefore leads generally to the formation of an oxido-derivative of the *trans*-isomer, brassidic acid. The reaction is thus similar to that observed in the gaseous oxidation of oleic acid where oxidoelaidic acid (*trans*) is the main product, oxido-oleic acid not being formed (Ellis, *loc. cit.*).

Erucic acid, however, at 70°, exceptionally, gives oxidoerucic acid, the lower temperature apparently preventing inversion, although methyl erucate, at the same temperature, forms the oxidobrassidic acid derivative.

Both oxido-acids are resistant to hydrolysis, which may account for the absence of dihydroxy-acids in the original oxidation product. After saponification of the complex, however, 13 : 14-dihydroxybehenic acid, m. p. 132°—the normal hydrolysis product of oxidobrassidic acid—is always formed in considerable quantity. Scission products of lower molecular weight were practically absent.

Unstable peroxides may also be among the initial products of oxygen uptake. From them aldehydic compounds could be formed which, either by reaction with other substances present, or by polymerisation, give rise to the resistant brown residue observed in all these oxidations.

EXPERIMENTAL.

Preparation of Erucic Acid.—800 G. of rape seed oil in 1 l. of 95% alcohol were heated for 6 hours with 200 g. of potassium hydroxide in 100 ml. of water. The alcohol was removed by distillation, the potassium salts treated with about 1·5 l. of water, and the syrup acidified with 10% hydrochloric acid and boiled. After cooling, the cake of fatty acids was washed and dried (yield, 700 g.). To remove liquid fatty acid impurities, the cake (700 g.) was dissolved in 2 l. of warm alcohol and cooled in ice with stirring. As soon as crystals formed, the solution was filtered, and the filtrate left for 1 day in the ice-chest. The erucic acid deposited was removed, and a second crop obtained after 1 more day. These crops were recrystallised several times from alcohol, giving 250 g. of erucic acid, m. p. 33·3°, I.V. 72·4. To remove solid fatty acids, the 250 g. of crude acid in 1·5 l. of 95% alcohol were treated with a solution containing 6 g. of lead acetate dissolved in the minimum quantity of water and made up to 1·5 l. with alcohol, both solutions being kept at 75°. After 12 hours at 20° the solid was removed; the filtrate, after 1 day at 0°, deposited an acid which, after several crystallisations from 500 ml. portions of absolute alcohol, gave 215 g. or 28% of erucic acid, m. p. 33·8°, I.V. 75·0, A.V. 166.

Preparation of Brassidic Acid.—(*a*) 10 G. of erucic acid, suspended in 250 ml. of an aqueous solution containing 75 ml. of nitric acid (*d* 1·42), were warmed to 50°, and 2 g. of finely powdered sodium nitrite gradually added. The fatty acid layer solidified and was remelted by warming at 70° for 15 minutes. After cooling, the solid was washed and crystallised several times from alcohol, giving brassidic acid, m. p. 60·8°, I.V. 73·8 (yield, 70%). (*b*) A mixture of 20 g. of erucic acid and 2 g. of powdered selenium was heated for 3 hours at 200—210°. The brown mass was extracted with 5% potassium hydroxide solution, the extract filtered and acidified, and the fatty acids removed in ether. The crude product was crystallised as before, leaving 8·5 g. or 42·5% of brassidic acid, m. p. 60·5°, I.V. 74.

Oxidation of Erucic Acid with Hydrogen Peroxide.—(a) *In acetone solution.* Erucic acid (2 g.) in 100 ml. of acetone with 20 ml. of hydrogen peroxide (100 vol.) was refluxed for 8 hours. After removal of the solvent, unchanged erucic acid (1·9 g.) was left. Heating for 50 hours gave the same result. Brassidic acid similarly was not oxidised.

(b) *In glacial acetic acid solution.* To 50 g. of erucic acid in 250 ml. of glacial acetic acid, 100 ml. of hydrogen peroxide (100 vol.) were added gradually during 2 hours at 100°. Refluxing was continued for a further 2 hours. An oily layer separated which gradually dissolved. The solution was poured into water, and the precipitate washed and crystallised from absolute alcohol, giving dihydroxybehenic acid (32 g.), m. p. 101°, I.V. 0 (Found: C, 70·9; H, 10·6. Calc. for $C_{22}H_{44}O_4$: C, 70·9; H, 11·8%). The m. p. was not depressed by the acid prepared by oxidation of brassidic acid with alkaline permanganate.

The alcoholic mother-liquors gave a pale yellow oil which liberated iodine from potassium iodide equivalent to 22·2% of erucic acid peroxide. About 33% distilled at 220—240°/3 mm., forming a white solid which, when crystallised from alcohol, gave oxidobrassidic acid, m. p. 69·5°, unchanged in admixture with a specimen made by the action of perbenzoic acid on brassidic acid.

Brassidic acid, when treated similarly (5 g. in 30 ml. of glacial acetic acid with 15 ml. of hydrogen peroxide; heating for 4—6 hours), gave dihydroxybehenic acid, m. p. 132°.

(c) *In glacial acetic acid solution with vanadium pentoxide.* 2 G. of erucic or brassidic acid in 25 ml. of acetic acid containing 0·1 g. of vanadium pentoxide, after treatment with 10 ml. of hydrogen peroxide for 10 days at room temperature or 40 hours at 70°, were recovered unchanged.

(d) *In glacial acetic acid solution with osmium tetroxide.* To 5 g. of erucic acid in 50 ml. of acetic acid containing 0·1 g. of osmium tetroxide, were added gradually 10 ml. of hydrogen peroxide. After 50 days at room temperature the solvent was removed, and the black residue extracted with alcohol. Traces of catalyst were removed by the addition of 20% of water and rapid filtration. After cooling in the ice chest and recrystallisation from alcohol, white crystals of dihydroxybehenic acid, m. p. 130°, I.V. 0, A.V. 151, were obtained. The m. p. was not depressed by an authentic specimen.

If, after the addition of hydrogen peroxide, the temperature was raised to 60° and maintained for 1 hour, the same result was obtained. Dihydroxybehenic acid, m. p. 131°, was formed; yield, 65% (Found: C, 70·8; H, 12·0. Calc.: C, 70·9; H, 11·8%).

Brassidic acid (2·5 g.), in 50 ml. of glacial acetic acid containing 0·1 g. of osmium tetroxide, was treated with 10 ml. of hydrogen peroxide at 30° and heated at 60° for 1 hour. After cooling in the ice-chest the solid was removed and after crystallisation from alcohol gave dihydroxybehenic acid, m. p. 100·3°, not depressed by an authentic specimen.

Oxidation of Oleic and Elaidic Acids with Hydrogen Peroxide in Acetic Acid Solution with Osmium Tetroxide.—2·5 G. of oleic acid were dissolved in 50 ml. of glacial acetic acid, cooled to room temperature, and 0·1 g. of osmium tetroxide added, followed by 10 ml. of hydrogen peroxide (100 vol.). The mixture was warmed at 60° for $\frac{1}{2}$ hour and cooled in the ice-chest overnight, the liquid filtered, and the residue washed with water and crystallised from alcohol. Dihydroxystearic acid, m. p. 131·2°, was obtained; yield, 60%.

Elaidic acid, treated similarly, gave dihydroxystearic acid, m. p. 95°, identical with that obtained by the action of hydrogen peroxide on oleic acid in glacial acetic acid solution alone.

Oxidation with Alkaline Potassium Permanganate.—2 G. of erucic acid in 5 ml. of absolute alcohol were treated with 4 g. of potassium hydroxide in 4 ml. of water. The alcohol was removed, and a solution of the residue in about 600 ml. of water was heated to 27°, 3 g. of potassium permanganate in 300 ml. of water rapidly added, and the whole maintained at 27° for 30 mins. with stirring. After treatment with sodium sulphite and excess of 20% hydrochloric acid, the solids were washed and crystallised from alcohol, giving 13 : 14-dihydroxybehenic acid, m. p. 132°. Yield, 85%.

Brassidic acid, treated in the same way, gave 13 : 14-dihydroxybehenic acid, m. p. 100·5°. Yield, 80%.

Oxidation of Potassium Erucate with Potassium Permanganate in Neutral Solution.—10 G. of erucic acid in the minimum quantity of alcohol were neutralised with N/2-alcoholic potassium hydroxide. The alcohol was removed, and the residue dissolved by adding water up to 1 l. and then diluted with hot water to 8 l. The solution was cooled to 40° (below which no reaction took place) and 9·8 g. of potassium permanganate in 1·5 l. of water, also at 40°, were run in with stirring, which was continued for 15 minutes. A solution of 32 g. of sodium sulphite in 300 ml. of water was added, followed by excess of dilute hydrochloric acid. The solid residue was washed and dried. It was extracted repeatedly with chloroform in small portions (total 150 ml.), the filtrate cooled in ice, and the crystals of dihydroxybehenic acid, m. p. 132°, removed. A small final crop was obtained on standing.

The chloroform was removed in a vacuum and the residue, while warm, was extracted with 400 ml. of light petroleum (b. p. 40—60°). After 24 hours at 0° a mixture of hydroxy-ketobehenic acids was deposited. A solution of this in 10 parts of chloroform was cooled to 0° and filtered, and the solvent removed in a vacuum. The residue, crystallised repeatedly from alcohol and acetone, gave crystals, m. p. 77°, setting point 73° (Found: C, 71·5; H, 11·5. *Hydroxyketobehenic acid*, $C_{22}H_{42}O_4$, requires C, 71·4; H, 11·4%).

The mixture of acids could not be separated by means of dilute alcohol, acetone or light petroleum. 2·4 G. of the mixed acids, m. p. 77°, in 4 ml. of alcohol were added to 2 g. of semicarbazide hydrochloride and 3 g. of sodium acetate dissolved in the minimum quantity of water (cf. King, J., 1936, 1789). The mixture was shaken, warmed to 60°, and kept. The solid was washed with ice-water, dried, and extracted with 20 ml. of boiling alcohol, and the solution left for 3 days at 0°. The semicarbazones obtained were purified further from absolute alcohol and dried, and 2 g. extracted with 50 ml. of ethylene dichloride at 60°. The filtrate, concentrated to 10 ml. and cooled, gave crystals, m. p. 134° after recrystallisation from 80% alcohol (Found: C, 63·8; H, 10·1. The *semicarbazone* of hydroxyketobehenic acid, $C_{23}H_{45}O_4N_3$, requires C, 64·6; H, 10·6%).

The residue insoluble in ethylene dichloride, when crystallised from 80% alcohol, gave crystals of the second semicarbazone, m. p. 157·5°. The acids were not isolated from these derivatives.

Oxidation of Erucic and Brassidic Acids with Perbenzoic Acid.—10 G. of erucic acid in 20 ml. of chloroform were mixed at 0° with 200 ml. of a solution of perbenzoic acid in chloroform containing 0·008 g. of active oxygen per ml. After 10 days at 0° and 1 day at room temperature the solvent was removed in a vacuum, and the residue extracted with hot water till free from benzoic acid. The oil obtained was dissolved in 8 times its weight of alcohol and cooled, and the crystals of oxidoerucic acid (7·5 g.) separated. After purification the m. p. was 63·5°, I.V. 0, A.V. 157 (Found: C, 74·5; H, 12·3. Calc. for $C_{22}H_{42}O_3$: C, 74·6; H, 11·9%). On hydrolysis by boiling for some hours with a large volume of aqueous alcoholic hydrochloric acid a solid was obtained which, crystallised from alcohol, yielded 13 : 14-dihydroxybehenic acid, m. p. 100°, not depressed by an authentic specimen.

7 G. of brassidic acid were treated with perbenzoic acid as above. The oxidobrassidic acid obtained (4·1 g.) had m. p. 70°, I.V. 0, A.V. 159 (Found: C, 74·8; H, 12·0. Calc. for $C_{22}H_{42}O_3$: C, 74·6; H, 11·9%). On hydrolysis 13 : 14-dihydroxybehenic acid, m. p. 132°, was obtained.

Chlorohydrin Synthesis of Oxidoerucic Acid.—To a solution of 15 g. of erucic acid in 250 ml. of ether, 230 ml. of 5% sodium hypochlorite solution were added. Carbon dioxide was passed into the liquid to saturation, the ether being replaced from time to time. After 12 hours the ether was washed and distilled, and the residue dissolved in 200 ml. of absolute alcohol, cooled to 0°, and filtered. Excess of sodium ethoxide was added, and the mixture warmed to 50°, left overnight, acidified with 5% hydrochloric acid, and cooled. The solid obtained gave oxidoerucic acid, m. p. 63·2°, after crystallisation from alcohol. Yield, 10%.

Preparation of Methyl Erucate and Methyl Brassidate.—100 G. of erucic acid, 300 ml. of anhydrous methyl alcohol, and 3·5 g. of concentrated sulphuric acid were refluxed for 6 hours, the bulk of the alcohol removed in a vacuum, the residue poured into cold water, and the oil taken up in ether, washed with dilute sodium carbonate solution and with water, and distilled. The fraction, b. p. 182—184°/0·2 mm., was methyl erucate (80·5 g.), I.V. 71·2, A.V. 0.

Methyl brassidate, similarly prepared and purified finally from alcohol, had m. p. 33°, I.V. 70·1, A.V. 0. Yield, 75%.

Oxidation of Methyl Erucate and Methyl Brassidate with Hydrogen Peroxide.—20 G. of methyl erucate in 40 ml. of glacial acetic acid were treated with 35 ml. of hydrogen peroxide (100 vol.). The oily layer formed disappeared after heating on the water-bath for 2 hours and after a further 2 hours the solution was poured into 300 ml. of water. The solid deposited at 0°, crystallised from methyl alcohol, gave *methyl* 13 : 14-*dihydroxybehenate*, m. p. 78° (Found: C, 71·3; H, 11·8. $C_{23}H_{46}O_4$ requires C, 71·5; H, 11·9%). On saponification it gave 13 : 14-dihydroxybehenic acid, m. p. 100°.

Methyl brassidate, when oxidised similarly with hydrogen peroxide, gave *methyl* 13 : 14-*dihydroxybehenate*, m. p. 111°, in good yield (Found: C, 71·2; H, 11·7%). On saponification it gave 13 : 14-dihydroxybehenic acid, m. p. 131°.

Oxidation of Methyl Erucate and Methyl Brassidate with Perbenzoic Acid.—15 G. of methyl erucate in 100 ml. of chloroform were treated at 0° with 400 ml. of a cold chloroform solution containing perbenzoic acid equivalent to 0·006 g. of active oxygen per ml. After 10 days (ice-chest) the temperature was allowed to rise to 20°, and the chloroform removed (vacuum). The residue was extracted with hot water and dissolved in ether, the solution washed with sodium carbonate and dried, and the solvent removed. The oil left was crystallised from methyl alcohol, giving *methyl oxidoerucate* (12 g.), m. p. 28°, A.V. 2·0, I.V. 0 (Found: C, 74·8; H, 11·9. $C_{23}H_{44}O_3$ requires C, 75·0; H, 11·9%). Saponification with 0·5N-alcoholic potassium hydroxide for 1 day at room temperature gave oxidoerucic acid, m. p. 62·3°, not depressed by an authentic specimen.

Methyl brassidate, oxidised in the same way, gave *methyl oxidobrassidate*, m. p. 42·3°, A.V. 0, I.V. 0 (Found: C, 74·9; H, 11·8. $C_{23}H_{44}O_3$ requires C, 75·0; H, 11·9%). Saponification in the cold gave oxidobrassidic acid, m. p. 70·1°, unchanged in admixture with an authentic specimen.

Oxidation of Methyl 13 : 14-*Dihydroxybehenate with Lead Tetra-acetate.*—10 G. of the ester, m. p. 78°, in 120 ml of glacial acetic acid were mixed with a solution of 33 g. of lead tetra-acetate in 250 ml. of hot glacial acetic acid. After 3 hours at 70° the mixture was poured into water. The product extracted by ether was dissolved in its own weight of light petroleum, washed, dried, and cooled to −10° for 1 day. The white solid obtained crystallised from 80% alcohol in plates, m. p. 51·8° (Found: C, 68·7; H, 10·1. *Methyl brassylate semialdehyde*, $C_{14}H_{26}O_3$, requires C, 69·4; H, 10·8%). As no aldehydic derivatives could be prepared, the identity of the product remains doubtful.

The filtrate from the light petroleum extract gave an oil which on distillation gave nonaldehyde, b. p. 50—52°/2·8 mm.; semicarbazone, m. p. 99·8°; 2 : 4-dinitrophenylhydrazone, m. p. 106°.

Oxidation of 13 : 14-*Dihydroxybehenic Acid, m. p.* 101°, *with Periodic Acid.*—16 G. of dihydroxybehenic acid in 400 ml. of 95% alcohol were mixed rapidly with a solution of 12 g. of potassium periodate in 600 ml. of N-sulphuric acid at 30°. After 15 mins. the cloudy solution was cooled and diluted with water. The product extracted by ether was distilled in steam. The distillate, extracted with ether, yielded an oil, one half of which, distilled (0·2 mm.), gave a main fraction, b. p. 51—53°, consisting of nonaldehyde (Found: C, 75·8; H, 12·7. Calc.: C, 76·0; H, 12·7%); semicarbazone, m. p. 99·5°; 2 : 4-dinitrophenylhydrazone, m. p. 106°.

The oil left after separation of the nonaldehyde rapidly darkened. The nonaldehyde was therefore removed from the second half of the original oil, and the residue at once cooled in ice. It was taken up in 95% alcohol and kept at 0°. Crystals (0·2 g.), m. p. 73°, separated; they gave no aldehydic reactions and were not further examined. The filtrate, after removal of the alcohol, left 3 g. of oil, which were heated for 30 mins. with 100 ml. of 8% sulphuric acid. The semi-solid material obtained was extracted with 50% alcohol and filtered hot. Crystalline plates, m. p. 87·5°, were obtained [Found: C, 68·0; H, 10·2; *M* (titration), 222. *Brassylic semialdehyde*, $C_{13}H_{24}O_3$, requires C, 68·4; H, 10·5%; *M*, 228]. The *semicarbazone* had m. p. 158·5° (Found: C, 59·2; H, 9·9. $C_{14}H_{27}O_3N_3$ requires C, 58·9; H, 9·5%). Oxidation gave brassylic acid, m. p. 111°, unchanged in admixture with an authentic specimen.

Oxidation of 13 : 14-*Dihydroxybehenic Acid, m. p.* 101°, *with Lead Tetra-acetate.*—20 G. of dihydroxybehenic acid in 250 ml. of glacial acetic acid were heated with 80 g. of lead tetra-acetate in 250 ml. of the same solvent at 70° for 3 hours, and the mixture poured into water. Ether extracted an oil, which on fractionation under low pressure gave a small quantity of acetic acid, followed by a mixture of acetic acid and nonaldehyde, b. p. up to 65°/8 mm., from which nonaldehyde (3·5 g.), b. p. 50—52°/2 mm., was separated. The residue in the flask which did not distil up to 130°/2 mm. weighed 8 g. It was dissolved in alcohol and, on cooling, gave 1·5 g. of fine crystals which after purification had m. p. 73°. This substance gave no aldehydic reactions. The alcoholic filtrate gave an oil which was heated with 200 ml. of 5% sulphuric acid for 30 mins. After cooling, the solid was removed, washed, and boiled out with 50% alcohol. The extract deposited crystalline plates which finally gave brassylic semialdehyde, m. p. 87·8° (Found: C, 68·8; H, 10·9%). The semicarbazone had m. p. 158°, unchanged in admixture with a sample prepared by the action of periodic acid on dihydroxybehenic acid. Oxidised with potassium permanganate, the aldehyde gave brassylic acid, m. p. 111°.

The oxidation of 13 : 14-dihydroxybehenic acid, m. p. 132°, with lead tetra-acetate gave the same scission products, nonaldehyde and brassylic semialdehyde.

The Rates of Reaction of the Two 13 : 14-*Dihydroxybehenic Acids with Lead Tetra-acetate.*—0·05 G. of the dihydroxy-acid in 20 ml. of glacial acetic acid was mixed with 10 ml. of 1·1N-lead tetra-acetate. The method of titration was that of Criegee (*loc. cit.*). The results are on p. 479.

General Method of Treatment with Oxygen.—Dry purified oxygen was passed at the rate of 5 l. per hour through the acid (25 g. units) in the apparatus described on p. 479. The catalyst, when used, was 0·6% of cobalt erucate in each case The amount of carbon dioxide produced was small (1—2%).

Oxidation of erucic acid at 120° *in presence of a catalyst.* 20 G. of the product obtained after 12 hours' treatment with oxygen were dissolved in 100 g. of 95% alcohol and kept at 0° for 2 days. The white solid was removed and crystallised several times from alcohol and acetone, giving oxidobrassidic acid, m. p. 70·5°. Yield, 12% (Found : C, 74·4; H, 12·1. Calc. : C, 74·6; H, 11·9%). On hydrolysis with aqueous alcoholic hydrochloric acid 13 : 14-dihydroxybehenic acid, m. p. 132°, was obtained.

The alcoholic filtrate was evaporated to dryness in a vacuum, and the residue (16 g.) dissolved in 100 ml. of light petroleum. On dilution with the solvent to 300 ml. a brown oil (8 g.) separated.

The solution in light petroleum might contain nonoic acid. It was kept at −20° for 8 hours, but no solid acid appeared. The solvent was removed, and the residue distilled in steam. Volatile acids were absent. Solution of the residue in alcohol and precipitation with lead acetate (20% of the total required) gave lead salts, which were extracted with hot alcohol. Lead nonoate would dissolve, but the acid could not be detected among the free acids obtained from the alcoholic extract. From the insoluble lead salts some erucic acid was obtained.

6 G. of the portion soluble in light petroleum were heated with alcoholic potassium hydroxide solution for 8 hours. The acids obtained on acidification were dissolved in 200 ml. of ether. The solution deposited a solid which, recrystallised from alcohol, left 0·6 g. (10%) of 13 : 14-dihydroxybehenic acid, m. p. 132°. This acid could not be detected in the brown oil (8 g.) insoluble in light petroleum, but after saponification of the oil as above 11% of 13 : 14-dihydroxybehenic acid was obtained.

A search for ketol-behenic acids was made by the method previously used for their isolation. The brown oil insoluble in light petroleum did not form a semicarbazone.

Oxidation of erucic acid at 120° *in the absence of a catalyst.* 17 G. of the product obtained after 12 hours' treatment were dissolved in 60 ml. of alcohol and kept below 0° for several days. The solid deposited gave oxidobrassidic acid, m. p. 70·5° (yield, 1%). The alcohol was removed, and the residue (16 g.) treated with light petroleum as before. The absence of nonoic acid and of dihydroxybehenic acid in the light petroleum-soluble portion (9 g.) was confirmed. After saponification for 8 hours as above, 8·5% of its weight of 13 : 14-dihydroxybehenic acid, m. p. 132°, was obtained. The light petroleum-insoluble fraction (8 g.) contained neither brassylic acid nor free dihydroxybehenic acid, but after saponification 16% of its weight of 13 : 14-dihydroxybehenic acid, m. p. 132°, was obtained.

Oxidation of erucic acid at 70° *in the presence of a catalyst.* 20 G. of the product obtained after 24 hours' treatment were dissolved in alcohol (100 ml.) and kept at 0° for 2 days. The solid deposited, after purification from alcohol and acetone and extraction with light petroleum, gave oxidoerucic acid, m. p. 63·7°, not depressed by a specimen prepared by the action of perbenzoic acid. Yield, 13·5% (Found : C, 74·3; H, 12·4. Calc. : C, 74·6; H, 11·9%). On hydrolysis 13 : 14-dihydroxybenenic acid, m. p. 100°, was formed.

The portion soluble in alcohol was treated with light petroleum as before, giving (*a*) a soluble fraction (48%), from which 6% of its weight of dihydroxybehenic acid, m. p. 132°, was obtained after saponification, and (*b*) an insoluble one (32%), giving 17% of its weight of the same acid when saponified. 6·5 G. of fraction (*b*) were extracted several times with hot 50% alcohol. The solution, after cooling at 0° for some days, deposited brassylic acid (0·3 g.), m. p. 111°, after purification. No brassylic semialdehyde was observed either before or after hydrolysis.

Oxidation of erucic acid at 70° *in the presence of acetic anhydride.* 10 G. of erucic acid in 20 g. of acetic anhydride with 0·6% of cobalt erucate were oxidised for 15 hours, fresh solvent being added from time to time. After 3 days the white solid formed was separated and gave oxidobrassidic acid, m. p. 70·8°. Yield, 12—15%. On hydrolysis with aqueous alcoholic hydrochloric acid, 13 : 14-dihydroxybehenic acid, m. p. 132°, was obtained.

The filtrate was poured into twice its weight of water, and sufficient ether added to dissolve the brown oil that separated. The solid deposited at 0° consisted of 13 : 14-dihydroxybehenic acid, m. p. 132°. Yield, 3%.

Oxidation of methyl erucate at 120° *in the presence of a catalyst.* 25 G. of methyl erucate with 0·6% of cobalt erucate were oxidised for 12 hours. 20 G. of the product were taken up with ether and extracted with potassium carbonate solution. The free oxidised acids obtained from the alkaline extract (15%) gave no pure compounds. The ethereal extract left 16·6 g. of oxidised esters, which were dissolved in 35 ml. of methyl alcohol and kept at 0° for 2 days. *Methyl oxidobrassidate* (2·6 g.) was deposited, giving 1·8 g. of the pure ester, m. p. 41·7°, I.V. 2 (Found : C, 74·9; H, 11·8. $C_{23}H_{44}O_3$ requires C, 75·0; H, 11·9%). Saponification gave oxidobrassidic acid, m. p. 70°.

The methyl-alcoholic filtrate contained 13·5 g. of residue, 3 g. of which were treated with alcoholic potassium hydroxide solution for 10 hours. The acids obtained on acidification were removed in ether (200 ml.) and from the solution 0·3 g. of dihydroxybehenic acid, m. p. 132°, was obtained.

Oxidation of methyl erucate at 70° *in the presence of a catalyst.* 25 G. of methyl erucate with 0·6% of cobalt erucate were oxidised similarly for 24 hours. 20 G. of the product in ether were extracted with potassium carbonate solution as above. The free oxidised fatty acids obtained (3·6 g.) could not be identified. The ethereal extract gave 15·2 g. of neutral oxidised esters, which were dissolved in 30 ml. of methyl alcohol, cooled to 0° for some days, and the liquid rapidly filtered. The solid, after purification, gave methyl oxidobrassidate (2·9 g.), m. p. 41·6° (Found : C, 74·8; H, 11·7%). After saponification oxidobrassidic acid, m. p. 70·5°, was obtained.

Oxidation of methyl erucate at 70° *in the presence of acetic anhydride and a catalyst.* 10 G. of methyl erucate in 20 ml. of acetic anhydride, with 0·06 g. of cobalt erucate, were oxidised in the same way, the volume being maintained by addition of acetic anhydride. After 12 hours the iodine value had fallen to 22. The solid product was removed and after purification consisted of methyl oxidobrassidate (2 g.), m. p. 41·8°.

CHELSEA POLYTECHNIC, LONDON, S.W. 3. [*Received, December* 29*th*, 1941.]