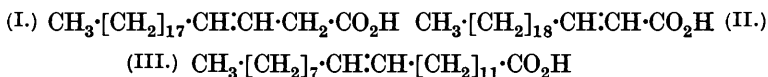


LVII.—*iso*Erucic Acid.

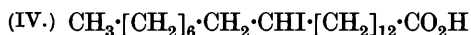
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*iso*ERUCIC acid was first obtained by Alexandrov and Saytzev (*J. pr. Chem.*, 1894, **49**, 58) by treating iodobehenic acid, prepared from erucic acid, with potassium hydroxide. Saytzev (*ibid.*, 1894, **50**, 65) showed that it also resulted when brassidic acid was converted into iodobehenic acid and the halogen acid treated with alkali. *iso*Erucic acid, m. p. 54—56°, was characterised by the preparation of a dibromobehenic acid, m. p. 44—46°, and by oxidation in alkaline solution with potassium permanganate to a dihydroxybehenic acid, m. p. 86—88°. At the time of these investigations, erucic acid was considered to have the constitution (I), and the above-mentioned authors regarded it as probable that *iso*erucic acid was the structural isomeride (II).



It was subsequently established that erucic acid and brassidic acid were the *cis*- and *trans*-modifications respectively of an acid (III), since on oxidation with ozone, followed by chromic acid, they both yielded brassylic and pelargonic acids (compare Noller and Adams, *J. Amer. Chem. Soc.*, 1926, **48**, 1074; Jegorov, *J. pr. Chem.*, 1912, **86**, 539). The view of Alexandrov and Saytzev (*loc. cit.*) being accepted, it followed that *iso*erucic acid would in all probability

have either formula (VI) or (VII), depending on whether iodobehenic acid from erucic and brassidic acids had formula (IV) or (V).



It was shown, however, by Ponzio (*Gazzetta*, 1904, **34**, ii, 50) that when *iso*erucic acid was oxidised by concentrated nitric acid, in a manner similar to that used in the oxidation of erucic acid (*J. pr. Chem.*, 1893, **48**, 323), it gave a mixture of acids from which brassylic and pelargonic acids were isolated and he showed further that the dibromo-acid (m. p. 44—46°), on treatment with alkali, yielded a behenolic acid identical with that obtained under the same conditions from the dibromo-acids derived from erucic and brassidic acids. As a result of these experiments he very legitimately concluded that *iso*erucic acid was not a structural isomeride of erucic and brassidic acids. In subsequent years, a number of investigations were carried out with the object of determining by physico-chemical methods the relationship of these three acids (Mascarelli and Toschi, *Gazzetta*, 1915, **45**, i, 314; Mascarelli and Sanna, *ibid.*, 1915, **45**, ii, 208, 315; Mascarelli, *ibid.*, 1917, **47**, i, 160). The conclusion was reached that in all probability brassidic and *iso*erucic acids were dimorphic forms of the *trans*-acid (III), but all attempts to convert one acid into the other failed.

Notwithstanding Ponzio's experiments, it appeared to us possible that the original view of Alexandrov and Saytzev might be correct, since the oxidation of an unsaturated fatty acid with concentrated nitric acid, owing to the extreme violence with which it proceeds, cannot be regarded as an entirely satisfactory method of orienting a double linking, whilst the conversion of the dibromobehenic acid into the acetylenic acid is carried out under conditions which are recognised as favourable to isomeric change.

Repetition of the oxidation of *iso*erucic acid with nitric acid has confirmed the formation of brassylic acid as one of the products of the reaction, but the yield of this dibasic acid is extremely small, the main substances formed being acids of lower molecular weight. We decided, therefore, to oxidise *iso*erucic acid, in the form of its ester, with ozone and also with potassium permanganate under the standard conditions used by Armstrong and Hilditch (*J. Soc. Chem. Ind.*, 1925, **44**, 43 τ) for the oxidation of methyl oleate.

The *iso*erucic acid used in these experiments was prepared by the method of Alexandrov and Saytzev (*loc. cit.*) and purified by

repeated crystallisation from alcohol (95%). It melted sharply at 55—57° and appeared to be homogeneous. Treatment of the *ethyl* ester with ozone gave, in addition to the main oxidation products, which will be discussed later, a not inconsiderable quantity of ethyl arachidate. There is no doubt that the *isoerucic acid* used in the earlier experiments was contaminated with arachidic acid, although the acid had the correct m. p. and crystallised extremely well. In our later experiments, the *isoerucic acid*, after crystallisation from alcohol to constant melting point, was further purified by fractional precipitation of the zinc salt, and any arachidic acid was thus removed in the least soluble fractions.

When ethyl *isoerucate* was oxidised with ozone, under conditions which, with erucic acid, were found to yield a readily separable mixture of brassylic and pelargonic acids (see p. 376), the oxidation product was a mixture which was somewhat difficult to resolve. As the quantity of this material was limited, we examined only the mixture of dibasic acids formed. We were able to isolate (a) decane- $\alpha\alpha$ -dicarboxylic acid, $\text{HO}_2\text{C}\cdot[\text{CH}_2]_{10}\cdot\text{CO}_2\text{H}$, m. p. 126—127°, identified by comparison with a synthetic specimen of the acid (Walker and Lumsden, J., 1901, 79, 1201), and (b) dodecane- $\alpha\alpha$ -dicarboxylic acid, $\text{HO}_2\text{C}\cdot[\text{CH}_2]_{12}\cdot\text{CO}_2\text{H}$, m. p. 121—122°, identified by analysis and by preparation of the methyl ester, m. p. 41°.

This result of the oxidation of ethyl *isoerucate* with ozone was surprising, and appeared to show that *isoerucic acid*, in spite of its sharp m. p. and well-defined crystalline form, was not homogeneous but was a mixture of the two unsaturated acids (VI) and (VII).

To confirm this conclusion, a quantity of very carefully purified methyl *isoerucate* was oxidised in acetone solution with potassium permanganate. From the oxidation products we were able to separate the two dibasic acids mentioned above and also *n*-octoic acid. Unfortunately, *n*-decoic acid, which must also have been formed, could not be obtained in a pure state.

This experiment confirmed in all respects the results obtained by oxidation with ozone and seems to leave no doubt that *isoerucic acid* is not a homogeneous substance, but is a mixture of Δ^{11} -*docosene-1-carboxylic acid* and Δ^{13} -*docosene-1-carboxylic acid*. From the yields of the oxidation acids the two acids would appear to be present in approximately equal amounts.

Since *isoerucic acid* itself was an inseparable mixture, we examined a number of derivatives to see whether any of them showed signs of heterogeneity. The *methyl* ester is crystalline, m. p. 24—26°, resolidifying at 22°; the *anilide* and *p-toluidide* both crystallise extremely well and both before and after crystallisation have the same m. p.; the *zinc* salt appears to be homogeneous.

As has already been mentioned, *iso*erucic acid is stated to yield a dibromo-derivative, m. p. 42—44°, or 46—46.6° according to Macbeth and Stewart (P., 1912, 28, 68). We have repeated the preparation of this substance several times, but in every case the bromination product had the appearance of a mixture and the m. p. was not sharp. We have not tried the oxidation of *iso*erucic acid to dihydroxybehenic acid, but it is probable that this is a mixture of two dihydroxy-acids.

The fact that *iso*erucic acid is an inseparable mixture of two acids yielding apparently homogeneous derivatives is somewhat unusual, but is not unique. Attention may be directed to the following somewhat similar cases: mononitro-*o*-veratraldehyde, m. p. 88° (Perkin, Roberts, and Robinson, J., 1914, 105, 2389), has been shown to be a mixture of two isomeric nitroveratraldehydes of m. p. 110° and 113° respectively (Perkin, Robinson, and Stoye, J., 1924, 125, 2355); anisic and veratric acids form a mixture, m. p. 145°, inseparable by crystallisation (Cain and Simonsen, J., 1912, 101, 1061); the geometrical isomerides of camphorquinone-oxime (*isonitrosocamphor*) are inseparable by solvents and produce a mixture melting higher than the more fusible modification (Forster, J., 1903, 83, 535); benzoic and *p*-nitrobenzoic acids in the proportion 2:1 form a mixture indivisible by solvents and melting at 182—198° (Forster and Saville, J., 1922, 121, 823).

During our preliminary experiments we investigated the oxidation of erucic and brassidic acids under various conditions and found the nature of the dihydroxy-acid formed to be dependent on the conditions used. In view of the recent publication of Hilditch (J., 1926, 1828) we do not intend to continue this side of the investigation. Experiments on the synthesis of the two unsaturated acids (VI and VII) are in progress and will, it is hoped, form the subject of a future communication.

EXPERIMENTAL.

*iso*Erucic acid prepared by Alexandrov and Saytzev's method (*loc. cit.*), after four crystallisations from alcohol, melted at 54—56°, but, as has already been mentioned, it was found as the result of oxidation experiments to contain a small percentage of arachidic acid. The acid was purified by fractional precipitation of the zinc salt; eight fractions were obtained, of which the first two were rejected, since they contained arachidic acid. After this purification, the acid had m. p. 55—57° and n_D^{25} 1.4469.*

*iso*Erucic acid is not affected by treatment with nitrous acid under conditions which convert erucic acid into brassidic acid, nor does it

* The refractive indices of erucic and brassidic acids at the same temperature were 1.4480 and 1.4472, respectively.

undergo any change when an alcoholic solution containing a trace of iodine is exposed to bright sunlight for some days.

The *zinc* salt crystallised from benzene in thin leaflets, m. p. 109°. No depression of the m. p. occurs on admixture with an equal amount of the zinc salt of brassidic acid (m. p. 112—113°), but the crystalline forms of the two salts are different, the latter salt crystallising in needles.

The *anilide* separated from alcohol in fine needles, m. p. 77—78.5° (Found : N, 3.6. $C_{25}H_{47}ON$ requires N, 3.4%), and the *p-toluidide* in needles, m. p. 85—86° (Found : N, 3.5. $C_{29}H_{49}ON$ requires N, 3.3%).

The *methyl* ester, prepared by treating the acid with methyl alcohol and sulphuric acid, crystallised in needles, b. p. 240°/14 mm., m. p. about 24—26°, resolidifying at 22° (thermometer in liquid). It is somewhat sparingly soluble in methyl alcohol (Found : *M*, 351.1; iod. val., 71.9. $C_{23}H_{44}O_2$ requires *M*, 352; iod. val., 72). The *ethyl* ester is a viscid oil, b. p. 243°/8 mm.

Oxidation of Methyl isoErucate with Potassium Permanganate.—Methyl *isoerucate* (50 g.) was dissolved in acetone (500 c.c.), and potassium permanganate (168 g.) gradually added. The oxidation proceeded vigorously and sufficient heat was generated to keep the acetone boiling. The reaction mixture was heated on the water-bath for 15 hours, the acetone distilled off, and the manganese dioxide sludge dissolved by the addition of dilute sulphuric acid and sodium bisulphite. The oil which had separated was dissolved in ether, and the ethereal extract was washed with sodium carbonate solution until no further acid was removed, dried, and evaporated (A). The sodium carbonate extract was mixed with an excess of sodium hydroxide solution, boiled for one hour, and acidified. The liberated organic acids were dissolved in ether; on removal of the solvent a semi-solid, crystalline mass remained (47 g.). The mixture of acids was digested with light petroleum (b. p. 40—60°), and the boiling solution filtered (residue B), a small quantity of solid which separated on cooling being added to B. The light-petroleum extract was evaporated and the liquid acids (20 g.) were distilled; a large fraction was then obtained, b. p. 230—270°/685 mm. The residue in the distilling flask (4 g.) crystallised and was added to B. On refractionation, a fraction was obtained, b. p. 232—235°/685 mm., which was identified as *n*-octoic acid by titration (Found : *M*, 146. Calc. : *M*, 144) and by preparation of the *p*-toluidide, m. p. 67—69°. This m. p. was not depressed on admixture with an authentic specimen (Found : N, 6.1. Calc. : N, 6.0%). It was not found possible to separate a constant-boiling fraction from the residue.

The solid acid (B), m. p. 80—100°, was a mixture which could not be resolved by fractional crystallisation. Preliminary experiments having shown that one of the acids yielded a magnesium salt which was readily soluble in water, the mixture of acids was dissolved in dilute sodium hydroxide solution (phenolphthalein), and the boiling solution treated with an excess of magnesium sulphate. The sparingly soluble magnesium salt, B₁, was collected after 12 hours, and the filtrate acidified; a voluminous, white precipitate then separated. This was taken up with ether (yield, 9 g.) and recrystallised from hot water and finally from ethyl acetate, flat needles being obtained (Found: C, 63.0; H, 9.6; *M*, 230.6. Calc.: C, 62.6; H, 9.5%; *M*, 230). It melted at 126—127°, alone or mixed with decane- $\alpha\kappa$ -dicarboxylic acid, prepared by Walker and Lumsden's method (*loc. cit.*).

The sparingly soluble magnesium salt B₁ was decomposed with dilute sulphuric acid. The acid thus obtained (16 g.), m. p. 90—95°, softening at 80° (*M*, 255.6), was fractionally converted into the magnesium salt, four fractions being obtained. Titration showed that the last fraction, which was soluble in water, was mainly decane- $\alpha\kappa$ -dicarboxylic acid (*M*, 235); this was also present in not inappreciable amount in fraction 3 (*M*, 247.4). The first two fractions (*M*, 259; 256), which were evidently identical, were combined and recrystallised from ethyl acetate; an acid then separated in leaflets, m. p. 121—122° (Found: C, 65.1; H, 10.3; *M*, 258.9. Calc.: C, 65.1; H, 10.1%; *M*, 258). The barium salt also was analysed (Found: Ba, 34.8. Calc.: Ba, 34.9%). This acid has the properties of dodecane- $\alpha\mu$ -dicarboxylic acid (Brown and Walker, *Annalen*, 1891, **261**, 123); direct comparison was not possible, but the methyl ester prepared from the silver salt separated in needles, m. p. 41°, which is stated to be the m. p. of methyl dodecane- $\alpha\mu$ -dicarboxylate.

The neutral oil A (see above; 9 g.) consisted of unchanged methyl *iso*erucate.

The actual yields of the oxidation acids obtained and those calculated on the assumption that *iso*erucic acid is an equimolecular mixture of the two unsaturated acids, allowance being made for the weight of methyl *iso*erucate recovered, are: monobasic acids obtained, 16 g.; calc., 17.8 g.; dibasic acids obtained, 26 g.; calc., 28.2 g.

Oxidation of Ethyl isoErucate with Ozone.—In a preliminary experiment made with the object of determining the most suitable conditions for the oxidation of ethyl *iso*erucate, erucic acid (10 g.) was oxidised with ozone, followed by chromic acid, under the conditions described below. The mixture of acids was taken up with ether

and on removal of the solvent an oil was obtained which partly crystallised. The solid, which melted at 109° after being washed with light petroleum and at 112 — 113° after crystallisation from benzene, was identified as brassylic acid by the method of mixed m. p. and by titration (Found : *M*, 243. Calc. : *M*, 244). The original filtrate, on dilution with light petroleum, deposited a further quantity of brassylic acid (m. p. 110°), and after the removal of this it was fractionated, b. p. 249 — $252^{\circ}/685$ mm., leaving a small residue which crystallised and probably consisted of brassylic acid, but was not further examined. The distillate was identified as pelargonic acid by titration (Found : *M*, 159.5. Calc. : *M*, 158).

Ozone was passed through a well-cooled solution of ethyl *isoerucate* (10 g.) in acetic acid (70 c.c.) until a test portion no longer decolorised bromine. After the addition of formic acid (10 c.c.), the solution was heated on the water-bath for 2 hours, cooled, and treated with an aqueous solution of chromic acid sufficient in quantity to convert the aldehydes present into the corresponding carboxylic acids. The mixture of acids (from 30 g. of ethyl *isoerucate*) was dissolved in ether and, after removal of the solvent, converted into the ethyl esters. On distillation under diminished pressure (8 mm.), the following fractions were obtained : (i) up to 150° (14 g.), (ii) 150 — 180° (5 g.), (iii) 180 — 190° (8 g.), (iv) 190 — 210° (6 g.), (v) above 210° (3 g.). Fraction (i) consisted of the esters of the monobasic acids and was not further examined; fraction (v) crystallised on keeping and was identified as ethyl arachidate, m. p. 50° (m. p. of acid, 77°) (Found : *M*, 311. Calc. : *M*, 312).

Since on redistillation the intermediate fractions could not be obtained pure, they were combined and after hydrolysis the acids were separated by the magnesium salt method described above. The fractions of the soluble and the insoluble magnesium salts were converted into the methyl esters through the silver salts; the soluble magnesium salt then yielded a methyl ester, b. p. 175 — $177^{\circ}/10$ mm. This was *methyl decane- α κ -dicarboxylate*, since on hydrolysis it gave decane- α κ -dicarboxylic acid, m. p. 126 — 127° (Found : *M*, 230.6. Calc. : *M*, 230).

The methyl ester from the acid yielding the sparingly soluble magnesium salt distilled at 191 — $192^{\circ}/10$ mm. and solidified on keeping; it melted at 41° after crystallisation from methyl alcohol. The acid obtained on hydrolysis had m. p. 121° (Found : *M*, 257.6. Calc. : *M*, 258).

Oxidation of Erucic and Brassidic Acids.—Erucic acid, on oxidation in alkaline solution under the conditions used by Lapworth and Mottram (J., 1925, **127**, 1629) for oleic acid, gave the high-melting dihydroxybehenic acid (m. p. 127 — 128° ; yield 36%). In cold

acetone solution, it gave the low-melting isomeride, m. p. 99—100°
Under similar conditions, brassidic acid yielded only the low-
melting dihydroxy-acid.

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