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Production of Polymers from the Seed Oil Of Crambe Abyssinica. I. Isolation of Tridecanedioic (Brassylic) Acid

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ABSTRACT

Methyl erucate has been separated from the mixed esters of the fatty acids obtained from the seed oil of Crambe abyssinica. Oxidative cleavage of erucic acid to give brassylic and pelargonic acids has been examined. The brassylic acid yield by nitric acid oxidation is less than that from reaction with potassium permanganate which in turn is less productive than ozonolysis. The overall yield of high-purity brassylic acid is 62.4% based on the methyl erucate fraction or 36.4% referred to the seed oil.

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INTRODUCTION

Crambe abyssinica is a high yielding crop, the seed oil of which has, as the glyceride, a particularly large content of cis-13-docosenoic (erucic) acid [1]. Investigation of the chemical utilization of crambe oil is not novel, and extensive work has been reported from the laboratories of the U. S. Department of Agriculture [2-9]. Much of this research has concentrated on the dicarboxylic acid, tridecandioic (brassylic) acid, obtained by oxidative cleavage of erucic acid. In the present reports [10-12] we describe the exploitation of brassylic acid for the formation of some polymers.

EXPERIMENTAL RESULTS

The Crambe abyssinica was grown at the Agricultural Institute (An Foras Taluntais), Oak Park, Eire; the seed was crushed (Rose, Downs and Thompson Ltd., Hull), the resulting oil was then saponified and the acid fraction was methylated (Victor Wolff and Co., Manchester). The composition of the methyl esters was found by GLC (Table 1) and is in good accord with earlier analyses.

In initial work the methyl erucate fraction was recovered by fractional distillation under a low pressure of nitrogen; the fraction was collected at 180-220°C/0.4-3.0 Torr in various runs. An electrically heated Hempel column packed with short lengths of glass tubing was used. In later, larger-scale, separations, the lower esters were removed below 180°C at pressures not greater than 3 Torr and the undistilled residue worked up. This contained 91-95% methyl erucate by GLC and was only fractionally less pure than the fraction cut in earlier runs. The methyl erucate fraction so separated amounted to 57-62% of the initial mass of mixed methyl esters supplied after saponification of the seed oil.

Studies by Wolff and co-workers [5] have shown that oxidative cleavage of erucic acid may be made efficiently by ozonolysis. As well as this method we have briefly examined oxidative cleavage by nitric acid and by permanganate. Most runs were made on erucic acid obtained by saponification of the methyl erucate fraction by refluxing with 2 N alcoholic potassium hydroxide for 2 hr, after which the alcohol was removed by distillation and the salt taken up in glacial acetic acid. However, to compare the various ways of cleaving the erucic acid, a single batch of commercial erucic acid, 89% pure (GLC), was employed as starting material.

Nitric acid oxidation involved adding 60 g of the acid to 500 ml

TABLE 1. Composition of Crambe Seed-Oil Acids (as Methyl Esters)

		Acid content (%)			
Acid		Present work	Ref. [1]	Ref. [2]	Ref. [9]
Hexadecanoic	(palmitic)	1.9	2	2.0	2
Octadecanoic	(stearic)	0.7	0.5	0.6	–
9-Octadecenoic	(oleic)	15.5	18	17.9	15
9,12-Octadecadienoic	(linolenic)	8.3	11	9.9	10
9,12,15-Octadecatrienoic	(linolenic)	7.2	4	5.0	7
Eicosanoic	(arachidic)	0.5	1	0.8	–
9-Eicosenoic	(gadoleic)	2.8	2	2.5	3
Docosanoic	(behenic)	1.0	1	1.0	2
13-Docosenoic	(erucic)	61.4	59	59.1	55-60
Docosadienoic		0.7	1	0.5	–
Tetracosenoic		n.d.	0	0.2	3

of 70% nitric acid containing 0.6 g ammonium vanadate at 90° C. This addition was made over 0.5 hr while the reaction mixture was continuously stirred; stirring was continued for a further 3 or 6 hr before the reaction mixture was poured into 2 liters of cold water. Precipitated acids were filtered, washed with water and dried in vacuo at 50-60° C. A sample was methylated with diazomethane and the brassylic acid content found by GLC; this examination showed the presence of a variety of products, the identification of which was not attempted.

Permanganate oxidation was carried out as follows. A 30-g portion of crude erucic acid was dissolved in 250 ml glacial acetic acid in a flask equipped with a mechanical stirrer. Then 70 g of finely powdered potassium permanganate was added in very small portions over a period of 1 hr and the flask cooled in cold water to moderate the effects of the reaction exotherm. After addition of the oxidizing agent the reaction mixture was stirred overnight at room temperature. The soluditon was diluted with 500 ml water and, after addition of acidified sodium metabisulfite to dissolve the precipitated manganese dioxide, was extracted with ether. The brassylic acid content of the recovered solid was found by GLC examination of a methylated sample. A repeat oxidation was made with methyl erucate as starting material.

Cleavage of erucic acid (30 g) by ozonolysis was carried out by bubbling the exit gases from an ozone generator (Gallenkamp GE 150) at 200 ml/min) through a solution of the acid in acetic acid at 20-25°C; the oxygen from the generator contained 5-6% ozone. Ozonolysis was continued until the gases emerging from the reaction flask produced visual evidence of iodine from an acidified solution of potassium iodide. The reaction mixture was treated with 30% hydrogen peroxide (30 ml) and was gradually warmed to 100°C and kept at this temperature for 2 hr. After cooling to room temperature excess peroxides were destroyed by addition of sodium metabisulfite until potassium iodide-starch paper gave a negative test. After standing overnight the brassylic acid which had crystallized out was filtered, washed, and dried in vacuo at 50-60°C.

The three methods of cleaving erucic acid are compared in Table 2; in this table the yield of brassylic acid is the percentage of the theoretical amount from cleavage of erucic acid and is based on the GLC analyses of the starting material and final product.

Having confirmed oxidative ozonolysis as the preferred method of cleavage the erucic acid separated from crambe seed oil was so

TABLE 2. Yield of Brassylic Acid Formed from Cleavage of Erucic Acid.

Method	Yield of tridecanedioic acid (%)
Nitric acid	17.2[a]
Nitric acid	21.2[b]
Potassium permanganate	43.0[c]
Potassium permanganate	62.0
Ozonolysis	73.0
Ozonolysis	75.0[d]

[a] 3 hr.
[b] 6 hr.
[c] From methyl erucate.
[d] Repeat experiment.

treated; after the procedure described above the crude brassylic acid was recrystallized twice from xylene (mixed isomers) to give a product of high purity, mp 113-114°C.

Equivalent weight 122.2 calcd, 121.7 found. Analysis calculated: C, 63.91%; H, 9.9%; O, 26.19%. Found: C, 63.9%; H, 9.9%.

The yield of pure brassylic acid isolated after two recrystallizations and based on the methyl erucate content of the seed oil varied between 59% and 69% of theoretical in six separate preparations with a mean yield of 62.4%. One experiment was made in which the methyl erucate fraction was cleaved prior to saponification. In this case the erucate was dissolved in ethyl acetate for ozonolysis after which the solvent was removed by rotary evaporation at low pressure. The product was saponified by refluxing with alcoholic potassium hydroxide and then treated with 30% hydrogen peroxide and further alcohol. After refluxing for 3 hr the alcohol was distilled off and water was added to dissolve the residues which were then acidified and treated with sodium bisulfite. The crystallised crude acids were then further recrystallized twice from xylene as before. The brassylic acid yield by this route was only 40%.

DISCUSSION

Several strategies to obtain brassylic acid from the starting material of mixed methyl esters of the crambe seed oil fatty acids may be proposed and which differ in the order of the separation, saponification and cleavage stages. The alternatives are summarized in the block diagram of Fig. 1.

The purity required of the brassylic acid will depend on its proposed application but, as a normal rule, polymer applications presuppose high purity material. If separation is postponed until after oxidative cleavage, an additional ten or more species will be present, not counting the products of oxidation side reactions. Finally, although separation methods for fatty acids based on fractional crystallization or complex formation are known, it is likely that fractional distillation procedures are the only feasible routes. Since the acids have relative high molecular weights and are high boiling, fractional distillation of esters rather than acids is preferred. This consideration effectively inserts an additional methylation stage into the right-hand routes of the block diagram; furthermore, these routes will consume greater quantities of oxidizing agents. Although our preferred route is that at the extreme left of Fig. 1, we have not made experimental tests of the schemes which rely on either hydrolysis or cleavage as the first stage.

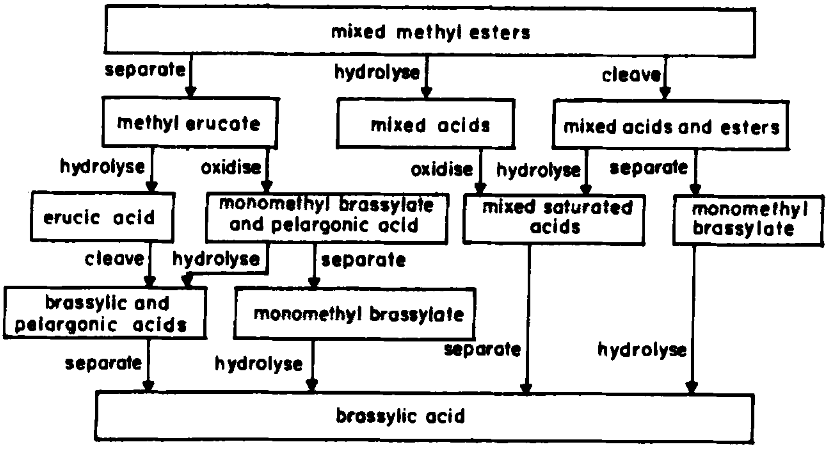

FIG. 1. Strategies to obtain brassylic acid from the mixed methyl esters from crambe oil.

Although an early report [13] claims a high efficiency of cleavage by nitric acid oxidation, more recent examination of the process [14] has established the presence of additional products arising from random attack on the hydrocarbon chain. The poor yield of tridecanedioic acid formed in this oxidative cleavage (Table 2) reflects the poor specificity of the primary site of oxidative attack.

Although the acids resulting from cleavage at the points of unsaturation are the main products of the oxidation of fatty acids by permanganate, various other products are formed [15], apparently as a consequence of the unequal reaction rates of some of the intermediate compounds; further, some 25% of the starting unsaturated acid may be unreacted [16]. Despite the report [17] that permanganate oxidation of erucic acid gives a 78% yield of brassylic acid, our experiments were substantially less productive.

Ozonolysis appears to be a much more specific mode of cleavage as is exemplified by its commercial exploitation for the production of nonanedioic (azeleic) acid and nonanoic (pelargonic) acid from 9-octadecenoic (oleic) acid [18]. Our formation yield at 74% is less than the mean value of 93% reported by the USDA workers [5]. The difference in isolated yields, USDA 70% of 98% purity brassylic acid compared with 62% of 99+% purity in the present work, is less striking and refers to different methods of recovery after ozonolysis. Higher yields of brassylic acid, at lower purity, should be possible if (a) discarded fractions in fractional distillation were recycled and (b) if ozonolysis and recrystallization supernatants were worked up. Nieschlag et al. [5] also found that isolation of brassylic acid in acceptable yields was troublesome; they considered the use of steam distillation and vacuum distillation to remove the pelargonic acid and also methylation followed by fractional distillation and resaponification. Economic considerations require an efficient separation of the valuable pelargonic acid.

On the basis of the present results, unit mass of seed oil will, assuming 98% efficiency on splitting, yield 0.984 units of mixed methyl esters and 0.092 units of glycerol. The mixed methyl esters will yield some 60% methyl erucate (94% pure), which is equivalent to 0.561 units of erucic acid and 0.371 units of by-product acids, assuming 1% loss on saponification. Our value of 62.4% for the isolated yield of pure brassylic acid is equivalent to 0.255 units of this product; assuming a similar efficiency for the isolation of pelargonic acid gives 0.165 units.

If the unit cost of seed oil is X and it costs Y to convert unit mass of it to erucic acid (94% pure) the unit cost of the latter is 1.78(X + Y), disregarding the value of the glycerol and by product mixed acids. If the cost of oxidative cleavage and product isolation is Z per unit mass of erucic acid, the final cost of pure brassylic acid is given by

$$2.20\,[1.78\,(X + Y) + Z] - [0.092\,G + 0.371\,Q + 0.165\,P]$$

where G, Q, and P are, respectively, the value of glycerol, mixed acids, and pure pelargonic acid. A recent report [19] quotes crambe seed oil at $0.18/lb; assuming realistic values for the other quantities in the above expression (X = 0.18, Y = 0.07, Z = 0.23, G = 0.55, Q = 0.14, P = 0.57) puts the production cost of high-purity brassylic acid at ca. $1.30/lb.

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