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Production of brassilic acid by ozonolysis of technical erucic acid

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Halina Szeląg and Henryk Niewiadomski

The Laboratory of the Chemistry and Technology of Fats of the Institute of Organic and Food Chemistry and Technology of the Gdańsk Polytechnic.

Production of Brassilic Acid by the Ozonolysis of Technical Erucic Acid

Ozonolysis of technical erucic acid (89.0%) was carried out. The effect of the water content in the acetic acid as the solvent, and the effect of the concentrations of erucic acid in the reaction mixture on the yield of the reaction were investigated. Brassilic acid was isolated from the post-reaction mixture with the help of two methods, and a 99.9% product, with a yield of 51.6% was obtained from one of these.

Edible vegetable oils and animal fats can also be a source of fatty acids for the chemical industry. The interest in fatty acids arises from the possibility of obtaining numerous derivatives as a result of the reaction of their carboxyl group or of double bonds in the chain$^{(1-5)*}$. Erucic acid$^{(4-7)}$ (cis-heneicosane-12-carboxyl-1) $CH_3(CH_2)_7CH = CH(CH_2)_{11}COOH$ has, in recent years, become the subject of study in many research centres. The natural source of erucic acid are the fats of cruciate plants. Rape seed oil,

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* **Translator's Note:** Raised figures in brackets, such as these, refer to items in the numbered bibliography at the end of the paper.

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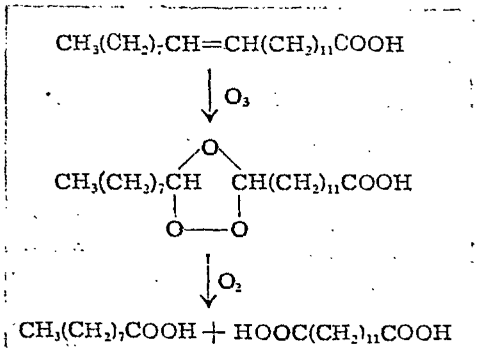
which belongs to this group of oils, contains about 50% erucic acid. One of the possible ways of using erucic acid in the chemical industry is to be found in its ozonization. The brassilic acid which is obtained in this way is a valuable stock product for obtaining plasticizers, artificial fibres and plastics, and lubricants(7-11).

The reaction of the ozonolysis of erucic acid takes place as follows:



As it appears from the above, from the erucic acid are obtained pelargonic acid (octanocarboxyl-1) and brassilic acid (undecano-dicarboxyl-1,11). Pelargonic acid can be used for obtaining suitable derivatives, and it can be partially recycled for the ozonolysis reaction as a solvent(9,12-14). There therefore exists a possibility of the complex utilization of the products of the ozonolysis of erucic acid.

Poland, as one of the chief producers of rape seed oil, must also realistically assess the possibility of its chemicalization, among other ways, by the ozonolysis of erucic acid. It is for this reason that, in spite of several earlier works carried out at foreign centres(5,6,8), it seemed expedient to instigate some research, the purpose of which was to investigate and describe in greater detail the conditions of the ozonolysis and the isolation of brassilic acid from the post reaction mixture. For the work of Niewiadomski and Wojeński(15) concerning the ozonolysis of erucic acid did not encompass the investigation of the effects of all the parameters of the reaction nor of the isolation of brassilic acid. The work of Grynberg and others(16), on the other hand, concerned the ozonolysis of the methyl ester of erucic acid.

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Experimental Section

Technical erucic acid obtained as a result of the distillation of the fatty acids of rape seed oil in the Strzemieszyce Chemical Works, STREM, was subjected to ozonolysis. The composition of this raw material was as follows:

palmitic acid	0.5%
stearic acid	0.3%
oleic acid	2.7%
linoleic acid	1.0%
eicozanic acid	0.7%
eicozenic acid	5.8%
erucic acid	89.0%

All the ozonolysis experiments were performed using a machine of the type LOZ-3 as the generator of the ozone. This machine is produced in the German Democratic Republic and has the following technical specifications: yield of ozone, 20-40 gms/hr, compression of ozone 5-10% oxygen, flow of O_2 30 litres/hr.

The reaction was carried out in a three-necked flask (capacity 0.25 or 2 litres) equipped with a sparger, a thermometer and a reflux condenser. After passing through the ozonizer, the oxygen was passed through the sparger to the reaction mass. In the first stage of the work, when the selection was being studied of the optimal conditions of carrying out the process of ozonolysis, the weight of the reaction mass was 150 gms. In the second part of the work, which consisted of isolating brassilic acid from the products of the reaction, this quantity was increased to 1200 gms. The ozonization was carried out at a temperature of 30°C. The completion of the process of the creation of ozonides was determined by carrying out a bromine test(3). The break-down of ozonides and the oxidation of the products of their decomposition into acids was carried out by passing oxygen through the reaction mass, while at the same time gradually raising the temperature to 95°C. The completion of the oxidation

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process was determined by carrying out a test with Fehling's solution for the presence of aldehyde groups(17).

The composition of the gases was determined by the method of gas chromatography. All the samples that were analysed were transformed into methyl esters, by heating them for four hours in methyl alcohol containing 1% sulphuric acid(5). The esters that were thus obtained were analysed /p.83/ on the Chrom I chromatograph, equipped with a flame ionization detector. Chromatographic columns were used of length 270 cm and diameter 0.6 cm, and filled with Chromosorb W (60-80 mesh) with a 15% carrier stationary phase DEGS(18,19). The temperature in the thermostat during the analysis was 194°C. The speed of the flow of the carrier gas (nitrogen) was equal to 45 ml/min. In order to carry out a quantitative analysis of the chosen acids only, the internal standard method was used (sebacic acid)(20).

Discussion of Results and Conclusions

The ozonolysis of erucic acid was performed using 80-90 percent glacial acetic acid as solvent. As it is apparent from the data shown in Table 1, the best yield of the ozonolysis reaction was obtained in the case where glacial acetic acid was used as solvent. Comparing the yield of the reaction when the initial concentration of the erucic acid in the reaction mixture is changed, it appears that an increase in this concentration causes a lowering in the yield of brassilic acid. A comparison of the data shown in Table 1 also makes it possible to state that the choice of solvent has a greater effect on the yield of the reaction than does the concentration of the substance being ozonized. It seems, however, that on an industrial scale it would be more profitable to give up the attempt of obtaining maximum yield in order to gain a better utilization of the apparatus and to have a smaller usage of the solvent, and smaller solvent recovery costs.

The fall in the yield of the ozonolysis reaction, both as a result of a change in solvent as also of a change in the concentration of erucic acid in the reaction mixture, is caused by the creation of other mono- and dicarboxyl

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acids, presumably as a result of the isomerization of the double bond.

Because of the large number of acids that appear in the post reaction mixture, differing very widely as regards the length of the hydrocarbon chain and the physio-chemical properties, the quantitative and qualitative identification of the short-chain constituents was omitted in this work, and only their total participation is given. The column entitled "short chain mono- and dicarboxyl acids" also embraces acetic acid in its role as solvent. Among the acids that enter into the composition of the post reaction mixture, the dicarboxyl acids deserve special attention. Their presence attests to the isomerization of the double bond during the process of ozonization. A change in the concentration of acetic acid has a particular effect upon the increase of the yield of by-products. The by-products of the ozonolysis reaction include the following acids: hexanodicarboxyl-1,6, nonanodicarboxyl-1,9, decanodicarboxyl-1,10, dodecanodicarboxyl-1,12 and tridecanodicarboxyl-1,13.

Schemat 1. Wyodrębnianie kwasu brasylowego po ozonolizie technicznego kwasu erukowego (60% techn. kwasu erukowego + 40% lod. kwasu octowego); metoda I

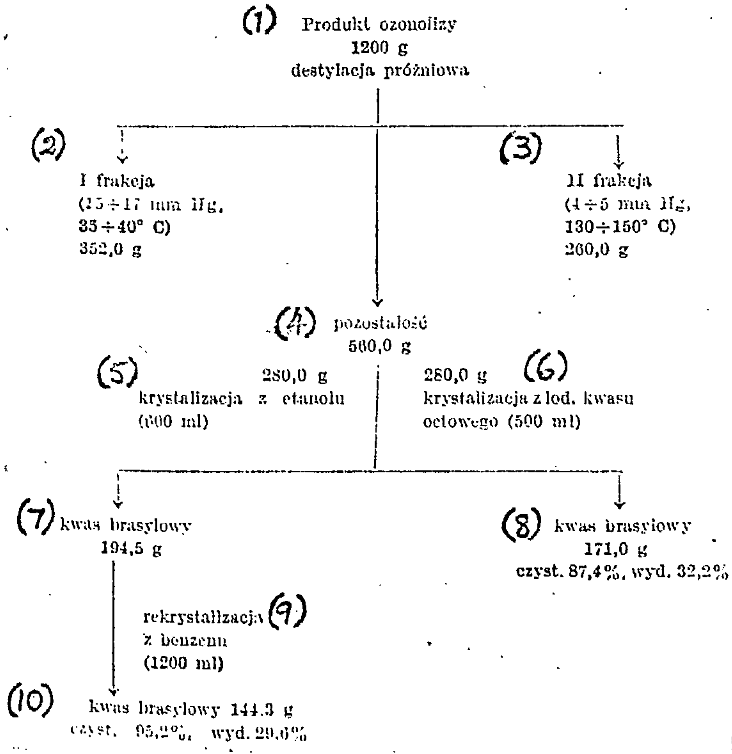

Figure 1. Isolation of brassilic acid after ozonolysis of technical erucic acid (60% technical erucic acid + 40% glacial acetic acid); Method I

(1) Product of ozonolysis 1200 gms vacuum distillation

(2) fraction I (15-17 mm Hg, 35-40°C) 352.0 gms

(3) fraction II (4-5 mm Hg, 130-150°C) 260.0 gms

(4) residue 560.0 gms

(5) 280.0 gms crystallization from ethanol (600 ml)

(6) 280.0 gms crystallization from glacial acetic acid (500 ml)

(7) brassilic acid 194.5 gms

(8) brassilic acid 171.0 gms purity 87.4%, yield 32.2%

(9) recrystallization from benzene (1200 ml)

(10) brassilic acid 144.3 gms purity 95.2%, yield 29.6%

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Table 1. The effect of the initial concentration of erucic acid; the concentrations of acetic acid used as solvent on the composition of the products of ozonolysis; temperature 30°C.

Tabela 1. Wpływ stężenia wyjściowego kwasu erukowego; stężenia kwasu octowego użytego jako rozpuszczalnika na skład produktów ozonolizy; temperatura 30° C

(1) Warunki ozonolizy		(2) Wydajność kwasu brasylowego [%]	(3) Skład produktów [%]									
(4) początkowe stężenie kwasu erukowego w mieszaninie [%]	(5) stężenie kwasu octowego jako rozpuszczalnika [%]		(6) kwasy o krótszych łańcuch.*)	(7) nasycone kwasy jednokarboksylowe		(8) kwasy dwukarboksylowe $HOOC(CH_2)_nCOOH$						
				C_{16}	C_{18}	n = 6	n = 7	n = 9	n = 10	n = 11	n = 12	n = 13
20	lodowaty (9)	96,0	83,2	0,2	—	0,2	0,5	0,6	0,6	12,3	0,7	0,7
20	90	92,2	82,8	0,2	—	0,3	0,5	0,7	1,1	11,8	1,3	1,3
20	80	83,2	83,6	0,1	0,1	0,2	0,5	0,9	0,7	10,7	1,3	1,9
40	lodowaty (9)	92,8	68,0	0,3	0,1	0,2	0,9	1,2	2,0	23,8	1,7	1,8
60	lodowaty (9)	89,6	49,0	0,4	0,3	1,1	1,6	1,8	2,4	34,6	1,6	2,2

*) jedno- i dwukarboksylowe. (10)

Key:

(1) Conditions of ozonolysis
(2) Yield of brassilic acid (%)
(3) Composition of products (%)
(4) initial concentration of erucic acid in the mixture (%)
(5) the concentration of acetic acid as solvent (%)
(6) acids with shorter chains*
(7) saturated monocarboxyl acids
(8) dicarboxyl acids $HOOC(CH_2)_nCOOH$
(9) glacial
*(10) mono- and dicarboxyl

Two methods were used for isolating brassilic acid from the post reaction mixture. The procedure that was used in method I is represented in figure 1., and the first part of table 2 shows how individual acids occurring in the post reaction mixture are removed in successive operations of the purification of the brassilic acid. After distilling off the volatile acids, the residue shows the presence of short chain acids together with the solvent, of saturated monocarboxyl acids that occur in the initial raw material and of numerous dicarboxyl acids. Subsequent crystallization from ethanol or from

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glacial acetic acid leads to a considerable increase in the content of brassilic acid. As a result of re-crystallization from benzene, a substance was obtained that had a 95.2% content of brassilic acid and a 2.1% content of short chain acids, mainly pelargonic and tridecanodicarboxyl-1,13.

In method II (figure 2) the isolation of brassilic acid was patterned upon the procedure published by Green and others(8). The filtrate, which is obtained after separating the raw brassilic acid,contained mainly acetic acid, and also pelargonic acid and other short chain acids, and brassilic acid. /p.84. Vacuum distillation of the filtrate makes it possible to recover the solvent and 6.4% of the brassilic acid (the second part of table 2).

Analysing the results obtained in both methods of isolating brassilic acid it can be stated that method II deserves especial interest. Employing this method, one can obtain brassilic acid of the highest degree of purity, which may be useful for the most refined syntheses, such as the obtaining of polyamide(4).

The results obtained in this paper allow the following conclusions to be drawn:

- the ozonolysis reaction at 30°C gives a maximum yield in glacial acetic acid with a 20 percent concentration of erucic acid;

- although a double or even triple increase in the concentration of erucic acid in the reaction mixture leads to a several percent lowering in the yield of the ozonolysis reaction, it makes possible a considerably larger yield of brassilic acid in one production cycle;

- crystallization of raw brassilic acid from the post reaction mixture and subsequent re-crystaliization make it possible to obtain brassilic acid of a very high degree of purity (99.9%).

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Table 2. The content of brassilic acid (and other acids) in products obtained during its isolation.

Tabela 2. Zawartość kwasu brasylowego (i innych kwasów) w produktach uzyskiwanych podczas jego wyodrębniania

	(1) Produkt	(2) Kwasy o krótszych łańcuchach*)	(3) Nasycone kwasy jednokarboksylowe		(4) Kwasy dwukarboksylowe $HOOC(CH_2)_nCOOH$						
			C_{16}	C_{18}	n = 6	n = 7	n = 9	n = 10	n = 11	n = 12	n = 13
(5) Metoda I	Produkt ozonolizy (60% kwasu erukowego + 40% kwasu octowego lodowatego) (a)	49,0	0,3	0,1	1,1	1,6	1,8	2,4	34,6	1,6	2,2
	pozostałość po oddestylowaniu kwasów lotnych (b)	10,0	1,1	1,0	1,5	3,2	3,5	5,1	67,0	3,5	4,1
	kwas brasylowy ekstr. etanolem (c)	4,3	0,6	0,4	1,0	0,3	0,6	0,8	88,9	0,7	3,2
	kwas brasylowy rekrystalizow. z benzenu (d)	2,1	—	—	—	—	—	—	95,2	—	2,7
	kwas brasylowy ekstr. lod. kwasem octowym (e)	5,7	1,1	1,2	—	—	—	—	87,4	—	4,6
(6) Metoda II	produkt ozonolizy (20% techn. kwasu erukowego + 80% lodow. kwasu octowego) (f)	84,2	0,2	—	0,2	0,5	0,6	0,6	12,3	0,7	0,7
	surowy kwas brasylowy (g)	26,2	—	—	—	—	0,5	0,4	70,1	0,5	2,0
	kwas brasylowy krystalizowany z etanolu (h)	2,2	—	—	—	—	0,6	0,6	93,3	1,1	2,2
	kwas brasylowy rekrystaliz. z benzenu (i)	0,1	—	—	—	—	—	—	99,9	—	—
	pozostałość po oddestylowaniu przesączu (j)	55,1	0,6	0,4	1,1	3,9	5,2	6,4	18,2	4,5	4,6
	kwas brasylowy po krystalizacji pozostał z lod. kwasu octowego (k)	42,6	—	—	0,9	1,5	2,2	3,0	41,3	2,5	6,0
	kwas brasylowy po rekryst. pozost. z alkoholu i benzenu (l)	0,8	—	—	—	1,8	1,2	1,5	69,3	1,9	5,0

*) jedno- i dwukarboksylowe (7)

Key:

(1) Product

(2) Acids with shorter chains*

(3) Saturated monocarboxyl acids

(4) Dicarboxyl acids $HOOC(CH_2)_nCOOH$

(5) Method I

(6) Method II

*(7) mono- and dicarboxyl

(a) Product of ozonolysis (60% erucic acid + 40% glacial acetic acid)
(b) residue after distilling off volatile acids
(c) brassilic acid extracted with ethanol
(d) brassilic acid recrystallized from benzene
(e) brassilic acid extracted with glacial acetic acid
(f) product of ozonolysis (20% technical erucic acid + 80% glacial acetic acid)
(g) raw brassilic acid
(h) brassilic acid crystallized from ethanol
(i) brassilic acid re-crystallized from benzene
(j) residue after distilling off the filtrate
(k) brassilic acid after crystallization of the residue from glacial acetic acid
(l) brassilic acid after recrystallization of the residue from alcohol and benzene

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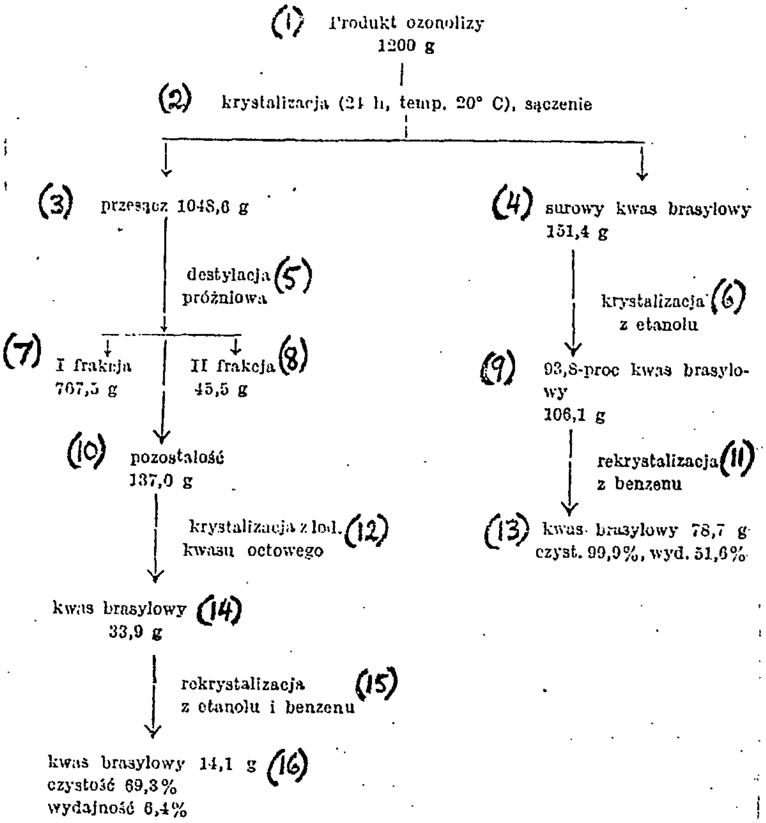
Figure 2. Isolation of brassilic acid after ozonolysis of technical erucic acid (20% technical erucic acid + 80% glacial acetic acid); Method II.

Schemat 3. Wyodrębnianie kwasu brasylowego po ozonolizie technicznego kwasu erukowego (20% technicznego kwasu erukowego + 80% lod. kwasu octowego); metoda II



Key:

(1) Product of ozonolysis 1200 gms
(2) crystallization (24 hours, temp. 20°C), filtration
(3) filtrate 1048.6 gms
(4) raw brassilic acid 151.4 gms
(5) vacuum distillation
(6) crystallization from ethanol
(7) fraction I 767.5 gms
(8) fraction II 45.5 gms
(9) 93.8 percent brassilic acid 106.1 gms
(10) residue 137.0 gms
(11) recrystallization from benzene
(12) crystallization from glacial acetic acid
(13) brassilic acid 78.7 gms purity 99.9%, yield 51.6%
(14) brassilic acid 33.9 gms
(15) recrystallization from ethanol and benzene
(16) brassilic acid 14.1 gms purity 69.3%, yield 6.4%

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SUMMARY

Production of Brassilic Acid by Ozonolysis of Technical Erucic Acid

The ozonolysis of technical erucic acid (89.0%) has been carried out. The influence of water content in acetic acid as a solvent and the erucic acid concentration in the reaction mixture have been investigated on the yield of reaction. Brassilic acid has been isolated from the post — reaction mixture by two methods, whereby at one of them the 99.9% product has been obtained with the yield of 51.6%.

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