STUDY ON THE EFFECT OF THINNERS ON THE COURSE OF ERUCIC ACID OZONOLYSIS

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The course of preparation brassilic acid involving ozonolysis of technical-grade erucic acid was investigated in relation to the thinner used in the ozonolysis reaction. The kind of thinner used was found to have a significant effect on the rate and course of the reaction.

The technology of production of dicarboxylic acids by ozonolysis of natural unsaturated fatty acids or their esters comprises the following steps:

— production of ozonides,

— decomposition of the ozonides with chain cleavage at the unsaturated bond,

— separation of ozonolysis products.

Because of the process complicacy, selection of conditions should depend on several factors, the most significant of which are:

a) the kind, degree of purity and the chemical character of the raw material to be used (acid or ester) [2, 10],

b) the desired form of the final product, that is, first of all the degree of purity and chemical character (ester, sami-ester, aldehyde--acid, acid, salt, etc.),

c) maintainment of suitable economic process indexes [9].

The type of reaction medium is a basic ozonolysis process variable, which has been inevstigated in relevant papers [1, 3-6, 8].

The aim of this paper is to investigate the thinner effect on the course of ozonolysis of technical-grade erucic acid.

The ozonolysis process was carried out in standard conditions on a laboratory scale in a glass apparatus.

Ozone was produced from technical-grade oxygen in an ozone generator constructed in this Institute.

Table 1

Characteristic of erucic acid

Property	Value
Neutralization value	168.4
Iodine value	67.4
Unsaponifiable substance content, %	2.3
Fatty acids composition, weight %	
$C_{22:1}$ (erucic)	90.0
$C_{20:1}$	2.2
$C_{18:1}$	1.6
$C_{20:0}$	1.8
$C_{18:0}$	1.9
$C_{16:0}$	1.6

Technical-grade erucic acid was obtained by crystallization (see Table 1).

The following parameters were kept constant:

— charge, 100 g,

— ozone flow, 2 g per hour,

— the ozonide forming step was discontinued, after a complete fall of the iodine value,

— ozonide decomposition was carried out at 90°C,

— the ozonide decomposition was continued for 24 hrs in the presence of 5% of water based on thinner.

The process variables were:

— the type of thinner (Table 2) and its amount relative to the erucic acid,

Table 2

Characteristic of the thinners used

Name	Dielectric constant [7] at 25°C
Water	80.4
n-Butyl alcohol	13.1
n-Octyl alcohol	11.3
Glacial acetic acid	6.2
Pelargonic acid	4*
n-Octane	1.9

* Approximate value.

— the temperature of the ozonide forming reaction.

Experiments were carried out according to an experiment design, which permitted a factorial analysis of the process (Table 3).

Table 3

Factorial experiment design

Symbol	Name of factor	Lower level	Upper level
a	Ratio of thinner to erucic acid	0.5	1.0
b	Temperature of ozonide forming step, °C	40	60

Experiment design for one thinner

	a	*b*
1	—	—
a	+	—
b	—	+
ab	+	+

Evaluation of the process was carried out as follows:

— the ozonide forming step was followed by measuring the through iodine value in samples taken at 1 hr intervals,

— the ozonolysis efficiency was evaluated by determining in the final product:

a) the neutralization value (after removal of the thinner in conservative conditions), and

b) the composition of fatty acids by GLC with identification of some products by mass spectroscopy.

Table 4

Results of ozonolysis as compared with theoretical values

Type of measurement	Theoretical value	Range of experimental values
Fall of iodine value in 2 hours of Ozonide formation	67.4	37.0—64.8
Neutralization value	409.7	321.3—397.2
Ratio of brassilic to pelargonic acids (*b*/*p*)	1.49	1.15—1.66
Brassilic and pelargonic acids (*b* + *p*), %	93.3	67.8—85.4
By-products, %	5	9—14

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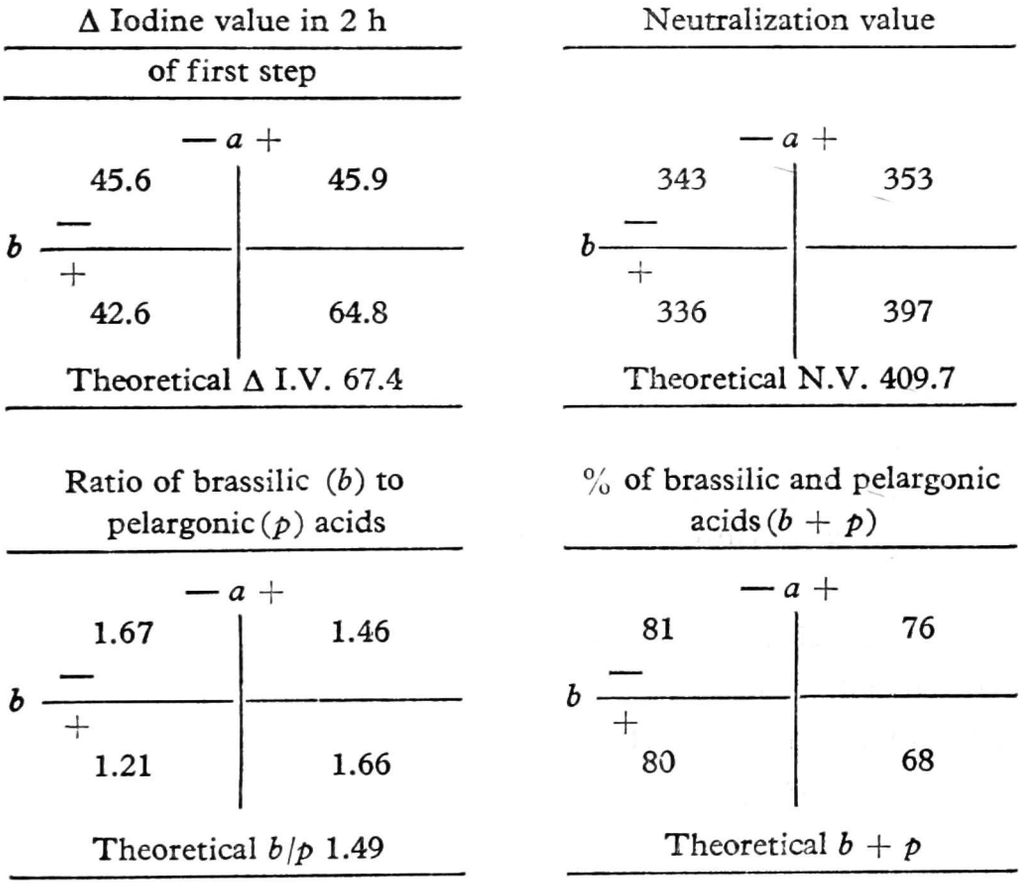

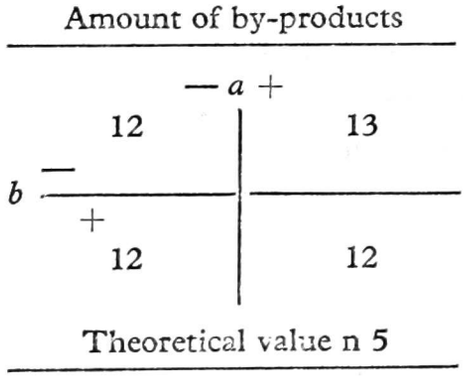

Fig. 1. Effect of variables on the course of ozonolysis

Chromatographic separation was performed in a Carlo Erba model GT apparatus equipped with a flame ionisation detector and a column 1 m long and 2 mm across, filled with 3% SE 30 on Celite. Temperature rise for the column was programmed at a rate of 5°C per minute between 80° and 220°C. Results were calculated relative to the theoretical values obtained from the raw material composition (Table 4). Analysis of the effect of the variables (Fig. 1) indicates the following relations:

— the first step of ozonolysis proceeds at the fastest rate at higher experimental temperatures, viz., at 60°C. When carried out at this temperature the reaction gives the final product with a iodine value closest to the theoretical,

— the brassilic acid-to-pelargonic acid ratio was closest to the theoretical when the reaction was carried out at a high dilution ($a = 1$), and at a temperature at the lower limit of the experimental range, viz., at 40°C,

— the percentage of the major components ($b + p$) was closest to the theoretical when the reaction was carried out at lower proportion of the tinner ($a = 0.5$),

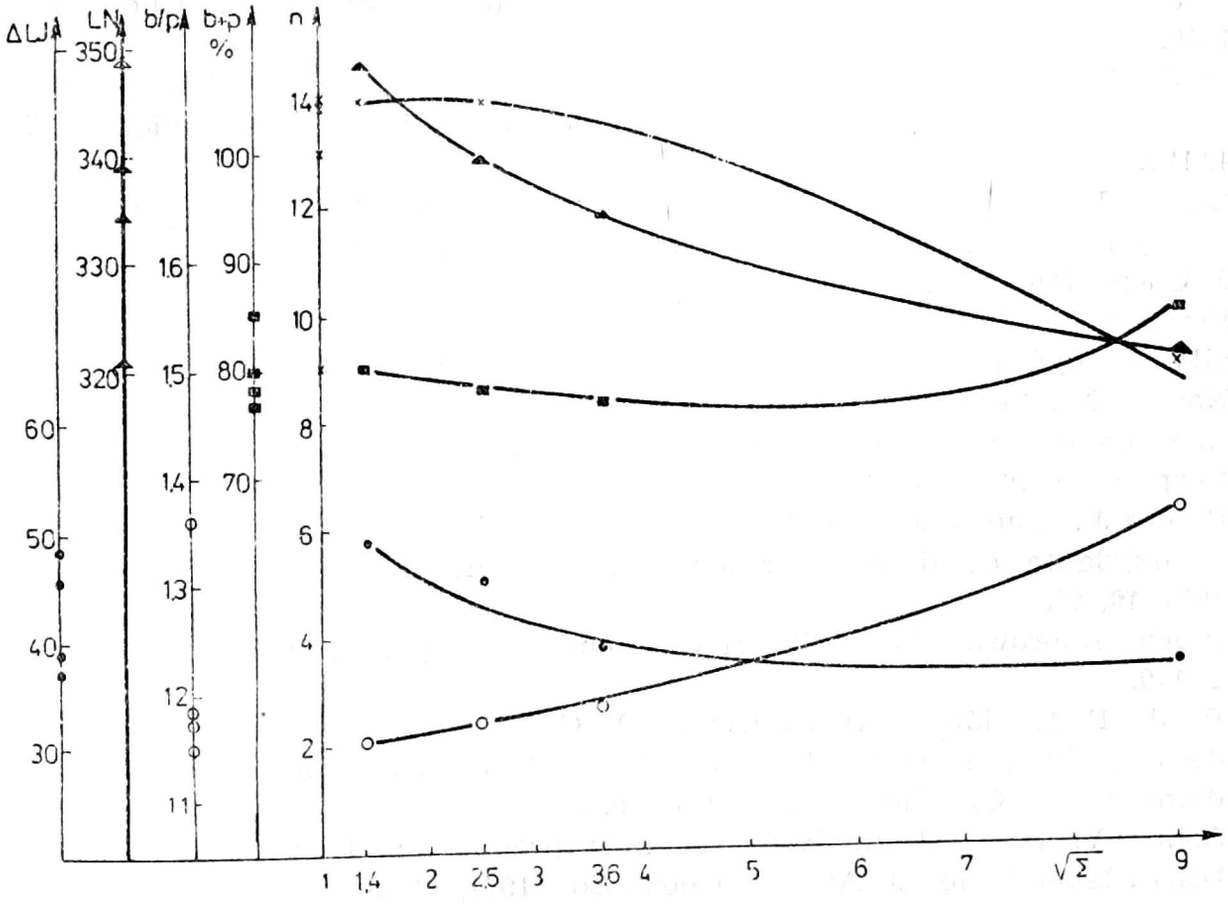

Fig. 2. Effect of the thimiers dielectric constant on course of erucic acid ozonolysis

— the variables tested were found to have no effect on the amount of by-products. The amount of by-products distinctly falls when water is used as a thinner for the reaction.

The effect of thinner polarity (expressed by dielectric constant) on the course of ozonolysis (Fig. 2) is such that:

— the lower is the thinners, ε-value, the faster is the first stage of ozonolysis and the closer is the neutralization value of the final product to the theory.

No distinct relation was found to exist between the yield of brassilic and pelargonic acids, their mutual ratio, number of components and the dielectric constant of the thinner.

As may be seen from the experimental data, selection of optimum process conditions is somewhat complicated, because the conditions securing the high-rate process differ from those providing for good selectivity. The process optimization of the process needs accurate description with in the whole factorial space.

Investigations on this problem are in progress.

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BADANIA WPŁYWU ROZPUSZCZALNIKÓW NA PRZEBIEG OZONOLIZY KWASU ERUKOWEGO

Streszczenie

Badano przebieg ozonolizy kwasu erukowego technicznego (90%) w obecności różnych rozcieńczalników polarnych i niepolarnych. Ozonowanie prowadzono w skali laboratoryjnej ok. 2 g 03/h w temp. ok. 40°C i 60°C w obecności rozcieńczalnika w stosunku objętościowym 1 : 1 oraz 1 : 0,5 względem kwasu erukowego. Rozkład ozonków i ich dotlenianie do kwasów prowadzono w temp. 95°C, dodając do środowiska reakcji około 5% wody w stosunku do rozcieńczalnika.

Przebieg ozonowania oceniano na podstawie spadku zawartości wiązań nienasyconych w kwasie erukowym. Rozkład ozonków oceniano na podstawie składu kwasów tłuszczowych metodą spektrometrii sprzężonej w GLC.

Wykonanie doświadczeń oparto na planowaniu statystycznym — doświadczenia czynnikowe.

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ИССЛЕДОВАНИЕ ВЛИЯНИЯ РАСТВОРИТЕЛЕЙ НА ХОД ОЗОНОЛИЗА ЭРУКОВОЙ КИСЛОТЫ

Резюме

Исследовали ход озонолиза технической эруковой кислоты (90%) в присутствии разных полярных и неполярных разбавителей. Озонизация проводилась в лабораторном масштабе ок. 2 г 0,3/час в температуре около 40°C и 60°C в присутствии растворителя в объемном соотношении 1:1 и 1:0,5 по отношению к эруковой кислоте.

Разложение озонидов и их дополнительное окисление до кислот проводилось в температуре 95°C, при добавлении к реакционной среде около 5% воды по отношению к разбавителю.

Ход озонизации оценивали на основании снижения количества ненасыщенных связей в эруковой кислоте. Разложение озонидов оценивали на основании состава жирных кислот по методу сопряженной спектрометрии в GLC.

При ведении опытов базировали на статистическом планировании — факторные опыты.