Reductive Ozonolysis of Soybean Oil: Laboratory Optimization of Process Variables

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ABSTRACT

Statistically designed experiments were carried out to determine the effect of reaction variables in the reductive ozonolysis of soybean oil to azelaaldehydic glyceride methyl acetal. Yields of this acetal were essentially quantitiative under optimum conditions, which include a 1:1 mixture of acetic acid and butanol as solvent, a solvent-oil ratio of 1.5:1, and hydrogenation at 150 psig and 50 C with palladium-on-charcoal catalyst.

INTRODUCTION

Previously, laboratory optimization of process variables was described for the reductive ozonolysis of methyl soyate to produce methyl azelaaldehydate dimethyl acetal (1). Another potentially useful intermediate is the azelaaldehydic glyceride or its methyl acetal formed by reductive ozonolysis of soybean oil (2-7). Accordingly, we carried out statistically designed experiments on the process variables for the glyceride as well. Aldehyde oils may be prepared by either complete (8,9) or partial (10) reductive ozonolysis, but for our purpose complete ozonolysis was selected.

EXPERIMENTAL PROCEDURES

Factorial Designs and Levels

Four separate experiments were carried out, each a one-third replicate of a 3^4 factorial design, for a total of 108 runs. The experiments were based on solvent (X) and carrier gas (Y) as independent variables in four combinations, X_0Y_0, X_0Y_1, X_1Y_0 and X_1Y_1, where the subscripts are levels identified as butanol-acetic acid (X_0), water (X_1), oxygen (Y_0) and air (Y_1). Additionally, four other independent variables (A-D) were tested at three levels each as described in Table I. The 1:1 butanol-acetic acid solvent (X_0) was selected for comparison with water and no solvent, on the basis of the high yields of methyl azelaaldehydate obtained from methyl oleate by its use (11).

Ozonolysis of Soybean Oil

Each experiment in the factorial design was based on a starting charge of 50.0 g alkali-refined soybean oil. After the charge was ozonized at 40 C and hydrogenated, the products were isolated as dimethyl acetals as previously reported (1). Soybean ozonolysis products formed without solvent were dissolved in 1:1 butanol-acetic acid before hydrogenation. The acetal products were weighed, and the volatile acetals (including caproaldehyde and pelargonaldehyde acetals) were removed in a falling film molecular still at reduced pressure. The volatile acetals were analyzed directly by gas liquid chromatography. The nonvolatile residue was hydrolyzed to the free aldehyde and analyzed for total carbonyl content. The percentage of azelaaldehydic glyceride in the residue was then calculated assuming that the average molecular weight, including saturated glycerides, was 720 (confirmed by a number of determinations by vapor pressure osmometry). For example, in one experiment of design X_0Y_0 (butanol-acetic acid solvent, oxygen carrier) the following conditions applied: (a) solvent-ester ratio: 1.5:1; (b) catalyst: Pd/C; (c) hydrogenation pressure: 150 psig; and (d) temperature: 50 C. After 103 min of ozonization with 102% of theoretical ozone uptake, the following results were obtained: weight of acetals isolated: 60.3 g; carbonyl in stripped oil: 8.40%; caproaldehyde dimethyl acetal: 5.2 wt %; pelargonaldehyde dimethyl acetal: 6.6 wt %; azelaaldehydic glyceride: 63.4 wt %; azelaaldehydic glyceride yield: 94.4 mol %; and pelargonaldehyde dimethyl acetal yield: 52.8 mol %.

The yields of acetals from the C_6 (caproaldehyde) and C_9 (pelargonaldehyde) monofunctional fragments were from 30 to 70% of the theoretical, depending on the conditions selected.

Yields of azelaaldehydic glyceride acetal in a few other experiments were: X_0Y_0(0000), 63.3%; X_0Y_0(0211), 97.6%; X_0Y_1(2110), 99.4%; X_0Y_1(0202), 67.7%; X_1Y_0(1102), 41.7%; X_1Y_0(1221), 87.2%; X_1Y_1(0000), 54.5%; and X_1Y_1(1021), 84.9%, where the integers within parentheses are the coded levels of the four independent variables A, B, C and D. Complete results of all 108 experiments are available from the Northern Regional Laboratory. For these statistically designed laboratory studies, methods were not developed for recovery and reuse of the reaction solvent liquor.

Analysis of Variance

Analysis of variance by standard statistical techniques (12) provided an independent estimate of experimental error, as well as tests of significance of main effects and first-order interactions at the 95% level. The standard deviation of azelaaldehydic glyceride yield was ±2.5%, and for C_9 dimethyl acetal yield, ±4%. The following main effects and first-order interactions were significant on azelaaldehydic glyceride acetal yield: X, solvent; A, solvent-oil ratio; C, hydrogenation pressure; D, hydrogenation temperature; XA, (solvent) (solvent-oil ratio); YA, (carrier gas) (solvent-oil ratio); and BD, (catalyst) (hydrogenation temperature). In this list of variables, appearance as a main effect does not connote greater importance than as a first-order combination. Yield of azelaaldehydic glyceride is affected by all six variables, although not necessarily equally.

For pelargonaldehyde acetal, the main effects and first-order interactions were: X, solvent; C, hydrogenation pressure; YA, (carrier gas) (solvent-oil ratio); YC, (carrier gas) (hydrogenation pressure); YD, (carrier gas) (hydrogena-

TABLE I

Independent Variable Codes

Variable	Level	Coded level
Solvent-oil weight ratio (A)	0.75:1	0
	0:1 (no solvent)	1
	1:50:1	2
Catalyst (B)	Pd/$BaSO_4$	0
	Pd/C	1
	Pd/SiO_2	2
Hydrogenation pressure (C)	15 psig	0
	150 psig	1
	300 psig	2
Hydrogenation temperature (D)	50 C	0
	75 C	1
	100 C	2

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tion temperature); and CD, (hydrogenation pressure) (hydrogenation temperature). For this compound, yield was independent of catalyst.

RESULTS AND DISCUSSION

Yield of azelaaldehydic glyceride depended on all six variables tested. Selection of certain of these variables, however, was imposed by certain process or economic limitations. Although satisfactory yields could be obtained with water as an ozonolysis medium, the slurry was so viscous that handling problems could be expected with large-scale processing. Of the remaining solvent choices, butanol-acetic acid is preferred to no solvent because ozonolysis products formed without solvent have greater instability and possibly a more hazardous nature. Another possibility–that of diluting the organic phase with caproaldehyde, perlargonaldehyde or their dimethyl acetals–has been discussed elsewhere (13). Oxygen is preferred for the carrier gas over air because ozone generation is more economical, and palladium on charcoal was selected as the catalyst because it is the most readily available.

Application of regression analysis (12) to the remaining variables resulted in the following equations for the yields of azelaaldehydic glyceride dimethyl acetal (AzODA) and perlargonaldehyde dimethyl acetal (PDA). AzODA, mol % = 122.20 + 9.001A - 0.8230D + 0.002161CD - $0.0003895C^2$.PDA, mol % = 60.25 - 0.4130C - 52.85A + 0.002432CD - 0.06411AC + $0.0009038C^2 + 35.10A^2$.

Solution by the IBM 1620/1311 Computing System of the AzODA regression equation could lead to thousands of combinations of reaction conditions. Computer selection of the set leading to the maximum yield (optimization) of azelaaldehydic glyceride was as follows: A, solvent-oil ratio: 1.50:1; C, hydrogenation pressure: 150 psig; and D, hydrogenation temperature: 50 C. Under these conditions, the yield of azelaaldehydic glyceride from soybean oil is predicted to be nearly quantitative. The accompanying yield of PDA under these conditions is predicted to be ca. 22 mol %. AzODA, mol % = 122.2 + 9.001(1.50) - 0.823(50) + 0.002161(150)(50) - $0.0003895(150)^2$ = 102.0 ± 2.5. PDA, mol % = 60.25 - 0.4130(150) - 52.85(1.50) + 0.002432(150)(50) - 0.06411(1.50)(150) + $0.0009038(150)^2 + 35.10(1.50)^2 = 22.0 \pm 4\%$. No attempt was made to determine the best PDA yield, since AzODA was considered to be the major product of interest. The prediction equations suggest that lowering pressure would tend to increase PDA yield without significantly changing AzODA yield.

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