Further Study on the One-Pot Synthesis of (*E*)-2-Nonenal from Castor Oil

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A one-step procedure is described for the synthesis of (*E*)-2-nonenal from commercial castor oil by ozonolysis in methanol, followed by reduction of the ozonide products with dimethyl sulfide and exposure of the resulting intermediate product to dilute sulfuric acid. The developed process allows the production of the aldehyde with a yield of 80% at a purity of 95%. The method has advantages over all those reported earlier, because of inexpensive raw material and reducing agent, recycling of the solvent and its unusual simplicity.

KEY WORDS: **Castor oil, 2-nonenal, ozonolysis.**

(*E*)-2-Nonenal is an important ingredient of natural flavors and fragrances. It is a microcomponent of volatiles from a number of plants (1). This aldehyde is used in the flavor industry, and all the commercially available flavorant is produced synthetically in a multi-step process. We recently reported a convenient and inexpensive procedure for the manufacture of (*E*)-2-nonenal by ozonolytic cleavage of castor oil (2). During the course of that study, we also observed that the ozonolysis of commercial-grade castor oil in acetic acid resulted in formation of the aldehyde in overall yield of *ca.* 35%, indicating that only one fatty acid in the glyceride molecule participated in the oxidation reaction. The extension of the ozonolysis time did not result in a noticeable increase of the yield. Apparently, under the conditions employed, the ozone addition occurred much more slowly with the other two fatty acids after the first one is oxidized. Here we report a better procedure for the preparation of 2-nonenal, the results of which rationalizes, to some extent, the above hypothesis.

EXPERIMENTAL PROCEDURES

Method A. Sodium (0.2 g) was dissolved in 200 mL absolute methanol, and 50 g commercial castor oil {n_D^{20} = 1.4778, $[\alpha]_D^{20}$ = + 5.6° (neat)} was added. The mixture was refluxed for 5 h and then cooled to −20°C. Oxygen containing 5 vol% of ozone was bubbled through the solution until a positive test with potassium iodide was reached. The mixture was then purged with nitrogen, and 12 g dimethyl sulfide was added dropwise, with agitation at a rate that kept the temperature of the reaction mixture below −10°C. The stirring was continued for another 2 h at −10 to 0°C and then for 5 h (or until a negative test with potassium iodide) at room temperature. The solvent was removed by vacuum distillation, and 80 mL of 5% sulfuric acid was added. The mixture was stirred, and the product was steam-distilled to deliver 22 g of crude aldehyde. (*E*)-2-Nonenal was purified by vacuum-distillation to give 14.5 g (74%) of product; boiling point 88–91°C/12 mm Hg, n_D^{20} = 1.4437. Spectral data of the aldehyde coincided with those reported previously (2).

Method B. A mixture of 150 g castor oil and 450 mL methanol was ozonized under the conditions described in Method A. The ozonide reduction (with 36 g dimethyl sulfide) and dehydration of the intermediate hydroxy aldehyde (with 120 mL of 5% sulfuric acid) was carried out in the same manner as in Method A to yield 54 g of crude product. Vacuum-distillation of this material yielded 46 g (80%) of (*E*)-2-nonenal; boiling point 98–101°C/20 mm Hg, n_D^{20} = 1.4440.

RESULTS AND DISCUSSION

In the first study, castor oil was transesterified with absolute methanol in the presence of sodium methanolate (3,4) (the reaction was monitored by ^{1}H nuclear magnetic resonance), and the crude methyl 12-hydroxy oleate (ricinoleate) was ozonized in methanol at −20°C (Method A) (Scheme 1). Then, the ozonide compounds formed were reduced with dimethyl sulfide (5) to give the intermediate 3-hydroxy nonanal, which was not isolated from the reaction medium. We employed several dehydrating agents, including *p*-toluene sulfonic acid, oxalic acid, iodine and sulfuric acid, for water elimination from the intermediate hydroxy aldehyde. The best results were obtained with 4–5% sulfuric acid by producing 2-nonenal in a yield of 74% (based on 85% glyceride). This method may present some interest if α,ω-formylester formed from the other moiety of the methyl ricinoleate is a desirable product. However, in the present study this anticipated compound has not been isolated.

Our assumption that the ozone addition to polyunsaturated compounds depends on the reaction conditions led to a second study. In this investigation (Method B), castor oil was dissolved in methanol, and the ozonolysis was carried out at −20°C. After ozonide reduction with dimethyl sulfide, the intermediate hydroxy aldehyde was dehydrated by steam distillation from the medium of a dilute sulfuric acid to deliver (*E*)-2-nonenal in a yield of 80% (based on 85% glyceride).

In both methods (A and B), the ozone consumption was about 2½ times higher than in the case of castor oil ozonolysis in acetic acid, indicating that three fatty acids in the glyceride molecule take part in the reaction.

The crude product was purified by vacuum distillation in a 20-cm vigreux column, and the resulting material was analyzed by gas chromatography (capillary column). In a typical experiment, the purified product contained 4% of two low-boiling compounds, (which were not identified) close in retention time and 95.5% 2-nonenal, including 3% of the (*Z*)-isomer. The same impurities, which are present in amounts up to 1% when ozonolysis is carried out in acetic acid, presumably originated from the ozonolysis of minor compounds in the castor oil.

For ecological and economical purposes, the methanol recovered from the process can be successfully reused.

We wish to stress that the developed new one-step procedure for the preparation of (*E*)-2-nonenal was an effective and inexpensive method of getting this natural aldehyde.

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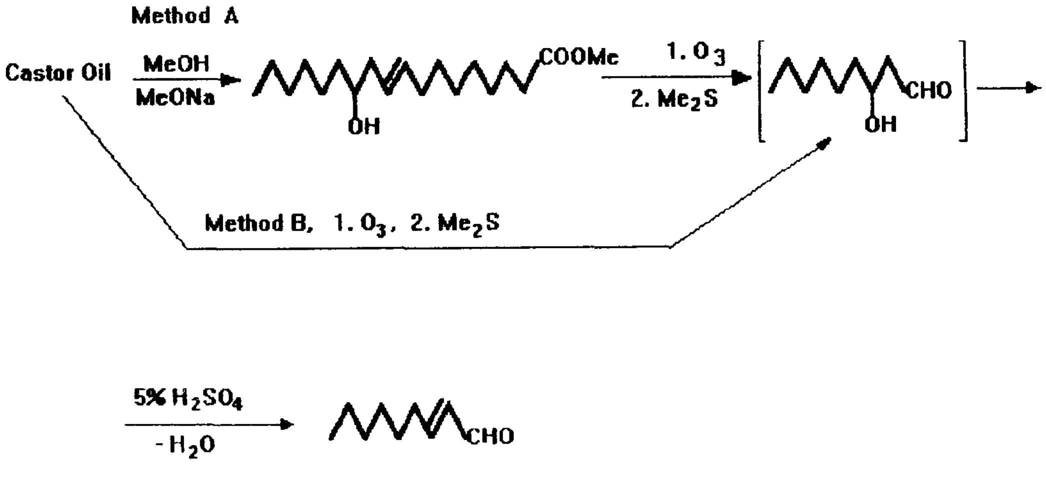

SCHEME 1

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