One-Pot Synthesis of (*E*)-2-Nonenal from Castor Oil

Jozef Kula* and **Halina Sadowska**
Institute of General Food Chemistry, Technical University, 90-924 Lodz, Poland

A one-step procedure for the preparation of (*E*)-2-nonenal from commercial castor oil by ozonolysis in acetic acid, followed by exposure of the resulting intermediate product to *p*-toluene sulfonic acid, is described. The manufactured aldehyde is of high purity and the method, by virtue of being simple and using inexpensive raw material, has advantages over those reported in the literature.

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

(*E*)-2-Nonenal, with its strong tallow odor, is an important ingredient of natural flavors and fragrances. Recent analytical studies have disclosed that the aldehyde is a microcomponent of volatiles from apricot fruit (1), rice (2), popcorn (3), narcissus (4) and *Centaurea solstitialis* L. (5). It is a major component of cucumber odor (6). The presence of (*E*)-2-nonenal, up to 1.46 mg/kg, has also been reported in a variety of meats (7,8).

Owing to its low odor threshold, 0.08 ppb (2), its participation in the creation of the total flavor can be significant even at low concentration. This aldehyde can be added to naturally or synthetically flavored foodstuffs, such as meat, coffee and other beverages, to improve or enhance the flavoring properties thereof and to make their flavor and aroma more natural (9).

(*E*)-2-Nonenal shows some biological activity as an attractant to olive fruit flies (10) and as a repellent to the cockroach *Periplaneta americana* (11).

Few (and elaborate) syntheses have been reported for this compound. Bedoukin (12) obtained 2-nonenal from nonanal in a 5-step procedure. Some other methods reported are based on the condensation reaction of heptaldehyde with malonic acid, followed by a three-step transformation of the resulting product (9,13,14). However, the total yields of 2-nonenal are rather moderate. The Wittig reaction of *n*-heptanal with formylmethylene-triphenylphosphorane may be a good method for the synthesis of (*E*)-2-nonenal, but the preparation of the Wittig agent is tedious and the product is isolated as the 2,4-dinitrophenylohydrazone (15) or by column chromatography (16). 2-Nonenal is also reported (17) to be manufactured from castor oil by its hydrogen peroxide hydroxylation to trihydroxyacid and oxidation by red lead (311 g of castor oil gives 50 g 2-nonenal of 94% purity).

EXPERIMENTAL PROCEDURES

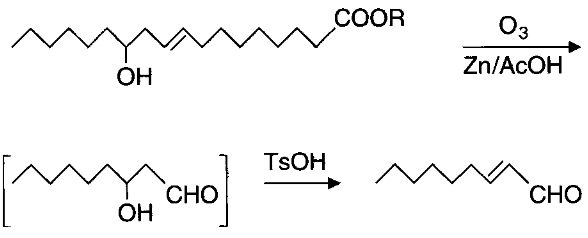
Through a solution of 100 g commercial castor oil {$n_D^{20} = 1.4775$, $[\alpha]_D^{20} = +5.6°$ (neat)} in 200 mL acetic acid was bubbled oxygen containing 5 vol% of ozone at 10°C until a positive test with potassium iodide (in 10% acetic acid) was reached. The mixture was then added dropwise to a stirred suspension of 20 g zinc dust in 250 mL water, at a rate that kept the temperature of the reaction mixture below 60°C. The crude intermediate products were extracted with toluene and washed neutral with a saturated solution of sodium bicarbonate and water. The extract was dried, 0.05 g *p*-toluene sulfonic acid was added and the mixture was refluxed for 3 h to collect *ca.* 3 mL water. The solution was washed free of acid, and the solvent was removed by vacuum evaporation. The residue was steam-distilled to yield 13.6 g of crude aldehyde. (*E*)-2-Nonenal was purified by vacuum-distillation to give 13 g of pure product [99% 2-nonenal, including 2.7% of (*Z*)-isomer]; b.p. 88–90°C/12 mm Hg, ^{1}H-nuclear magnetic resonance (NMR) (80 MHz, $CDCl_3$): δ 9.5 (1H, *d*, $J = 7.6$ Hz), 6.86 (1H, *dt*, $J = 15.6$ and 6.6 Hz), 6.09 (1H, *ddt*, $J = 15.6$, 7.6 and 1.3 Hz), 2.36 (2H, *m*), 1.32 (8H, *m*), 0.89 (3H, *t*, $J = 5.5$ Hz).

RESULTS AND DISCUSSION

It follows from the review that the reported synthetic methods for the manufacture of (*E*)-2-nonenal suffer from several disadvantages, such as multi-stage preparations and expensive chemicals. On the other hand, there are no known rich natural sources of this compound. These circumstances are incorporated in the relatively high price of the aldehyde.

In this paper we disclose a new synthesis of (*E*)-2-nonenal by means of castor oil ozonolysis. Nonedible castor oil, due to its high content of 12-hydroxy oleic acid (ricinoleic acid), has been extensively used in several branches of industry, *e.g.*, for lubricant and paint manufacturing. It is also ozonized to produce a laxative, to reduce toxicity and to create a germicidal effect (18–20). Ozonolysis has been used for years in the industry for the oxidative cleavage of unsaturated fatty acids to produce pelargonic acid and azelaic acid from oleic acid or brassylic acid from erucic acid (21). That inspired us to study the conversion of castor oil into 2-nonenal.

The ozonolysis of commercial-grade castor oil was carried out in acetic acid solution, and the ozonide compounds formed were reduced with zinc dust to give the intermediate 3-hydroxy nonanal that was not isolated from the reaction medium:



Dehydration of the intermediate product by *p*-toluene sulfonic acid led to thermodynamically more stable (*E*)-2-nonenal that contained only a few percent of the (*Z*)-isomer. The structure of the title compound was confirmed by infrared, H-NMR and elemental analysis. Thus, the olefinic proton at C-3 in the NMR spectrum of the aldehyde appeared at 6.86 ppm as a triple doublet with $J = 15.6$ Hz due to *trans* coupling with the C-2 olefinic

---

*To whom correspondence should be addressed at Institute of General Food Chemistry, Technical University of Lodz, ul. Stefanowskiego 4/10, 90-924 Lodz, Poland.

Copyright © 1993 by the American Oil Chemists' Society

proton. The olefinic proton at C-2 appeared at 6.09 ppm as a *ddt* with $J = 15.6$ Hz, the value of which clearly indicates *trans*-geometry of the double bond.

The fate of the other part of the cleaved molecule was not determined. However, judging from the yield of the aldehyde, it is likely that under the conditions studied, only one fatty acid in the glyceride molecule participates in the reaction. Such a selectivity in the addition of ozone to polyunsaturated compounds is often observed (22–24). A study to improve the yield of the process is in progress.

Interestingly, the majority of methods reported in the literature for the synthesis of (*E*)-2-nonenal use *n*-heptanal as a starting material, which generally is manufactured by pyrolysis of castor oil (25,26).

The described method, by virtue of being simple and cost effective, seems to be of enormous practical potential.

REFERENCES

1. Takeoka, G.R., R.A. Flath, T.R. Mon, R. Teranishi and M. Guentert, *J. Agric. Food Chem. 38:*471 (1990).
2. Buttery, R.G., J.G. Turnbaugh and L.C. Ling, *Ibid. 36:*1006 (1988).
3. Schieberle, P., *Ibid. 39:*1141 (1991).
4. Ehret, C., P. Maupetit and M. Petrzilka, *J. Ess. Oil Res. 4:*41 (1992).
5. Binder, R., Ch.E. Turner and R.A. Flath, *J. Agric. Food Chem. 38:*764 (1990).
6. Grosch, W., and H.D. Belitz, *Naturwissenschaften 65:*58 (1978).
7. Ramarathnam, N., L.J. Rubin and L.L. Diosady, *J. Agric. Food Chem. 39:*1839 (1991).
8. Chung-May, W., and S-E. Liou, *Ibid. 40:*838 (1992).
9. Parliment, T.H., W.P. Clinton, R. Scarpellino, R.J. Soukup and M.F. Epstein, U.S. Patent 3962321; *Chem. Abstr. 85:*159432 (1976).
10. Guerin, P.M., U. Remund, E.F. Boller, B. Katsoyannos and G. Delrio, *Comm. Eur. Communities (Rep.) Eur.,* 8384; *Chem. Abstr. 99:*173356 (1983).
11. Seruven, R., and C.E. Meloan, *Ohio J. Sci. 84:*82 (1984).
12. Bedoukin, P.Z., *J. Am. Chem. Soc. 79:*889 (1957).
13. Gadkari, R.G., and A.H. Kapadi, *Biovigyanam 15:*111 (1989).
14. Makin, S.M., S.M. Gabrelyan and A.S. Chebotarer, *Zh. Org. Khim. 10:*2044 (1974).
15. Trippett, B.S., and D.M. Walker, *Chem. Ind.,* 202 (1960).
16. Cresp, T.M., M.V. Sargent and P. Vogel, *J. Chem. Soc. Perkin Trans. 1:*37 (1974).
17. Scalan, J.T., and D. Swern, *J. Am. Chem. Soc. 62:*2309 (1940).
18. Knox, W.J., U.S. Patent 1210949; *Chem. Abstr. 11:*687 (1917).
19. De Villez, R.L., U.S. Patent 4451480; *Chem. Abstr. 101:*78861 (1984).
20. De Villez, R.L., U.S. Patent 4591602; *Chem. Abstr. 105:*66485 (1986).
21. Goebel, C.G., A.C. Brown, H.F. Oehlschlaeger and R.P. Rolfes, U.S. Patent 2813113 (1957).
22. Schulte-Elte, K.H., A. Hauser and G. Ohloff, *Helv. Chim. Acta 62:*2673 (1979).
23. Odinokov, W.N., R.I. Galejeva, R.S. Bakejeva, R.S. Grishkova and G.A. Tolstikov, *Zh. Org. Khim. 15:*1403 (1979).
24. Kula, J., and J. Podlejski, *Liebigs Ann. Chem.,* 2098 (1985).
25. Kirk-Othmer, R.E., *Encyclopedia of Chemical Technology,* 2nd edn., Vol. 8, 1965, p. 822.
26. Fulin, M., *Taiyuan Gongye Daxue Xuebao (3):*65 (1987); *Chem. Abstr. 108:*7843 (1988).

[Received October 15, 1992; accepted March 30, 1993]