Decolorization of Meadowfoam Estolides Using Sodium Borohydride

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ABSTRACT: Estolides are condensed oligomers of fatty acids made by introducing an ester linkage at sites of unsaturation. Estolides made from meadowfoam (*Limnanthes alba*) oil fatty acids have positive effects in personal care formulations and a patent has been applied for. However, estolides prepared by acid catalysis had a color of 12 (Gardner scale) and industrial cooperators desired lower color to increase marketability of meadowfoam estolides. Hydrogen peroxide and hydrogenation did not lower the color of estolide but 1% w/w sodium borohydride at 80°C for 12 h reduced color to 7 on the Gardner scale which was acceptable to the industrial partners for further development. Sodium borohydride decolorization gives a product with good color at a reasonable cost. The sodium borohydride does not have to be used in concentrations higher than 1% w/w and the product loss, which can be several percent with a clay-based process, is negligible using sodium borohydride.

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KEY WORDS: Bleaching, decolorization, estolides, hydrogenation, hydrogen peroxide, meadowfoam, platinum, sodium borohydride.

Limnanthes alba, meadowfoam, is a crop currently cultivated in the Willamette valley of Oregon. Meadowfoam contains 83% delta-13 and delta-5-monoenoic fatty acids that grant unique properties to estolides. Meadowfoam estolides are oligomeric esters (1), resulting from selfcondensation of meadowfoam fatty acids in the presence of 0.05 molar equivalent $HClO_4$ at 65°C after 31 h (1). Meadowfoam estolides significantly improve conditioning, shine, comb-out, and other properties of shampoos (a patent application has been filed). Although the current process conditions (1) produce estolide in high yield, the color of the estolide is darker than desired by our commercial partners, The Fanning Corp., for applications in the personal care market. The Gardner scale is used for color determinations in the cosmetics industry. Optimally, cosmetic ingredients should be colorless (Gardner = 0), but a Gardner of 5 to 7 was deemed acceptable and greater than 10 was unacceptable (Wohlman, A., The Fanning Corp., personal communication). Meadowfoam estolides can also be obtained using a clay-based process (2,3) but the yield is only 10–20% and the product is also dark. Therefore, we investigated three decolorization methods to lighten the color of estolides. Existing methods for bleaching vegetable oils and fatty acids are bleaching earths, clays, and amorphous silicas and/or activated carbon (4). Originally, the most common process involved the use of bentonite, known as Fullers' earth (5). Currently, bleaching earths are most often activated with various strong mineral acids (5,6). Magnesium oxide can also be used to enhance the bleaching effect (7). The key process in bleaching is the removal of pigments (chromophores) from the oil by adsorption. The pigments are often carotenoids, chlorophyll pigments, gossypol, and products from condensation, storage, and handling (8,9). The effect of bleaching earth is not only by adsorption of chromophores but also by breakdown of hydroperoxides on the adsorbent surface, followed by the adsorption of carbonyl compounds that are the secondary oxidation products. Furthermore, amorphous silica can be used sequentially, without intermediate filtration, to adsorb soap, phosphatides, and trace metals (10). If the removal of polyaromatic hydrocarbons (PAH) is required, activated carbon can be used. Furthermore, there are reports of an enzymatic peracid method (11,12) and distillation (13) is sometimes helpful. All of the decolorization methods cited are for chromophores in crude vegetable oils; they may have served a similar purpose in estolides although the chromophores in estolides were not yet identified. Bleaching is an often generally applicable method for decolorization. The enzymatic peracid method could not be used with meadowfoam estolides due to patent infringement; also, the molecular weight (boiling point) of the estolides is too high for distillation. Earlier work at this laboratory was unsuccessful in reducing estolide color using official activated bleaching earths, silica, or activated charcoal (AOCS, Champaign, IL) (Selim Erhan, private communication). There have been reports of the use of sodium borohydride for alkali refining and the beneficial effect of lighter color was noted (14). We investigated several additional methods for estolide decolorization and found sodium borohydride to be effective.

EXPERIMENTAL PROCEDURES

Materials. Meadowfoam fatty acid estolides were obtained by the Isbell method (1). Sodium borohydrides were obtained from the Aldrich Chemical Co. (Milwaukee, WI). Both Ven-Pure (granular and powder) grades are trademarks of Morton

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Chemical (Danvers, MA). Filter papers were obtained from Whatman (Maidstone, England). Platinum on carbon catalyst, 5% type B21142-5, was a kind gift from Johnson Matthey (West Deptford, NJ). Hydrogen peroxide was obtained from Fisher Scientific (Fairlawn, NJ).

Color determinations. Gardner color was measured on a Lovibond 3-Field Comparator from Tintometer Ltd. (Salisbury, England).

Decolorization. Meadowfoam estolides (5 g) were measured for Gardner color then mixed with 0.5–2% w/w of sodium borohydride in a 50-mL round-bottom flask fitted with a thermocouple. The reaction mixture was magnetically stirred and heated to 60–90°C. Hydrogen evolution was observed during the sodium borohydride reaction with the estolide. Sodium borohydride did not dissolve in the estolide. After 6–48 h, spent sodium borohydride was filtered off and Gardner color was measured again.

Hydrogenation. Meadowfoam estolides (50 g) were measured for Gardner color then mixed with 0.5–2% w/w of platinum catalyst in a 100 mL autoclave, then 6895 kPa of hydrogen pressure was applied. The bleaching effect by hydrogenation was evaluated at temperatures between 35 and 90°C. The reaction mixture was mixed by overhead stirring. After 1–24 h, the spent platinum catalyst was filtered off and Gardner color was measured.

Hydrogen peroxide treatment. Meadowfoam estolides (5 g) were measured for Gardner color then mixed with 0.5–2% w/w of hydrogen peroxide in a 50-mL round-bottom flask fitted with a thermocouple. The reaction mixture was magnetically stirred and heated from 25–90°C. The hydrogen peroxide did not dissolve in the estolide. After 4–12 h, the reaction mixture was cooled to room temperature and the estolide washed with water. The estolide was dried over Na_2SO_4, filtered, and Gardner color was measured.

TABLE 1
Bleaching of Meadowfoam Estolides Using Different Grades of Sodium Borohydride at 70°C

Sodium borohydride grade[a]	Time (h)	Gardner before treatment	Gardner after treatment
Aldrich	12	12	8
VenPure powder	12	12	9
VenPure granulate	12	12	9

[a] 1% w/w.

TABLE 3
Effect of Time on the Bleaching of Meadowfoam Estolides[a]

Reaction times	Gardner before treatment	Gardner after treatment
6	12	9
12	12	7
18	12	8
24	12	11
48	12	11

[a] Reaction run at 80°C with commercial $NaBH_4$, VenPure 1% w/w.

TABLE 4
Bleaching of Meadowfoam Estolides at Different Concentrations of Sodium Borohydride[a]

Concentration (%) w/w sodium borohydride	Gardner before treatment	Gardner after treatment
0.5	12	10
1	12	8
2	12	8

[a] Reaction run at 80°C for 18 h on meadowfoam estolide with VenPure granulate $NaBH_4$.

RESULTS AND DISCUSSION

Gardner color of estolides was 11–12 after hydrogenation and hydrogen peroxide treatment. Color was not reduced by these methods. Sodium borohydride bleached meadowfoam estolides from a color of 12 to 7. The bleaching effectiveness was dependent on sodium borohydride grade, reaction temperature, reaction time, and sodium borohydride concentration (Tables 1–4).

Aldrich laboratory grade $NaBH_4$ was found to give the best initial bleaching (Table 1). However, the commercial sodium borohydride granulate (VenPure granulate) was the most effective grade over time. The granulate preparation has reduced surface area, thus this grade is less susceptible to decomposition by air moisture. Even after long-term dry storage the granulate preparation retained its activity while the powder preparations lost some of their potency. The bleaching effect was found to be temperature dependent with the optimal temperature of 80°C (Table 2). Higher temperatures did not add any additional bleaching effect. The optimal reaction time at 80°C was found to be around 12 h with longer reaction times decreasing the bleaching effect (Table 3). We suspect that a reduced bleaching effect over longer reaction times

TABLE 2
Sodium Borohydride Bleaching of Meadowfoam Estolides at Different Temperatures

Sodium borohydride grade[a]	Temperature (°C)	Reaction time (h)	Gardner before treatment	Gardner after treatment
Aldrich	60	12	12	10
Aldrich	70	12	12	8
Aldrich	80	12	12	7
VenPure granulate	80	12	12	7
VenPure granulate	90	12	12	7

[a] 1% w/w.

is due to oxidation by prolonged air contact at these elevated temperatures. The optimal concentration of sodium borohydride was found to be 1% w/w with higher concentrations offering no additional benefit (Table 4).

Although we do not yet fully understand the mechanism of bleaching of meadowfoam estolide, we suspect that hydrogenation of certain pigments (chromophores) is the primary effect. These chromophores must be more easily hydrogenated than the meadowfoam estolides since there is only need for 1% w/w sodium borohydride to obtain a significant effect.

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REFERENCES

1. Isbell, T.A., and R. Kleiman, Mineral Acid Catalyzed Condensation of Meadowfoam Fatty Acids to Estolides, *J. Am. Oil Chem. Soc. 73:*1097–1107 (1997).
2. Erhan, S.M., R. Kleiman, and T. Isbell, Methods for Increasing Estolide Yields in a Batch Reactor, *Ibid. 72:*671–674 (1995).
3. Erhan, S.M., and T.A. Isbell, Estolide Production with Modified Clay Catalysts and Processing Conditions, *Ibid. 74:*249–254 (1997).
4. Gunstone, F.D., J.L. Harwood, and F.B. Padley, Bleaching, in *The Lipid Handbook,* 2nd edn., Chapman & Hall, London, 1994, pp. 267–270.
5. Richardson, L.L., Use of Bleaching Clays in Processing Edible Oils, *J. Am. Oil Chem. Soc. 55:*777–780 (1978).
6. Koma, T., K. Hatamoto, and Y. Iyoda, Palm Oil Refining, Japanese Patent 55007816 (1980).
7. Thomopoulos, C.D., C.E. Tzia, K.G. Papathanasiou, and I.E. Anghelopoulou, Improvement of the Bleaching Earth Activity by the Addition of Magnesium Oxide, *Grasas Aceites 40:*90–96 (1989).
8. Mag, T.K., Bleaching-Theory and Practice, *Proceedings of the Edible Fats and Oils Processing World Conference,* edited by D.R. Erickson, American Oil Chemists' Society, Champaign, 1990, pp. 107–116.
9. Taylor, D.R., Adsorptive Purification, *Proceedings of the Oilseed Technology Utilization World Conference,* edited by T.H. Applewhite, American Oil Chemists' Society, Champaign, 1993, pp. 152–165.
10. Bogdanor, J.M., and W.A. Welsh, Silica Refining of Edible Oil, *J. Am. Oil Chem. Soc. 64:*669–670 (1987).
11. Wiersema, R.J., A.G. Stanislowski, G.L. Gray, A.J. Poulose, and S.D. Power, Enzymatic Per Acid Bleaching System, European Patent 268456 (1988).
12. Poulose, A.J., and S.A. Anderson, Enzymatic Peracid Bleaching System with Modified Enzyme, European Patent 375102 (1990).
13. Hollo, J., and E. Kurucz, Possibility of Use of Molecular Distillation as a Separation Method in the Vegetable Oil Industry, *Riv. Ital. Sostanze Grasse 44:*249–259 (1967).
14. Helebra, S.F., R.A. Mikulski, and M.M. Cook, Purification of Natural Oils with Alkali Metal Borohyrides, European Patent 0116408 (1984).

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