Some Chemical Processes Utilizing Oleic Safflower Oil

M. J. DIAMOND AND GLENN FULLER, Albany, California 94710

Abstract

Oleic safflower seed (UC-1) produces an oil containing approximately 80% oleic acid and 12% linoleic acid. The oil is a source of high quality oleic acid, and fatty acids from the oil may be used without further separation in some applications where technical oleic acid is now used, since oleic safflower free fatty acids have a a higher oleic acid content than good commercial grades of oleic acid. A high purity oleic acid can be produced by urea fractionation. Ozonization of the oil followed by reductive cleavage yields pelargonaldehyde and nearly colorless aldehyde oils. Ozonization of a crude mixture of oleic safflower acids followed by oxidative cleavage provides high yields of azelaic acid and pelargonic acid. In contrast, ozonization of free fatty acids from polyunsaturated vegetable oils produces azelaic acid and mixtures of lower molecular weight carboxylic acids with smaller amounts of pelargonic acid. Furthermore, ozone consumption is lower and reaction time is shorter when oleic safflower acids are used in place of more highly unsaturated fatty acids.

Introduction

Oleic safflower seed (UC-1), introduced by Knowles et al. (1) contains an oil comprised of approximately 80% oleic acid and 12% linoleic acid. A comparison of the fatty acid composition of oleic safflower oil with that of several other vegetable oils was shown earlier (2,3). With the exception of olive oil, oleic safflower oil has the highest oleic acid content of commercially available oils. Some chemical characteristics of the oils are compared in Table I. Oleic safflower oil is shown to have the highest content of unsaturation in the 9,10 position, and highest total content of acids with C_{18} chain length.

Previous studies indicate that oleic safflower oil is stable, edible and resistant to autooxidation (2–4). Hydrogen peroxide converts the oil to uncolored epoxy oils in good yield (3).

In the present investigation, oleic safflower oil is converted to a high purity oleic acid. Also, ozonization of high-oleic safflower oil is compared with that of several other oils reported in the literature (5–19). Reduction of the ozonides to aldehydic materials and oxidative cleavage to acidic products are described.

Experimental Procedures and Data

Materials

Oleic safflower oil, free of additives, was obtained from Pacific Vegetable Oil Corporation and the J. G. Boswell Co. Soybean oil, refined and bleached, but not deodorized, was supplied by A. E. Staley Manufacturing Co., Decatur, Ill. Olive oil, marketed by J. T. Baker, Co. was used. Cottonseed oil, refined and unbleached, was supplied by Ranchers Cotton Oil, Fresno, Calif. Corn oil, commercial corn oil, "Mazola," was purchased locally. Free fatty acids: The free fatty acid mixtures were prepared by saponification of the respective oils (20).

TABLE I

Fats and Oils: Chain Length and Unsaturation

Source	% C_{18} Fatty acids	% Acids with double-bond in 9,10 position	IV
Safflower, UC-1	95	93	93
Safflower, *commercial*	94	90	144
Olive	92	90	89
Soybean	89	85	132
Sunflower, U.S.	94	92	130
Cottonseed	78	76	112
Corn	87	83	129
Tallow	64	47	45

Analytical Techniques

Aldehydic products were analyzed by titration with hydroxylamine hydrochloride solution in aqueous ethanol according to Siggia (21) as modified by Pryde et al. (5d). A Leeds-Northrup 7405 pH meter was used for determining the end point at approximately pH 3.2. Carboxylic acid products were analyzed by first converting them to methyl esters according to the AOCS method (22) followed by separation of the esters using gas liquid chromatography (GLC). Programmed-temperature, GLC analyses were performed on an F&M, Model 720, Gas Chromatograph with a thermal conductivity detector. The column was a 4 ft, 0.25 in. O.D. stainless steel tube packed with 15% DEGS on Gas-Chrom P. A helium flow-rate of 50 ml/min with programming from 60–220 C at 10 C/min was used.

A Welsbach Laboratory Ozonator, Model T-23, was used to generate ozone in a stream of pure oxygen. This stream was passed into a glass reactor having an extra coarse fritted glass plug (19).

Preparation of Purified Oleic Acid

The urea adduct of oleic safflower free fatty acids was formed and fractionated by a modification of the method of Rubin and Paisley (20). A 245 g quantity of mixed oleic oil fatty acids was added to a solution of 120 g of urea in 700 ml of methanol. The mixture was heated until homogeneous and allowed to cool. The first crystals (Table II, Fraction 1) contained 22% saturated fatty acids and 76% oleic acid (by GLC of methyl esters). Then 300 g of urea was added and again brought into solution. On cooling, the second batch of crystals was obtained (Fraction 2). Another 300 g of urea was added and brought into solution by heating. Methanol was removed by distillation until the liquid had one half the original volume. Cooling the mixture produced Fraction 3. Fraction 4 was obtained from the mother liquor. Fatty acids were recovered from the urea adduct crystals by addition of water and extraction with ether.

Preparation of Aldehyde Oils

Sixty-gram portions of unsaturated oil were dissolved in 720 ml of 20% methanol-80% ethyl acetate

TABLE II

Urea Separation of Fatty Acids From Oleic Safflower Oil

Fraction, %		Fatty acid composition (% wt)			
		16:0	18:0	18:1	18:2
1	8.2	15	7	76	2
2	35.6	0	<1	93	6
3	38.4	0	0	94	6
4	7.2	0	0	24	76
Total	89.4				
Loss	10.6				

TABLE III

Production of Aldehyde Oils by Ozonolysis[a]

Conditions	Oil source				
	Oleic safflower, UC-1	Olive	Cottonseed	Soybean	Triolein (theor.)
Iodine value of oil	93	88	112	132	85.8
Moles O_3 consumed per mole fatty acid, theor.	1.10	1.03	1.33	1.59	1.00
Ozonization reaction time, min	95	91	139	145	.....
Ozone consumed, % theor.	97	98	121	111	100
Weight, g	37.2	42.6	42.4	39.1	37.6
Per cent yield based on unsaturated fatty acids	96	108	95	97	100
Aldehyde oil Carbonyl content mM/g	4.33	3.54	2.35	3.87	5.41
Color, Gardner	3	7	9	13	.....

[a] From 60 g oil dissolved in 720 ml solvent, followed by reduction with zinc and acetic acid.

and treated with ozone at 5 C. An oxygen flow rate of approximately 2.7 liters/min with 40 mg/liter of ozone was maintained until the reaction was complete as indicated by a dark red color in the KI trap. The resultant ozonides then were reduced by treatment with 30 g zinc dust and 60 ml glacial acetic acid (5).

Preparation of Azelaic Acid and By-Products

Twelve-gram quantities of the unsaturated free fatty acids obtained by saponification of the various oils were ozonized to completion in 50 ml of acetic acid. The ozonides were oxidized without removal from the reaction vessel by adding 15 ml of 88% formic acid and 15 ml of 50% hydrogen peroxide (16). Reaction mixtures were distilled at reduced pressure to yield a residue of crude azelaic acid and a distillate of more volatile carboxylic acids. The samples of crude azelaic acid were recrystallized from hot water to yield products of >97% purity.

Results and Discussion

The fatty acid composition of oleic safflower oil (UC-1) fractions separated from urea adducts are presented in Table II. Greater than 70% yield of oleic acid of 93+% purity is obtained, by a relatively simple crystallization procedure.

Reaction conditions and yields of aldehyde oils obtained by ozonization followed by zinc-acetic acid reduction of several unsaturated oils are summarized in Table III. As expected, ozone consumptions and reaction times are smaller for monounsaturated oils than for polyunsaturated oils. Pryde et al. (5c) have stressed that ozonolysis of polyunsaturated oils yields large molar amounts of malonaldehyde fragments which are attacked further by ozone to yield mixtures containing tartronic acid, mesoxalic acid, oxalic acid and carbon dioxide. Ozone consumption above 100% of theoretical for the polyunsaturated cottonseed and soybean oils can be attributed to such side reactions. Also, since oleic acid is the major component in oleic safflower oil and olive oil, yields of the less volatile pelargonaldehyde are higher while by-products, caproaldehyde and propionaldehyde, will be lower. Oleic safflower aldehyde oil had the highest available carbonyl content of the commercial oil products. Another advantage of aldehyde oils produced from oleic safflower oil is light color of end-product as indicated by the lowest Gardner color number of all the tabulated aldehyde oils. Crude oleic safflower aldehyde oil is colored very light yellow, whereas all the other aldehyde oils are yellow to dark orange.

TABLE IV

Production of Azelaic Acid and Pelargonic Acid by Ozonolysis of Fatty Acids From Commercial Oils[a]

Conditions	Source of FFA				
	Oleic Safflower, UC-1	Soybean	Cottonseed	Corn	Theoretical yield from oleic acid
Ozonization reaction time, min[b]	41	81	101	73	.....
Moles O_3 consumed ——— (theor.) / Moles FFA	1.10	1.59	1.33	1.53	1.00
Actual O_3 consumed, % of requirement for pure oleic acid	105	122	144	120	100
Crude azelaic acid obtained, g	8.1	8.2	8.2	8.0	7.99
Azelaic acid content of crude, % of theory for oleic acid	84	82	72	77	100
Weight of distillate, g	4.2	2.5	2.1	2.5	6.72
Pelargonic acid content of distillate, %	94	62	71	79	100
Weight unidentified volatiles in trap, g	0.2	1.1	0.9	0.9	.....

[a] From 12 g FFA dissolved in 50 ml acetic acid, followed by oxidation with H_2O_2–formic acid.

[b] A constant ozone flow rate was maintained during reaction with oleic safflower FFA, but with all other acids the flow was reduced during reaction because excessive foaming was produced as the reaction progressed. The times listed are the shortest ones recorded for the various free fatty acids used in this particular apparatus.

Polyunsaturated free fatty acids, such as those from soybean, cottonseed and corn, may be ozonized and then oxidatively cleaved to produce azelaic acid and mixtures of lower molecular weight carboxylic acids including caproic acid, malonic acid, pelargonic acid and sometimes propionic acid. Since oleic safflower fatty acids are composed primarily of monounsaturated oleic acid, ozonization of the oleic oil fatty acids forms high yields of azelaic acid and pelargonic acid. Reaction conditions and product yields for ozonolysis of unsaturated free fatty acid mixtures are summarized in Table IV. The last column of Table IV lists the theoretical attainable yields from the ozonolysis of pure oleic acid. The same advantages of low ozone consumption and shorter reaction time apply to the use of oleic safflower acids for producing azelaic acid as compared to using the fatty acid mixtures obtained from other unsaturated oils. An advantage to laboratory ozonization in acetic acid followed by oxidizing with formic acid-hydrogen peroxide is that solvent evaporation between the two steps is eliminated (16). Mixtures of azelaic-pelargonic esters are used extensively as plasticizers and lubricants (23) and such esters could be prepared directly from the ozonolysis products of oleic safflower acids without prior fractionation. Use of oleic safflower acid derivatives in ozonolysis reactions offers the further advantage over polyunsaturated derivatives of less troublesome foam formation.

As a basic commodity, oleic safflower oil offers many advantages over similar competing materials: lower cost, high content of a single component, less colored end products and greater oxidative stability. With increasing demand by industry for higher purity and greater uniformity in commercial fatty acid derivatives, oleic safflower oil can contribute to satisfying this need.

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REFERENCES

1. Knowles, P. F., A. B. Hill and J. E. Ruckman, Calif. Agr. *19*, 15 (1965).
2. Fuller, G., G. O. Kohler and T. H. Applewhite, JAOCS *43*, 477–478 (1966).
3. Fuller, G., M. J. Diamond and T. H. Applewhite, Ibid. *44*, 264–266 (1967).
4. Purdy, R. H. and B. J. Campbell, Food Tech. *21*, 349 (1967).
5. (a) Pryde, E. H., D. E. Anders, H. M. Teeter and J. C. Cowan, J. Org. Chem. *25*, 618–621 (1960); (b) Ibid. *27*, 3055–3059 (1962); (c) JAOCS *38*, 375–379 (1961); (d) Ibid. *40*, 497–499 (1963).
6. Fitton, P., E. H. Pryde and J. C. Cowan, JAOCS *42*, 14–16 (1965).
7. Anders, D. E., E. H. Pryde and J. C. Cowan, Ibid. *42*, 236–243 (1965).
8. Pryde, E. H., R. A. Awl and J. C. Cowan, Ibid. *42*, 549–553 (1965).
9. Moore, D. J., E. H. Pryde and J. C. Cowan, Ibid. *42*, 894–898 (1965).
10. Awl, R. A. and E. H. Pryde, Ibid. *43*, 35–37 (1966).
11. Beal, R. E., Ibid. *43*, 122–124 (1966).
12. Beal, R. E., D. E. Anders and L. T. Black, Ibid. *44*, 55–58 (1967).
13. Throckmorton, P. E., L. D. Hansen, R. C. Christenson and E. H. Pryde, Ibid. *45*, 59–62 (1968).
14. Goebel, C. G., A. C. Brown, H. F. Oehlschlaeger and R. P. Rolfes, U.S. Patent 2,813,113 (1957).
15. Oehlschlaeger, H. F., and H. G. Rodenburg, U.S. Patent 3,402,108 (1968).
16. Bailey, P. S., Ind. Eng. Chem. *50*, 993–996 (1958).
17. Ackman, R. G., M. E. Retson, L. R. Gallay and F. A. Vandenheuvel, Canad. J. Chem. *39*, 1956–1963 (1961).
18. Naudet, M. and J. Pasero, Fette Seifen Anstrichm. *62*, 1110–1112 (1960).
19. Pasero, J., and M. Naudet, Rev. Fr. Corps Gras *7*, 189–200 (1960); Ibid. *10*, 453–462 (1963).
20. Rubin, L. J., and W. Paisley, Biochem. Prep. *9*, 113–116 (1960).
21. Siggia, S., "Quantitative Organic Analysis Via Functional Groups," John Wiley and Sons, New York, 1949, p. 63–64.
22. AOCS Method Ce 2–66, 3rd Edition, Rev. 1968.
23. Fedor, W. S., Chem. Eng. News *39*(46), 118 (1961).
24. Swern, D., Editor, "Bailey's Industrial Oil and Fat Products," 3rd Edition, Interscience Publishers, New York, 1964, p. 592.

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