TABLE III

Infrared Bands[a] of Cis and Trans Dipentyldioxolane Below 2000 cm^{-1} [b]

Trans cm^{-1}	*Cis* cm^{-1}	*Trans* cm^{-1}	*Cis* cm^{-1}
1736 w	1738 vw	1048 s	1044 s } br
1466 s	1466 s	1030 sh	1020 sh }
1461 sh	1462 sh	990 m	992 sh
1457 sh	1458 sh	947 m	944 m
1433 m	1435 m	913 m, sh	921 m
1410 m	1415 m	905 m	899 m
1378 m	1378 s	820 w	819 w
1341 m	1352 sh	786 vw	788 w
1302 vw	1340	768 w	767 w
1280 vw	1307 w	726 m	726 m
1267 vw	1280 w	710 sh	710 w
1233 w	1268 w	545 w, br	648 vw, br
1218 w	1236 w	535 w	538 w
1190 vw	1195 w		
1140 vs, br	1141 vw } br		
1112 vs	1115 vs }		
1075 m	1072 m		

[a] Key: br, broad; m, medium; s, strong; sh, shoulder; vs, very strong; vw, very weak; w, weak.
[b] All bands have precision of ± 2 cm^{-1}.

may form in the mixture on standing. However, acetals are known to form under anhydrous conditions, and, because of the absence of 1,2-heptandiol, methanol, and pentanol, our acetals must have formed by another mechanism. It is uncertain that our analytical procedures are capable of detecting 1,2-heptanediol in the condensate.

Pentyl hexanoate is also somewhat anomalous, in that the abundance of methyl octanoate (compare peak 27 and peak 15) would lead one to expect a relatively large amount of pentyl octanoate. No pentyl octanoate was observed. Butanol and hexanol are observed as the free alcohols but are not observed in any combination (ester, acetal, etc.). Pentanol is not observed as the free alcohol but is detected in significant abundance combined as an ester or as the mixed acetal (peak 36). Pentane was observed as has been previously noted (18).

ACKNOWLEDGMENTS

Dr. T. H. Applewhite gave valuable discussion and guidance in interpretation of some data; Dr. R. G. Buttery aided in the collection of GLC fractions; Dr. R. E. Lundin performed the NMR analysis, and Dr. J. R. Scherer performed the IR analysis.

Research was supported in part by funds from the Office of Civil Defense, Department of Defense.

REFERENCES

1. McFadden, W. H., and R. Teranishi, Nature *200*, 329 (1963).
2. McFadden, W. H., R. Teranishi, D. R. Black and J. C. Day, J. Food Sci. *28*, 316 (1963) (paper presented at 10th Ann. Meeting, ASTM Comm. E-14, Mass Spectrometry, June, 1962).
3. Swern, D., and W. Parker, J. Oil Chem. *30*, 5 (1953).
4. Teranishi, R., R. G. Buttery, W. H. McFadden, T. R. Mon and J. Wasserman, Anal. Chem. *36*, 1509 (1964).
5. Forss, D. A., J. Dairy Sci. *47*, 245 (1964).
6. Hoffmann, G., JAOCS *39*, 439 (1962).
7. Badings, H. T., Ibid. *36*, 648 (1959).
8. Swift, C. E., R. T. O'Connor, L. E. Brown and F. G. Dollear, JAOCS *26*, 297 (1949).
9. Patton, S., Ibid. *36*, 280 (1959).
10. Johnson, O. C., S. S. Chang and F. A. Kummerow, Ibid. *30*, 317 (1953).
11. Lillard, D. A., and E. A. Day, Ibid. *47*, 549 (1964).
12. Stark, W., and D. A. Forss, J. Dairy Res. *29*, 173 (1962).
13. Batterson, D. B., J. Org. Chem. *22*, 662 (1957).
14. Lucas, H. J., and M. S. Guthrie, J. Am. Chem. Soc. *72*, 5490 (1950).
15. Barker, S. A., E. J. Bourne, R. M. Pinkard, M. Stacey and D. H. Whiffen, J. Chem. Soc., 3232 (1958).
16. Salomaa, P., and A. Kankaanpera, Acta Chim. Scand. *15*, 871 (1961).
17. Fritsch, C. W., and F. E. Deatherage, JAOCS *33*, 109 (1956).
18. Horvat, R. J., W. G. Lane, H. Ng and A. D. Shepherd, Nature *203*, 523 (1964).

[Received June 14, 1965—Accepted September 3, 1965]

Production of Cyclic Fatty Acids: Water as the Reaction Solvent[1]

R. E. BEAL, R. A. EISENHAUER and V. E. SOHNS
Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

In an attempt to lower processing costs of producing cyclic fatty acids by a high-temperature alkali treatment, water was tested as the reaction solvent instead of ethylene glycol, previously used. Based on extensive tests in a high-pressure autoclave, saturated cyclic (cyclohexanoic) fatty acids were produced under economic reaction conditions, including a temperature of about 300C; a 4:1 solvent ratio and 50% excess sodium hydroxide catalyst. The lower yield of saturated cyclic fatty acids by the water process is more than offset by the fewer steps and reduced evaporation costs.

Introduction

CYCLIC FATTY ACIDS (CFA) derived from linolenic acid offer a unique new chemical to increase the use of linseed oil. They have valuable properties for coatings, cosmetics, plasticizers and lubricants and should find a sizable industrial market (2,4,7,8). Previously data have been given on product yields obtained with various reaction temperatures, catalyst concentrations and either solvent-to-oil or solvent-to-fatty acid ratios (5,6). Results with ethylene glycol, diethylene glycol and t-butanol as solvents and with sodium hydroxide, potassium hydroxide, potassium t-butoxide and the monosodium salt of ethylene glycol as catalysts, have been described. On the basis of limited data, water was not originally considered to be a suitable solvent. Because of certain disadvantages with using glycols, water has been reevaluated as a reaction solvent and found to offer a distinct economic advantage when used under optimum operating conditions.

Under the conditions of reaction used to prepare CFA, ethylene glycol undergoes partial condensation to form diethylene glycol as shown by gas chromatographic analysis of the recovered reaction solvent. Apparently higher glycols are also formed. Secondly, distillation of the used glycol solvent, necessary to purify it for reuse in subsequent reactions, increases the cost of the process, and the presence of high-boiling polyglycols increases solvent losses. Thirdly, a small but appreciable amount of ester is formed between the glycol and the fatty acids following the reaction and neutralization of the catalyst, despite careful use of the stoichiometric amount of dilute sulfuric acid. This fatty acid-glycol ester is recovered in the polymer because it does not distill under the

[1] Presented at the AOCS Meeting, Chicago, Ill., 1964.
[2] A laboratory of the No. Utiliz. Res. & Dev. Div., ARS, USDA.

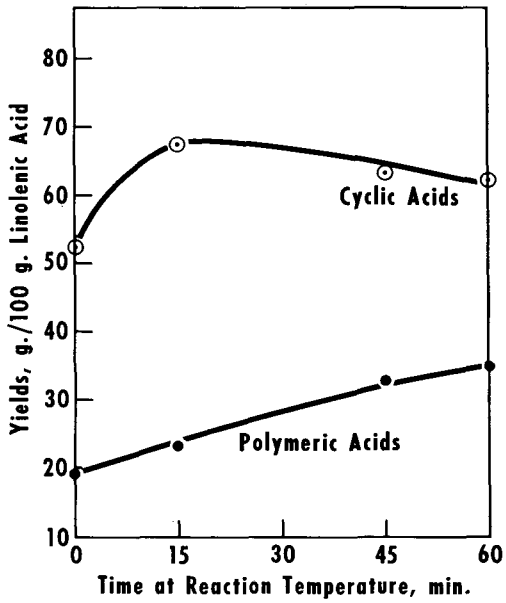

FIG. 1. Relation of reaction time to product yields. Reaction conditions: temperature, 295C; catalyst amount, 100% excess; solvent ratio, 4:1.

conditions of temperature and pressure used to separate monomeric and polymeric fatty acids. It must be subsequently hydrolyzed to recover the monomeric fatty acids therefrom. These factors are principally responsible for the difference in cost between a process using ethylene glycol and one using water as reaction solvent. It will be shown that the cost of producing CFA is significantly reduced by using water instead of glycol as the solvent for the reaction.

Experimental

Reactions for making CFA with water as the solvent were conducted in a 1-liter autoclave designed for 5,000 psi maximum working pressure and equipped with electrical heating and a vertically reciprocating, magnetically driven agitator. The reactants (water, linseed oil and sodium hydroxide) were charged to the cold autoclave which was closed, evacuated, placed under nitrogen and heated to the

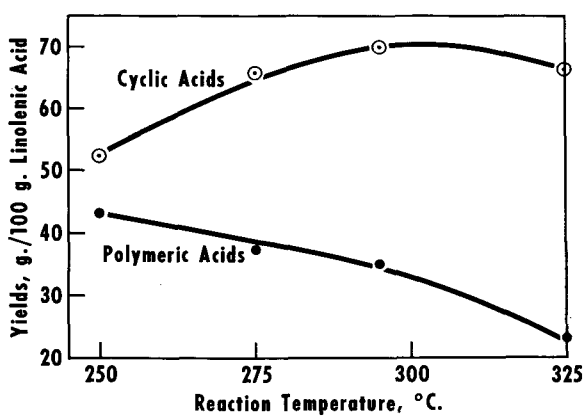

FIG. 2. Effect of reaction temperature on yields. Reaction conditions: catalyst amount, 100% excess; solvent ratio, 4:1.

Reaction temp., °C	Time at temp. for max. yield. hr.
250	4½
275	1½
295	⅔
325	0 (max. yield during heat-up)

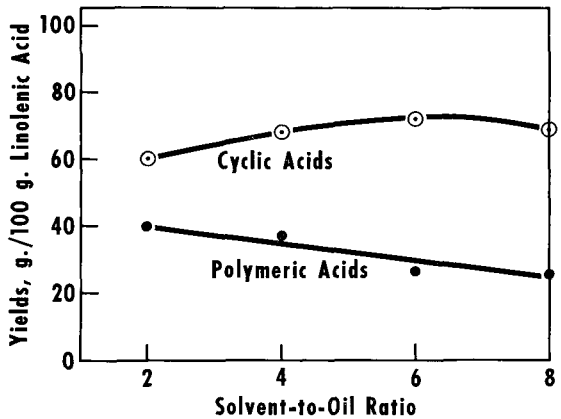

FIG. 3. Effect of solvent ratio on yields. Reaction conditions: temperature, 295C; catalyst amount, 100% excess.

Solvent ratio	Time at temp. for max. yield. min.
8	10
6	15
4	45
2	60

desired reaction tempertaure. Heat-up time to reach a reaction temperature of 295C was about 1 hr and the pressure at this temperature was about 1,200 psi. Samples were removed during the reaction through a draw-off valve and were collected in a beaker containing dry ice and surrounded by dry ice to prevent oxidation and provide rapid cooling. Samples taken during the reaction and from the final product were acidified and the fatty acids recovered and vacuum distilled to separate the monomeric acids. The polymer content was determined by weighing the undistilled material. The monomer fraction was completely hydrogenated and converted to the methyl esters, which were analyzed by gas-liquid chromatography to determine CFA content. Details of the procedure for analysis have been described previously (3).

Results

Nonbreak linseed oil was used in one series of experiments and the series was partially repeated with distilled linseed oil fatty acids as the reactant. The results, reported on a basis of yield per unit of linolenic acid, show that comparable yields were obtained either with the oil or the fatty acids.

Experimental reactions were run at temperatures of 250, 275, 295 and 325C, at solvent-to-oil or fatty acid ratios of 2, 4, 6 and 8 by weight and at catalyst concentrations between 3.5 and 150% excess sodium hydroxide. Four samples were taken during a test at selected intervals and yields plotted on a graph to show the maximum yield of CFA.

Yields of cyclic and polymeric fatty acids in a typical test are shown in Figure 1. At the time when the maximum CFA yield occurred, the corresponding yield of polymeric acids was recorded. To determine optimum conditions, maximum CFA yields and corresponding polymer yields were plotted against reaction conditions.

Figure 2 shows the relation of reaction temperature and CFA yields, shown as a percentage of the linolenic acid present in the linseed oil or fatty acids. A solvent-to-oil ratio of 4 and a catalyst concentration of 100% excess were used for these tests. The highest yield was obtained at a reaction temperature of about 295C. Total yield of CFA plus polymer de-

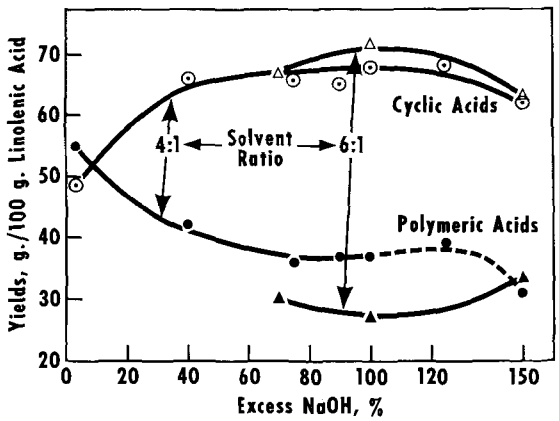

FIG. 4. Effect of catalyst concentration on yields. Reaction temperatures: 295C.

Excess NaOH, % (4:1)	Time at temp. for max. yield. min.
3.5	180
40	105
75	60
100	45
150	15

creases above 300C. This decrease may be due to bond shift to other than conjugated positions above 300C since there was no evidence of decomposition at 325C to account for lower yields. Because of the possibility of decomposition at temperatures above 325C (1) and because at 325C maximum yield is obtained during the heat-up period, no higher temperature was investigated. Possibly a higher CFA yield could be obtained if the heat-up time were less because lower temperatures through which the reactants pass during the heat-up period favor the formation of polymeric rather than CFA. Triene conjugation is necessary for CFA formation, whereas only diene conjugation is necessary for a polymer to form. Triene conjugation is probably favored at about 300C as evidenced by the highest CFA yields being obtained at this temperature.

The effect of solvent ratio on yield is shown in Figure 3. Reaction conditions were 295C and 100% excess catalyst. Increased solvent ratio gave increased cyclic and decreased polymeric yields. Although yield at a solvent ratio of 6 improves slightly over that at 4, the increased cost for larger capacity equipment to handle more solvent is probably not justified economically.

CFA yields as affected by the amount of excess sodium hydroxide catalyst used in the reaction are shown in Figure 4. Percent excess catalyst is the amount greater than that required to saponify the oil used in the reaction. At a solvent-to-oil ratio of 4 there was little increase in yield above 50% excess but at a ratio of 6, a maximum of CFA yield was obtained at 100% excess. Probably yield is a function of both alkali concentration and solvent ratio. Thus, high concentration may favor triene conjugation, whereas dilution favors monomolecular cyclization over bimolecular Diels-Alder polymerizaion. Generally high yields of CFA are accompanied by low yields of polymer; however, at the high alkali concentration of 150% excess and a solvent ratio of 4 both polymer and CFA yields are low. This result, repeatedly obtained, suggests that at high alkali concentrations some double bonds may not move to conjugated positions but instead undergo some other type of shift such as the Varrentrapp reaction (9), and therefore

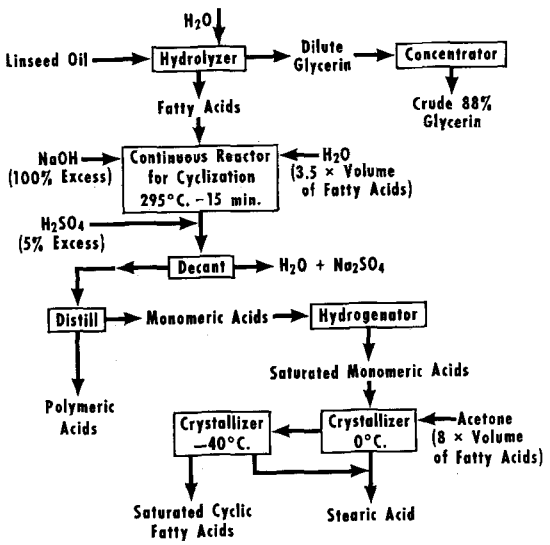

FIG. 5. Production of saturated cyclic fatty acids from linseed oil in H_2O solvent system.

are not in a position to form either cyclic or polymeric acids.

Cost Evaluation

Preliminary comparative cost estimates of the production of saturated CFA from linseed oil have been made for hypothetical plants to produce 4 million pounds of CFA annually: one based on a process with water as the reaction solvent, and one with ethylene glycol as the solvent.

Figure 5 is a flowsheet of the water process from which yields of 35.1 lb of saturated CFA and 15.2 lb of polymeric acids are obtained from 100 lb of linseed oil. Based on 100 lb of fatty acids, respective yields are 37 and 16 lb. Yields are based on batch reactions, but a continuous reaction is assumed in the estimate because of the high cost of batch high-pressure reactors. Feasibilty of the continuous method was shown previously (1). Although yields by the continuous method may be less than those obtained in a batch reactor, the relationship of the yields from

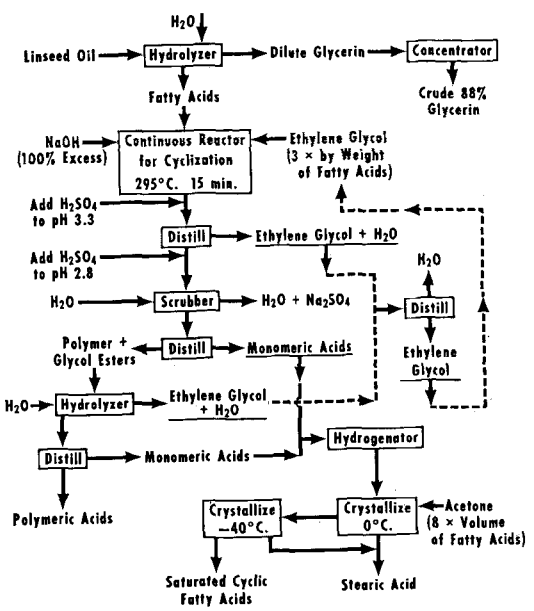

FIG. 6. Production of saturated cyclic fatty acids from linseed oil in ethylene glycol solvent system.

TABLE I

Estimated Fixed Capital Investments for Plants Producing Saturated Cyclic Fatty Acids from Linseed Oil by Either a Water or a Glycol Solvent System; Basis of Operations: 300 days/year, 24 hr/day, 4,000,000 lb product/year

Equipment, delivered	Solvent	
	Water	Glycol
1 Continuous fat-splitting column	$ 80,000	$ 80,000
4 Pumps, positive displacement	5,000	5,000
1 Glycerin concentrator	12,000	10,000
1 Continuous reactor for cyclic acid production with pump and heat exchanger	15,000	15,000
1 Distillation unit for stripping glycol		30,000
1 Scrubber for removal of sodium sulfate		1,500
1 Distillation system for monomer-polymer separation	13,000	13,000
1 Continuous hydrolyzer for polymer-glycol ester mixture		16,000
1 Distillation unit for glycol concentration		16,000
2 Hydrogenators	60,000	60,000
1 Filter for catalyst removal	2,500	2,500
Heat exchangers	8,100	4,600
2 Continuous filters for stearic acid removal	47,000	47,000
2 Refrigeration units	70,000	65,000
1 Conveyor, jacketed with condenser	6,000	5,000
1 Kettle for acetone recovery	15,000	14,500
1 Flaker for stearic acid	15,000	12,000
2 Vaporizing units for low-pressure, high-temperature vapor heating	45,000	45,000
Tanks for processing and storage	141,000	166,400
Pumps for transferring and processing	13,000	14,000
Packaging equipment for stearic acid	6,000	5,000
Subtotal	553,600	627,500
Installation of equipment	166,100	188,500
Piping, wiring, instruments, etc.	251,900	286,000
Engineering and contractors' fees	193,700	221,000
Contingencies	145,700	165,000
Building	144,000	152,000
Land and improvements	50,000	50,000
Estimated fixed capital investment for 4,000,000 lb/year plant	$1,505,000	$1,690,000
Estimated fixed capital investment for 2,000,000 lb/year plant	$ 950,000	$1,070,000

the glycol and water systems is estimated to be the same for either operation, since reaction time for maximum yield is about the same for either solvent at optimum operating conditions.

Linseed oil is first hydrolyzed, and the fatty acids from it are used in the reaction. This step ensures maximum value for the glycerin. If linseed oil is used in the CFA reaction, the glycerin undergoes side reactions (condensation for one) and recovery is not quantitative. The fatty acids, water and sodium hydroxide are heated to 295C and held for 14 min in a continuous flow reactor, then the mixture is cooled to about 60C and dilute sulfuric acid is added to neutralize the catalyst and convert the soaps to fatty acids. Sodium hydroxide excess is assumed here to be 100% for comparative cost estimation. The acids are distilled at an absolute pressure of 1 ml of mercury, and the distilled monomeric acids are completely hydrogenated with palladium-on-carbon catalyst at 200C, 600 psi. The saturated monomeric acids are crystallized from acetone at an 8:1 solvent-to-fatty acid ratio by volume to a final temperature of −40C, and the saturated CFA are recovered from the filtrate by evaporation. Byproducts from the reaction include glycerol; polymeric fatty acids, which are principally dimeric; and the stearic acid fraction, which contains about 35% palmitic acid. Recovery of sodium sulfate is not assumed.

Figure 6 is a flowsheet for a process that has ethylene glycol as the reaction solvent. The process is similar to the water process except that the solvent and the water added with the dilute acid during neutralization must be distilled and fractionated to recover the glycol free of water and sodium sulfate for reuse. After removal of monomer by fractional distillation, the polymer fraction must be hydrolyzed to recover a further quantity of glycol solvent and monomeric acids. Yields from the glycol process are 42.7 lb of CFA, 7.6 lb of polymeric acids and 43.7 lb of stearic acid per 100 lb of linseed oil. As compared to the water process, there is an increase in yield of 7.6 lb of CFA per 100 lb of oil and a corresponding decrease in yield of polymeric acids. Glycol loss is estimated from experimental data to be as much as 0.35 lb per lb of CFA. Actual loss incurred by repeated recovery and reuse of solvent was not determined.

TABLE II

Estimated "Cost to Make" of Saturated Cyclic Fatty Acids from Linseed Oil by Either a Water or a Glycol Solvent System; Basis of Operations: 300 days/year, 24 hr/day

Item	Solvent			
	Water		Glycol	
	Million pounds product per year			
	Four	Two	Four	Two
	cents/lb	cents/lb	cents/lb	cents/lb
Raw material				
Linseed oil at 14¢ lb	39.9	39.9	32.7	32.7
Hydrogen at $4/M ft[3]	2.2	2.2	2.0	2.0
Sodium hydroxide at 5.2¢/lb	4.1	4.1	3.2	3.2
Sulfuric acid at 1.1¢/lb	1.2	1.2	0.8	0.8
Acetone at 6.5¢/lb	0.5	0.5	0.5	0.5
Palladium-carbon catalyst at $45/lb	1.0	1.0	0.9	0.9
Ethylene glycol at 13.5¢/lb			4.7	4.7
Subtotal	48.9	48.9	44.8	44.8
Utilities				
Steam at 80¢/M lb	0.8	0.8	1.5	1.5
Water at 10¢/M gal	0.4	0.4	0.6	0.6
Electricity at 1.5¢/kw hr	0.4	0.4	0.4	0.4
Gas at 25¢/M ft[3]	0.3	0.3	0.3	0.3
Subtotal	1.9	1.9	2.8	2.8
Labor and supervision	7.6	12.3	9.3	15.7
Maintenance [a]	1.7	2.7	2.0	3.2
Fixed charges [b]	4.5	7.1	5.1	8.0
Miscellaneous factory supplies and expenses	0.3	0.3	0.3	0.4
Charge on working capital	0.6	0.6	0.6	0.6
General plant overhead	3.7	6.0	4.5	7.6
Estimated gross cost to make, cents/lb	69.2	79.8	69.4	83.1
Byproduct credit [c]				
Polymer at 25¢/lb				
0.43 lb/lb product	10.8	10.8		
0.18 lb/lb product			4.5	4.5
Stearic acid at 17¢/ lb				
1.24 lb/lb product	21.1	21.1		
1.02 lb/lb product			17.3	17.3
Crude glycerin at 15¢ lb				
0.30 lb/lb product	4.5	4.5		
0.25 lb/lb product			3.8	3.8
Byproduct credit, total cents/lb product	36.4	36.4	25.6	25.6
Estimated net cost to make, cents/lb	32.8	43.4	43.8	57.5

[a] Maintenance calculated at 5%/year on total erected equipment cost and 2%/year on land and building.

[b] Fixed charges include depreciation, calculated at 10%/year (straight-line basis) on total erected equipment cost and 3%/year on building, plus taxes and insurance calculated at 3%/year on estimated fixed capital investment.

[c] Prices for byproducts based on late 1964 data published by various technical sources.

The estimated fixed capital investment as shown in Table I is about $1.5 million for a plant to produce 4 million pounds of CFA per year by the water process and $1.7 million for a plant by the glycol process.

Table II shows a summary of the costs and byproduct credits for the two solvent processes and the net cost to make of 32.8 cents per pound of saturated CFA for the water process and 43.8 cents per pound for the glycol process assuming an annual production of 4 million pounds of CFA per year.

As shown in Figures 5 and 6, the glycol process involves more operations than the water process, consequently the charges per pound of product for utilities, labor and supervision and other items are higher for the glycol process. The raw material charge is lower principally because less linseed oil is needed to produce a pound of CFA. Byproduct credits for the water process are higher because of the greater amount of byproducts per pound of product.

The cost-to-make figures for the two methods reported here are intended primarily to be comparative rather than precise absolute cost figures. Certain

simplifying assumptions have been used, as previously pointed out and, moreover, continuing process studies may allow further cost reduction. However, the reduction in cost accomplished by using water as the solvent for the CFA reaction is substantial.

ACKNOWLEDGMENT

Assistance in conducting experiments and analyses by L. T. Black, R. L. Reichert and L. Carlson.

REFERENCES

1. Beal, R. E., R. A. Eisenhauer and E. L. Griffin, Jr., JAOCS *41*, 683–685 (1964).
2. Bell, E. W., J. P. Friedrich, L. E. Gast and J. C. Cowan, Abstracts of Papers, No. 77, 37th Fall Meeting, AOCS, Minneapolis, Minn., 1963.
3. Black, L. T., and R. A. Eisenhauer, JAOCS *40*, 272–274 (1963).
4. DeJarlais, W. J. and H. M. Teeter, *Ibid. 39*, 421–424 (1962).
5. Eisenhauer, R. A., R. E. Beal and E. L. Griffin, Jr., *Ibid. 40*, 129–131 (1963).
6. Friedrich, J. P., and R. E. Beal, *Ibid. 39*, 528–533 (1962).
7. Friedrich, J. P., E. W. Bell and L. E. Gast, Abstracts of Papers, No. 52, 55th Annual Meeting, AOCS, New Orleans, La., 1964.
8. Miller, W. R., H. M. Teeter, A. W. Schwab and J. C. Cowan, JAOCS *39*, 173–176 (1962).
9. Varrentrapp, F., Ann. Chem. *35*, 196 (1840).

[Received April 20, 1965—Accepted September 27, 1965]

The Oxygenated Fatty Acid of Calendula Seed Oil

R. C. BADAMI[1] and L. J. MORRIS,[2] Brunel College, Acton, London W.3., England

Abstract

The seed oil of *Calendula officinalis* L. contains a monohydroxy acid amounting to some 5% of its component acids. This acid has been isolated and shown to be D-(+)-9-hydroxy-10,12-octadecadienoic acid, probably 10-*trans*,12-*cis*.

Introduction

THE SEED OIL OF *Calendula officinalis* L. (family *Compositae*) has been examined in recent years in three laboratories. McLean and Clark (1) demonstrated that a high proportion of the fatty acids consisted of a conjugated trienoic acid, which was isolated in its isomerised all-*trans* form and shown to be 8,10,12-octadecatrienoic acid. Chisholm and Hopkins (2) isolated the acid in its natural configuration, proved conclusively that it was *trans*-8, *trans*-10,*cis*-12-octadecatrienoic acid and estimated that it comprised 47% of the oil. Earle et al. (3,4) in their examination of a large number of seed oils from *Compositae* and other families also noted the presence of conjugated trienoic acid in *Calendula* oil, estimated at 51–53% of the fatty acids, other components being palmitic (5%), stearic (2%), oleic (5.5%) and linoleic (34%) acids. In addition, they obtained a carbonyl value corresponding to 4% of the oil, if calculated as a C_{18} keto-acid, and also noted an apparent "dimorphecolic acid" (i.e., 9-OH-*trans*-10,*trans*-12-octadecadienoic acid) content of 4%, as determined by their hydrogen bromide titration method (4).

Long-chain keto-acids are very rare in nature and for this reason it was considered worthwhile to examine more closely any oxygenated acid present in *Calendula* oil. Only one oxygenated acid was detected. This was isolated and shown to be D-(+)-9-hydroxy-10,12-octadecadienoic acid, probably 10-*trans*,12-*cis*.

Experimental and Results

Seeds of *Calendula officinalis* L. were harvested from the garden of one of us, the original seed having been purchased from a reputable seedsman. The fresh seed (165 g) was finely ground and extracted three times with light petroleum at room temperature over a period of 24 hr. The solvent was removed from the clear filtered extract, at less than 30° in a rotary evaporator, to yield 16.7 g of oil. The oil was hydrolysed by standing overnight at room temperature with 5% ethanolic potassium hydroxide and nonsaponifiable material was removed by ether extraction. After careful acidification to pH 5 with 1 N sulfuric acid, the mixed acids were immediately extracted into diethyl ether. The ether solution was washed with water till neutral, dried and the solvent removed to yield 14.7 g of mixed fatty acids. Thin-layer chromatography (TLC), with ether-hexane-formic acid (50:50:1) as solvent, of the mixed acids alongside suitable standards revealed no trace of a keto acid component but a small amount of a hydroxy acid which had similar migration characteristics to a dimorphecolic acid standard.

The hydroxy acid fraction (914 mg, 6.2% of the total mixed acids) was concentrated in 70% aqueous ethanol by a three-funnel six-withdrawal distribution against hexane as stationary solvent. This concentrate was esterified with diazomethane and separated by preparative TLC with ether-hexane (1:1) as developing solvent, to yield 690 mg (4.7% of total mixed acids) of monohydroxy methyl ester which migrated as a single component on analytical TLC, with the same solvent system.

Spectrophotometry

The isolated hydroxy ester had an ultraviolet absorption maximum at 233mμ, $\Sigma = 23{,}150$, corresponding to a conjugated diene grouping. There was no measurable absorption in the conjugated triene region. The spectrum of a sample treated with anhydrous hydrogen bromide in ether showed some residual absorption at 233 mμ and a strong band with maxima at 260, 269 and 280 mμ indicating an all-*trans* conjugated triene group. This effect of hydrogen bromide treatment is characteristic of a vicinal hydroxydiene grouping and arises by partial dehydration to conjugated triene accompanied by partial substitution of bromine for hydroxyl (5).

The infrared spectrum of a dilute (ca. 0.3% w/v) solution of the hydroxy ester in carbon tetrachloride showed a single sharp band at 2.76 μ in the hydroxyl stretching region. This corresponded exactly to the intramolecularly associated hydroxyl band of a conjugated dienol grouping such as methyl dimorphecolate and differed from the dilute solution spectra of other unsaturated hydroxyl groupings (6). The infrared spectrum of a thin film of the ester showed bands of near equal intensity at 10.13 μ and 10.51

[1] D.S.I.R. Fellow (1963–64) at Brunel College; present address: Department of Chemistry, Karnatak University, Dharwar, Mysore State, India.
[2] Unilever Research Fellow (1961–64) at Brunel College; present address: Unilever Research Laboratory, Colworth House, Sharnbrook, Bedford, England.