paper and nitromethane-petroleum ether columns. A 2,4-dinitrophenylhydrazone isolated from the nitromethane column with an absorption maximum at 367 mμ, in agreement with that of the authentic derivative of vinylethyl ketone. The isolated material had the same R_f as the authentic derivative when chromatographed on silica gel-silver nitrate plates, or when rechromatographed on silica gel plates and kerosene impregnated paper.

This evidence suggests that vinylethyl ketone in combination with other carbonyl compounds produces flavor A typical of the early stages of soybean oil autoxidation, just as vinylamyl ketone in combination with any of several aldehydes produces the oxidized flavor typical of the early stages of autoxidation in milk fat. The importance of these vinyl ketones in the flavor is not due to their high concentrations relative to other carbonyl compounds, but rather to their extremely low flavor thresholds.

ACKNOWLEDGMENTS

Dr. M. Winter provided *cis*-3-hexanal; technical assistance was given by Mrs. Carolyn Boatman.

Journal Paper No. J-4995 of the Iowa Agriculture and Home Economics Experiment Station, Ames, Iowa. Project No. 1517. This investigation was supported in part by a PHS research grant EF-84 from the Division of Environmental and Food Engineering and Food Protection, Public Health Service.

REFERENCES

1. Barrett, C. B., M. S. J. Dallas and F. B. Padley, JAOCS *40,* 580-584 (1963).
2. Chang, S. S., and F. A. Kummerow, *Ibid. 31,* 324-327 (1954).
3. Day, E. A., R. Bassette and M. Kenney, J. Dairy Sci. *43,* 463-474 (1960).
4. Day, E. A., D. A. Lillard and M. W. Montgomery, *Ibid. 46,* 291-294 (1963).
5. El-Negoumy, A. M., D. M. Miles and E. G. Hammond, *Ibid. 44,* 1047-1056 (1961).
6. El-Negoumy, A. M., M. S. de Puchal and E. G. Hammond, *Ibid. 45,* 311-316 (1964).
7. Hammond, E. G., and F. D. Hill, JAOCS *41,* 180-184 (1964).
8. Schultz, H. W., E. A. Day and R. O. Sinnhuber, "Lipids and Their Oxidation", Avi Publishing Co. Inc., Wesport, Conn., 1962, pp. 215-229.
9. *Ibid,* pp. 224.
10. Schwab, A. W., and H. J. Dutton, JAOCS *25,* 57-59 (1948).
11. Shine, H. J., J. Org. Chem. *24,* 1790-1791 (1959).

[Received November 27, 1964—Accepted July 21, 1965]

Hydrogenation of Linolenate.
XII. Effect of Solvents on Selectivity[1]

SAMBASIVARAO KORITALA and H. J. DUTTON,
Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

Selectivity of heterogeneous catalysts for hydrogenation of linolenate over linoleate is increased by the presence of certain polar solvents. A ratio of specific reaction rate constants for linolenate to linoleate of 4 was obtained with a 5% palladium-on-alumina catalyst when dimethyl formamide (DMF) was used as the solvent. This high selectivity of DMF was independent of temperature and catalyst concentration. Other solvents that improved selectivity include furfural, acetonitrile, tetramethyl urea and trimethyl phosphate.

Introduction

THE CAUSE FOR CERTAIN undesirable flavors in soybean oil has been attributed to the presence of linolenic ester groups (1). A cooking or salad oil of increased stability can be obtained from soybean oil by a two-step process: a) selective hydrogenation, to reduce linolenate from its original 7–9% to 2–3%, and b) winterization, to remove the solid high-melting fatty acid esters formed during hydrogenation (2). Commercially available catalysts have selectivity ratios (^{K}linolenate/^{K}linoleate) of 1.8–2.9 (3,4). A ratio of 4 or greater, as calculated on an analog computer (5), is required to reduce the linolenate content in a liquid soybean oil to 2% or less without substantial loss of linoleate or increase in high melting glycerides, and such ratios increase the yield of liquid oil during winterization or may eliminate the need for that processing step.

When evaluating solvents for the selective extraction of linolenic acid-containing triglycerides from soybean oil, the possibility was suggested of hydrogenating in a two-phase oil-solvent system. By suspending a catalyst in the selective solvent layer, it was hoped to reduce preferentially the more unsaturated triglycerides and improve selectivity. As reduction proceeded, an equilibrium would be maintained between oil and solvent phases; thus during the hydrogenation the more unsaturated triglycerides from the oil phase would tend to move into the solvent layer and the more saturated triglycerides produced in the solvent phase would tend to migrate into the oil phase. Hydrogenating in the presence of solvents has been covered in Maryott's patent (6), and the concept of hydrogenating in a selective solvent phase has been disclosed in another (7). However, the purpose of the second patent was to reduce the polyunsaturated esters to monounsaturated esters without producing any saturated esters, whereas our study is concerned with increasing the hydrogenation rate of linolenate to linoleate.

Experimental

Materials

Solvents evaluated were of the purest grade commercially available and were used without further

TABLE I

Hydrogenation of Linseed: Safflower Oil Mixture
(Temp. 25C, atmospheric pressure, 0.06% of 5% Pd-on-alumina catalyst)

Sample	Time of hydrogenation min.	Composition, % 01	Lo	Le	IV Calcd	*trans* %	Selectivitity (^{K}Le/^{K}Lo)
Starting material	—	16.2	37.8	36.7	175.3	—	—
No solvent	70	34.6	41.2	14.2	138.3	14.4	1.85
5 Volumes DMF + 1 Volume oil	18	31.5	49.6	9.7	138.4	13.0	3.98

---

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

TABLE II

Effect of Temperature on Selective Hydrogenation in Dimethyl Formamide
(0.06% of 5% Pd-on-Al_2O_3 catalyst, DMF/oil = 4)

Temp., C	Selectivity (^{K}Le/^{K}Lo)	*trans*, %
15	3.3	9.2
25	3.9	—
30	3.7	13.9
40	3.9	14.3
50	3.8	15.9
60	3.8	17.5

purification except for acetonitrile, hexane and methoxyethanol, which were distilled, and furfural, which was freshly distilled under reduced pressure and stabilized with hydroquinone. Peroxides were removed from 1,2-dimethoxyethane by passage through alumina followed by distillation over sodium.

Hydrogenations

Catalytic reductions were performed in glass manometric apparatus as described previously (3). Linseed and safflower oils were combined in such proportions as to yield a mixture containing equal amounts of linolenate (Le) and linoleate (Lo). The mixture (1 ml) hydrogenated with solvent and a 5% palladium-on-alumina catalyst was compared to a similar hydrogenation without any solvent. Hydrogenation was stopped after adding 1 mole of hydrogen per mole of Le. Use of the equimixture and this experimental design facilitate a more accurate determination of selectivity ratio (8). Selectivity ratio (^{K}Le/^{K}Lo) was determined from the fatty acid compositions of the linseed-safflower oil mixture before and after hydrogenation (8).

Analytical Methods

Methyl esters were prepared by refluxing the oil mixture with 0.5% sodium methoxide and a great excess of methanol for 1 hr. The percent *trans* was determined from infrared absorption of the methyl esters at 10.36 μ region by using methyl elaidate as the standard (3). Fatty acid compositions were determined by gas-liquid chromatography (GLC) of the methyl esters. A Pye argon gas chromatograph equipped with a 4 ft × ¼ in. glass column, packed with 14% EGSS-X on Gas-Chrom P, 100–120 mesh (Organosilicon polyester packing obtained from Applied Science Laboratories, Inc., State College, Pa.) and with a radium D ionization detector was operated at 180C with an argon gas flow of 45-ml per min. The area under each peak was determined from an electronically integrated curve.

Results and Discussion

Analyses of the hydrogenated linseed-safflower oil mixture with and without dimethyl formamide (DMF) are given in Table I. The addition of solvent doubled selectivity without a concomitant increase in *trans* content. The rate of hydrogenation was considerably increased.

Figure 1 illustrates the effect of increasing the amount of DMF on selectivity. As little as 1 ml DMF per milliliter oil gave nearly maximal selectivity. Increasing the solvent above 5 ml decreased selectivity; the optimum was from 3 to 5 ml. The claim of no upper limit to the amount of solvent used (7) for selective hydrogenation of polyunsaturated esters does not hold for selective reduction of linolenate.

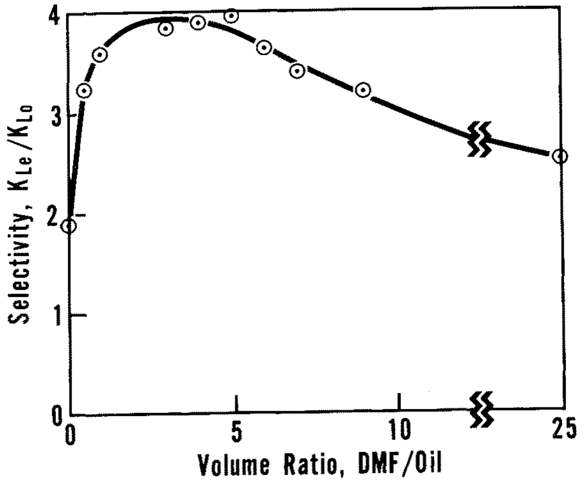

FIG. 1. Effect of increasing dimethyl formamide on selective hydrogenation of a linseed:safflower oil mixture.

The relationship between selectivity and temperature of hydrogenation is given in Table II. Below room temperature selectivity decreased, whereas above room temperature it remained essentially constant. The *trans* content increased with increase in temperature of hydrogenation, an observation which is in agreement with previous reports (9–12). Above 50C

TABLE III

Effect of Catalyst Concentration on Selectivity
(temp. 25C; DMF/oil = 4)

Catalyst concn., % Pd	Pd on Al_2O_3, % Pd	Selectivity (^{K}Le/^{K}Lo)
0.1	5.0	3.6
0.05	5.0	3.6
0.01	0.5	4.0
0.005	0.5	3.9

TABLE IV

Effect of Solvents on Selectivity of 5% Pd on Al_2O_3

Solvent	Ml solvent/ml oil	Hydrogenation temp., C	Rate of hydrogenation ml/min	*trans*, %	Selectivity (^{K}Le/^{K}Lo)
None		25	0.42	13.0	1.9
DMF (DuPont, tech. grade)	3	25	1.78	13.8	3.6
DMF (Matheson, Coleman and Bell, chem, grade)	4	25	1.78	—	3.0
Diethyl formamide (spectrograde)	2	25	2.62	16.7	3.2
Dimethyl acetamide	3	25	1.95	—	2.5
Furfural	2	40	1.11	34.0	3.6
Trimethyl phosphate[a]	3	100	0.27	33.0	3.3
Tetramethyl urea	2	25	1.60	14.0	3.4
Acetonitrile	4	50	4.99	19.5	3.2
Propionitrile	2	25	3.20	—	2.5
Ethoxy proionitrile	3	25	1.18	—	2.5
Butyrolactone	1	30	1.00	16.7	2.0
1,2-Propanediol cyclic carbonate	1	30	1.10	15.8	2.2
N-Methyl-2-pyrrolidinone	1	25	0.74	14.4	2.5
Methoxyethanol	4	30	2.20	—	2.2
1,2-Dimethoxyethane (peroxides)	2	30	2.24	23.3	4.0
1,2-Dimethoxyethane (peroxide free)	2	30	5.36	17.8	2.3
Tetraethylene glycol dimethyl ether	1	25	0.85	—	1.8
tert-Butyl alcohol	1	25	1.42	—	1.8
Acetone	3	25	4.05	25.5	2.2
Diethyl carbonate	2	30	2.87	12.9	2.3
Dimethyl carbonate	3	30	3.43	15.7	2.0
Dimethyl malonate	1	30	1.41	14.4	1.9
Diethyl oxalate	1	30	2.35	14.4	1.9
Methyl formate	3	0	1.79	11.4	1.9
Trimethyl borate	1	30	4.04	14.4	1.5
Hexane (tech. distilled)	2	25	3.04	13.8	2.0

[a] Hydrogenation was carried out with a commercial nickel catalyst.

the oil was completely miscible with the solvent, but selectivity was the same, contrary to our original hypothesis of two-phase hydrogenation. Thus a polar solvent does not need to form a two-phase system to improve selectivity. Though this observation refutes our earlier hypothesis, the experimental application of this concept remains unaffected.

Table III lists the selectivities at various catalyst concentrations. Within experimental error, selectivity remained constant over a wide range of catalyst concentrations.

In an effort to find other solvents useful for selective hydrogenation, a survey was made; the results are shown in Table IV. All solvents were tested with 5% palladium-on-alumina catalyst at room temperature and atmospheric pressure, except for trimethyl phosphate which was used with a commercial nickel catalyst at 100C. Hydrogenation with methyl formate was performed at 0C. As can be seen from Table IV, highly polar solvents like DMF, furfural and tetramethyl urea improved selectivity, whereas less polar and nonpolar solvents were not beneficial despite an increase in hydrogenation rates. Furfural and trimethyl phosphate produced large amounts of *trans* isomers possibly because of the presence of catalyst poisons in the solvents. If 1,2-dimethoxyethane containing peroxides was used, a high selectivity of 4.0 was obtained. A high *trans* content was also produced, which is probably indicative of the peroxides acting as selective poisons (13). After removal of peroxides from the solvent, selectivity dropped to a nearly normal value. The *trans* was still slightly higher possibly due to traces of peroxides which are removed with difficulty. With acetone, the high *trans* content also indicates poisons; but selectivity is not improved. It appears that selectivity can often be improved by poisoning the catalyst. However, since the *trans* content did not increase with DMF or tetramethyl urea, it might be inferred that these two solvents act by a process other than catalyst poisoning. The two-phase hydrogenation hypothesis proposed earlier is not a necessary prerequisite for improving selectivity since the same high selectivity was obtained even when there is only one phase. A more likely explanation is that of McQuillin et al. (14), namely, the solvent influences the polarity of the catalyst surface so that the highly unsaturated molecules are adsorbed on the catalyst surface in preference to the less unsaturated triglycerides.

A technical grade DMF gave a selectivity of 3.6; a chemical grade, 3.0. The spectro grade DMF used gave higher values than either of the other two samples. These differences may reflect the extent of impurities present in the solvent.

Selectivities achieved, when applied to soybean oil, should produce a liquid oil of greater flavor stability. Since hydrogenations are carried out at low temperatures, the flavor stability may further be improved by the suppression of many side reactions that normally accompany a high-temperature hydrogenation.

ACKNOWLEDGMENT

Infrared analyses for *trans* determinations were performed by Mrs. Helen Peters.

REFERENCES

1. Dutton, H. J., C. R. Lancaster, C. D. Evans and J. C. Cowan, JAOCS *28*, 115–118 (1951).
2. Evans, C. D., R. E. Beal, D. G. McConnell, L. T. Black and J. C. Cowan, *Ibid. 41*, 260–263 (1964).
3. Johnston, A. E., D. Macmillan, H. J. Dutton and J. C. Cowan, *Ibid. 39*, 273–276 (1962).
4. Riesz, C. H., and H. S. Weber, *Ibid. 41*, 400–403 (1964).
5. Butterfield, R. O., private communication.
6. Maryott, C. H., U.S. 1,097,456 (1914).
7. Sanders, J. H. (Procter and Gamble Co.), U.S. 2,520,440 (1950).
8. Dutton, H. J., JAOCS *39*, 95–97 (1962).
9. Johnston, A. E., H. M. Ven Horst, J. C. Cowan and H. J. Dutton, *Ibid. 40*, 285–286 (1963).
10. Allen, R. R., *Ibid. 37*, 521–523 (1960).
11. Cousins, E. R., Wilma Guice and R. O. Feuge, *Ibid. 36*, 24–28 (1959).
12. Feuge, R. O., E. R. Cousins, S. P. Fore, E. E. Dupre and R. T. O'Connor, *Ibid. 30*, 454–460 (1953).
13. Bailey, A. E., "Industrial Oil and Fat Products," 2nd ed., Interscience Publishers, Inc., New York, 1951, p. 717.
14. McQuillin, F. J., W. O. Ord and P. L. Simpson, J. Chem. Soc., 5996–6003 (1963).

[Received July 14, 1965—Accepted September 7, 1965]

Effect of Internal Distributors in a Packed Column on the Steam Stripping of Hexane from Soybean Oil

LIONEL K. ARNOLD and RAY SCHUTTER, Department of Chemical Engineering, Iowa State University of Science and Technology, Ames, Iowa

Abstract

Internal distributors were designed and installed in a 6-in. diameter column with an 8-ft bed of ½-in. berl saddles. The distribution pattern of a liquid (water) flowing down the column was first determined. The distributors picked up the water from the wall of the column and redistributed it towards the center producing definitely better distribution across the column than obtained without them. Steam stripping of hexane from soybean oil was next carried out in the column both with and without the distributors. The residual hexane in the oil varied exponentially with the steam-oil ratio. Under the experimental conditions 18% less steam was required for comparable stripping with the distributors in the column than without them.

Introduction

PACKED COLUMNS have had considerable use in stream-stripping the residual solvent from oil miscellas following the initial separation of most of the solvent in an evaporator. Dumped packings such as raschig rings and berl saddles, are usually used in preference to stacked packings because of lower cost and higher capacities. A major problem in the efficient use of packed columns for either stripping or absorption is that of securing uniform distribution of the liquid over the surface of the packing. When the falling liquid is applied uniformly to the top surface of the packing, the uniform distribution exists only momentarily. As the liquid moves downward it spreads outward accumulating on the column wall. When the liquid is applied by a center feed it distributes outwardly as it moves down. Uniform distribution exists only as a flat plane theoretically