Automatizing the separation of gum or soap stock from vegetable oil is an innovation which, when combined with the basic control methods described, satisfies all the requirements of precise and vigilant operation of a continuous process. Plants have operated 24 hours per day, seven days a week, for periods of six months and longer without interruption.

In conclusion, we emphasize the advantages of this automatic control system. Increased production and quality control are attributed to elimination of the human element. Centralized control and graphic presentation simplify supervision of plant operation. The flashing alarm system pinpoints trouble locations immediately, preventing oil loss otherwise unnoticed. Automation of this type eliminates the necessity for operators skilled in the art of vegetable oil refining. They need only to be given the analysis of the feed stock; then they can set the controls and press the buttons.

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REFERENCE

1. Podbielniak, W. J., Gavin, A. M., and Kaiser, H. R., J. Am. Oil Chemists' Soc., 36, 238–241 (1959).

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n-Deca-2,4-Dienal, Its Origin from Linoleate and Flavor Significance in Fats[1, 2]

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A SERIES of methyl ketones, characterized as their 2,4-dinitrophenylhydrazones,[4] recently was identified in the deodorization distillate of fresh milk fat at this laboratory (12). This series was composed of the straight-chain members containing odd numbers of carbons from C_3 through C_{15}. Whether other common fats and oils might yield the same group of ketones under similar conditions was considered worthy of investigation. It was found difficult, if not impossible, to make the conditions for handling other fats the same as for milk fat. Distillates from cottonseed oil, soybean oil, beef tallow, and lard were evaluated. Since the preliminary processing of these fats was beyond our control, the negative findings obtained with respect to the series of ketones in their distillates are of questionable value. However the predominance of n-deca 2,4-dienal, as detected through its DNP- hydrazone, among the carbonyl compounds in distillates from all four fats was impressive and served as the stimulus for the investigations described below. Decadienal is "fantastically" potent as a flavor compound. Its flavor threshold value in water was determined to be 0.5 parts per billion. As will be shown, its formation through action of moisture and heat seems predictable from any fat which contains linoleate.

Experimental

Decadienal from Commercial Fats. Steam deodorization of fats and collection of distillates were performed for us through the kind services of R. J. Sims and associates of Swift and Company. The fats employed in the study were cottonseed oil, soybean oil, beef tallow, and lard, all in good condition and considered to be representative of the materials processed by industry. They were steam-deodorized in amounts of 3 liters each at 225°C. and 1 mm. Hg for 3 to 5 hr., using conventional laboratory deodorizing equipment (12). The beef tallow, a fresh steam-rendered product, was deodorized at this laboratory. The thawed distillates from the four fats all had very pronounced odor reminiscent of fat used many times for frying. DNPhydrazones of carbonyl compounds in the distillates were prepared as follows. Each distillate, amounting to about 200–300 ml., was saturated with NaCl and then extracted four times with 50-ml. volumes of ethyl ether. To the combined ether extracts was added a DNPhydrazine solution prepared by dissolving 200 mg. of the solid reagent in 1 ml. of concentrated H_2SO_4, 2 ml. of H_2O, and 5 ml. of ethanol (abs). Extract and reagent were mixed with a stirrer for 1 hr., 25 ml. of H_2O were added, and the stirring was continued for an additional 15 min. The ether layer containing the hydrazones was evaporated under reduced pressure (water aspirator), and the residue was extracted by mechanical shaking for 1 hr. with 50 ml. of n-hexane. Hexane solutions derived from distillates of the four fats were employed as the source of samples for column and paper chromatographic separation of the DNPhydrazones. The column separation used Celite as support, nitromethane as immobile phase, and n-hexane as moving phase. This method was developed and brought to our attention by Bassette *et al.* (1) and is very similar to that of Monty (7). Use of the method in this investigation was precisely as described in reference 12. To follow separation of hydrazone bands on the chromatography column and to aid identification, the paper chromatographic method of Huelin (5) was employed. Although there was evidence of numerous hydrazones, in both paper and column separations, one red derivative (R_f 0.71, by the Huelin method, retention volume on a 50-g. [Celite] column 800 ± 20 ml. of hexane) predominated in intensity from all four fats.[5]

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[4] 2,4-Dinitrophenyl is hereinafter abbreviated DNP.

[5] There were the following numbers of definitely observable hydrazone bands with mobilities greater than that of the acetone derivative: cottonseed oil—6, soybean oil—7, beef tallow—6, lard—9. Since hexane extraction seems to recover only DNPhydrazones of monofunctional carbonyl compounds with any degree of efficiency, the number of bands observed is considered only a partial accounting of the carbonyls in the distillate. At this point a decision was made to attempt identification of only the prominent red hydrazone and thus determine whether or not the same compound derived from all four fats.

Approximately one-half (25 ml.) of each of the original hexane solutions of the mixed hydrazones was separated, 5 ml. per chromatographic column, and the eluted bands corresponding to the red hydrazone from each fat were combined and evaporated to dryness. The absorption maxima of the crude derivatives, suitably diluted with chloroform, were determined in the 350 to 400 mμ region with a Beckman DU spectrophotometer. The derivatives from the three fats all showed absorption maxima at 390 ± 1 mμ. They also exhibited the same R_f value (0.71) on paper chromatograms. These observations and considerations from the literature (2, 16) suggested that the red hydrazones from the three fats were identical and probably that of n-deca-2,4-dienal. Through the kind generosity of E. L. Pippen, Western Utilization Research and Development Laboratories, U.S.D.A., authentic samples of both the indicated dienal and the most commonly encountered form of its DNP-hydrazone were procured. Details of their preparation have been published (13). We were particularly impressed with the potent "deep-fried" odor of the dienal since it seemed to account substantially for the odor of the fat distillates.

The crude red hydrazones from the four fats were crystallized twice from hexane and then once from methanol. The resulting purified derivatives were submitted to melting point determinations (Kofler hot-stage), both alone and mixed with the authentic DNPhydrazone of decadienal. Pertinent data showing the coidentity of all these preparations are given in Table I. With the exception of melting-point data, these findings were confirmed for distillates from a second set of fat samples (beef tallow not included).

Decadienal from Linoleate. It has been postulated by Swift *et al.* (16) that the origin of decadienal from cottonseed oil is linoleic acid. In a general way the quantities of decadienal DNPhydrazone from the four fats in this study, as judged by color intensity of column bands, correlated with linoleic acid content of the fats, namely, cottonseed oil most intense, soybean oil somewhat less, and beef tallow and lard decidedly less intense. The point regarding origin seemed worthy of confirmation. The successful line of experimentation was as follows. Ten grams of methyl linoleate (Hormel Foundation) were placed in a 50-ml. Claisen flask. The flask then was fitted with a thermometer in the straight neck with the mercury well in the linoleate. The bent neck was fitted with a separatory funnel containing 50 ml. of distilled H_2O, and the side-arm delivered to a cold-water condenser, which in turn delivered to a 500-ml. distilling flask. The linoleate was adjusted to 200°C. with the aid of a heating mantle controlled by a transformer. Water was added from the funnel, a drop at a time, in a manner to maintain the temperature of the linoleate between 200 and 250°C. In all, 33 ml. of H_2O were added during a period of 2 hr. (air present throughout).

TABLE I

Identification Data for n-Deca-2,4-Dienal as Its 2,4-Dinitrophenylhydrazone, in the Steam Distillates of Several Fats

	Properties of the hydrazones			
	R_f[a]	Max. (mμ in $CHCl_3$)	m.p. (°C.)	
			Single	Mixed
Lard	0.71	389	142–3	142–4
Beef tallow	0.71	391	143.5–5	143.5–5
Soybean	0.71	391	143–4.5	143–5
Cottonseed	0.71	390	142–3	142–5
Decadienal	0.71	391	143.5–5	....

[a] Method of Huelin (5).

Considerable spattering and entrainment of linoleate in the distillate occurred. The residue in the Claisen flask and material in the condenser were washed into the receiving flask with 150 ml. of warm H_2O. The receiving flask then was connected to a clean condenser, and 100 ml. were distilled from it into a 500-ml. glass-stoppered flask. This distillate had a strong odor of decadienal, in contrast to the nearly odorless, fresh linoleate. To the distillate were added 200 mg. of DNPhydrazine and 25 ml. of concentrated HCl. The mixture was mechanically shaken 2 hr. and held over-night. The next morning the reaction mixture was shaken for 2 hr. with 50 ml. of n-hexane to recover the DNPhydrazones. The hexane solution was evaporated to dryness. The residue was dissolved in 2 ml. of hexane, which solution was transferred to a chromatography column as described above. Development of the column revealed three bands. The first band in the order of elution was relatively faint and appeared to be elongating by the time it reached the bottom of the column. Rechromatographing of this band on a small column (5 g. of Celite) confirmed the presence of two components. These were designated IA and IB in that order of elution. Band 2 was the most intense and corresponded in color and retention volume to the derivative of decadienal. All three bands were collected and evaporated under reduced pressure. The residues were suitably diluted with chloroform for the measurement of absorption maxima and optical densities.

On the basis of the data so obtained, the band components were paper-chromatographed in comparison with appropriate authentic DNPhydrazones. Components of band IA and IB were not recovered in quantities to yield crystalline products for identification. However bands 2 and 3 could be so manipulated. Band 2 produced red plates from methanol after crystallization from hexane and band 3 produced orange-red needles from hexane. Data, including single and mixed melting points, on the established (bands 2 and 3) and postulated (bands IA and IB) identities of the compounds involved in this experiment are presented in Table II. All significant aspects of the data in this table were confirmed by the results of a second, essentially identical experiment. The compounds thus arising from linoleate were mainly n-deca-2,4-dienal and n-hept-2-enal with much lesser amounts of presumably n-dec-2-enal and n-non-2-enal.

Initial experimentation in this area, which had proved fruitless with respect to the production of decadienal, involved shaking linoleate-water mixtures and holding at room temperature for several days to induce oxidation. The mixture then was steam-distilled, and individual carbonyl DNPhydrazones were obtained as described above. When several such experiments yielded no encouraging evidence of decadienal, the line of investigation was changed. However it subsequently became evident that some difference existed in the number and identity of carbonyl compounds produced under the two sets of conditions. In addition to the absence of decadienal in the room-temperature-induced deterioration, the production, under such conditions, of n-hexanal was conclusively established by the types of data given in Tables I and II. This product and

TABLE II

Identification Data for Carbonyl Compounds, as 2,4-Dinitrophenylhydrazones, in the Steam Distillate from Methyl Linoleate

Band No.	Optical density [a]	Postulated identity	R_f[b]		λ Max. (mμ in $CHCl_3$)		m.p. (°C)		
			Unknown	Known	Unknown	Known	Unknown	Known	Mixed
1A	0.108	n-dec-2-enal	0.84	0.84	378	377	......	......	......
1B		n-non-2-enal	0.80	0.80	378	377	......	......	......
2	1.37	n-deca-2,4-dienal	0.71	0.71	391	391	145	143.5–5	143.5–5
3	0.303	n-hept-2-enal	0.64	0.64	377	377	130–1	131–2	130–2

[a] Values determined at wavelength maxima for the bands.
[b] Method of Huelin (5).

n-oct-2-enal, which have been reported (16) in fat distillates, were not found among the carbonyls produced by 200°C.-decomposition of linoleate.

Flavor Properties of Decadienal. The interesting odor properties of authentic decadienal and the probability that its generation is commonplace in the cooking of various foods suggested that some effort should be made to measure the compound's flavor potency. Its flavor threshold in water was determined by the method of Patton and Josephson (8). Concentrations of decadienal ranging from 0.1 p.p.m. to 0.1 p.p.b. in distilled water were prepared by serial dilution from 1 ml. of a stock solution containing 1 mg./ml. of the compound in ethanol (abs.). Five taste observers evaluated each concentration five times. Recognition at the various concentrations by the observers is shown in Table III. A graphic plot of the data indicated that the flavor threshold was approximately 0.5 p.p.b. when the threshold is defined as that concentration which elicits a positive response 50% of the times it is presented. This finding was confirmed by further observations on a second set of samples, which were made from a freshly prepared stock solution. The taste observers were requested to describe the qualitative flavor character of decadienal above threshold. Common terms used were "deep-fried," "restaurant-like," and "oily."

TABLE III

Flavor Threshold Data for n-Deca-2,4-Dienal in Water [a]

	Concentration (p.p.b.)					
	100	25	5	1	0.1	0
Recognition (%)	100	100	96	68	40	12
Positive responses	25	25	24	17	10	3

[a] Five observers evaluating each concentration five times.

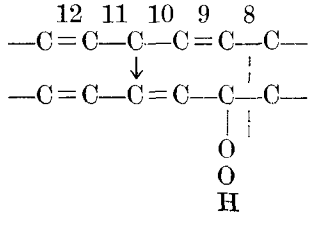
Decadienal in Certain Fat Oxidation Tests. The earlier work at this laboratory (9, 10) established that malonic dialdehyde gives the characteristic pink colors (maxima at 543 and 532 mμ, respectively) which oxidized lipides produce in the Kreis[6] and thiobarbituric acid (TBA) tests. More recently 2-enals were evaluated in the TBA test (11), and it was observed that freshly prepared compounds do not give the pink color in the test but that on standing exposed to air or in the presence of cupric ions they do give a positive test. It was of interest to study decadienal in this connection. This compound appeared to behave in much the same manner as the 2-enals. It gave a muddy yellow color in the TBA test when analyzed fresh (stored in the dark under nitrogen). On exposure to air (48 hr.) or when tested in the presence of 40 p.p.m. of copper (as $CuSO_4$), it gave the typical pink color. Likewise it was negative (yellow green) to the Kreis test when fresh but gave the characteristic pink color after exposure to air or when the test solution was treated with 1 ml. of 3% H_2O_2. These color tests were conducted in the conventional manner (for example 9, 10) on a solution of decadienal in ethanol, 1 mg./ml.

Control Experiments. In addition to the control measures described above, an effort was made to evaluate the solvents employed (ethanol, ethyl ether, and n-hexane) as a source of carbonyls. It was found, under the experimental conditions used, that acetaldehyde and acetone were the only problematical contaminants that could not be eliminated from the solvents for a practical period of time. Consequently no particular significance was attached to the DNPhydrazones of these two compounds when encountered in this investigation.

It was desirable at times to regenerate decadienal from its DNPhydrazone as further confirming evidence of identity by odor. A procedure, brought to our attention by Bassette *et al.* (1) which works very effectively, is to dissolve one or two small crystals of the derivative in 1 ml. of concentrated H_2SO_4 and then add slowly, with shaking, 2 ml. of H_2O.

Discussion

Decadienal has been demonstrated in the distillates from cottonseed oil (16), soybean oil (15), peanut oil (6), and chicken fat (14). It has also been detected among numerous other mono- and dienals produced in the copper-induced flavor deterioration of skimmed milk (4). The present study has confirmed derivation of the compound from cottonseed and soybean oils and has added beef tallow and lard to the list of origins. Thus it is evident that decadienal is derived from most, if not all, the common edible fats. Evidence from the literature, as well as from this study, indicates that high temperatures (200–250°C.) favor formation of the compound. The postulation of Swift *et al.* (16) that decadienal may come *via* decomposition of linoleate is clearly confirmed herein. They have proposed that the mechanism of formation involves shift of the 9 double bond in linoleate to the 10 position and hydroperoxidic attack of the 9 carbon followed by chain cleavage at the 8 position. The essence of this mechanism, which seems plausible, may be represented as follows:



$$\begin{array}{l} \quad\;\; 12 \quad 11 \quad 10 \quad 9 \quad 8 \\ -C{=}C{-}C{-}C{=}C{-}C{-} \\ \qquad\quad\;\; \downarrow \\ -C{=}C{-}C{=}C{-}\underset{\underset{\underset{H}{|}}{O}}{\underset{O}{|}}{C}{-}C{-} \end{array}$$

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[6] Pure epihydrinaldehyde (glycidaldehyde) has recently been reported as negative in this test (C and E News, April 20, 1959, and Payne, G. B., J. Am. Chem. Soc., in press).

In contrast to the finding of Swift *et al.* of n-hexanal and n-oct-2-enal as additional products from cottonseed oil, we found n-hept-2-enal and much smaller amounts of C_9 and C_{10} 2-enals as additional products from methyl linoleate. Autoxidation of the cottonseed oil prior to deodorization may have some bearing on this difference. The probability of differences in products between room- and elevated-temperature decomposition of linoleate warrants further investigation.

The flavor potency of decadienal is quite remarkable. With a flavor threshold of approximately 0.5 p.p.b. it ranks with very powerful sulfur compounds (8). Forss (3) independently has confirmed that several other n-alkyl-2,4-dienals have flavor strengths of the same order observed in this work for decadienal. The intense flavor properties of the compound coupled with its potential of formation from the major edible fats, or more generally from any fat containing linoleate, suggest that it is a very commonplace component in food odors and flavors. More particularly, it is postulated that decadienal contributes to the flavor and aroma of foods in which the fat comes in contact with moisture at relatively high temperatures. The classic example is deep-fat frying, but broiling, frying, and baking also fit the definition under certain conditions. The baking of pie-crust probably is a good example.

Summary

n-Deca-2,4-dienal was identified as a major component of the carbonyl compounds in deodorization distillates from cottonseed oil, soybean oil, beef tallow, and lard. This compound also was demonstrated as a principal carbonyl component in the heat decomposition of methyl linoleate in the presence of moisture. n-Hept-2-enal and C_{10} and C_9 2-enals also were detected in the latter system. The flavor threshold of decadienal in water was found to be approximately 0.5 parts per billion. Flavor and odor qualities of the dienal perhaps are described best by the term "deep-fried." The compound's significance in fried and baked foods and its performance in the Kreis and 2-thiobarbituric acid tests for fat oxidation are discussed.

Acknowledgments

Donation of n-deca-2,4-dienal and its dinitrophenylhydrazone by E. L. Pippen and the services of R. J. Sims and associates in deodorizing fat samples were indispensable contributions to this investigation, for which the authors are very grateful.

REFERENCES

1. Bassette, R., Day., E. A., and Keeney, M., personal communication (1958).
2. Braude, E. A., and Jones, E. R. H., J. Chem. Soc., 498–503 (1945).
3. Forss, D. A., personal communication (1958).
4. Forss, D. A., Pont, E. G., and Stark, W., J. Dairy Research, *22*, 345–348 (1955).
5. Huelin, F. E., Austral. J. Sci., Research, *5B*, 328–334 (1952).
6. LeFort, D., Bull. mens. *inform.* ITERG, *7*, 383–386 (1953) (cited in C.A. 48: 388d, 1954).
7. Monty, K. J., Anal. Chem., *30*, 1350–1352 (1958).
8. Patton, S., and Josephson, D. V., Food Research, *22*, 316-318 (1957).
9. Patton, S., Keeney, M., and Kurtz, G. W., J. Am. Oil Chemists' Soc., *28*, 391–393 (1951).
10. Patton, S., and Kurtz, G. W., J. Dairy Sci., *34*, 669–674 (1951).
11. Patton, S., and Kurtz, G. W., J. Dairy Sci., *38*, 901 (1955).
12. Patton, S., and Tharp, B., J. Dairy Sci., *42*, 49–55 (1959).
13. Pippen, E. L., and Nonaka, M., J. Org. Chem., *23*, 1580–1582 (1958).
14. Pippen, E. L., Nonaka, M., Jones, F. T., and Stitt, F., Food Research, *23*, 103–113 (1958).
15. Stapf, R. J., and Daubert, B. F., J. Am. Oil Chemists' Soc., *27*, 374–377 (1950).
16. Swift, L. E., O'Connor, R. T., Brown, L. E., and Dollear, F. G., J. Am. Oil Chemists' Soc., *26*, 297–300 (1949).

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Epoxy Resins from Fats. I. Epoxidized Glycerides Cured with Phthalic Anhydride[1]

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A large potential market exists for fatty acid derivatives in the rapidly expanding epoxy resin industry. Predictions have been made that by 1960, 82 million pounds of epoxy resins will be produced annually (5). Thermosetting resins of this type are very hard and have good impact resistance, excellent chemical resistance, and excellent electrical properties. They are finding widespread use as casting and potting resins, for adhesives and laminates, and for use in protective coatings of all kinds.

Chemically epoxy resins are cross-linked polymers obtained by curing glycidyl ethers of polyfunctional phenols with a polyfunctional chemical, such as diethylenetriamine or phthalic anhydride. The most common glycidyl ethers used commercially are obtained from the reaction of bisphenol A and epichlorohydrin. The intermediate condensation product may be the simple structure A (Figure 1) or, more usually, it contains further condensation products B where n is a low integer. Curing results from the reaction of the epoxide group with the curing agent. When anhydrides are used as curing agents, the hydroxyl groups also may react. The nature of the reactive groups present in B suggests that epoxy resin intermediates may be modified by reaction with fatty acid derivatives.

To a degree such fatty derivatives have already been investigated, and some are in commercial use. For example: a) epoxidized soybean oil has been used to modify epoxy resins, to impart flexibility, and to prolong the working pot life (3, 4); b) polyamides (9, 10), which are condensation polymers of dimerized (or trimerized) unsaturated fatty acids and polyamines, have found similar uses; c) fatty diamines, such as Duomeen S,[4] have been used as flexibilizers in epoxy systems to impart physical characteristics simi-

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[4] Trademark of Armour and Company, Chicago, Ill.