soybean oil and corn oil. Sidwell *et al.* (20), in applying this method, found no increase in carbonyls during the oxidation of butter but did find an increase during the oxidation of lard and vegetable oils. The labile nature of aldehydes, especially the α,β-unsaturated and the dialdehydes formed in fat oxidation products, makes any determination of these compounds difficult to reproduce. Better and more specific methods, along with improved techniques, are definitely needed to evaluate and interpret chemical data in flavor work.

Summary

Oxidation prior to deodorization was shown to be detrimental to the flavor and oxidative stability of soybean oil. The increase in the nonvolatile carbonyl content of freshly deodorized oils was proportional to the peroxide value of the oils before deodorization. Rate of loss of flavor and oxidative stability of the oil were related to the extent of carbonyl development. All oils, whether or not they had been submitted to any known oxidation, contained some nonvolatile carbonyls. The loss in stability was not due to a loss of the antioxidant tocopherol.

Oxidized soybean oil methyl esters were shown to develop nonvolatile carbonyl compounds upon heating at deodorization temperatures. The addition of isolated methyl ester peroxide decomposition products to deodorized soybean oil reduced its flavor and oxidative stability in proportion to the amount added. The results obtained were parallel and similar to those obtained by oxidizing soybean oil prior to deodorization.

Flavor deterioration and undesirable flavors were typical of aging soybean oil whether or not the oils were oxidized before deodorization or whether an equivalent amount of nonvolatile thermal decomposition products was added to the oil. These oxidatively derived, nonvolatile carbonyl materials are believed to enter into the sequence of reactions that contribute to flavor instability and quality deterioration of soybean oil. The structure of these materials is not known.

This work indicates the importance of minimizing autoxidation in soybean oil particularly before deodorization to insure good oxidative and flavor stability.

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[Received December 8, 1959]

Quantitative Gas Chromatography of Fatty Derivatives. Relative Detector Responses to C_6-C_{14} Saturated Methyl Esters

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The relative response of a thermal conductivity cell, in terms of peak area produced per mole of compound, has been determined for the fatty methyl esters caproate through myristate. The values were found to be a linear function of molecular weight.

IN GAS CHROMATOGRAPHY of fatty derivatives, using thermal conductivity detectors, claims have been made that the peak areas are proportional to the weights of the corresponding components of the sample, and this assumption has been applied in the quantitative analysis of such materials (2,5). Increasingly sophisticated approaches to quantitative gas chromatography have revealed that the situation is not as simple as previously thought, and two different effects have been postulated to account for the fact that, in homologous series, the peak areas become progressively smaller than would have been predicted. One mechanism is that advanced by Orr and Callen (8): transesterification occurring between the sample components and polyester column liquids results in a decrease in the amounts of these components actually reaching the detector. The extent of the reaction, and corresponding decrease in the amounts eluted, would be progressively greater for those substances with longer retention-times; the effect was emphasized at higher temperatures. Other workers have attributed this trend to "minor errors associated with the technique of calculating areas" (6).

The second mechanism has been elegantly documented by Rosie *et al.* (7,9) for an impressive variety of C_1–C_{10} compounds. They showed that the peak areas were directly proportional to mole-percentages when adjusted for differences in thermal conductivity by means of empirical constants, which are linear in molecular weight for each homologous series. The constants referred to as "relative responses" with respect to the area produced by benzene, which was arbitrarily assigned the value of 100.0, will be designated by the symbol R_m in the following discussion. Johns (4) has reported limited data, which agree with those of Rosie.

The generality and accuracy of the foregoing techniques suggested that the results reported for the fatty series might be caused by fortuitous combination of the facts that, in homologous series of high molecular weight, mole-percentages are very similar to weight percentages and thermal conductivity differences might be small. For the accurate analysis of mixtures containing a wide range of molecular weights it appeared that a more reliable interpretation of the chromatograms would be possible if a set of relative detector responses were known for the individual compounds encountered.

Although Hudy (3) has thrown doubt on the transesterification theory by reporting that similar data result from the use of polyester and Apiezon N columns, it remained of interest to determine whether the linearity of the relative responses persists beyond the range reported by Rosie. This note summarizes results obtained on methyl esters of even-numbered normal acids from C_6 through C_{14}. The apparatus used was a Podbielniak Chromacon, Series 9580, equipped with a 1-mv. Minneapolis-Honeywell electronic recorder and a ball-disk integrator (Disc Instruments Inc.). Helium was passed at 70 ml./min. through the column, which was maintained at 210°C., and consisted of 4 ft. of ¼-in. o.d. stainless steel tubing, packed with Craig polyester on Chromosorb W. The detector cell contained tungsten filaments operated at 12.4 volts and 315 milliamp., and was maintained at 220°C. Samples of *ca.* 2 μl were introduced through the silicone rubber septum by means of a Hamilton microsyringe; more precise control was shown to be unnecessary (see discussion of the data in Table I). The individual esters were purified by repeated careful fractionation through a 20-in. Stedman column; their quality was such that, upon gas chromatographic analysis under the conditions already described, no detectable recorder deflection was produced by any other compound although the expected peak was off-scale at the same attenuation. Twelve mixtures, each containing two to four components, were analyzed three to six times. Repeatability of the peak area ratios is indicated by the typical set of data in Table I, resulting from six analyses of a three-component mixture.

TABLE I

Repeatability of Park Area Ratio Determinations

	1	2	3	4	5	6
Peak A	251	342	308	345	357	320
B	311	418	377	432	444	391
C	468	620	566	636	658	575
Ratio B/A	1.239	1.222	1.224	1.252	1.244	1.222
C/B	1.505	1.483	1.501	1.472	1.482	1.471

The values of the ratio B/A show a standard deviation (s.d.) of 0.01294, and a coefficient of variation (c.v.) of only 1.05% (1a); similarly the C/B values have s.d. = 0.01436 and c.v. = 0.966%. The ratios display no significant correlation with sample size (as represented by the sums of the three peak areas); it therefore appears unnecessary to control the sample size more closely than ± *ca.* 20%.

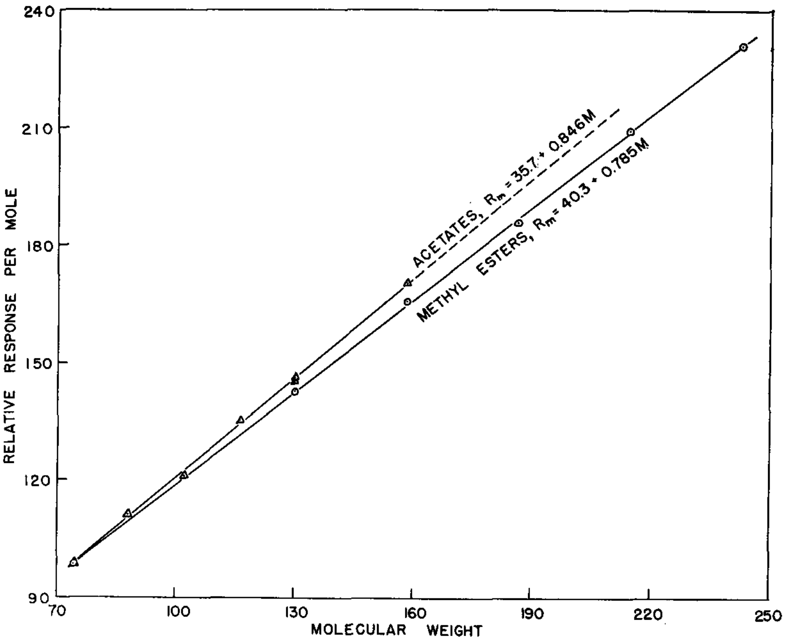

FIG. 1. Relative detector responses of straight-chain acetates and methyl esters.

Establishment of these area-ratios for mixtures of known composition makes possible the calculation of relative responses on either a mole or a weight basis:

$$\frac{A_i/A_j}{m_i/m_j} = \frac{A_i/m_i}{A_j/m_j} = \frac{(R_m)_i}{(R_m)_j};$$

$$\frac{A_i/A_j}{w_i/w_j} = \frac{A_i/w_i}{A_j/w_j} = \frac{(R_w)_i}{(R_w)_j};$$

where A_i/A_j = ratio of areas of peaks produced by components i and j, m_i/m_j = ratio of numbers of moles of components i and j, w_i/w_j = ratio of weights of components i and j, and R_w = relative response per gram. R_w values are better suited for application to analysis of unknown mixtures while R_m values lend themselves to linear correlations of the type shown by Rosie.

The relative responses obtained in this work are listed in Table II. Since no compound of known Rosie R_m value was present, the data are expressed (column A) as multiples of the relative response of methyl caproate.

The second column (column B) of R_m values represents a tentative assignment of the results of this work to the Rosie scale (benzene = 100.0), based on the following argument. R_m for methyl acetate can be calculated from the least-squares line for Rosie's six acetates; this value must also fall on the line representing the straight-chain methyl esters. It is possible to calculate a new least-squares line passing through this point and of such slope that the R_m for the fatty equation $R_m = 40.3 + 0.785$ M, where M = molecular weight. Figure 1 depicts this derivation and also displays the high linearity of the data of Table II; the coefficient of determination (1b) is 0.9996. The excellent linearity of these data indicates that the extrapolation to palmitate and stearate is probably valid and invocation of the transesterification theory is not required at least up to the C_{15} compound.

TABLE II

Relative Detector Responses of Fatty Methyl Esters

Compound	Detector responses		
	Area/mole, Rm		Area/gram, Rw
	(A)	(B)	
Methyl caproate	(1.000)	142.4	(1.000)
Methyl caprylate	1.160	165.2	0.954
Methyl caprate	1.301	185.3	0.909
Methyl laurate	1.467	208.9	0.891
Methyl myristate	1.619	230.5	0.869
Methyl palmitate[a]	1.773	252.6	0.854
Methyl stearate[a]	1.927	274.6	0.840

[a] Extrapolated.

Acknowledgment

The authors are indebted to S. T. Preston and John Mark of Podbielniak Inc. for making available the gas chromatograph on which these measurements were made.

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[Received February 3, 1960]

Extraction of Soybean and Cottonseed Oil by Four Solvents[1]

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VARIOUS SOLVENTS have been both studied and used commercially for the solvent extraction of vegetable oils. Benzol (benzene) has been popular in Europe. Ethyl alcohol has been used in Asia largely because of its ready availability and low cost. In the United States the solvents commonly used are petroleum fractions, mainly the hexane fraction. The common method of determining this fraction by its boiling point does not necessarily establish its chemical composition. The commercial product may contain as low as 60% or as high as 88% n-hexane. Other constituents commonly present are methyl cyclopentane, methyl pentanes, and benzene. Little or no data are available showing the effect of these nonhexane constituents on the solubility of vegetable oils or on the quality of the oil extracted by them.

Studies were made on the rate of extraction of soybeans and cottonseed with pure hexane, pure benzene, and two varieties of commercial hexane commonly used in oil extraction. Composition data on the three hexanes are shown in Table I. The benzene was "reagent" grade. Cracked soybeans containing 7 to 8% moisture were heated to 160°F. and rolled into flakes with an average thickness of 16 mils. The extractions were carried out in laboratory-rate extraction apparatus similar to that used in previous studies in this laboratory (1), except somewhat larger. The extraction chamber was 12 in. high by 2 in. in diameter allowing the use of 100-gram samples. The extraction chamber and the incoming solvent were heated to 135 to 140°F. The solvent passed through the flakes at a rate producing 10 ml. per minute of miscella. Samples were taken at 10-minute intervals. The solvent was evaporated from each fraction under vacuum and the oil weighed. The residual oil content of each sample was determined in Soxhlet apparatus using the solvent drained from the sample in the rate extractor as the extracting solvent. Cottonseed meats were extracted in a similar manner. Results for both are shown in Table II.

TABLE I

Composition of the "Hexanes"[a]—Amounts in Volume Percentages

Constituents	Pure	High purity	Commercial
N-Hexane	99.5	88.4	59.7
Methyl cyclopentane	0.0	7.6	22.4
2-Methyl pentane	0.0	0.0	5.4
3-Methyl pentane	0.0	0.0	11.3
2- and 3-Methyl pentanes	0.0	3.0	0.0
2,2-Dimethyl butane	0.0	0.3	0.0
2,4-Dimethyl pentane	0.0	0.7	0.0
2,3-Dimethyl butane	0.0	0.0	0.3
Cyclo hexane	0.4	0.0	0.9
Benzene	<0.001	<0.001	0.0

[a] Hexanes and their composition data supplied by Phillips Petroleum Company.

Composites of the oil aliquots from each complete extraction were examined for quality with the results

TABLE II

Extraction Data

	Extraction time in min.	Residual extractable oil, % of original[a]			
		"Commercial" hexane	"High purity" hexane	"Pure" hexane	Benzene
Soybean oil	10	69.5	69.5	73.6	64.8
	20	45.2	47.4	53.7	39.9
	30	29.7	32.4	38.9	25.5
	40	19.7	21.4	27.1	15.8
	50	12.8	13.8	20.2	11.2
	60	8.0	8.7	14.2	8.5
	70	4.8	5.0	10.0	7.0
	80	3.0	2.8	7.0	6.2
Cottonseed oil	10	82.8	79.5	80.5	82.8
	20	63.6	63.7	61.4	65.8
	30	48.0	47.4	46.3	50.6
	40	35.4	34.8	34.6	37.1
	50	26.1	25.4	25.3	28.6
	60	19.0	18.8	18.5	20.7
	70	13.6	13.5	13.5	14.8
	80	9.8	9.8	9.9	10.6
	90	7.1	7.2	7.2	7.7
	100	5.1	5.1	5.3	5.7

[a] Original oil content of the flakes, 19.08% (dry basis). A residual extractable oil of 3.0% would be equivalent to 0.7% of the dry extracted meal.

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[1] Presented at the 51st annual spring meeting, American Oil Chemists' Society, Dallas, Tex., April 3–6, 1960.