A New Color Reaction of Sesame Oil

COLOR REACTIONS owing to characteristic compounds of sesame oil (*Sesamum indicum*) are extensively reviewed by Budowski and Markley (1) and by Budowski (2).

We have found an altogether new reaction which gives a characteristic color with sesame oil. When trichloroacetic acid is added to sesame oil, an initial blue color, which turns to green after a few hours, is noticed. The test is performed as follows. To 1 ml of 50% solution (v/v) of sesame oil in petroleum ether, 2 ml of chloroform solution of trichloroacetic acid (40% concentration, w/v) are added. After a few seconds, a faint blue color develops. The color increases in intensity and first becomes sky blue, then green after a few hours. Oils from brown as well as white seed give this test. Alkali refining and adsorption bleaching with earth and carbon accentuate the intensity of the response.

The reaction appears to be of the redox type. It takes place in the presence of peroxides or persalts. No blue color develops when hydroquinone is first added to the oil. If hydroquinone is added after the color has developed, the color is immediately discharged; upon addition of excess benzoyl or other peroxide, the blue color is revived.

The characteristic blue color with trichloroacetic acid may be attributed to the presence of sesamol and related compounds. Sesame oils which have been chromatographed on a column of alumina (eluted with n-hexane and with methanol:ether 975:25) do not respond to the test. Crude sesamol (Shulton Inc., Clifton, N.J.) added to petroleum ether along with a peroxide gives a blue color which later turns to green. Similarly sesamin, isolated from sesame oil by molecular distillation and low-temperature crystallization, also responds, although to a lesser extent. Sesamol, sesamin, and sesame oil are sensitive to the extent of 0.01, 0.2, and 20.0% by weight respectively in petroleum ether toward this test. For example, 0.0001 g of sesamol, 0.002 g of sesamin, and 0.2 g of sesame oil, added separately in 1 ml of petroleum ether, respond to the test.

Sesamol and sesamin dissolved in paraffin oil do not give a blue color with the trichloroacetic acid reagent alone. However, if benzoyl peroxide is added, a blue color appears immediately. Sesame oil, which invariably contains some peroxide because of autoxidation, responds positively when dissolved in paraffin oil. Piperonal does not give the test; but if piperonal is oxidized with peracetic acid, according to the Böeseken, Coden, and Kip method (3), the resulting sesamol acetate gives the blue color with trichloroacetic acid in the presence of benzoyl peroxide.

From these observations it may be postulated that the methylenedioxyphenoxy group characteristic of compounds which are present in sesame oil and trichloroacetic acid take part in a reaction in which peroxides might be involved through a free radical mechanism that results in the blue color.

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REFERENCES

1. Budowski, P., and K. S. Markley, Chem. Rev. *48*(1), 136–139 (1951).
2. Budowski, P., JAOCS *41*, 280–285 (1964).
3. Böeseken, J., W. D. Coden and C. J. Kip, Rec. trav. Chim. *55*, 815–20 (1936).

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Gas Flowmeter from a Leak Detector and Potentiometer

CARRIER-GAS FLOW from a flame ionization detector (FID) is often troublesome to measure because the burner housings must be opened or partially dismantled. A Gow-Mac Leak Detector (GM-LD), formerly Gas Hound, can be operated as a specialized flowmeter that particularly applies to this measurement problem.

A 50K ten-turn potentiometer with locking duodial when wired in the meter line of the GM-LD allows its sensitivity to be attenuated so that, on the "low" range, large amounts of helium carrier-gas may be monitored against a background of air from the FID. Usually the measurement is made with no hydrogen flowing through the burners. However if the flames are adjusted to combust the hydrogen stoichiometrically, helium measurements may be made while the burners are operating. Results are best without hydrogen since no water vapor will be introduced into the GM-LD.

A typical GM-LD/flowmeter calibration procedure is as follows:

1) Hydrogen and helium to detector temporarily shut off.

2) Airstream through burner housing adjusted to 200 cc/min with the aid of a soap-film flowmeter.

3) Helium carrier turned on and adjusted to 70 cc/min (soap-film meter).

4) GM-LD used to monitor FID effluent from any convenient opening in the burner housings while 50K potentiometer is adjusted so that 70 cc/min helium in 200 cc/min air causes full-scale meter deflection. The potentiometer adjustment is locked and recorded so that it may be returned to this value without recalibration. Measurements should be made at the same opening in the FID housing so that readings are not influenced by variations in probe location.

5) Helium flow reduced, measured with the soap-film meter, and recorded;

6) GM-LD meter deflection at this lower helium flow recorded; and

7) Repeat steps 5 and 6.

Typical calibration data are:

Actual He Flow (measured with) soap-film meter) cc/min	GM-LD Meter Deflection (divisions right)
8	12
16	19
24	24
31	28
38	32
46	35
53	38
59	42
66	44
72	47

This table or a plot from its data allows a quick and fairly accurate measurement of column flow without dismantling the FID assembly. The adjustable 50K resistance, when turned to its lowest value, restores the GM-LD to its former sensitivity.

Addition of this single potentiometer is a simple modification that has made the GM-LD in this laboratory a more useful instrument.

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Homogeneous Hydrogenation of Soybean Fatty Esters by the Ziegler Type of Catalyst Systems

It has already been shown that soybean oil esters are partially hydrogenated by such homogeneous catalysts as iron pentacarbonyl (1) and dicobalt octacarbonyl (2) or by such heterogeneous catalysts as palladium complexes (3), sodium borohydride-catalysts (4), and copper-chrome catalysts (5). Meanwhile hydrogenation of soybean methyl esters with metal acetylacetonate (abbreviated as $M[acac]_3$), such as $Ni(acac)_3$, $Co(acac)_3$, $Cu(acac)_2$, and $Fe(acac)_3$ activated by methanol, has been reported by Emken et al. (6).

Most of these catalysts promote the reduction of polyunsaturated fatty esters with positional and geometric isomerization of double bonds, and the degree of isomerization varies with the catalyst. But it has also been reported (7) that a number of transition metal compounds, for example, $Ti(O\ i\text{-}C_3H_7)_4$, $VO(O\ n\text{-}C_4H_9)_3$, $Cr(acac)_3$, etc., combined with organometallic derivatives are active catalysts for the hydrogenation of olefins (such as cyclohexene, 1-octene, etc.).

In this paper homogeneous hydrogenation of soybean fatty esters (methyl linoleate, methyl linolenate) by the binary catalyst systems of transition metal compounds and organo-aluminium compounds is reported. Transition metal compounds which were tried were $Ni(acac)_3$, $CoCl_2$, $Co(acac)_3$, and $FeCl_3$. Triethyl aluminum was used as an organo-aluminium compound.

A description of the hydrogenation reaction follows. In an autoclave (100 ml) were placed 1 mmol of transition metal compound, 5 mmol of $AlEt_3$, 50 ml of hexane (as a solvent), and 8.5 g of soybean oil methyl esters (methyl linoleate, methyl linolenate) under inert atmosphere. Then hydrogen was introduced up to 150 kg/cm². The hydrogenation reactions were carried out at 150C for 2 hr with vigorous agitation.

After the reaction the reduced products were analyzed directly after washing. Countercurrent distribution between *n*-hexane and acetonitrile was used to fractionate the reduced products. Individual fractions were monitored by GLC (2). For GLC a 200-ft column, coated with Apiezon L, was used with a Barber-Colman chromatograph equipped with a Radium D ionization detector. The operation was carried out at 175 C with a nitrogen flow of 35 ml/min. The percentage of isolated *trans* double bonds in the hydrogenated products was determined by comparing the IR absorption of the methyl esters in a carbon disulfide solution with the 10.36 mμ region with that of methyl elaidate. The diene conjugation was measured by UV absorption in the 231–234 mμ region.

Table I shows the results of the hydrogenation reaction of soybean methyl esters. With each catalyst system (1–4) the contents of triene and diene in the reaction products were decreased and the content of monoene was increased with the reaction time. The content of saturated esters (stearate, palmitate) remained constant. Table II shows the results of the hydrogenation of methyl linoleate and methyl linolenate. The same tendency is observed in Table II as in Table I. The decrease in diene and triene and the increase in *trans* unsaturation are related to the degree of hydrogenation. There was essentially no monoene hydrogenation to saturated; only a trace of stearate was formed. During each hydrogenation reaction only a small accumulation of conjugated dienes was observed.

From these results the conjugated dienes which were formed during the reaction may be considered intermediates. The scheme via conjugated dienes is presumed to be like that of Frankel (2):

trienes → dienes → conjugated dienes → monoenes

As for the reduction mechanism, the following

TABLE I

Hydrogenation of Soybean Fatty Esters[a]

Catalyst systems[b]	Palmitate (%)	Stearate (%)	Monoene (%)	Diene (%)	Triene (%)	IV (calculated	Conj. diene (232 mμ)	*trans* (%)
S	10.9	4.1	25.4	52.1	7.5	132.0	0	0
1	10.5	4.0	48.2	34.5	2.8	108.0	1.15	19.4
2	10.5	4.2	62.6	21.5	1.2	92.5	1.28	30.3
3	10.7	3.8	64.6	20.1	0.8	90.1	1.01	48.5
4	11.0	3.9	71.3	13.8	trace	82.5	0.50	49.2

[a] The reactions were carried out at 150C for 2 hr (hydrogen pressure of 150 kg/cm²); 1 mmol of transition metal compound, 5 mmol of $AlEt_3$, 50 ml of hexane as solvent, and 8.5 g of soybean *methyl esters were used in each experiment.*

[b] Catalyst systems: 1. $FeCl_3 \sim AlEt_3$; 2. $CoCl_2 \smile AlEt_3$; 3. $Co(acac)_3 \smile AlEt_3$; 4. $Ni(acac)_3 \sim AlEt_3$.