Determination of the Fatty Acid Composition of Partially Hydrogenated Tung Oils

RALPH W. PLANCK, FRANK C. PACK, DOROTHY C. HEINZELMAN, MACK F. STANSBURY, and ROBERT T. O'CONNOR, *Southern Regional Research Laboratory,*[1] *New Orleans, Louisiana*

KNOWLEDGE of the process whereby conjugated triene systems add hydrogen has remained incomplete because of a lack of satisfactory methods for analyzing the intermediate, partially hydrogenated products. In the introduction to the 1951 revision of the American Oil Chemists' Society's Tentative Method for Polyunsaturated Acids, Cd-7-48 (1), it is stated that "this method is applicable to unhydrogenated animal and vegetable fats containing only small amounts of preconjugated material . . . ." The same restrictions apply to related methods (11, 12) which have been applied to partially hydrogenated trienoic materials even though those methods fail to make adequate correction for the influence of trienoic materials on absorption in the diene region (233 mμ). Hilditch and Pathak (4) followed the course of the hydrogenation of methyl alpha-eleostearate, alone and with other methyl esters, using halogenation and oxidation methods in various combinations with spectrophotometric methods (3), recently discussed elsewhere (6). Isolinoleic acids were not determined as such but were grouped with other dienoic acids. Thompson (11), at the conclusion of an article on the hydrogenation of a tung oil-linseed oil mixture, states that "because of the limitations of the analytical methods, particularly the spectrophotometric methods used for linolein, conjugated linolein, and linolenin, and the arbitrary procedures of arriving at corrected values for these constituents, the composition data . . . must be regarded as only approximations."

The major difficulties that hampered investigators in this field have been overcome by utilizing and extending a recently reported method (6) for the determination of conjugated dienoic and conjugatable linoleic acids in the presence of large amounts of diene and triene conjugation.

Methods of Analysis

Tung oil or partially hydrogenated tung oil was dissolved in cyclohexane and analyzed spectrophotometrically for α- and β-eleostearic acids by the usual method (5). Conjugated dienoic acids were determined on the same solutions, making corrections for eleostearic acids present (6). Conjugatable linoleic acids were converted to conjugated structures by alkali treatment, using the procedures of the American Oil Chemists' Society's Tentative Method for Polyunsaturated Acids, Cd-7-48 (1), (180°, 6.6% KOH in ethylene glycol, 25 min.) and determined by measuring the absorption at 233 mμ, making corrections for various interfering materials (6). The total unsaturation of each hydrogenated oil was obtained by quantitative hydrogenation (7) and checked by a new bromination procedure (9). The content of saturated fatty acids was obtained by a Bertram oxidation procedure (2), modified as indicated below.

Enough oil to yield 1.0-1.5 g. of saturated acids (about 35 g. for tung oil) was placed in a 500-ml. flask with 15 ml. of 0.5 N alcoholic KOH per g. of oil. After refluxing for 25 min. the product was transferred to a casserole, diluted with water, and the alcohol removed on a steam bath. Additional KOH (1 ml. of 50% aq. KOH per g. of oil used) and enough water to form a fluid solution were added. This soap solution was added dropwise from a separatory funnel into a stirred permanganate slurry (200-300 g. of $KMnO_4$, 500 ml. H_2O) in a 4,000-ml. beaker surrounded by circulating cooling water. The rates of addition of the soap solution and of the flow of the cooling water were adjusted to keep the temperature of the permanganate solution below 40°C. After all of the soap solution had been added, the $KMnO_4$ solution was set aside at room temperature for 16-20 hours before being acidified with H_2SO_4, and the excess permanganate reduced with SO_2. The saturated acids were extracted from this solution in the usual manner, and the long-chain ones were purified as described by Pelikan and von Mikusch (8) with the exception that sintered glass filter sticks were used for removing filtrates from the magnesium soaps.

Having learned the content of eleostearic acids, conjugated dienoic acids, and conjugatable dienoic acids from spectrophotometric data, the saturated fatty acids by oxidation, and the hydrogen iodine value (HIV) of the oil, the isolinoleic acid content was calculated from the equation:

$$\text{Isolinoleic acid, } \% = c_i = 1.097 \times \text{HIV} \\ -2.014\, c_e - c_l - c_d + 0.986\, c_s - 94.00,$$

where HIV is the hydrogen iodine value and c_e, c_l, c_d, and c_s are the percentages of eleostearic, linoleic (conjugatable), conjugated dienoic, and saturated acids, respectively. This equation was derived by solving two simultaneous equations, one of which relates the hydrogen iodine value of an oil to its unsaturated acid composition, and a second which takes 95.4 as the fatty acid content of the hydrogenated tung oil after making allowance for the unsaponifiable material normally present in such oils. The monoethenoic acids were determined by difference according to the equation:

$$\text{Monoethenoic acids, } \% = C_m = 95.4 - c_e - \\ c_l - c_d - c_i - c_s$$

Hydrogenation of Oil and Discussion of Results

A sample of screw-pressed, domestic tung oil (1950 crop) of the species *Aleurites fordii* was hydrogenated at 170° with rapid stirring in the presence of 0.1% dry-reduced nickel catalyst and under a pressure of hydrogen of 5 p.s.i.g. Samples for analysis were withdrawn without stopping the hydrogenation, and six of these samples were analyzed by the methods described above. The data are presented in Table I and Figure 1.

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

TABLE I

Composition of Partially hydrogenated tung oils

Hydrogen iodine value	Fatty acid composition, %[a]						
	Eleostearic		Dienoic			Monoethenoic	Saturated
	Alpha	Beta	Conjugated	Conjugatable (linoleic)[b]	Nonconjugatable (isolinoleic)		
231.4	70.0	7.4	1.3	9.2	0(—2.2)	3.1	4.4
195.0	48.9	5.7	7.7	8.4	0(−1.7)	20.2	(4.5)[c]
168.1	32.9	4.1	11.4	(10.8)[d]	0(−1.8)	31.6	(4.6)[c]
140.1	18.8	2.4	13.4	6.2	2.0	47.9	4.7
103.8	3.0	0.9	8.8	5.5	2.4	70.0	4.8
78.8	0.4	0.01	0.7	0.4	2.2	79.8	11.9

[a] Oil basis.
[b] Average value for 2 or more determinations.
[c] Interpolated value.
[d] This value appears to be erroneously high.

The changes in composition of the oil during the course of the hydrogenation agree in general with observations made in other recent investigations (4, 10, 11). The reduction of conjugated triene to diene under the experimental conditions described above is only partially selective in one sense for it is accompanied by a simultaneous, yet somewhat slower, reduction of dienes to monoethenoids. In another sense the addition of the first mole of hydrogen is quite selective as shown by the fact that the conjugated dienoic constituent is the only dienoic constituent that increasd in quantity during the early part of the hydrogenation process. The reduction of polyenes to monoethenoids is shown to be highly selective since nearly all eleostearates and linoleates disappeared before the saturated constituents increased significantly. The persistence of 2% of isolinoleic acid after most of the other polyenoic acids were hydrogenated may be attributed to the low activity of the double bonds in the isolinoleic acids.

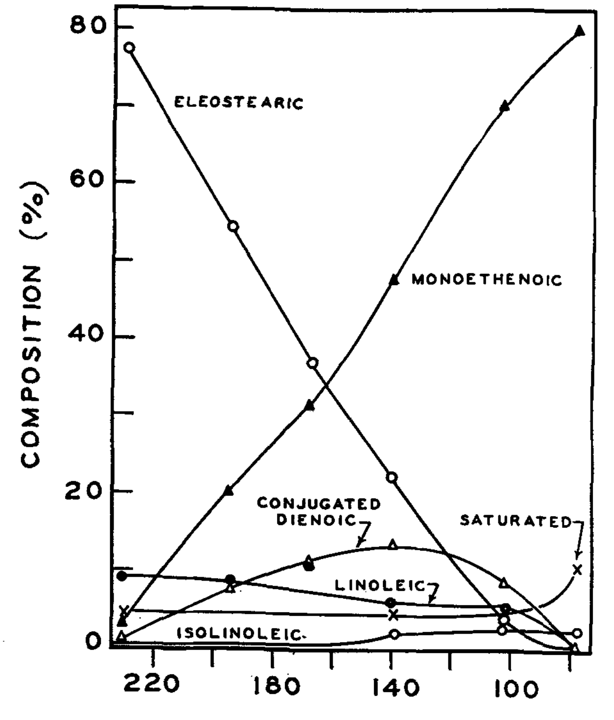

FIG. 1. Changes in fatty acid composition occurring during hydrogenation of tung oil.

Another experiment in which tung oil was hydrogenated at 140° and 50 p.s.i.g. of hydrogen produced similar changes in composition with the exception that less of the conjugated dienoic acids was formed. The maximum was 7% at an iodine value of 130.

The results obtained in this work indicate that with one exception, average values obtained by the analytical methods described above are consistent within about ± 1 percentage unit for all constituents except isolinoleic and monoethenoic acids, for which consistency is reduced to about ± 2.5 percentage units.

Summary

Recently developed spectrophotometric methods for the determination of linoleic and conjugated dienoic acids in the presence of large amounts of eleostearic acid have been applied to the determination of the fatty acid composition of a series of progressively hydrogenated tung oils. Utilizing hydrogen-iodine values and independently obtained values for saturated fatty acids, it has become possible to calculate concentrations of isolinoleic and of monoethenoic acids. Use of these methods gives a more complete and accurate knowledge of the fatty acid composition of a partially hydrogenated tung oil, or mixture of other oils containing the same types of components, than has been obtainable by previously published spectrophotometric methods. They are also much less time-consuming than solvent fractionation methods.

Data are presented which show the changes in fatty acid composition occurring during the hydrogenation (170°, 5 p.s.i.g. H_2, 0.1% Ni) of a domestic tung oil from an iodine value of 231 to 78.

Acknowledgment

The authors wish to thank E. R. Cousins of the Oil Processing Section of the Oilseed Division of this laboratory for assistance in hydrogenating the tung oil.

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[Received July 16, 1953]