EXPRESSED BRAZIL NUT OIL

By H. A. SCHUETTE AND W. W. F. ENZ

The seeds of the Brazil nut tree, *Bertholletea excelsa*, yield an oil whose individuality depends upon the mode of recovery. For example, a "virgin" oil of a color lying between water-white and pale yellow is obtainable by expression, whereas an inferior and materially darker product results when the residual pulp is exhausted with a suitable solvent. Qualitatively there appear to be few, if any, significant differences in the chemical composition of the constituent glycerides of these oils. That they are quantitative was, in a sense, indicated in an earlier communication[1] by the statement that the virgin oil readily solidifies (5–10°) whereas the residual oil does not show a similar behavior.

The evident desirability of verifying this statement has prompted us to repeat quantitatively an analysis once reported qualitatively.[1] Pertinent data are recorded in this communication.

I. Preparation of Materials and Methods of Analysis

The nuts from which this oil was expressed[2] were purchased in the open market during the Christmas holiday season, when the stocks were fresh, confirmatory evidence for which was found in the very low acidity (0.006% as oleic) of the oil. A division of the fatty acids into two groups was effected by application of the lead salt–ether method[3a] with the necessary correction for the small amount of unsaturated acids contaminating the saturated when this procedure is used.[3b] The former (71.74%) were separated and identified by means of their bromine addition products,[4] while the latter (20.28%) were isolated as methyl esters.[5]

II. Analysis of Oil

(a) **Titer Test.**—The solidifying point of the insoluble fatty acids (titer test) is one of the few remaining constants of virgin Brazil nut oil which have not been heretofore reported. It was determined by the usual procedure[6]—the fatty acids were prepared by the glycerol–potassium hydroxide method of saponification—and found to be 33.3°. This value agrees with that reported[1] for the residual oil.

(b) **Unsaturated Acids.**—That linolenic acid is not a constituent of this group was apparent from the fact that no hexabromide separated from the ether solution of the

[1] Schuette, Thomas and Duthey, THIS JOURNAL, **52**, 4114 (1930).

[2] Acknowledgment is made of the assistance given us by Miss Mabel Duthey, who expressed the oil used in this investigation. Filtration was the only operation required for its purification.

[3] (a) Gusserow, *Arch. Apoth.-Vereins nord Teutschland*, **27**, 153 (1828); Varrentrapp, *Ann.*, **25**, 197 (1840); (b) Jamieson, *J. Assoc. Official Agri. Chem.*, **11**, 303 (1928).

[4] Eibener and Muggenthaler, *Farben-Z.*, **18**, 131 (1912).

[5] Baughman and Jamieson, THIS JOURNAL, **42**, 157 (1920).

[6] Association of Official Agricultural Chemists, "Methods of Analysis," Washington, D. C., **1925**, 2d ed., p. 286.

brominated product at $-10°$.   Linoleic and oleic acids, however, are present in appre-
ciable amounts.   The presence of the former was shown in the formation of its tetra-
bromide (m. p. 114°), whereas the latter was indicated by its dibromo derivative (Br,
39.85%).   Using this value and the theoretical iodine numbers of oleic and linoleic acids,
the percentage composition of the whole was then calculated[5] with the results shown in
Table I.

TABLE I

COMPOSITION OF THE UNSATURATED ACID FRACTION

Acid	In oil, %	Glycerides in oil, %	Total,[a] %
Oleic	36.67	41.61	42.79
Linoleic	22.72	25.80	26.54

[a] This column includes the unsaturated acids present with the saturated.

(c)   **Saturated Acids.**—The methyl esters of the saturated acids were separated into
five fractions (Table II) whose boiling range lay between 147 and 163° (3 mm.).   The

TABLE II

RESULTS OF ANALYSIS OF METHYL ESTERS OF THE SATURATED ACIDS

Fraction	Wt., g.	Iodine no.	Sapon. no.	Mean mol. wt.	Unsatd. acids, wt.	Myristic acid, g.	Palmitic acid, g.	Stearic acid, g.
1	10.23	7.3	209.8	267.5	0.73	1.53	7.48	..
2	17.62	5.5	202.8	276.6	0.94	..	12.74	3.09
3	31.00	6.6	200.0	280.5	1.99	..	18.44	9.12
4	9.71	7.5	197.8	283.6	0.71	..	4.71	3.84
5	3.62	7.6	195.3	287.2	0.27	..	1.33	1.86
Res.	4.94	12.9	...	...	..	..	..	..
Total	..	...	...	...	..	1.53	44.70	17.91

mean molecular weights of the respective fractions as calculated from saponification and
iodine numbers—the latter serving as a basis for correcting each for the presence of un-
saturated acids—indicated the presence of acids in the C_{14} to C_{18} group.   These data lead
to the following statement of the percentage composition of the saturated acid fraction.

TABLE III

COMPOSITION OF THE SATURATED ACID FRACTION

Acid	In oil, %	Glycerides in oil, %
Myristic	0.47	0.48
Palmitic	11.97	13.74
Stearic	4.80	5.45
Undetermined	1.61	..

Summary

    The approximate percentage composition of a sample of virgin Brazil nut
oil has been found to be myristin, 0.48; palmitin, 13.74; stearin, 5.45;
olein, 42.79; linolein, 26.54.   Its solidifying point is higher than that of
the oil recoverable from the residual pulp, a difference which is apparently
largely due to a lower olein content.   The linolein and palmitin contents
of both grades of oil are of the same order of magnitude.   Myristin, on the
other hand, is present in the virgin oil to the extent of one-fourth as much

as in the product of lower quality. The former contains approximately twice as much stearin as the latter.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE REDUCTION OF AROMATIC KETONES AND BENZILS BY TRIPHENYLMETHYLMAGNESIUM BROMIDE
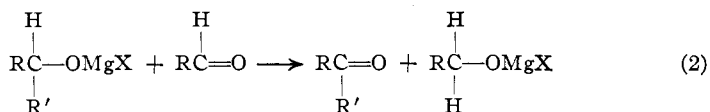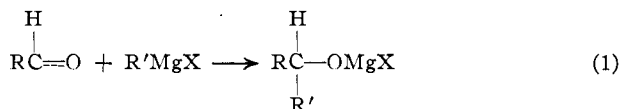
BY W. E. BACHMANN

It is clear that the reduction which so frequently occurs in the Grignard reaction may be occasioned in several ways.[1] It has long been known that aliphatic Grignard reagents can exercise a reducing action toward certain compounds; as a rule an unsaturated hydrocarbon is formed in addition to the reduction product.

The work of Gomberg and Bachmann[2] on the reducing action of a mixture of magnesium and magnesium iodide has made it obvious that the Grignard reagent must be filtered from unused magnesium if reduction by this system is to be avoided. A number of instances have been reported in which reduction occurred when unused magnesium was allowed to remain in the Grignard reagent.[3]

Marshall[4] discovered that a mutual oxidation and reduction reaction may occur between excess of an aldehyde and the normal addition compound which is formed by the action of a Grignard reagent on the aldehyde. The reaction which occurs may be formulated as follows

$$\underset{\text{R}\overset{\displaystyle H}{\overset{|}{\text{C}}}{=}\text{O}}{} + \text{R'MgX} \longrightarrow \text{R}\overset{\displaystyle H}{\underset{\displaystyle \text{R'}}{\overset{|}{\underset{|}{\text{C}}}}}\text{—OMgX} \qquad (1)$$

$$\text{R}\overset{\displaystyle H}{\underset{\displaystyle \text{R'}}{\overset{|}{\underset{|}{\text{C}}}}}\text{—OMgX} + \text{R}\overset{\displaystyle H}{\overset{|}{\text{C}}}{=}\text{O} \longrightarrow \text{R}\overset{\displaystyle H}{\underset{\displaystyle \text{R'}}{\overset{|}{\underset{|}{\text{C}}}}}{=}\text{O} + \text{R}\overset{\displaystyle H}{\underset{\displaystyle \text{H}}{\overset{|}{\underset{|}{\text{C}}}}}\text{—OMgX} \qquad (2)$$

The reaction involves a transfer of H and MgX from a molecule of the secondary alcohol to a molecule of aldehyde; the products are a ketone and a primary alcohol. The importance of this mode of reduction has been overlooked to a great extent; its applicability has been indicated by

[1] See Noller, THIS JOURNAL, 53, 635 (1931).

[2] Gomberg and Bachmann, ibid., 49, 236 (1927); 49, 2584 (1927); 50, 2762 (1928); 52, 4967 (1930).

[3] See for example Boyd and Hatt, J. Chem. Soc., 898 (1927); Hatt, ibid., 1623 (1929); Barnett, Cook and Nixon, ibid., 505 (1927); Lagrave, Ann. chim., [10] 8, 363 (1927).

[4] Marshall, J. Chem. Soc., 105, 527 (1914); 107, 509 (1915); 127, 2184 (1925).