

was heated under reflux in an oil-bath at 110–120° for two hours. Distillation of the reaction mixture yielded small amounts of unreacted acrylic and secondary amino esters and 11.6 g. (80%) of tertiary amino ester (II).

Summary

It has been found that when ethyl β -methylaminopropionate is allowed to react with either ethyl β -bromoisobutyrate or ethyl α -methylacrylate the product obtained is not the expected β -carbethoxyethyl- β -carbethoxypropylmethylamine, but is β, β' -dicarbethoxyethylmethylamine which is formed by the elimination of methyl amine (or its salt) from two molecules of the secondary amino ester.

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RYE GERM OIL

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Little published information¹ on the composition of the oil in rye, *Secale cereale* L., is available. That which has found its way into the literature is of European origin and is not pertinent to the same type of product in each instance inasmuch as the whole kernel,^{1a,d,h} its bran,^{1b} its embryo^{1g} and its flour^{1c,h} and breads^{1h} baked therefrom have been used as the sources of the oil or "ether extract," under examination. The inevitable result of this diversity in selection of raw material has been a lack of correlation of data.² Furthermore, with one exception,^{1h} all of the reports in question are incomplete when viewed in the light of the newer trends in the technique of fatty oil analysis.

Unlike the embryo oils of other cereals such as corn and wheat, rye oil finds at present no important technical or alimentary use. The facts that it is apparently rich in the carotinoid pigments, that it contains a high percentage of lecithin-bearing unsaponifiable matter, and that the antimony trichloride test which is presumed to be indicative of the presence of vitamin A is positive, suggest the thought that the clinical advantages of

¹ (a) König, *Landw. Vers. Sta.*, **17**, 1 (1874); (b) Stellwaag, *ibid.*, **37**, 135 (1890); (c) Spaeth, *Forschungsber. Lebensm.*, **3**, 251 (1896), through *Z. Nahr. Genussm.*, **11**, 410 (1896); (d) Meyer, *Chem.-Ztg.*, **27**, 958 (1903); (e) Grimme, *Seifensieder-Ztg.*, **45**, 704 (1918); (f) Herbig, *Seifenfabrikant*, **38**, 497 (1918); (g) Alpers, *Chem.-Ztg.*, **42**, 37 (1918); (h) Croxford, *Analyst*, **55**, 735 (1930).

² This is particularly noticeable in the description of the color—it has been variously reported as being dark green to yellowish-brown—and other external characteristics of the oil and in the records of its simpler chemical constants. Iodine numbers, for example, have been reported as lying between 81.8 and 127.7; saponification numbers between 172.8 and 196.0; and the content of unsaponifiable matter to vary between 8.2 and 11.20%.

the presence of rye oil in the diet might profitably be investigated. There are, however, obvious needs both for a definition of the term rye oil and a better knowledge of the chemistry of the lipin which is elaborated in the embryo or germ of the kernel. Precedent and consistency, it seems, dictate that, apart from all the substances recoverable by solvent extraction from this cereal grain and its products, the term rye oil should be reserved for the constituent in question in the embryo.

A re-investigation of this oil appears then justified in view of the unsatisfactory state of our knowledge of its chemistry and the fact that no record appears to be extant on a domestic product which had been recovered exclusively from the embryo. A report of such a study is made the subject of this communication.

I. Preparation of Material

The oil in question was obtained by extracting with sulfur-free petroleum ether (b. p. 30–60°) rye embryo (oil content 11%) recovered by repeated sifting and air cleaning of so-called rye germ stock,³ a by-product in the milling of the grain. The last traces of solvent were removed by distillation at reduced pressures on a water-bath and in the presence of carbon dioxide. The oil was found to be of a deep golden-brown color. It possesses an odor suggestive of the grain itself and, in contradistinction to the report that rye oil is of a semi-solid consistency at 15°,^{1h} was found still to be plastic at –60°.

II. Analysis of the Oil

(a) **Chemical and Physical Characteristics.**—The important chemical and physical constants (Table I) were determined by recognized procedures.⁴ In the determination of the thiocyanogen number of the fatty acids and the interpretation of this constant the procedure of Kaufmann was followed.⁵ Because of the presence of the relatively large quantities of unsaponifiable matter, this was first removed before the acids were subjected to analysis. Separation of the fatty acids into saturated and unsaturated groups was effected by the lead salt-ether^{6a} method, after which corrections were made for the small amount of unsaturated acids contaminating the former, when this procedure is used,^{6b} and for the unsaponifiable matter accompanying the insoluble acids.

³ Acknowledgment is made to the Messrs. Frank H. Blodgett, Inc., of Janesville, Wisconsin, who by gratuitously placing at our disposal some two hundred pounds of this material, made possible this investigation.

⁴ Association of Official Agricultural Chemists, "Methods of Analysis," Washington, D. C., 1930, 3d ed., pp. 314–330.

⁵ Kaufmann, *Z. nahr. Genusssm.*, 51, 15 (1926); "Deutsche Einheitsmethoden," 1930, Wizoff, Stuttgart, 1930, pp. 94–97.

⁶ (a) Gusserow, *Arch. Apoth.-Vereins nord. Teutschland*, 27, 153 (1828); Varrentrapp, *Ann.*, 35, 196 (1840); (b) Jamieson, *J. Assoc. Official Agri. Chem.*, 11, 303 (1928).

TABLE I
CHEMICAL AND PHYSICAL CHARACTERISTICS OF RYE GERM OIL

Specific gravity 20/20°	0.9229
Index of refraction, 20°	1.4779
Titer test, °C.	25.2
Iodine number ^a (Wijs)	139.91
Saponification number	176.81
Reichert-Meissl number	0.05
Polenske number	.3
Free fatty acids (per cent. oleic)	2.9
Acetyl number	20.19
Soluble acids (per cent. as butyric)	trace
Insoluble acids (Hegner number) ^b	84.45
Iodine number (Wijs) of insoluble fatty acids ^b	133.57
Thiocyanogen number of insoluble fatty acids ^b	85.05
Unsaturated acids (per cent.) corrected	77.46
Saturated fatty acids (per cent.) corrected	10.12
Iodine number of unsaturated acids (Wijs)	158.90
Saponification number of unsaturated acids	172.6
Unsaponifiable matter (per cent.)	7.28

^a The iodine number when determined by the Hanus method was found to be 134.0. This figure represents an average of four determinations. ^b Corrected for unsaponifiable matter.

(b) **Unsaturated Acids.**—Separation of the unsaturated acids was effected through the preparation of their bromo addition compounds and the fractional separation of the mixture into its components by the use, in turn, of diethyl and petroleum ethers.⁷ The presence of linolenic acid was indicated by the formation of an ethyl ether-insoluble precipitate in the cold (-10°). Analysis proved the latter to be the hexabromide of this acid. A considerable quantity of the tetrabromo derivative of linoleic acid (Br, 53.62%) separated from the cold petroleum ether solution. The bromine content (43.43%) of the dibromide fraction showed it to be a mixture of this compound and the tetrabromo derivative. Using the latter value and those expressing the bromine content of the oleic and linoleic derivatives, respectively, the percentage composition of the mixture was calculated.⁸

The composition of this fraction was also arrived at, and perhaps with greater accuracy of results since gravimetric separations are not involved, by the mode of procedure suggested by Kaufmann,⁵ a scheme of analysis in which the iodine (133.57) and thiocyanogen (85.05) numbers of the purified fatty acids become the point of departure in a mathematical calculation. Exact agreement was not obtained by these two different methods of approach, yet the order of magnitude of the quantities of each acid present is substantially the same (Table II).

⁷ Eibener and Muggenthaler, *Farben-Ztg.*, **18**, 131 (1912).

⁸ Baughman and Jamieson, *THIS JOURNAL*, **42**, 157 (1920).

TABLE II
PERCENTAGE COMPOSITION OF THE UNSATURATED ACID FRACTION

Acid	In oil		Glycerides in oil	
	Obs. ^a	Calcd. ^b	Obs. ^a	Calcd. ^b
Oleic	36.17	30.54	37.79	31.92
Linoleic	38.92	42.14	40.68	44.05
Linolenic	2.37	4.78	2.48	4.99

^a From bromine addition products. ^b From thiocyanogen number.

(c) **Saturated Acids.**—The methyl esters of the saturated acids were separated into five fractions (Table III) of boiling range 163 to 181° (5 mm). The average 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 unsaturated acids—indicated the presence of acids in the C₁₄ to C₁₈ group.

TABLE III
RESULTS OF ANALYSES OF METHYL ESTERS OF THE SATURATED FATTY ACIDS

Fraction	Wt., g.	Iodine no.	Sapon. no.	Mean mol. wt.	Myristic ester	Palmitic ester	Stearic ester
1	7.30	2.76	215.6	257.6	3.203	3.894	...
2	9.72	3.37	211.2	265.0	1.745	7.759	...
3	15.68	7.56	209.5	266.4	2.024	11.876	...
4	2.30	22.59	209.3	263.8	0.450	1.507	...
5	1.01	43.25	196.5	270.7	...	0.686	...
Res.	3.35					.432	0.598
Total					7.422	26.154	.598

These data lead to the following statement of the percentage composition of the saturated acid fraction.

TABLE IV
PERCENTAGE COMPOSITION OF THE SATURATED ACID FRACTION

Acid	Myristic	Palmitic	Stearic
In oil	2.21	7.73	0.17
Glycerides in oil	2.33	8.11	.18

(d) **Miscellaneous.**—The phosphorus content of both the oil itself and its unsaponifiable matter was determined in the usual manner after the organic matter, saturated with sodium hydroxide solution, had been destroyed by incinerating it. From the data so obtained the lecithin equivalent of a hypothetical di-oleyl derivative (C₄₄H₈₆O₉NP) was calculated. It was found to be 1.33% for the oil and 3.05% for its unsaponifiable matter. The former value is somewhat higher than the lecithin content (1.04%) of a purified rye oil reported by Alpers¹⁸ but less than that found by him (3.04%) in a crude oil. It compares very favorably with the lecithin content of a corn oil (1.49%) examined by Hopkins⁹ but is

⁹ Hopkins, THIS JOURNAL, 20, 948 (1898).

lower than that found in wheat germ oil (2.00%) by Frankforter and Harding.¹⁰

The deep golden-brown color of this oil suggests the presence of the carotinoid pigments. In view of the fact that vitamin A potency is now generally associated with carotene, and since the antimony chloride reaction¹¹ is presumed to indicate its presence, application of this test bid fair to lead to affirmative results.

When the oil itself was added to a chloroform solution of this salt, a strong blue coloration appeared. The unsaponifiable matter which had been extracted with ethyl ether gave a stronger reaction than did that recovered by treatment with petroleum ether, a condition which is probably due to the fact that the latter removes less coloring matter from the oil than does the former.

Summary

The more important physical and chemical characteristics and the approximate percentage composition of rye germ oil have been determined. It is a semi-drying oil which is characterized by the quantity of heavily pigmented unsaponifiable matter which it contains. Correlation of its constants with those obtained by others, with perhaps one exception,¹⁸ cannot satisfactorily be made because of the diversity of products which have been included under the name rye oil.

The percentage composition of this oil was found to be as follows: myristin, 2.33; palmitin, 8.11; stearin, 0.18; olein, 31.92; linolein, 44.05; linolenin, 4.99; unsaponifiable matter, 7.28; undetermined, 1.14.

¹⁰ Frankforter and Harding, *THIS JOURNAL*, 21, 758 (1899).

¹¹ Carr and Price, *Biochem. J.*, 20, 497 (1926).

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[CONTRIBUTION FROM THE EXPERIMENTAL RESEARCH LABORATORIES, BURROUGHS
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MIXED BENZOINS. VIII. FURTHER DETERMINATIONS OF STRUCTURES. QUESTION OF ISOMERS

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The present paper deals mainly with the determination of the structure of a number of mixed benzoin, most of them new, in continuation of the authors' purpose to characterize a sufficiently large number of mixed benzoin to enable worth-while deductions to be made regarding the reactivity of aldehydes. The method used depends on the Beckmann transformation of the second type, previously used and described in Part IV.¹ The reaction appears to be trustworthy, as no results so far obtained contradict

¹ Buck and Ide, *THIS JOURNAL*, 53, 1912 (1931).