[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

Rye Oil. II. Properties as Affected by Choice of Menstruum

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Because of the variety of solvents available for the extraction of fatty oils and the fact that the menstruum employed is characterized to some extent by the kind and amount of the non-oil constituents which it removes from the mother substance, there arises a need for data pertinent to rye oil, the subject[1] of an investigation in this Laboratory. Such data are herein communicated with respect to three chlorinated hydrocarbons, one sulfur- and two oxygen-containing compounds, a cyclic hydrocarbon, and petroleum ether (b. p. 40–60°).

Experimental Procedure

One-kg. lots of thoroughly cleaned rye embryos which had been milled from the 1932 crop were exhausted in an intermittent type of extractor with redistilled solvents, the criterion of purity being the boiling point ascribed in the literature to the compound in question. Purification of the resulting oil was simple: removal of the last traces of the solvent by low-temperature distillation under reduced pressure and in the presence of carbon dioxide, then filtration through asbestos. The resulting oils were clear and bright but not of the same color.

The degree of pigmentation of a 1% petroleum ether solution of the oil was measured with a Rosenheim–Schuster colorimeter by means of which one arrives at the color in the Lovibond system. Unsaponifiable matter was determined by the method recommended by the Sub-Committee on Determination of Unsaponifiable Matter in Fats and Oils of the Society of Public Analysts.[2] A modification[3] of the Denigès ceruleomolybdic method was used for the determination of phosphorus. These data are here tentatively reported in terms of the lecithin equivalent of a hypothetical di-oleyl derivative ($C_{44}H_{88}O_9NP$). The other analytical procedures were the standard ones recommended for the purpose in question.

Results

When the solvents (Table I) are arranged in the order of ascending yields of oil obtained, it appears that petroleum ether is the least but that acetone is the most efficient menstruum. The latter follows chloroform in this respect, yet carbon tetrachloride does not fit into such a picture. Parallels cannot be drawn throughout the series as a whole except, perhaps, in the case of a few pairs. For example, the oxygen-containing solvents, ethyl ether and acetone, produce oils of practically the same density and content of phosphorus and unsaponifiable matter. Those oils which are the products of recovery with chloroform and carbon tetrachloride possess the same refractive index and approximately the same content of unsaponifiable matter, or 8.09 and 8.25%, respectively. But here the points of similarity end. A particularly noticeable difference is apparent in the phosphorus content of the oils recovered with the aid of these solvents, the former containing over twice (2.3 times) as much as the latter. It has been pointed out previously that one of the characteristics[1] of this oil is the quantity of unsaponifiable matter which it contains. This observation may now be amended to the extent of stating that rye oils obtained by extraction with carbon disulfide are particularly rich in this constituent.

TABLE I

CERTAIN CHARACTERISTICS OF RYE OIL AS AFFECTED BY SOLVENT USED IN ITS EXTRACTION FROM THE EMBRYO

Solvent	Oil yield, %	Color[a] Yellow	Color[a] Red	Sp. gr. 25/25°	Index of refr., 20°	Iodine no. (Wijs)	Unsaponifiable matter, %	Lecithin ($P \times 26$), %
Petroleum ether	11.46	3.5	0.5	0.9220	1.4750	138.42	9.34	1.03
Ethyl ether	13.66	3.2	.5	.9297	1.4732	135.05	8.95	1.78
Carbon tetrachloride	13.84	2.1	.8	.9341	1.4773	137.44	8.25	3.18
Ethylene dichloride	14.13	4.9	.6	.9329	1.4781	139.03	8.86	3.75
Carbon disulfide	14.14	6.1	.4	.9296	1.4780	139.50	10.00	2.97
Benzene	14.45	4.4	.5	.9308	1.4789	133.80	9.08	4.11
Chloroform	15.57	3.5	.6	.9483	1.4772	133.90	8.09	7.26
Acetone	17.23	3.7	.7	.9286	1.4753	136.85	9.01	1.67

[a] Dilution of oil: one per cent. solution in petroleum ether.

Summary

As a result of this investigation of the relation of eight different solvents to the properties of rye oil,

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[1] Stout and Schuette, THIS JOURNAL, **54**, 3298 (1932).

[2] *Analyst*, **58**, 203 (1933).

[3] Juday *et al.*, *Trans. Wisconsin Acad. Sci.*, **23**, 233 (1927).

it is evident that the quantity of the latter (11.46 to 17.23%) which can be recovered from the germ or embryo is a function of the former. Furthermore, this observation holds true also of the degree of pigmentation of the oil, its physical and chemical constants, and the content of unsaponifiable matter and phosphorus. It appears also that the yields of oil which may be expected assume the following order: petroleum ether $<$ ethyl ether $<$ carbon tetrachloride $<$ ethylene dichloride $<$ carbon disulfide $<$ benzene $<$ chloroform $<$ acetone.

The following minima and maxima were noted: d^{25} 0.9220 and 0.9483; n^{20} 1.4732 and 1.4789; iodine number 133.8 and 139.5; percentage of unsaponifiable matter 8.09 and 10.00; percentage of phosphorus (tentatively recorded as lecithin equivalent) 1.03 and 7.26.

MADISON, WIS. RECEIVED SEPTEMBER 14, 1933

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Tautomerism of Alpha Diketones. I. Benzyl Phenyl Diketone

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At the time this investigation was planned little was known about the enolization of alpha diketones and still less concerning the manner in which they are alkylated and acylated. The work was hardly under way when Dufraisse and Moureu[1] published the first of a series of papers dealing with the preparation and properties of alpha diketones. Their work was continued by Moureu and finally presented as an admirable study of benzyl methyl diketone, benzyl phenyl diketone and a few other related substances.[2] Moureu supplied the answer to many of the questions we were asking, but since he emphasized the great similarity of alpha and beta diketones while we were interested especially in the differences between these closely related types, he also left a number unanswered.

Our interest in the physical properties of the tautomeric modifications of the diketone centered in chelation. The only plausible explanation for the relatively high volatility of the enolic modification of acetoacetic ester, its great solubility in non-polar solvents and the physical properties of many of its metallic derivatives has been offered by Sidgwick,[3] who accounted for these peculiarities by means of the cyclic formula proposed by Hantzsch.[4] In view of the work of Mills and Gotts[5] it can scarcely be doubted that the enolic modifications of beta ketonic esters and beta diketones are chelated at the ordinary temperature but it is surprising that these rings should persist at the high temperatures at which these substances boil. It was desirable, therefore, to compare the physical properties of a pair of tautomers in which chelation is less probable. Benzyl phenyl diketone served this purpose.

Since 5-rings with but one double bond are relatively unstable it is improbable that the enolic modification of an alpha diketone could form a chelate ring involving a hydrogen bond; alpha diketones should, therefore, lack the peculiar physical properties of acetoacetic ester. We found, in agreement with Moureu, that the enol of benzyl phenyl diketone is far less volatile than the ketone. And we also found that while the solubility of the two forms is almost the same in alcohol and chloroform, the enol is almost completely insoluble in petroleum ether. In contrast with acetoacetic ester, the physical properties of the two modifications are those which would be expected if one were a hydroxyl and the other a carbonyl compound.

With respect to the chemical properties, we were interested first of all in the autoxidation. Many years ago it was found that the enolic modifications of certain mono ketones combine rapidly with oxygen to form crystalline peroxides.[6] Despite many attempts it has not been possible to find any other type of enol capable of combining with oxygen or any other ethylenic compound that would form a monomeric crystalline peroxide. When we discovered the avidity with which alkaline solutions of alpha oxido ketones combine with oxygen we attributed it to the enolic forms and hoped to secure the peroxides. We found that a peroxide of some kind is formed when oxygen is passed into solutions of benzyl

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(1) Dufraisse and Moureu, *Bull. soc. chim.*, [4] **41**, 1613 (1912).

(2) Moureu, *Ann. chim.*, [10] **14**, 303 (1930).

(3) Sidgwick, *J. Chem. Soc.*, **127**, 907 (1925).

(4) Hantzsch, *Ber.*, **43**, 3053 (1910).

(5) Mills and Gotts, *J. Chem. Soc.*, 3121 (1926).

(6) Kohler, *Am. Chem. J.*, **36**, 177 (1906).