The Chemical Composition of Ergot Oil

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ERGOT is the dried sclerotium of *Claviceps pur purea* (Tulasne) developed on rye plants. The same fungus, or one closely related, grows on a number of other grasses. It was the original source of ergosterol (Tanret Ann. Chim. Phys. (6), *20*, 289 (1890); ibid (8), *15*, 313 (1908)), but this sterol has now been identified in a wide range of lower plants, for example, certain yeasts and in a number of animal and vegetable fatty oils. Rosenheim and Webster (Biochem. Jour. *21*, 389 (1927)) also Windaus and Hess (Nachr. Ges. Wiss. Göttingen, 1927, 175) have advanced the opinion that ergosterol or a highly unsaturated sterol of similar constitution is the natural parent substance of antirachitic vitamin D, and is converted into vitamin D by irradiation with ultra-violet light.

Ergot contains a fatty oil which it is necessary to extract with petroleum ether before preparing the fluid extract used in medicine (U. S. Pharmacopœia X, pp. 133, 167). This oil has been the subject of investigations at different times for many years, Wiggers (Annalen *1*, 129 (1832) as early as 1832 reported that ergot contained 35 per cent of fatty oil. Herrmann, (Jahresber, Pharm. 1869), Ludwig (ibid 1869, 25) and Gauser (ibid 1871, 13) made short communications concerning the oil. Most of the investigators have found that the oil gives a high acetyl number and have described it as containing hydroxyoleic acid. Mjöen (Arch. Pharm. 234, 278 (1896)) gave 62.9 as the acetyl number, and stated that he found the oil to contain glycerides of palmitic acid, oleic acid, and a hydroxy fatty acid which he had not succeeded in isolating. Rathje (Arch. Pharm., *246*, 696 (1908)) reported the acetyl number as 27.4, and the percentage composition as follows: oleic acid, 68 per cent; hydroxyoleic acid, 22 per cent; and palmitic acid, 5 per cent. The composition obtained by Dieterle, Diester and Thimann (Archiv. Pharm., *265*, 171 (1927)) as a result of their elaborate investigation was: palmitic, daturic, and other saturated acids, 20.5 per cent; ω-linolic acid, 4.6 per cent; and oleic acid, 71.0 per cent. They could not prove the presence of hydroxy fatty acid. The oil used by them gave an acetyl number of 60.4, but the insoluble fatty acids prepared from this oil gave an acetyl number of only 20.6, and they expressed the opinion that the high acetyl number of the oil may have been caused by the presence of mono- and diglycerides. Finally, Matthes and Schütz (Arch. Pharm., *265*, 541 (1927)) claim to have isolated hydroxyoleic acid and dibromide from the bromides of the liquid acids by treatment with petroleum ether at low temperature and to have obtained pure hydroxyoleic acid by reducing this dibromide with zinc.

The authors recently received a two-liter sample of ergot oil from the Drug Control Laboratory, Food,

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Drug and Insecticide Administration, Department of Agriculture, and on account of the meager knowledge regarding the composition of the oil available in the literature it was thought worth while to make a rather extensive examination of it. The oil had been extracted in the Drug Laboratory with petroleum ether from a composite sample of Russian, Spanish, and Austrian ergot. This composite sample of ergot contained 5.50 per cent moisture and 32.75 per cent oil, which is equivalent to 34.66 per cent (dry basis) oil. This sample of oil was dark red by transmitted light, but by reflected light there was a dark brownish yellow fluorescence. However, other samples of ergot oil have been seen which had a light yellow color. At room temperature the oil was viscous but less so than castor oil. After standing in the ice box (10°-12° C.) for a month it became more viscous of course, but did not deposit any stearin.

Chemical and Physical Characteristics. — The more important characteristics were determined, and the results are reported in Table I. The iodine number indicates that it is a non-drying oil, and the very low Reichert-Meissl and Polenske numbers show that glycerides of volatile acids are absent. The acetyl value is low and indicates that hydroxylated acid is not present in an appreciable quantity. A second sample of oil extracted from a different lot of ergot gave an acetyl value of 11.0. The percentages of saturated and unsaturated fatty acids were determined by the lead salt-ether method, and corrections were made for the small quantity of unsaturated acids that separates with the saturated acids fraction as indicated by the iodine number of the saturated acids fraction (J. A. C. S. *42*, 2398 (1920); Cotton Oil Press *6*, No. 1, 41 (1922)) and it was also taken into account that the unsaponifiable matter separates with the unsaturated acids fraction, in this determination.

TABLE I

Ergot Oil

Chemical and Physical Characteristics

Specific gravity 25°/25°	0.9222
Refractive index, 25°	1.4691
Acid value	3.02
Iodine number (Hanus)	73.8
Saponification value	196.9
Unsaponifiable matter (%)	1.18
Acetyl value	7.3
Reichert-Meissl number	0.3
Polenske number	0.4
Saturated acids as determined (%)	27.2*
Unsaturated acids plus unsaponifiable matter as determined (%)	68.6
Iodine number of unsaturated acids	101.2
Saturated acids (corrected) (%)	26.5
Unsaturated acids (corrected) (%)	68.1

*Iodine number, 2.6

Unsaturated Acids.—The iodine number of the unsaturated acids fraction (101.2) lies between the theoretical iodine numbers of oleic acid (90.1) and linolic acid (181.4). The saponification value, as determined, of the unsaturated acids fraction containing the unsaponifiable matter is. 193.8. Making allowance for the unsaponifiable matter the saponification value of the unsaturated acids becomes 197.2. This figure is close to the theoretical values for oleic acid (198.65) and linolic acid (200.1). These data indicate that this fraction of the fatty acids consists of oleic and linolic acids. The following percentages were calculated from the foregoing iodine numbers.

	Per cent	In original oil Per cent	Glycerides in original oil Per cent
Oleic acid	87.84	59.8	62.5
Linolic acid	12.16	8.3	8.7
	100.00	68.1	71.2

Saturated Acids.—A quantity of saturated acids, prepared by the lead salt-ether method, was esterified with methyl alcohol (J. A. C. S. *42*, 1200 (1920)). The mixture of methyl esters, which weighed 118 g., was fractionally distilled under diminished pressure. The data for this distillation are given in Table II. A preliminary distillation from a 1-liter Claissen flask resulted in six fractions designated by the letters A to F, and a residue. These preliminary fractions were redistilled from a 250 cc. Ladenburg flask as indicated in the table, and seven fractions and a residue were obtained.

The iodine numbers, which are measures of the contaminating unsaturated acids, and the saponification values of the final fractions were determined, Columns 2 and 3 of Table III give the results. From these data the mean molecular weights of the saturated acid esters in each fraction were calculated; the results are recorded in Column, 6, Table III (J. A. C. S., *42*, 152, 1197 (1920)). The results in Column 6 indicate what saturated acid esters may be present in the various fractions. The result for Fraction 1 lies between the molecular weights of methyl myristate (242.3) and methyl palmitate (270.3) and suggests therefore the presence of these two esters. The indicated constituents for Fractions 2 to 6 are methyl palmitate and methyl stearate (298.4), and for Fraction 7, methyl stearate and methyl arachidate (326.4).

The free acids were recovered from some of these fractions, and the constituent saturated acids were isolated by fractional crystallization from alcohol. Their identities were established by their melting points and by observing whether or not these melting points were lowered when the substances were mixed with equal quantities of the respective acids which they were suspected of being, the purity of which had been established previously by elementary anaylsis. In all cases the melting points of the isolated acids confirmed the deductions drawn from the mean

molecular weights of the fractions.

Pure myristic acid was isolated from Fraction 1; pure palmitic acid was obtained from Fractions 1 and 3; stearic acid, from Fractions 2 and 3; and arachidic acid, from Fraction 7 and from the final residue. This residue, however, was composed mostly of decomposition products and was not taken into account in calculating the quantities of saturated acids.

The quantities in the various fractions were calculated from the mean molecular weights of the saturated acid esters (Col. 6, Table III), and the theoretical molecular weights of the two esters in each fraction. The results are given in Columns 7-14, Table III. The saturated acids data are summed up in Table IV, and the equivalent percentages of glycerides in the original oil are given in Column 4.

TABLE II

Ergot Oil

Fractional Distillation of Methyl Esters of Saturated Acids

(118 g. subjected to distillation.) Distillation at 8 mm. pressure

	Fraction	Temperature °C.	Weight g.
	A	183–5	19.9
	B	185	21.6
	C	186–7	22.8
	D	187–8	22.4
	E	188–198	21.1
	F	198-218	6.1
	Residue		4.1
Fractions A and B redistilled.....	1	183–4	6.8
	2	185–7	23.0
Fractions C and D added.....	3	188	23.7
	4	188	23.5
Fraction E added	5	190–5	22.0
Fraction F and residue added.....	6	197–207	12.4
	7	207–225	6.2
	Residue		0.4

TABLE III

Ergot Oil

Results of Analyses of Fractions Obtained by Distilling Methyl Esters of Saturated Acids

Fraction	Iodine Number	Saponification Value	Mean Molecular Weight	Esters of Unsaturated Acids, %	Mean Molecular Weight of Esters of Saturated Acid	Myristic Acid		Palmitic Acid		Stearic Acid		Arachidic Acid	
						%	g.	%	g.	%	g.	%	g.
1	1.2	211.3	265.5	1.24	265.1	17.28	1.18	76.25	5.18	....	....	....	....
2	0.7	206.9	271.1	0.73	271.0	....	...	91.79	21.11	2.35	0.54	....	....
3	1.3	205.5	273.0	1.35	272.9	....	...	84.88	20.12	8.70	2.06	....	....
4	1.3	204.9	273.8	1.35	273.5	....	...	82.88	19.48	10.71	2.52	....	....
5	3.6	201.3	278.7	3.73	278.1	....	...	65.95	14.51	25.47	5.60	....	....
6	6.9	193.4	290.1	7.16	289.6	....	...	27.57	3.42	60.77	7.54	....	....
7	12.6	180.7	310.5	13.07	312.9	....	...	....	....	39.94	2.48	43.09	2.67
	....	.....	.....	....	....	....	1.18	....	83.82	....	20.74	....	2.67

TABLE IV

Ergot Oil—Saturated Acids

Acid	Acids in saturated acid fraction		Acids in original oil	Glycerides in original oil
	Grams	Per cent	Per cent	Per cent
Myristic	1.18	1.09	0.29	0.3
Palmitic	83.82	77.32	20.49	21.5
Stearic	20.74	19.13	5.07	5.3
Arachidic	2.67	2.46	0.65	0.7
	108.41	100.00	26.50	27.8

Summary

The chemical composition of ergot oil has been determined with the results given below:

		Per cent
Glycerides of	Oleic acid	62.5
	Linolic acid	8.7
	Myristic acid	0.3
	Palmitic acid	21.5
	Stearic acid	5.3
	Arachidic acid	0.7
Unsaponifiable matter		1.2

It was not possible to detect in this oil either daturic acid or hydroxylated acid, which have been reported as present by other investigators.

Book Reviews

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