NON-HEPTANE CONSTITUENTS OF DIGGER PINE (PINUS SABINANA).

BY ARTHUR H. UHL.*

In 1928, Foote (1), in coöperation with the Ethyl Gasolene Corporation of Yonkers, N. Y., rectified the principal constituent of Jeffrey Pine oil, heptane. The non-heptane constituents of the oil were further investigated. This investigation revealed the presence of *n*-octylic, *n*-nonylic and *n*-decylic aldehydes.

Approximately 20 gallons of that portion of the oil of digger pine which boils above 110° was received from the California Chemical Corporation. The heptane which constitutes approximately 90–93 per cent (2) of the oil had been previously removed. The 20 gallons, therefore, represented between 1800 and 1900 gallons of the original oil.

Isolation of the Aldehydes.—The aldehydes were removed from the oil by shaking with a 30% solution of sodium acid sulphite. The solid addition product was separated on a force filter and washed with ether. The aldehydes were regenerated by treatment with sodium carbonate and separated by steam distillation. There resulted 625 Gm. of aldehydes. The aqueous sulphite mother liquor was treated likewise and an additional 51 Gm. were obtained.

Identification of the Aldehydes.—Because excess heating was likely to destroy or change some of the higher aldehydes, the first fractionation was run as rapidly as possible. The 625 Gm. of aldehydes were fractionated, under a pressure of 3 mm., into ten convenient fractions using a short Vigreaux column.

	B. P.	Sp. Gr.
1	– 45°	0.8182
2	45– 50°	0.8236
3	50– 60°	0.8260
4	60– 70°	0.8281
5	70– 80°	0.8400
6	80– 90°	0.8560
7	90–100°	0.8563
8	100–110°	0.8501
9	110–120°	0.8520
10	120–130°	0.8495
11	Residue	

Inasmuch as decomposition took place in Fractions 9 and 10, distillation was discontinued.

Although the fractions obtained gave some indication as to the possible aldehydes present, the melting points of derivatives were inconsistent and not sharp. The individual fractions were refractionated under a pressure of 10 mm. using a 12-inch Widmer column.

The various fractions yielded:

Fraction No. 1.		Fraction No. 4.	
a	–56°	*a*	74–76°
b	56–58°	*b*	76–78°
c	58–60°	*c*	78–80°
d	Residue	*d*	Residue

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Fraction No. 2.	Fraction No. 5.
a 60–62°	*a* 84–86°
b 62–64°	*b* 86–88°
c 64–66°	*c* 88–90°
d Residue	*d* Residue
Fraction No. 3.	**Fraction No. 6.**
a 66–68°	*a* 90–92°
b 68–70°	*b* 92–94°
c 70–74°	*c* 94–98°
d Residue	*d* Residue

Fraction No. 7.

Decomposition began and distillation was discontinued.

By way of comparison, the constants of the aldehydes and derivatives of previous workers may be tabulated with those found.

FRACTION No. 2.

	Found.	Recorded for *n*-Octyl Aldehyde.
B. p.	60–62°	60–63° at 10 mm. (3)
Sp. Gr.	0.8236 at 20°	0.8211 at 20° (3)
n_D	1.4206 at 20°	1.4955 (4)
α_D	±0	±0 (4)
M. p. of thiosemicarbazone	94–94.5°	94–95° (5)

This fraction corresponds to *n*-octyl aldehyde.

FRACTION No. 3.

	Found.	Recorded for *n*-Nonylic Aldehyde.
B. p.	70–74° at 10 mm.	72° at 10 mm. (6)
Sp. Gr.	0.8297 at 20°	0.8277 at 15° (7)
n_D	1.4273 at 20°	1.42452 at 16° (7)
α_D	±0°	±0° (7)
M. p. of thiosemicarbazone	77°	77° (5)

This fraction corresponds to *n*-nonyl aldehyde.

FRACTION No. 6.

	Found.	Recorded for *n*-Decyl Aldehyde.
B. p.	90–92° at 10 mm.	92° at 10 mm. (8)
Sp. Gr.	0.8502 at 20°	0.8538 at 15° (9)
n_D	1.4287 at 20°	1.4273 (9)
α_D	±0°	±0° (9)
M. p. of thiosemicarbazone	99–100°	99–100° (5)

This fraction corresponds to *n*-decyl aldehyde.

On standing in a refrigerator, Fractions 7, 8 and 9 became partly solid. The solid white material was collected on a force filter, recrystallized from alcohol and dried. It had a melting point of 42° to 43°. After further purification by recrystallization from alcohol the melting point remained unchanged.

Lauric Aldehyde.	Found.	Recorded.
M. p.	42–43°	44.5° (10)
M. p. thiosemicarbazone	100–100.5°	101.5–102.5° (11)

This fraction corresponds closely to lauric aldehyde which is indicated.

The mother liquor was placed in a refrigerator and again solid material separated which partly liquefied when an attempt was made to collect it at room temperature. The solidifying point was determined and found to be 22.5°.

Myristic Aldehyde.	Found.	Recorded.
M. p.	22.5°	23° (12)
M. p. oxime	82.5–83.5°	82.5° (12)
M. p. semicarbazone	101.5°	100–101° (13)
		106° (12)

This fraction corresponds to myristic aldehyde.

There are indications of other aldehydes present, especially those with a larger number of carbon atoms, but it was impossible to obtain derivatives pure enough to characterize the compounds.

CONCLUSION.

N-octylic, *n*-nonylic, *n*-decylic and *n*-myristic aldehydes have been isolated and identified and *n*-lauric aldehyde is indicated.

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RUSSIAN ERGOT.

BY H. H. RUSBY.

No specific account of Russian ergot, cured as our Pharmacopœia directs, and preserved in its natural state, has come to my attention. All published information that I have seen has related to commercial supplies, which have been accurately described by Henning as "usually arriving in a damp and moldy condition."

More than a year ago, I entered into communication with the Russian department of agriculture for the procural of samples officially prepared and sent direct, so as to arrive in an unaltered state. I made it clear that my criticisms of Russian ergot had no relation to Russia or its products as such, but had been made wholly in the interest of improvement of the materia medica. Several years ago, I had urged our food and drug authorities to secure, through our State Department, cooperation with Russia in the investigation of this subject and in the improvement of the latter's product, but without result. The Committee of Revision has taken no steps, as a part of their research work, to ascertain the facts regarding this drug. Thus I, perforce, took it up myself.