PHYTOCHEMICAL NOTES.[1]

83. The Volatile Oil of Canada Balsam.[2]

BY MAX PHILLIPS.[3]

Although Canada balsam is one of the early contributions made by America to the materia medica, the chemistry of this substance is but little understood. Of the two products into which this drug resolves itself upon steam distillation, the volatile oil has yielded but one of its constituents, namely, *l*-pinene.

Inasmuch as the occasion had arisen to prepare a larger amount of *l*-pinene for certain experiments with this hydrocarbon, 15.9 K. of commercial Canada balsam were subjected to steam distillation. 3725 grammes of oil resulted, corresponding to a yield of 23.4 percent. With the oil there came over a flocculent substance which was removed by filtration. The residue remaining in the still was a hard, yellow resin.

The density of the oil at 20° C. was 0.8472; $[\alpha]_{D_{20}}$ —27.8°; $n_{D_{20}}$ 1.4718. These constants, with the exception of the density, come within the limits of those previously observed.

The oil was then fractionated. In order to prevent unnecessary decomposition, amounts of 500 Cc. were distilled in an ordinary fractionating flask at a fairly rapid rate. In no case was much more than one-half hour consumed to bring about the first rough separation. The last lot amounted to but 190 Cc. The following table records the amounts obtained in each fraction, also the time consumed in each operation:

—153°.	153–158°.	158–163°.	163–168°.	168–173°.	173–178°.	178–183°.	Residue.	Time.
				Vol. in Cc.				
9 Cc.	16 Cc.	26.8 Cc.	190 Cc.	142 Cc.	47.5 Cc.	28.8 Cc.	49 Cc.	32 m.
6	6	18	167	164	58	28	55	38
6.2	4	18	175	165	54.5	31	50	26
5.6	3.5	30	175	157	52	29	52	36
6.2	5.4	25.2	200	142	53	25	49	26
6	4.6	30.6	200	133	55	30	46	30
5	4.6	33.4	190	137	55	27	49	32
6.6	5	41	190	137	51	27	49	29
4	4	25.4	110.6	80	26	13.8	28	17

Although the oil is reported to contain about 50 percent of pinene, the above table reveals but a small total in fraction 153–158°. The residue had a decided limonene odor. That decomposition had taken place became apparent, not only from the vapors formed at temperatures above 175°, but also from the yellow resinous character of the residue, although distillation had been interrupted at 183° C.

A refractionation with a column of three bulbs was undertaken. That there was an appreciable lowering, in part at least, of the boiling point, becomes apparent from the data recorded in the following table:

---

[1] From the laboratory of Edward Kremers.

[2] Read before Scientific Section, A. Ph. A., Chicago meeting, 1918.

[3] Fritzsche Bros. Fellow.

Original fraction.	—153°.	153°+.						
—153°	8.2 Cc.	43 Cc.						
		153–8°.	158°+.					
153–158°	3.8 Cc.	6 Cc.	77 Cc.					
			158–63°.	163°+.				
158–163°	8 Cc.	8.2	143 Cc.	143				
				163–8°.	168°+.			
163–168°	4.4 Cc.	11.2	516 Cc.	839 Cc.	372 Cc.			
					168–73°.	173°+.		
168–173	0	4.6	44.4 Cc.	810 Cc.	435 Cc.	296		
						173–8°.	178°+.	
173–178	0	0	0	13 Cc.	343 Cc.	163 Cc.	218	
							178–83°.	183°+.
178–183	0	0	1 Cc.	5.6 Cc.	46 Cc.	140 Cc.	63 Cc.	190 Cc.

The specific gravity and angle of rotation of the respective fractions are recorded in the next table.

	—153°.	153–8°.	158–63°.	163–8°.	168–73°.	173–8°.	178–83°.
Sp. gr. at 20.....	0.819	0.838	0.852	0.853	0.853	0.848	0.842
Optical rotation in 1 dcm. tube.....	17.03	—22.54	—23.54	—25.56	—27.83	—28.21	—28.02

The residue, that is, the material which had boiled above 183° C. in the first fractionation, was distilled under a pressure of only 38 mm. The following table contains a list of the various fractions obtained together with the sp. gr. of each:

Fractions.									
—75°.	75–95°.	95–105°.	105–15°.	115–25°.	125–35°.	135–45°.	145–55°.	155–65°.	Residue.
Vol. in Cc.									
39.5	100	132	47.5	27	46	35	45	26.6	42 g.
Sp. Gr. at 20° C.									
0.844	0.847	0.837	0.832	0.833	0.837	0.847	0.862	0.893	

PREPARATION OF NITROSOCHLORIDES.

Nitrosochlorides were prepared from some of the fractions given below according to the method of Wallach for the preparation of pinene nitrosochloride. For each preparation 29.5 Cc. of oil were used. The results obtained are tabulated below.

Fraction.	Wt. of nitrosochloride.	Yield.	Rotation of oil.
158–163	2.32 Gm.	9.2 percent	—23.54
163–168	1.62 Gm.	6.4 percent	—25.51
168–173	0.71 Gm.	2.8 percent	—27.83
173–178	0.14 Gm.	0.55 percent	—28.21

The amount obtained diminished in accordance with the well known rule that the yield of optically active pinene nitrosochloride diminishes as the angle of rotation of the pinene increases. In this case, however, the diminution in the yield is out of all proportion to the slight increase in the angle of rotation and must, no doubt, be attributed in part to other causes.

CONVERSION OF NITROSOCHLORIDES TO BENZYLAMINE AND PIPERIDENE BASES AND TO NITROSOPINENE.

The nitrosochloride obtained from fraction 153–163 was converted to nitrosopinene. (Heusler-Pond, p. 43.) The purified compound melted at 132° C. (m. p. of nitrosopinene = 132° C. Heusler-Pond).

From the nitrosochloride of fraction 163–168° the nitrolbenzylamine base was prepared, according to the method given in Heusler-Pond p. 43. It melted at 122° C. (m. p. of nitrolbenzylamine base of pinene = 122° C.).

The nitrosochloride of fraction 168–173° was converted to the nitrolpiperidide base. The pure compound melted at 118° C. (m. p. of nitrolpiperidide of pinene is 118–119° C.).

From the nitrosochloride of fraction 173–178° a nitrolbenzylamine base was prepared. It was found to melt rather low. The compound was recrystallized several times and was then found to melt rather sharply at 91–93° C. This melting point is far too low for the nitrolbenzylamine base of pinene. Moreover, the nitrolbenzylamine base of limonene melts at 93° C., which fact would seem to indicate that in fraction 173–178° limonene is present. However, no tetrabromide could be prepared from this fraction.

SUMMARY AND CONCLUSION.

A rather preliminary chemical investigation of the volatile oil of Canada balsam has been made. The presence of pinene, previously reported by Fluekiger has been confirmed. That there is at least one other terpene present in this oil is indicated by the boiling points of certain fractions and by the benzylamine base of fraction 173–178°.

---

84. An Unusual Oil from Monardo Punctata.*

BY MAX PHILLIPS.†

In connection with the experiments on the cultivation of *Monardo punctata* it became necessary to collect a larger amount of seeds. Hence, between October 18 and 20, 1917, forty-five pounds of matured flower tops were collected. The corollas had dropped long ago, so that only the calyces with the mature fruit remained on the expanded base of the former influorescence. Having been stored for about a month, the fruit heads were threshed, 3.5 lbs. (= 7.7 percent) of seed being obtained. However, there also resulted 40 lbs. (18,181 Gm.) of chaff which was not devoid of odor. Hence, this material was subjected to steam distillation. The original oil (152 Gm.) and the cohobated oil (12 Gm.) were mixed, affording a total of 164 Gm. or 0.9 percent. This is an unusually high yield of oil for Monarda material collected so late in the season.[1]

---

* Read before Scientific Section, A. Ph. A., Chicago meeting, 1918.

† Fritzsche Bros. Fellow.

[1] From the work that has been done upon *Monarda punctata*, it seems that the largest yield of oil is obtained from young plants not yet in blossom. Last November 800 lbs. of dry plants were distilled at this station and a 0.77 percent yield of oil was obtained. (See also N. Wakeman, "The Monardas," p. 24 of Univ. of Wis., *Bull.* 448.)