PHYTOCHEMICAL NOTES.*

No. 86. A Comparison of Eastern and Western Hemlock Oils.

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The needle oil of *Abies canadensis* L. was first investigated by Bertram and Walbaum[1] in Germany, where it is known more commonly as *Canadisches Tannenoel* (spruce oil), in the year 1893. They gave as the characteristics of this oil the following: specific gravity, 0.907; optical rotation, —20° 54′ in a 100 mm. tube; bornyl acetate content, 36 p. c. This oil was said to yield a pinene nitrosochloride (m. p., 102° to 103°) and contained a sesquiterpene in its highest boiling fraction. Power[2] is of the opinion that the above-investigated oil was obtained from *Picea alba* Link (White Spruce) or *Picea nigra* Link (Black Spruce) and not from *Abies canadensis* Michx. (popularly known in America as "Hemlock Spruce") which he regards as the source of the commercial oil of hemlock. Camphene was detected in hemlock oil obtained from the needles of *Abies canadensis* Michaux in 1894 by Schimmel and Company.[3]

In the latter part of September 1894, Hunkel[4] collected a quantity of leaves and twigs of the tree hemlock, *Tsuga canadensis*, better known in pharmaceutical literature at that time as *Abies canadensis* Michaux, at the Dells of the Wisconsin River. The yield of oil from this material was said to be comparatively small. This oil possessed a yellowish color and had the characteristic odor of hemlock. Its physical properties were: specific gravity (of the dried oil), 0.9288 at 20°; specific angle of optical rotation, $[\alpha]_D$ 18.399° at 20° C. The ester content of this oil, calculated as bornyl acetate, was 51.5 p. c. and 52.0 p. c. Laevo pinene was shown to be present by the formation of the nitrolbenzylamine base of this compound with a melting point of 122° C. The above investigator concludes that this oil when distilled in September consists principally of about equal parts of 1-bornyl acetate and 1-pinene.

Schimmel and Company[5] in 1897 present the following information concerning "Hemlocktannen-Oel" (hemlock oil) from the needles of *Abies canadensis* L. = *Tsuga canadensis* Carriere: specific gravity, 0.911; specific optical rotation, —25° 22′ at 16° C.; bornyl acetate content, 38 p. c. This oil is reported as being soluble in one and more parts of 90 percent alcohol.

In 1905 Pancoast and Graham published[6] an interesting report on "Commercial Volatile Oils of the Conifers" which threw some light upon the commercial production of hemlock oil. In answer to a questionnaire which they sent to about ten oil dealers in Boston and New York asking whether those employed in gathering of coniferous needles took care to keep the hemlock, spruce and cedar needles, boughs and twigs separate, they received the reply that the leaves and small twigs of the three varieties, hemlock, spruce and cedar, are distilled separately for each variety of oil and are never mixed with the cones.

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* From the laboratory of Edward Kremers.

[1] *Archiv. der Pharm.*, 231, p. 290.

[2] "Descriptive Catalogue of Essential Oils and Organic Preparations" (June 1894), p. 74.

[3] S. & Co.'s *Bericht*, Oct. 1894, p. 21.

[4] *Pharm. Rev.*, 14, 34, 1896.

[5] S. & Co.'s *Bericht*, Oct. 1897, p. 25.

[6] Proc. Pa. Pharm. Assoc., 28, p. 184.

This report contained a description of the still used by one distiller. The authors point out the fact that they have not found any oil of commerce that has complied with Hunkel's figures for that obtained from *Tsuga canadensis*. They mention that in the spring of 1904 a lot of authentic needles and twigs of the above variety with no admixture of other needles was procured which contained "no oil or not enough to examine." In the fall another lot of this material was secured which yielded but a rather scanty amount of light green colored oil with characteristic odor. This resulting oil upon examination possessed the following physical constants: specific gravity, 0.9665; optical rotation, —11° 31′, and was soluble in all proportions of 95 p. c. alcohol. The bornyl acetate content could not be taken as the amount of oil was so small.

The experimental results obtained by Pancoast and Graham in working with various commercial samples and the authentic one are summarized by them in the following table:

OIL OF HEMLOCK (*Tsuga canadensis*).

No. samples.	Sp. gr. 15° C.	Optical rotn.	Bornyl acet.	B. p.
7.....	0.882 to 0.9172	—11°30′ to —18°14′	24.7 to 27.24	155–205°
8.....	0.902 to 0.911	—23°24′ to —28°48′	29 to 41.3	160–225°
1.....	0.9665	—11°31′	....	....

Hanson and Babcock[1] in the year 1906 made two distillations of leaves and twigs from a large hemlock tree. The first gave a yield of 0.4 p. c. of oil which had a specific gravity of 0.9238 at 15° C., and the second gave a yield of 0.46 p. c. with a corresponding specific gravity of 0.9273 at 15° C. The change in the specific gravities of these oils, while still fresh, for 1° C. was 0.0010.

From the above review, it becomes apparent that the question of the physical and chemical constants of hemlock oil, not to dwell upon its chemical composition, is anything but settled. It seemed desirable, therefore, to subject the oil to a more thorough investigation. Moreover, the utilization of the waste hemlock bough as a precautionary measure against forest fires seemed to make it necessary to find extended use for this oil, if possible. Such may be anticipated in the production of borneol and camphor. The bornyl acetate of the oil can readily be saponified to borneol and sodium acetate. The former could be used as such or oxidized to camphor. The latter would have been welcome during the war period. A complete separation of the borneol from the pinene would not at all be necessary, for the latter, with the borneol impurity, could be used in the artificial production of camphor. The consideration of this problem suggested that the western hemlock be included in this investigation, since at present it might prove of greater economic significance than the eastern hemlock of which our forests have already been largely depleted. Because of this possible economic significance the geographical distribution of both hemlocks was taken into consideration.

For the material the writer is indebted to lumber companies, also the Forest Service.[2] In the first distillation a separation into stems, leaves, and cones had

[1] *Journ. Amer. Chem. Soc.*, 28, p. 1198.

[2] For a more detailed description of the material and its source, see Donald E. Cable, "Needle Oils of Eastern Hemlock and Western Hemlock." A thesis submitted for the degree of Master of Science, University of Wisconsin, 1920.

carefully been effected by handpicking and the materials thus differentiated distilled separately. Finding that the branches, or rather twigs, yielded no separable oil, the branches or twigs were thereafter distilled as received. After distillation it was a relatively easy matter to separate the needles from the twigs and compute their relative proportion.

EASTERN HEMLOCK.

Five lots of *Tsuga canadensis* from as many states were collected and distilled during the months of June, July and August: No. I from East Tawas, Michigan, in June 1920; No. II from Armstrong, Wisconsin, in July 1919; No. III from Coos Co., New Hampshire, in July 1920; No. IV from McFarland, Tennessee, in August 1920; and No. V from Harrisonburg, Virginia, in August 1920. The results of the distillations, also the physical and chemical constants, so far as determined, are herewith tabulated for convenient comparison.

Sample number.	I.	II.	III.	IV.	V.
Yield of oil from stripped leaves.	0.29 p. c.	0.35 p. c.	0.53 p. c.	0.52 p. c.	0.65 p. c.
Sp. gr. 20°/15°	0.9172	0.9234	0.9190	0.9020	0.9165
Ref. ind. $n_{D20°}$	1.4704	1.4691	1.4699	1.4694	1.4694
$[\alpha]_{D20°}$	—21.65	—14.80	—18.80	—16.14	—19.10
Acid number	0.55	0.70	0.67	0.33	0.37
Ester number	131.8	147.35	132.7	103.8	129.6
Ester number after acet.	139.6	171.94	144.7	113.5	139.5
Ester as bornyl acet.	46.13 p. c.	51.57 p. c.	46.45 p. c.	36.33 p. c.	45.36 p. c.
Borneol as ester	36.25 p. c.	40.52 p. c.	36.50 p. c.	28.55 p. c.	35.64 p. c.
Free alc. as borneol	2.16 p. c.	5.89 p. c.	3.33 p. c.	2.69 p. c.	2.74 p. c.
Total borneol	38.41 p. c.	47.41 p. c.	39.83 p. c.	31.24 p. c.	38.38 p. c.
Substances other than bornyl acetate and free borneol	51.71 p. c.	41.54 p. c.	50.22 p. c.	60.98 p. c.	51.90 p. c.

The data given in the above table show a very close similarity in properties of the oil of eastern hemlock obtained from leaves grown in rather widely separated localities in the region of this species. There are, however, very appreciable differences in yields of oil in the five cases. The real cause for these differences in values need not necessarily be ascribed to differences of locality. An adequate explanation would require a much more thorough investigation of involved relationships than has previously been undertaken.

The ester content of the oil from Armstrong, Wisconsin, is about five percent larger than that of three of the other oils, and fifteen percent larger than that from Tennessee; however, it is almost identical with the corresponding value obtained by Hunkel[4] for that secured from leaves grown near Kilbourn, Wisconsin. The free borneol content of the Armstrong oil is also decidedly larger than the corresponding value for each of the other four oils. These two factors are seen to give a total borneol content of the former which is 8 to 16 p.c. in excess of the amounts obtained in the cases of the other four oils.

WESTERN HEMLOCK.[1]

Three lots of material were obtained from the west, all from Coeur d'Alene, Idaho; No. I in May, No. II in June, and No. III in July 1920. The results of

[1] A map showing the distribution of *Tsuga heterophylla* will be found in ***Bull.*** 680, U. S. Dept. of Agriculture, Map. No. 4.

the distillations as well as the physical and chemical constants, so far as determined, are tabulated for convenient comparison.

Sample number.	I.	II.	III.
Yield of oil from stripped leaves	0.36 p. c.	0.32 p. c.	0.32 p. c.
Sp. gr. 20°/15°	0.8444	0.8521	0.8490
Ref. ind. $n_{D20°}$	1.4790	1.4840	1.4806
$[\alpha]_{D20°}$	—6.74°	—16.99°	—20.00°
Acid number	2.57	3.4	3.2
Ester number	17.25	17.2	6.7
Ester no. after acet	27.64	33.4	19.6
Ester as bornyl acet	6.04 p. c.	6.02 p. c.	2.35 p. c.
Borneol as ester	4.75 p. c.	4.73 p. c.	1.85 p. c.
Free alcohol as bornyl	3.87 p. c.	4.51 p. c.	3.58 p. c.
Total borneol	8.62 p. c.	9.24 p. c.	5.43 p. c.
Substances other than bornyl acetate and free borneol.	90.09 p. c.	89.74 p. c.	94.07 p. c.

The table reveals that there is no appreciable variation in the yield of oil for the three months over which the investigation was extended. This observation agrees with that of another investigator[1] of needle oils of western conifers who covered the longer period from May to November.

Attention should also be directed to the striking differences in the angle of rotation and the ester content. The latter in the case of western hemlock oil is seen to be much lower than that of eastern hemlock oil.

The amounts of oil obtained did not admit of a careful chemical study of these products. Preliminary fractional distillations,[2] however, have already revealed striking differences between the eastern and western oils. It is to be hoped that larger amounts of oil may some day become available for a thorough chemical study.

COMMERCIAL HEMLOCK OILS.

For the purpose of acquiring a better idea of the hemlock oils of commerce several samples were examined as to their physical and chemical constants, the results being herewith tabulated. All three samples were cabinet specimens. From their labels the following information may be gleaned: No. I Fritzsche Brothers, 1909; No. II Fritzsche Brothers, Sap. No. 109, ester content 38.15 p.c. (no date); No. III E. H. Sargent & Co., July 1919.

Sample number.	I.	II.	III.
Sp. gr. 20°/15°	0.9664	0.9190	0.9310
Ref. ind. $n_{D20°}$	1.4796	1.4721	1.4760
$[\alpha]_{D20°}$	—14.18	—24.85	—19.92
Acid number	18.45	3.59	1.51
Ester number	108.05	115.41	105.09
Ester no. after acet	....	150.83	149.51
Ester as bornyl acet	37.82 p. c.	40.39 p. c.	36.78 p. c.
Borneol as ester	29.71 p. c.	31.74 p. c.	28.91 p. c.
Free alcohol as borneol	....	10.00 p. c.	12.64 p. c.
Total borneol	....	41.74 p. c.	41.55 p. c.
Substances other than bornyl acetate and free borneol	....	49.61 p. c.	50.58 p. c.

The writer desires to thank the officers of the Forest Service also others who have kindly supplied the material that made this investigation possible.

[1] G. M. Hunt, "Steam Distillation of Needles, Twigs and Cones of Western Conifers," Dec. 29, 1913. Available in the files of the Forest Products Laboratory.

[2] See thesis for records.