PHYTOCHEMICAL NOTES.

79. *Oleoresin of Pseudotsuga taxifolia (Lam.) Britton.*

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Acting upon the request of Acting Director Howard F. Weiss, of the Forest Products Laboratory, Assistant Forest Ranger F. W. Stablman, of the Santian National Forest, stationed at Detroit, Oregon, collected oleoresin, also twigs and cones of the "Douglas Fir." The identity of the latter was confirmed by Professor R. H. Denniston, of the Botany Department of the University. The tree is also known to botanists by the synonyms, *Pseudotsuga mucronata* (Raf.) Sudw. and *Pseudotsuga Douglasii* (Lindl.) Carr., and is commonly known as Douglas fir, red fir and Douglas spruce.[1] As a possible source of the Oregon balsam, the Douglas fir and its oleoresin are of special interest to the phytochemist as well as to the pharmaceutical and analytical chemist. As was learned after this examination had been made, the oleoresin in question had been obtained, not by puncturing the pustules but by boring into the trunk.

Setting aside about 100 grams as reserve material and as specimen, the remaining oleoresin, about 336 grams, was subjected to steam distillation, thus resolving it into its volatile oil and resin. These, together with the original oleoresin, were examined as to their physical and chemical constants. The amount of material was too small for anything more than a preliminary survey.

The oleoresin when received was not clear like that obtained from *Abies amabilis* which was examined in 1904 and 1905, respectively, by Rabak,[2] but had more of the emulsion-like appearance of ordinary turpentines, though decidedly liquid like the balsams. However, attempts to separate water by dissolving the oleoresin in chloroform or by distilling with xylene gave negative results. After standing for several months, however, it became perfectly clear, a slight white sediment having been deposited.

Frankforter states that "Fir pitch as it runs from the trees is a perfectly clear liquid. * * * Usually it is water-white and quite mobile. On exposure to the air it changes its color and slowly becomes viscous."[5]

The angle of rotation of a 20 percent alcoholic solution was determined in both a 100 mm. and in 200 mm. tube and in each case the specific angle of rotation was computed to be $+1.48°$.

One gram of oleoresin, dissolved in 10 cc. of perfectly neutral alcohol and titrated with standardized alcoholic potassa, gave an acid value of 100.5. Heated for an hour on a water bath with an excess of alcoholic potassa, and titrated back, the saponification number was found to be 102.0. Duplicate determinations were made in both cases.

Of volatile oil, 51.5 grams or about 15 percent were obtained. Its specific

[1] A detailed synonomy, quoted from Sargent's Sylva, will be found in Brandel and Sweet's article in the Ph. Rev., 26, p. 326. See also Rabak, Ph. Rev., 22, p 29[illegible].

[2] Ph. Rev., 22, p. 293; also 23, p. 46.

gravity at 15° was 0.8705; its angle of rotation in a 100 mm. tube —40.46°, hence $[\alpha]_D = -46.47°$.

When freshly distilled the oil had an agreeable terebinthinate, slightly camphoraceous odor. Five cc. yielded about 0.2 grams of a nitrosochloride, presumably pinene nitrosochloride. The small yield is in conformity with the high angle of rotation.

The resin obtained upon steam distillation became hard upon standing. It was clear but by no means of the light yellow color like that obtained from *Abies amabilis*.[3]

To determine the angle of rotation, the resin was purified by evaporating the filtered chloroform solution. In a 20 percent alcoholic solution (d=0.845) it deviated the angle of polarized light 3.34° to the right, hence $[\alpha]_D = +19.6°$.

The acid value of the resin was found to be 129, the sponification value 141. Duplicate determinations were made in both cases. The discrepancy between the two values as determined for the oleoresin and the resin, respectively, cannot be explained at present.

There are on record at least two earlier preliminary examinations of the volatile oil of the Douglas fir, the first by Blasdale[4] in 1901, the other by Frankforter[5] in 1906. The needle oil was examined by Brandel and Sweet[6] in 1908.

The tabulation of a few of the data recorded may enable a better comparison.

	Blasdale.	Frankforter.	Beath.
Yield of oil	about 9 p.c.	22 p.c.	15 p.c.
Sp. gr.	0.8583 at 15°	0.8621 at 20°	0.8705 at 15°
Index of refraction	1.4754 at 15°	1.47299	.....
Specific rotation $[\alpha]_D$	—41° 12′	—47.2°	—46.47°

The variations in the physical constants as recorded are such as might be expected from an oil of the same species, although differences in the specific gravity are rather large. The variation in the yield, however, is more remarkable.

Since the Douglas fir has oleoresin-bearing pustules under the bark, the oleoresin from this species has been suggested as a possible source for the Oregon balsam of commerce. Its chemical examination, therefore, is of commercial as well as of phytochemical interest. Hence a further comparison of the properties of this oleoresin with those of the oleoresin of *Abies amabilis*, another possible source of Oregon balsam, should give an added interest to the subject. For this purpose the data compiled by Rabak in the publication referred to above are utilized. Attention should, however, be once more directed to the fact that after this examination had been made it was learned that the oleoresin in question had not been obtained from the pustules but by boring into the trunk. If this method yields an oleoresin similar in appearance to Canada balsam, it becomes apparent why the Oregon balsam of commerce should be much cheaper than Canada balsam. Hence the comparison of data in the following table loses

[3] Comp. 1, c.

[4] Journ. Am. Chem. Soc., 23, p. 162.

[5] Ibidem, 28, p. 1467.

[6] Ph. Rev., 26, p. 326.

none of its analytical significance and interest, though phytochemically the products are not directly comparable.

OLEORESIN.

	Pseudotsuga taxifolia	Abies amabilis	Oregon balsam, commercial "1903"	"1904"	"Portland"	"Dowzard"
Sp. Gr.....	.....	0.969	1.01	0.985	0.988	0.993
[α]D	+1.48°	±0°	+4° 13′	+2° 13′	+3° 5′	—3° 12′
Acid No.....	100	44	116	103	114	.....

VOLATILE OIL.

	Pseudotsuga taxifolia	Abies amabilis	Oregon balsam, commercial "1903"	"1904"	"Portland"	"Dowzard"
Yield	15 p.c.	40 p.c.	.....	25 p.c.	.....	.....
Sp. Gr.....	0.8705	0.852	0.857	0.882	.....	0.8652
[α]D	—46.47°	—12.17°	—37° 46′	—34° 37′	.....	—37° 24′

RESIN.

	Pseudotsuga taxifolia	Abies amabilis	Oregon balsam, commercial "1903"	"1904"	"Portland"	"Dowzard"
[α]D	+19.6°	±0°	.....	.....	.....	.....
Acid No.....	129	70	.....	.....	.....	153

A comparison of the above data justifies the conclusion that we are not much nearer to an understanding as to the botanical source of commercial Oregon balsam than before, except possibly in so far that one more botanical possibility seems to have been eliminated. In addition to the constants tabulated above, it should be pointed out that whereas the oleoresin of *Abies amabilis* examined closely resembled the commercial oleoresin in color and general appearance, the oleoresin from Pseudotsuga taxifolia was milky in appearance and in this condition could scarcely have been substituted for either Oregon or Canada balsam. However, upon prolonged standing it became clear but "water-white," not yellow as the Canada and Oregon balsams of commerce.

BIBLIOGRAPHY.

Blasdale, W. C.....1901
On heptane from coniferous trees.
Jour. Amer. Chem. Soc., 23, p. 162.

The author found the oleoresin of *Pseudotsuga taxifolia* to yield an oil of the following nature:

Specific gravity at 15°.....	0.8583
Index of refraction at 15°.....	1.4754
Specific rotation	—41° 12′
Iodine absorption	"high"
Yield of oil.....	about 9 p.c.

Frankforter, G. B.....1906
The pitch and the terpenes of the Norway pine and the Douglas fir.
Jour. Amer. Chem. Soc., 28, p. 1467.

The author reviews the yield of fir "pitch" from different grades of wood and outlines the physical and chemical constants of the oleoresin and volatile oil.

Oleoresin (exudation) of Douglas fir:

Specific gravity at —20°.....	0.9821
Index of refraction at 20°.....	1.51745
Optical activity	—8.82

Volatile oil of Douglas fir:

	Steam Distilled.	Destructive Distilled
Specific gravity at 20°.....	0.8621	0.8662
Boiling point.....	153.5—154°	157—160°
Index of refraction.....	1.47299	1.47246
Optical activity.....	—47.2°	—29.40°
Yield of "turpentine in fir pitch".....	22 p.c.	.....

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