

PHYTOCHEMICAL NOTES.*

No. 93. Balsam of White Fir.¹

BY. S. S. AIYAR.

A number of years ago a special study was made of the so-called Oregon balsam. Not only were the physical and chemical constants of this substitute² for Canada balsam determined in connection with commercial specimens, but an attempt was also made to ascertain its botanical source. For the latter purpose a number of balsams were secured and examined.³ It was in this connection that the U. S. Forest Service had collected between July 24 and 30, near Camptonville, California, in the Tahoe National Forest⁴ a small amount (about 8 ounces) of balsam from white fir, presumably *Abies concolor* (Gord.) Parry.⁵ This material has at last been examined.

The balsam was almost colorless when it arrived and has remained thus after these many years. It is still semifluid though not quite as mobile as when fresh. In the course of years it has deposited a white flocculent precipitate. Its odor is still not unpleasantly terbinthinate.

The density, determined at 20° in a specific gravity flask, was 0.989. Its optical rotation in a 50 mm. tube was +5.53°. The angle of rotation of its 25 p. c. chloroformic solution was +4° 61' in a 100 mm. tube. In alcohol it is soluble for the most part but leaves a white residue. This is likewise true of such solvents as acetone, and benzene in the cold. In the case of benzene, the residue is very small. In chloroform and ether the balsam is completely soluble. Distilled with steam, the oleoresin yielded 27.7 p. c. of oil, the resin remaining as a brittle amorphous mass when cool.

VOLATILE OIL.

The volatile oil was colorless and had a distinctly terebinthinate but pleasant odor. $d_{20} 0.865$; $\alpha_D + 11.88^\circ$.

Upon direct distillation it yielded the following fractions:

<i>t.</i>	Amt., Gm.
-154°	1.4
154-156°	3.0
156-164°	16.9
164-166°	6.0
166-174°	1.9
174-176°	0.35
176°+	0.3

Total, 29.85

* From the laboratory of Edward Kremers.

¹ Scientific Section, A. Ph. A., Cleveland meeting, 1922.

² See "Phytochemical Notes No. 56," *Ph. Rev.*, 22, p. 293.

³ "Phytochemical Notes," 59 (*Ibid.*, 23, p. 46) and 79 (*JOUR. A. PH. A.*, 2, p. 1566).

⁴ The label on the bottle recorded the dates given above, but not the year. The correspondence with U. S. Forest Service contains a letter with reference to red fir, but not to white fir, hence the year cannot be supplied.

⁵ This is the botanical designation as given by Schorger in his article: "The Leaf and Twig, and Bark Oils of White Fir," *Jour. Ind. Eng. Chem.*, 6, p. 809.

As will be seen, the bulk of the oil came over between the pinene and no pinene fractions. Fraction 164-166° deviated the ray of polarized light +12.92°, hence its angle of rotation differed but little from that of the entire oil.

The presence of pinene in fraction 154-156° was readily demonstrated by converting it into the nitrosochloride and this into the nitrolamine base. However, the latter melted at 126-127°, whereas the melting point of pinene nitrolpiperidine is recorded at 118-119°. Possibly this difference is due to impurities in the reagent discovered later.

RESIN.

In order to obtain, if possible, a crystalline resin acid from the resin left after steam distillation of the oleoresin an attempt was made to dissolve the former in alcohol. However, in this solvent it is found to be but sparingly soluble. The hot alcoholic solution, upon cooling, deposited a granular white precipitate. More of it was soluble in acetone, which solution, upon evaporation of the solvent, deposited a transparent amorphous resin. Benzene dissolved it even more completely. In ether and chloroform the resin is readily soluble.

In order to effect at least a partial separation of the several constituents, the bulk of the small amount of resin available, was extracted with alcohol, the hot alcoholic solution filtered and the filtrate allowed to cool. Thus a very small amount of a white crystalline powder was deposited, too small indeed for further investigation.

The alcohol insoluble resin was then extracted with acetone. The acetone extracted a large portion of the resin, but would not crystallize it out. Hence the solution was concentrated by evaporation and allowed to cool, when the whole mass cooled down to a thick syrupy liquid. As no crystals could be obtained, all the acetone was driven off and the resin obtained as a brown translucent mass easily pulverized.

The residue was again extracted with alcohol-benzene mixture. A small portion of the resin was soluble but would not crystallize even on concentrating the solution. When all the solvent was driven off a yellow plastic resin was left.

The residue was a white solid with a saponification value of 130.5 and 115.3. The reason for this difference in value of the duplicates is due to the fact that the resin melts to a globule, and does not expose a free surface to the reacting liquids.

The original resin itself had a saponification number of 120.9. The resin extracted by acetone gave a saponification number of 143.4. It seems as though the acetone takes up more of the acid material. Again another sample of original resin 30 Gm. in weight was extracted with 400 cc alcohol. On cooling the solution a small quantity of white precipitate was obtained.