benzbromamide is the brominating agent. Furthermore, it is not easy to see why a substance as insoluble as benzoylphenylurea should be much affected by dilute bromine water.

The improvement in the quality of benzbromamide when only small quantities were prepared, is doubtless to be explained by the fact that, under these circumstances, it is easier to maintain a low temperature throughout, less of the benzbromamide being decomposed to form isocyanate or carbamate.

SUMMARY.

When benzbromamide is prepared by the method of Hoogewerff and Van Dorp, it is liable to contain benzoyl-*p*-bromphenylurea. The amount of this substance may sometimes exceed 10 per cent.

Benzoyl-*p*-bromphenylurea is a bulky, colorless, crystalline solid. It melts in a closed tube at 230° and decomposes at 232°. It is soluble with difficulty in most of the ordinary organic solvents.

The constitution assigned to this compound is most conclusively proved by its synthesis from *p*-bromphenyl isocyanate and benzamide, but it is also consistent with its preparation by three other syntheses, with the analysis, and with its whole behavior.

The formation of the benzoyl-*p*-bromphenylurea in the preparation of benzbromamide is to be accounted for as the result of the bromination of the benzoylphenylurea first formed. This bromination is probably effected by the benzbromamide itself.

The authors perform a pleasant duty in acknowledging their indebtedness to Dr. Richard B. Earle, instructor in organic chemistry at the institute, for many helpful suggestions.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.
June 5, 1906.

NOTES ON SOME OF THE CONIFER OILS.

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Received June 20, 1906.

AN apparent want of conformity in the present literature on some of the conifer oils has led us to investigate several of them, and we hereby embody the results of our work.

Our investigation has been confined to the following oils:

(A) Black spruce (*Picea Mariana*) leaves.
Hemlock (*Tsuga Canadensis*) leaves.
(B) American larch (*Larix Americana*) leaves.
White spruce (*Picea Canadensis*) leaves.
White spruce (*Picea Canadensis*) cones.
Red spruce (*Picea rubens*) leaves.
Red spruce (*Picea rubens*) cones.
Pitch pine (*Pinus rigida*) leaves.
Red pine (*Pinus resinosa*).
Juniper (*Juniperus communis*) leaves.

All of the oils in division marked B are, to the best of our knowledge, distilled and herein described for the first time.

Throughout the work we have carefully identified all materials from which the oils have been distilled and have personally superintended the distillation to insure the purity of the oils.

(1) *Oil of Black Spruce* contains 48.85 per cent. bornyl acetate (Kremers), sp. gr. 0.922 at 20° (Gildmeister and Hoffmann). An oil distilled by us was obtained in a yield of 0.57 per cent. and had a sp. gr. of 0.9274 at 19°. Change in the specific gravity of its fresh oil for 1°, 0.0010; for oil which has stood for some time 0.0014.

(2) *Oil of Hemlock* contains 51.5–52 per cent. of bornyl acetate —sp. gr. 0.9288 at 20° (Hunkel). According to Gildmeister and Hoffmann, it contains 36 per cent. bornyl acetate, sp. gr. 0.907–0.913. An oil distilled by us from leaves and twigs of a large tree was obtained in a yield of 0.4 per cent., sp. gr. 0.9238 at 15°. A second distillation from the leaves and twigs of a small tree gave a yield of 0.46 per cent., sp. gr. 0.9273 at 15°. Change in its specific gravity of the fresh oil for 1°, 0.0010.

(3) *Oil Picea Canadensis* (Cat Spruce) has apparently not been investigated, although we have reason to believe it is often confused with black spruce in the distillation of the latter. We obtained this oil in a yield of 0.103 per cent., sp. gr. 0.9216 at 15°. Change in the specific gravity for 1°, 0.0012. It contains 25.7 per cent. of ester, calculated as bornyl acetate, which is a low ester content in comparison with the other spruce oils. The odor of this oil is distinctly different from that of black spruce and hemlock oils, suggesting limonene or dipentene. We are at

present engaged upon the identification of the terpenes present in this oil.

(4) *Oil Picea Rubens* (Red Spruce).—This oil is remarkable for its high specific gravity and high percentage of ester. The distillation gave a yield of 0.204 per cent., sp. gr. 0.9539 at 16°. Change in the specific gravity for 1°, 0.0014. This oil contains 66.2 per cent. of bornyl acetate and 7.76 per cent. of free borneol. On saponification, large quantities of crystals having a distinct odor of borneol separated out. After recrystallizing several times from petroleum ether the borneol appeared as white, shining, hexagonal plates melting, but not sharply, in the neighborhood of 200°. Lack of sufficient quantity of oil prevented us from obtaining crystals with the melting-point of pure borneol, 206°, or from forming derivatives and thus making a positive identification.

The oil itself had a very agreeable odor, strongly suggestive of borneol acetate.

(5) *Oil Larix Americana.*—This oil, distilled from the leaves and twigs was obtained in a yield of 0.149 per cent., sp. gr. 0.8816 at 15°, ester content 15.1 per cent., calculated as bornyl acetate.

Fractional distillation gave the following results:

155°–170°	= 20	per cent.
170°–180°	= 38.4	" "
180°–190°	= 11.2	" "
190°–200°	= 9.2	" "
200°–240°	= 14.8	" "
Residue	= 6.4	" "
Total	= 100	" "

The fraction 170–180° was redistilled when 62 per cent. boiled below 171°; 20.5 per cent. boiled at 171–181°. The remainder was the residue, boiling above 181°.

The fractions distilling *below* 171° were combined. The specific gravity of these combined fractions was 0.8578 at 15°. Two more redistillations of the fractions below 171° yielded a fraction boiling at 155–162°. From this last fraction we were enabled to obtain a nitrosochloride which melted sharply at 108°. This is the melting-point of pure pinene nitrosochloride.[1] Owing to paucity of material, we did not attempt to form the nitrol-

[1] Van Romburgh: See Schimmel's Report, April, 1901.

benzylamine compound, which would have established still more firmly the presence of pinene.

According to our investigations, 15.1 per cent. of this oil is ester (calculated as bornyl acetate) and the remainder is largely pinene.

(6) *Picea Rubens* (*Cones*).—This oil was obtained in a yield of 0.38 per cent., sp. gr. 0.8600 at 15°, with a golden yellow color and a fir-balsam-like odor.

(7) *Oil of Picea Canadensis* (*Cones*).—This oil was obtained in a yield of 0.25 per cent., sp. gr. 0.899 at 15°. It was of a yellow color and a pronounced limonene-like odor. These constants were taken some time after the oil had been distilled, and the high specific gravity may be due to a subsequent thickening.

(8) *Oil Pinus Rigida.*—The yield of this oil was extremely small. From 12 kg. of leaves and twigs we obtained only 0.2 cc. Oil was yellow in color and had an extremely pungent odor.

(9) *Oil Pinus Resinosa.*—The yield of this oil was also very small, about 0.001 per cent. The color of the oil was a brownish red. Its odor was very pungent and disagreeable.

(10) *Oil Juniperus Communis.*—Leaves and twigs, devoid of berries, were used in the distillation of this oil. The oil was obtained in a yield of 0.18 per cent. in one distillation, while a second distillation of material from other ground gave nearly the same yield, 0.15 per cent. These distillations were carried on in the spring about the first of May. Specific gravity of the oil was 0.8531 at 20°. Oil was of a light yellow color and characteristic juniper odor.

(11) *Oil Juniperus Virginiana* (*Leaves*).—An oil distilled by us had a slightly higher density than is generally given. Sp. gr. 0.900 at 16°.

Owing to lack of sufficient quantities of the oils we have been unable to carry these investigations further as yet. Arrangements are being made, however, for the distillation of larger quantities of several of them as well as other new oils of the same species. We hope to be able to present more complete results in the near future.

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