Tertiary bases add directly to give salts of quaternary bases, $S(CH_2CH_2NR_3Cl)_2$, $OS(CH_2CH_2NR_3Cl)_2$ and $O_2S(CH_2CH_2NR_3Cl)_2$.

The results obtained are consistent with the theory that the vesicant action of β,β'-dichloro-ethyl sulfide is due to its reactions with constituents of the living cell.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

BORNEOL IN SPRUCE TURPENTINE

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RECEIVED JULY 29, 1925 PUBLISHED NOVEMBER 5, 1925

In an investigation of the sulfite liquor obtained from the paper mills of northern Europe, Klason and Segerfelt[1] isolated a solid white, optically inactive substance of camphor-like odor and composition $C_{10}H_{18}O$; m. p., 207°. They regarded it as inactive borneol. Later Bergstrom[2] obtained a white solid which distilled at 205–210° and had the composition given above. In 1913 Klason and Segerfelt[3] isolated the same compound apparently, and called it a terpene alcohol. In 1915 Bergstrom[4] reported this product as inactive borneol. More recently Homberg and Sunesson[5] re-examined the product and showed that it was optically active, containing 14–22% of *l*-borneol. Since the composition of the spruce turpentine of northern Europe may easily be different from that of other localities, we examined the spruce turpentine from the paper mills of Erie, Pennsylvania, some of our material being very kindly furnished by the Eastman Kodak Company.

That portion of the spruce turpentine left after distilling the *p*-cymene fraction, b. p. 175–178°, was used for this work. Five hundred g. of this residue was distilled under a vacuum of 3 mm., using a 30cm. Glinsky fractionating column. After three fractionations, the portion coming over from 70° to 80° was cooled to —10° with a freezing mixture. Crystallization took place and 9 g. of a white solid was filtered off. This represents 1.8% of the original cymene residue, but doubtless a considerable portion remained in solution, for the solid is very soluble in the oil. On recrystallizing the product from dil. alcohol, it was obtained in large, hexagonal plates; m. p., 206°.

Anal. Subs., 0.2096: CO_2, 0.5996; H, 0.2193. Calcd. for $C_{10}H_{18}O$: C, 77.85; H, 11.76. Found: C, 77.99; H, 11.72.

A molecular-weight determination was made by the lowering of the freezing point of its benzene solution.

Calcd. for $C_{10}H_{18}O$: mol. wt., 154.2. Found: 153.

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[1] Klason and Segerfelt, *Svensk Kem. Tid.*, **23**, 149 (1911).

[2] Bergstrom, *Papier-Fabr.*, **13**, 229 (1915).

[3] Klason and Segerfelt, *Arkiv. Kemi. Min. Geol.*, **4**, No. 20, 3 pp. (1913).

[4] Bergstrom, Ref. 2, p. 229; *Svensk Pappers-Tid.*, **18**, 62 (1915).

[5] Homberg and Sunesson, *Svensk Kem. Tid.*, **35**, 215 (1923).

It was further identified as borneol by its phenylurethan and by its oxidation to camphor.

Borneol-phenylurethan.—One g. of the substance was mixed with 0.77 g. of phenylisocyanate. The product, recrystallized several times from hot petroleum ether, was obtained in fine, white needles; m. p., 140–141°. Haller[6] gives 137.75° as the melting point of *d*- and *l*-borneol and 140° for the *dl*-borneol derivative.

Oxidation to Camphor.—Two g. of the substance was added in small amounts to 6 g. of nitric acid (d., 1.45). The mixture was shaken for 40 minutes, while the temperature was kept at 20–25°, and was then poured over cracked ice. The white solid thus obtained was purified by steam distillation from an alkaline solution of potassium permanganate; yield, 1.75 g. of camphor; m. p., 176°. Its semicarbazone, made in acetic acid solution, consisted of fine white needles, from alcohol; m. p., 242°. Rimini,[7] gives 245°.

Optical Activity.—Our borneol showed an optical rotation of $[\alpha]_D^{20}$, —13.64°, using a 5% solution in alcohol. The product contains, therefore, 36% of *l*-borneol, a much higher amount of this isomer than is found in the borneol of northern Europe.

The question as to the presence of any isoborneol was answered by the method of Haller,[8] who showed that the rotation of isoborneol varies in different solvents while that of *d*- and *l*-borneol remains constant.

Solvent	Erie borneol	*l*-Borneol	*l*-Isoborneol
Alcohol	−13.64°	−37.3°	−32.9°
Ethyl acetate	−13.93°	−37.6°	−22.8°
Benzene	−13.69°	−37.9°	−18.9°

Designating our borneol as "Erie" borneol it is seen that its constant specific rotation precludes the presence of any isoborneol. This conclusion is also supported by the melting point and angle of rotation of the phenylurethan. Haller[6] gives the following values for the phenylurethan obtained from the borneols and their mixtures (equal amounts of *d* and *l*).

Borneol	*d*	*l*	*dl*	*d*-Borneol + *l*-isoborneol	*l*-Borneol + *d*-isoborneol	*l*-iso
M. p., ° C.	137	137	140	133	133	130
$[\alpha]_D^{20}$	+34	−34	0	−7.5	+7.5	−56.7

The phenylurethan of "Erie" borneol melted at 140–141° and showed a rotation of $[\alpha]_D^{20}$, —12.1°. The presence of isoborneol would cause the melting point to be lower and the angle of rotation to be higher than that obtained.

Summary

1. Borneol has been isolated from spruce turpentine, a by-product in the sulfite method of making paper pulp at Erie, Pennsylvania. The amount obtained was about 2% of the turpentine after removal of the *p*-cymene. It contains about 36% of *l*-borneol, calculated from its angle of rotation; $[\alpha]_D^{20}$, —13.64°. Borneol obtained from a similar source in northern Europe contained 14–22% of *l*-borneol.

[6] Haller, *Compt. rend.*, **110**, 149 (1890).

[7] Rimini, *Atti accad. Lincei*, [5] **9**, I, 212 (1900).

[8] Haller, *Compt. rend.*, **112**, 143 (1891).

2. It was proved to be borneol by conversion into its phenylurethan, m. p. 140–141°, and its oxidation to camphor, m. p. 176°.

3. It was proved to be free from isoborneol.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON PYRIMIDINES. C111. THE DISCOVERY OF 5-METHYL-CYTOSINE IN TUBERCULINIC ACID, THE NUCLEIC ACID OF THE TUBERCLE BACILLUS[1]

BY TREAT B. JOHNSON AND ROBERT D. COGHILL[2]

RECEIVED AUGUST 5, 1925 PUBLISHED NOVEMBER 5, 1925

Introduction[3]

The problems of the greatest interest and importance to the organic chemist who is interested in the life processes of animal and plant cellular organisms are those dealing with a more accurate determination and definition of the composition and molecular structure of the fundamental, constructive constituents of the cell. The biological development of cellular organisms is dependent upon the interaction of characteristic organic combinations functioning in the living cell, and the normal life changes taking place during its growth are only revelations of profound and progressive alterations in chemical structures.

Of the many forms of bacterial cells which have been shown to exist in nature, that group which embraces the pathogenic type and operates as an enemy to mankind deserves the first consideration. Fortunately, the tubercle bacillus, which has probably received more attention than any other representative of this group, is an organism which can now be obtained easily in large quantity and thereby made available for accurate chemical research. Due to the progress that has been made in the artificial cultivation of this pathogenic organism, and through the assistance of the Research Committee of the National Tuberculosis Association, it has been made possible for us to obtain the interesting chemical results which we now report in this paper. The questions whether any constitutional differences exist between pathogenic and non-pathogenic organisms and whether such differences are detectable by application of the chemical method of research, are important ones and will receive attention during

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[1] This research was supported and made possible by a special grant given by the National Tuberculosis Association, for which the writers hereby desire to express their thanks and sincere appreciation.

[2] Holder of the National Tuberculosis Association Research Fellowship, 1924–1925.

[3] A report of the results of this research was presented before the Organic Division of the American Chemical Society, at the Spring Meeting in Baltimore, April, 1925.