

LXVI.—*The Production of Camphor from Turpentine.*

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THE formation of camphor from turpentine has been accomplished by several chemists, but, probably owing to the smallness of the yield, the camphor so obtained has never been very fully examined, nor has its relationship to natural camphor, on the one hand, and to turpentine on the other, been satisfactorily ascertained.

In this preliminary note we describe two methods by which

camphor can be obtained from turpentine in fairly large quantity; and at the same time we give some account of the various products obtained, which are of interest in tracing the connection between turpentine, camphene, and camphor.

Both processes depend, in the first instance, on the production of the solid hydrochloride of turpentine, the so-called "artificial camphor."

In the first process employed, this hydrochloride is distilled over moderately hot soda-lime, to obtain camphene; then, after a partial purification, the camphene is shaken up with a strong solution of hydrochloric acid to convert it into camphene hydrochloride. This is heated with acetate of potassium and glacial acetic acid to give acetate of borneol; and finally, the acetate of borneol, when saponified with alcoholic potash, yields *borneol*.

The second process employed is simple, and seems to give a more satisfactory yield. The terpene hydrochloride is heated with potassium acetate and glacial acetic acid in sealed tubes at about 250°, when it gives a high-boiling liquid which, on saponification, yields *borneol*.

The turpentine employed was the ordinary dextrorotatory australene. It was allowed to stand for some time over dry carbonate of potash, and then distilled, when it boiled fairly constantly at 158—159°, the temperature being allowed to rise to 163° at the end. Its sp. gr. was found to be—

$$0.8705 \text{ at } \frac{9.5^\circ \text{ turpentine}}{15.5^\circ \text{ water}}.$$

Its rotatory power (determined with a Laurent half-shade polarimeter) was found to be—

$$[\alpha]_D = +11.3^\circ \text{ at } 9.5^\circ.$$

The hydrochloride was prepared by saturating the turpentine with gaseous hydrogen chloride, and crystallising from alcohol the solid product obtained.

The rotatory power of the hydrochloride was determined in alcoholic solution—

$$[\alpha]_D = +4.8^\circ.*$$

* We are unable to confirm the observation of Wallach and Conrady (*Annalen*, 252, 156) or of Pesci (Abstr., 1889, 158), that dextropinene chlorhydrate is inactive. We have made several determinations, and always found the substance to be dextrorotatory, but it is not the optical isomer of the chlorhydrate of French turpentine. The names + and - pinene are therefore hardly suitable for these terpenes.

Production of Camphene.

Several methods for obtaining camphene from terpene hydrochloride were tried, for example, distilling with soap, and heating with alcoholic potash. The most satisfactory method for obtaining the substance quickly, and in large quantity, was found to be the distillation of the hydrochloride over moderately heated granular soda-lime. The camphene so obtained boils at about 160° , and is a liquid, being kept in solution evidently by small quantities of liquid impurity. Indication was, however, obtained that the camphene could be separated in the solid form, either by freezing or by partial oxidation with chromic mixture. But these processes were not adopted, as being unnecessary for our purpose.

Preparation of Borneol.

The camphene was then shaken up with fuming hydrochloric acid, and the solid substance which separated was collected on a filter, pressed, and dried. This was heated with potassium acetate and glacial acetic acid at about 200° for three hours. On then separating and distilling, it gave some camphene and a considerable quantity of a higher-boiling liquid, presumably the acetate of borneol, which was not specially purified, but at once saponified with alcoholic potash.

The product of saponification, when distilled, yielded a solid of high melting point and camphorous odour. A portion was still further purified, by sublimation, for analysis. It melted at about 200° , and gave:—

	Found.	Calculated for $C_{10}H_{18}O$.
C	78.04 per cent.	77.92 per cent.
H	12.16 ,,	11.68 ,,

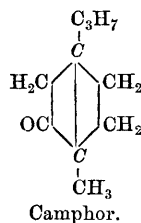
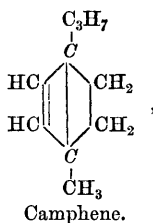
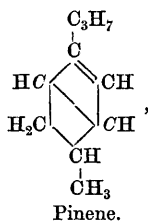
The substance is, therefore, borneol.

Borneol direct from Terpene Hydrochloride.

The second method for obtaining borneol is much less tedious than the one just described in that it is not necessary to first prepare camphene. Wallach (*Annalen*, **239**, 6) has given a method for preparing camphene by heating terpene hydrochloride, 1 part, sodium acetate, 1 part, and glacial acetic acid, 2 parts, for 3—4 hours, at a temperature approaching 200° . A slight modification of this process yields acetate of borneol, as well as, and apparently in larger quantity than, camphene.

The mixture was heated in sealed tubes for 3—4 hours at about 250°, each tube containing 20 grams of terpene hydrochloride, 12 of potassium acetate, and 10 c.c. of glacial acetic acid. When cold, the contents of the tubes were distilled in steam, the distillate separated from water, dried, and distilled. From the lower-boiling portion camphene was readily obtained in the solid state (b. p. 154—156°), whilst a considerable portion distilled above 190°, condensing as a liquid. This was saponified with alcoholic potash, when borneol was obtained. This crude borneol was oxidised by nitric acid, when an inactive camphoric acid was obtained.

Professor Wallach, in his masterly investigation of the terpenes, has given some consideration to the constitution of turpentine, which he calls pinene, of camphene, and of camphor. He represents their constitution by the following formulæ:—



Such formulæ as these, whatever their justification, are certainly open to criticism, both on general and on particular grounds. In the first place, are the compounds which they represent to be regarded as hexamethylene- or as double tetramethylene-derivatives? In the latter case, why should hexagonal symbols be retained? In the former case, have we any evidence of cross-linking between carbon-atoms in the 1 : 4-position? And if we adduce anthracene as an instance, ought not pinene to resemble anthracene, and be capable of yielding a quinone on oxidation? Consider further the remarkable rearrangement of nuclei in passing from pinene to camphene, as expressed by the symbols. Have we any analogy for such a change? It is, for example, as if quinoline, by a simple reaction, could yield isquinoline, or as if a homonuclear substituted naphthalene could yield a heteronuclear, and *vice versa*. Then, again, the more obvious characters of camphoric acid are inconsistent with Wallach's camphor formula.

But, perhaps, the strongest argument against these formulæ is derived from the application to them of the hypothesis of the asymmetric carbon-atom. Professor Wallach accepts, in general, that the rotatory power of a body is conditioned by the presence of an asymmetric carbon-atom, but he is scarcely consistent in following out the

consequences of the theory. One of these consequences is, that any exchange of groups or linkages about an asymmetric carbon-atom must lead to the production of an inactive body, as far as concerns the rotatory power due to that carbon-atom. For since there is an equal chance for the formation of both optically opposite isomers, they will both be found in equal quantity.

On the other hand, simple substitution, or the alteration of groups by oxidation, &c., will not necessarily affect the optical isomerism.

Camphor then and camphoric acid obtained from an active pinene, which has been found to yield an active camphene, should be themselves active. We find, however, that camphoric acid obtained from active pinene is inactive. Moreover, if camphene and camphor are to be regarded, according to Wallach's formulæ, simply as unsaturated hexamethylene-derivatives, then they are in no case capable of rotatory power, for the formulæ do not possess a non-superposable image.

Without in any way presuming to detract from the high merit of Professor Wallach's experimental work, we venture to submit that his formulæ for pinene, camphene, and camphor are inconsistent with the properties and reactions of those compounds, and without analogy in organic chemistry.

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