A NEW DITERPENE—γ-CAMPHORENE.

By Kinzô KAFUKU, Taichirô OYAMADA and Masura NISHI.

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It was F. W. Semmler and Irene Rosenberg(1) who first liberated the diterpenes α- and β-camphorenes out of the high-boiling fraction of camphor oil, and shortly afterwards these were synthetically prepared by Semmler and K. G. Jonas(2) from the aliphatic terpene myrcene by the action of heat and pressure on it. These diterpenes are regarded as monocyclic as they give tetrahydrochlorides as well as octahydro-compounds, and also as their molecular refractions accord with $C_{20}H_{32} \models_{4}$, but, as to their constitutional formulae, nothing exact is yet known. Only, L. Ruzicka and M. Stoll(3) have suggested the following one for α-camphorene from considerations of its mode of formation from myrcene and of the oxidative destruction of its octahydro-derivative, taking into account that myrcene which represents isopentenyl-isoprene, ought to undergo an analogous polymerization as isoprene does to form dipentene, but this deduction is not rigorous enough.

One of the present authors (K), during his former experiments with Formosa lemongrass oil, proceeded with his terpene fraction exactly as described by Semmler and Jonas, in order to identify myrcene in it, and it was that his crude α-camphorene tetrahydrochloride appeared under the microscope to be a conglomerated mixture of two distinctly differently shaped crystals—the one representing thin hexagon plates, the other tiny needle-shaped prisms. Furthermore, he observed that pure α-camphorene tetrahydrochloride corresponding to the descriptions of Semmler and others could only be attained after several consecutive recrystallizations of this crude product from hot ethyl alcohol, and that at the pure stage, no more needle-like crystals were to be seen under the microscope except in very small amount. With a view to clear up the nature of this prismatic contamination, the present authors recently resumed the study in this field of research, and, after a series of experiments, at last arrived at the conclusion that among the diterpenes resulting from the polymerization of myrcene, there existed a hitherto unknown diterpene which leads to a new hydrochloride melting at 96–98°C., and which crystallizes

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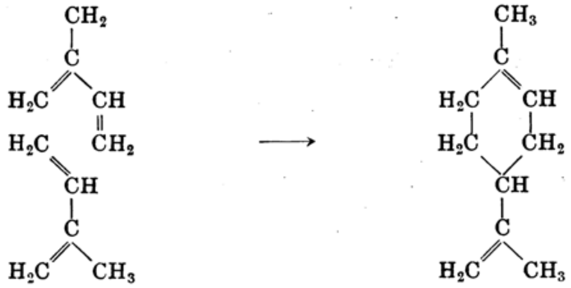
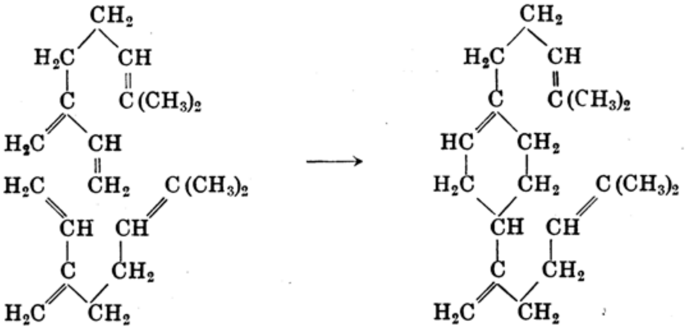
(1) *Ber.* **46** (1913), 768.

(2) *Ber.* **46** (1913), 1566; **47** (1914), 2077.

(3) *Helv. Chim. Acta*, **7** (1924), 271.



Isoprene. Dipentene.



Myrcene α-Camphorene

in prismatic needles. The reason why this diterpene slipped the elaborate hands of such renowned chemist as Semmler, is because this hydrochloride is readily decomposed by hot alcohol never to crystallize again. To this new diterpene, the authors propose the name "*γ-camphorene.*"

γ-Camphorene has almost the same physical properties as the α-modification as can be seen from the following data:—

	α-Camphorene	γ-Camphorene
b. p. / 4.5 mm.	178°	176–178°
d	$0.8864_{(21/4)}$	$0.8875_{(19/4)}$
n_D	$1.4998_{(21)}$	$1.5030_{(19)}$
M. R.	90.7	90.6
Do. calc. as $C_{20}H_{32} \models_4$	90.48	

γ-Camphorene tetrahydrochloride is readily soluble in cold petroleum ether while α-camphorene tetrahydrochloride is not, and thus the two can easily be separated from each other. The γ-hydrochloride can be recrystallized from warm petroleum ether without decomposition, and the purified crystals melt at 96–98°C. The γ-hydrochloride, on treatment with alcoholic potash, regenerates γ-camphorene and this regenerated hydrocarbon, on being acted on by dry hydrogen chloride gas, redeposits the needle-crystalline γ-camphorene tetrahydrochloride only, and no more plate crystals of α-camphorene tetrahydrochloride with it. By the action of hydrogen bromide gas, α-camphorene gives a tetrahydrobromide melting at 133–134°C., while γ-camphorene yields a corresponding hydrobromide melting at 111–114°C.

Experimental.

Myrcene. The starting material myrcene was obtained partly from Formosa lemongrass oil and partly from linalool. That from the former was prepared by carefully fractionating the crude oil dried over anhydrous sodium sulphate under 50 mm. pressure, and then shaking the terpene fraction thus obtained with 40% sodium bisulphite solution, and finally distilling the product over metallic sodium. The other portion from linalool was obtained in the following way: To pure linalool kept in a flask and heated to 100–120°C., iodine in form of fine powder was slowly added, when a violent reaction took place. The mass was distilled under 100 mm. pressure, and the process was repeated with the distillate until all linalool decomposed. Then the product was distilled over metallic sodium and was rectified under 12 mm. pressure. Myrcene thus obtained showed the following physical properties:—

b. p. / 12 mm.	55°C.
d	$0.8030(_{19}/_{4})$
n_D	1.4680

Polymerization of Myrcene. Myrcene was heated in a sealed tube in a bomb furnace up to 240–260°C. for four hours. After cooling, the content of the tube was fractionated under 6 mm. pressure, when about 30% came over between 51° and 55°C., which turned out to be an isomerized monocyclic terpene with some unchanged myrcene, the properties of which are as follows:

b. p.	51—55°C. / 6 mm.
d	$0.8420(_{22}/_{4})$
n_D	$1.4680(_{22})$
M. R.	44.9
Do. calc. as $C_{10}H_{16} \models_2$	44.90

The next 44% distilled between 162° and 176°C., and showed the following constant:

b. p.	162—176°C. / 6 mm.
d	$0.9203_{(24/4)}$
n_D	$1.4960_{(24)}$
M. R.	88.3
Do. calc as $C_{20}H_{32}\ \|\!=_4$	90.48

These constants are in accordance with Semmler's data for crude camphorene.

α- and γ-Camphorene Tetrahydrochloride. The crude camphorene thus obtained was dissolved in its own volume of absolute ether and was saturated with dry hydrogen chloride gas and stood overnight in cold. The gruel-like mass of crystals thus produced was freed from the adhering liquid on porous porcelain and then it was boiled with light petroleum ether and filtered while warm. From the filtrate there precipitated on cooling the needle-like crystals of γ-camphorene tetrahydrochloride m.p. 96–98°C. The filtered crystals were washed with warm petroleum ether several times, dried, and then recrystallized from hot alcohol. The crop of crystals so obtained, on inspection under the microscope contained no more needle-shaped crystals of γ-camphorene tetrahydrochloride, and melted at 129–131°C., representing pure α-camphorene tetrahydrochloride.

Anal.: Crystals (m.p. 96–98°C.) = 2.730; AgCl = 3.762 mg.
Found: Cl = 34.17%. Calc. for $C_{20}H_{36}Cl_4$: Cl = 33.91%.
Crystals (m.p. 129°–131°C.) = 3.386; AgCl = 4.480 mg.
Found: Cl = 33.50%. Calc. for $C_{20}H_{36}Cl_4$: Cl = 33.91%.

Regeneration of α- and γ-Camphorenes. Ten grams each of α- and γ-camphorene tetrahydrochlorides were separately dissolved in an excess of 10% alcoholic potash, boiled under reflux for seven hours on the water-bath, saturated with carbon dioxide, filtered from depositing solid matters, alcohol distilled off, and finally the residual substance was distilled in vacuo over metallic sodium. The yield of the ultimate product in each case amounted, in the case of α-camphorene to about 98%, and in that of γ-camphorene to about 75% of the theory, and each exhibited such properties as given in the preceeding page. These, on treatment with hydrogen chloride, gave the respective hydrochlorides only, and not the mixture of the two hydrochlorides.

α- and γ-Camphorene Tetrahydrobromides. On treatment of these two diterpenes with hydrogen bromide gas, tetrabromides resulted. From α-camphorene lustrous scaly crystals crystallized out which after purification melted at 133–134°C., while from γ-camphorene, prismatic needle crystals separated out with m.p. 111–114°C. Both could be recrystallized from petroleum ether, but the γ-modification was more soluble than the α-hydrobromide, and moreover, it exhibited a remarkable tendency to decompose on dissolving in hot alcohol.

Anal.: α-Hydrobromide = 5.910; AgBr = 7.500 mg.
Found: Br = 53.96%. Calc. for $C_{20}H_{36}Br_4$: Br = 53.66%.
γ-Hydrobromide = 4.937; AgBr = 6.180 mg.
Found: Br = 53.34%. Calc. for $C_{20}H_{36}Br_4$: Br = 53.66%.

Camphorene Octabromide. By the action of bromine, α- and γ-camphorenes give an undefined crystalline octabromide, seemingly identical. For this purpose, an ethereal solution of each hydrocarbon was treated by an excess of bromine, also in the same medium. The reaction mass was stood still in an ice chamber overnight, excess of bromine and ether expelled in vacuo, the residue which at first assumed a syrupy consistency, gradually solidified on keeping. Then, it was powdered, redissolved in ether, a little methyl alcohol added thereto, filtered, and evaporated in cold. Thus, from both hydrocarbons, a white crystalline powder was obtained which melted between 70° and 80°C., showing no lowering of the melting point by mixing with each other. Other methods of purification were tried to attain to a more definite melting point but in vain.

Anal.: Substance from α-camphorene = 6.105; AgBr = 10.026 mg.
Substance from γ-camphorene = 4.237; AgBr = 6.871 mg.
Found: Br = 69.91; 69.01%. Calc. for $C_{20}H_{32}Br_8$: Br = 70.17%.

Laboratory of Organic Chemistry,
Taihoku Imperial University, Taihoku.