

13047
49.

A STUDY
of

C A M P H O R O X I M E .

oooOooo

A THESIS

Submitted to the Examining Committee of the Faculty

at the

University of Minnesota

for the Degree of

D O C T O R o f P H I L O S O P H Y

by

Paul Maurice Glasoe, M. S.

oooOooo

Minneapolis Minn.

May 19, 1902.

MOD
G 46

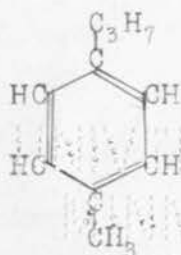
HISTORICAL PART.

AUG 1 8 1910

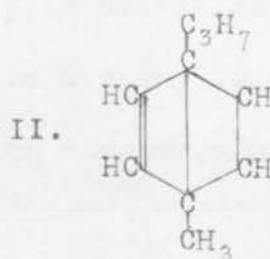
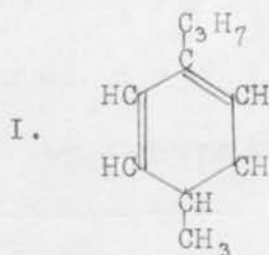
The peculiar odors of many blossoms, juices of fruits and saps of trees, especially of the Coniferae and varieties of Citrus, are due to a series of volatile or etherial oils, known by the general name of terpenes. The oils are obtained either by distillation with steam or by pressure. The close relation existing between the para-benzole compounds, cymol, thymol, carvol, carvacrol, an-thol, eugenol, etc., and the terpenes and camphor deriva-tives, establishes to a great extent their formulas. Thus terpine goes directly into cymol when heated with io-dine and yields various benzole derivatives upon oxydation. That they are unsaturated compounds may be seen from the ease with which they form addition products with bromine and halogen hydride.

From a study of the chemical and physical properties of the terpenes, they may be divided into three classes:
1) those with two double bonds, which are able to unite with four univalent atoms or radicles, and upon oxydation

yield acids of the fatty series; 2) those with one double bond, capable of uniting with two atoms of a univalent substance and on oxidation pass into camphor; 3) those which have no double bonds, but form nitrosites with nitrous acid. Representing cymol as para-isopropyl-methyl benzole,



the first class, to which belong citrene, dipentene, isoprene, terpinolene and sylvestrene, may be represented by formula I, of which seven varieties are possible, four active and three inactive; the second class, with one unsaturated linkage by formula II, of which there are three isomers possible, two with two asymmetric carbon atoms and one with three.



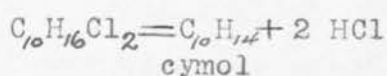
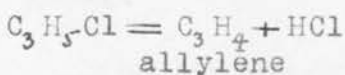
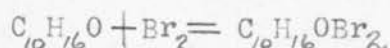
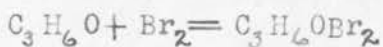
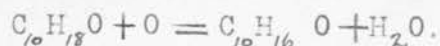
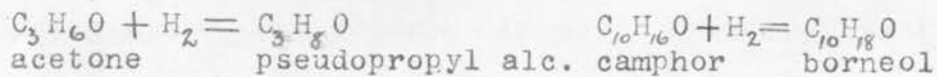
(3)

To the second class belong australene, pinene, and terebenthene. The third class with isopropyl and methyl in the para position must be either

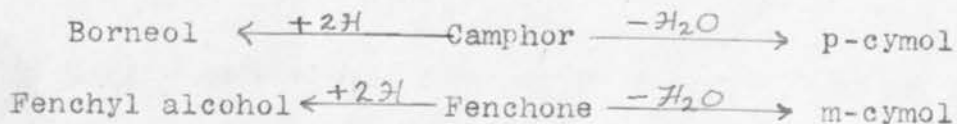


By addition of hydrogen the terpenes become hydro-terpenes, which give rise to a large number of alcohols and ketones, classed under the general name of camphors. The camphors differ from the terpenes in that they are all solid while only one solid terpene is known. Borneo camphor or Borneol, $C_{10}H_{17}OH$, and Menthol $C_{10}H_{19}OH$, have long been recognized as alicyclic alcohols, forming esters with organic acids, xanthogenates with bisulphide of carbon and passing into camphene and menthene on removal of a molecule of water. Treating borneol with nitric acid camphor is produced, $C_{10}H_{16}O$. This, which is distinguished from the rest of the camphor group as Japan camphor, was proven to

be a ketone by its similar behavior to acetone, which may be shown as follows:



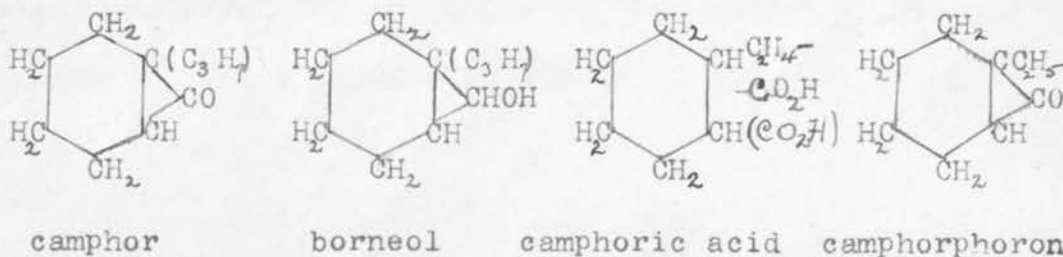
Ordinary or Japan camphor occurs in three varieties in nature, two optically active and one inactive. Then there is a substance isomeric with camphor which has been named fenchone, apparently identical with it in chemical and physical properties, but which must be different in structure inasmuch as it yields different products upon treatment with dehydrating or reducing agents. The difference may be represented as follows:



Japan camphor is found in the camphor tree (*Laurus camphora*); is obtained by distillation with steam and purified by sublimation. It has a melting point of 175°C.

boils at 204° ; $[\alpha]_D = 44.22$ in alcohol. Artificially it can be prepared by oxidizing borneol with nitric acid and camphene with chromic acid. It has a specific gravity of .985. Yields pure cymol when distilled slowly with phosphoric anhydride, and on boiling with iodine it forms carvacrol.

Berthelot¹⁾ as early as 1858 had discovered that camphor would yield with alcoholic potash the compound $C_{10}H_{18}O$, or borneol, and from that time on numerous attempts have been made to express the structural formula of camphor and allied compounds. Kachler²⁾ in 1872 gave the following:

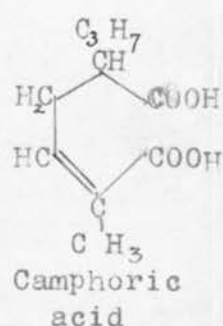
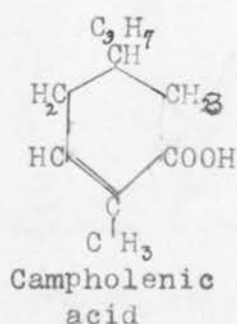
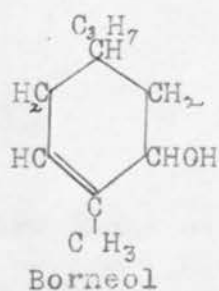
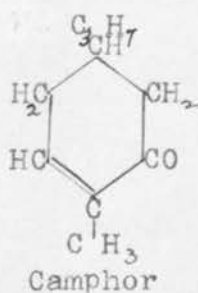


Kekulé³⁾ made a more exhaustive study of camphor and terpenes than any of the previous investigators. Although formulas had been proposed by Victor Meyer, Kachler and others he held that the difficulties in the way of deter-

¹⁾ Jahresberichte, 1858-441.

²⁾ Jahresberichte, 1873-929.

ining the structure of camphor had increased rather than decreased, and that to meet with success one had to collect data from which to derive a formula and then make new experiments on camphor derivatives and varieties. In developing his formula he had the following facts in mind: that camphor is essentially of an indifferent nature; that it changes into the alcoholic body borneol; the building of of a monobasic campholenic acid through the influence of alkalies; the change through oxydation into the dibasic camphoric acid. He also reasoned that going so easily into cymol it likely contained both methyl and isopropyl groups. These considerations led him to propose these formulas for camphor and its immediate derivatives:



This considers camphor a ketone having a CO group

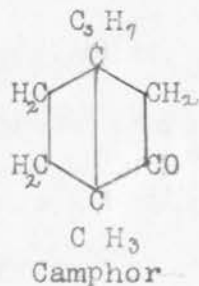
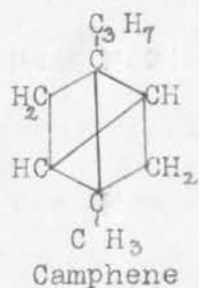
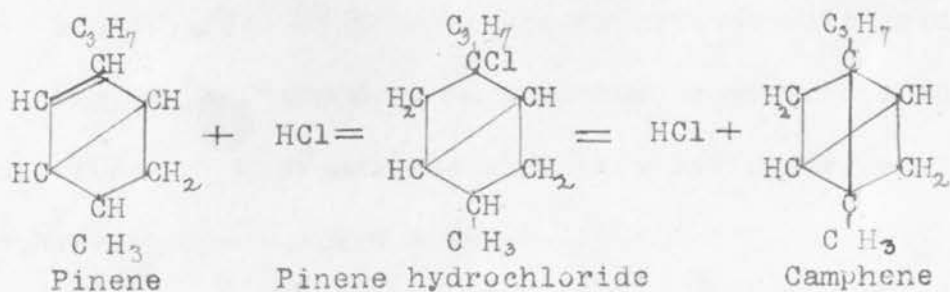
connected on both sides to a carbon chain. It shows its relation to cymol by a six atom carbon ring.

After the discovery of Dale and Gladstone's law a great deal of work was done on organic compounds as it was found that the physical arrangement of the molecules exerted a definite influence upon the molecular refractive constant. Thus Kanonnikoff investigated ethylcamphor and from its refractive constant concluded that it did not possess a double linking as expressed by the Kekulé formula. Brühl confirmed this view by using the theoretical formula $(\frac{n^2-1}{n^2+2})\frac{P}{d}$, while Kanonnikoff used the old Gladstone and Dale formula and came to the same conclusions. To conform to this view he suggested writing ^{the} Kekulé formula either

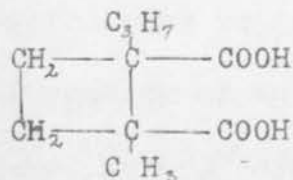


Berthelot and Riban succeeded in converting pinene into camphor, and this reaction may be represented by the following changes:

(8)



Later in a very extensive study of camphoric acid and its esters, Brühl¹⁾ compared the Kekulé and diagonal formulas. The Kekulé formula for camphoric acid may be written thus: $\text{HOOC}-\underset{\text{C}_3\text{H}_7}{\text{CH}}-\text{CH}_2-\underset{\text{C H}_3}{\text{CH}}=\text{C}-\text{COOH}$, which would be α -methyl- δ -isopropyl $\Delta^{\alpha/\beta}$ hydromuconic acid, but the researches of von Baeyer have proven that $\Delta^{\alpha/\beta}$ hydromuconic acid has the formula: $\text{HOOC}-\text{CH}_2-\underset{\beta}{\text{CH}_2}-\underset{\alpha}{\text{CH}}=\text{CH}-\text{COOH}$. The diagonal formula on the other hand would be,



1) Berichte-14-3373

or a derivative of tetramethylene dicarboxylic acid. The problem was therefore to show whether camphoric acid is a substituted hydromuconic acid or a derivative of tetramethylene dicarboxylic acid.

Menschutkin¹⁾ showed that the formation of esters takes place most rapidly in the primary acids, and slowest in the tertiary, and that camphoric acid possess the properties of a tertiary acid. It was shown also by Victor Meyer, Auwers, Bischoff, that the difficulty of forming anhydrides of the acids of the succinic type increases in proportion to the number of alkyl radicles which have been substituted for hydrogen. Reasoning from this it is not surprising that such a tetra substituted compound— ethylene-methyl-isopropyl-succinic acid, should show it to a large extent. Brühl makes the following conclusion: The entire chemical behavior of camphoric acid toward oxydizing and reducing agents, toward halogen hydride and bromine; further its weak tendency to form acids and its resistance toward the formation of an anhydride, go to prove that it is not a derivative of $\Delta^{\alpha\beta}$ -hydromuconic acid, while

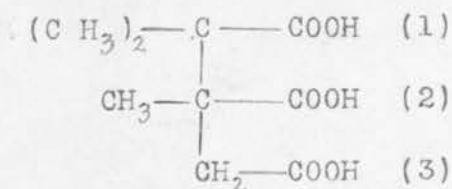
1) Berichte, 14-2631; 1881.

it bespeaks most plainly the succinic structure. Viewed side by side it can be seen that of the hydromuconic acid derivative there can be only three isomeric forms, one dextro rotatory, one laevo- and one inactive, while in reality there are four known for a certainty, and two more have been suspected by Wreden and others. Considering it a tetra methylene derivative there are six forms possible, because it contains two assymmetric carbon atoms, one united to the methyl the other to the isopropyl group. The possible forms are, one strongly positive, one equally strongly negative; one weakly positive and one equally weakly negative, and two racemic varieties. If then camphoric acid is considered proven to be a succinic acid derivative it becomes necessary to represent camphor as a double tetra methylene ring with isopropyl and methyl in the para position. The change from camphor to camphoric acid may be represented thus:



For twenty years or more the Kekulé formula, with the diagonal modification remained the standard for camphor and its derivatives. A large number of compounds were however made which could not be explained on the basis of the Kekulé formula. Bredt carried out a very exhaustive series of experiments on the oxydation products of camphor and came to the conclusion that none of the formulas yet proposed could explain the changes which took place, and hence did not express the true formula of camphor or its derivatives. He found that on oxydation camphor yields camphoric acid $C_{10}H_{16}O_4$, camphanic acid $C_{10}H_{16}O_5$, and camphoronic acid $C_9H_{14}O_6$. He worked especially on camphoronic acid with the hope of clearing up through it the structure of camphor and camphoric acid. In its behavior it resembles tricarballic acid and passes on slow distillation, under atmospheric pressure, into carbon dioxide, water, carbon, isobutyric acid, trimethylsuccinic acid and a small amount of phoron like substance. He tried to express these facts by building a formula for camphoronic acid which becomes then trimethylsuccinic acid in which one hydrogen at-

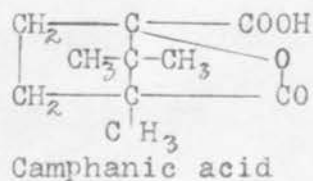
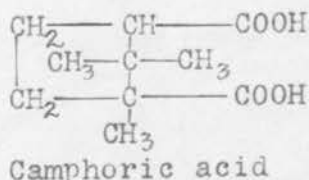
om has been replaced by the group $-\text{CH}_2\text{COOH}$, and and may be expressed by the following scheme:



Breaking this up between 1 and 2 there appear two molecules of isobutyric acid and one molecule of carbon dioxide. If it breaks between 2 and 3 it gives rise to trimethylsuccinic acid with carbon dioxide and free carbon remaining, thus:

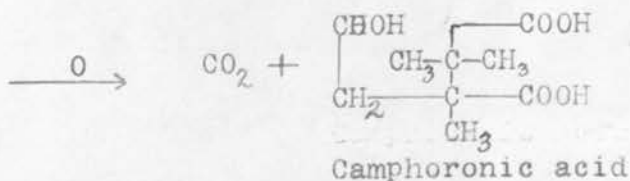
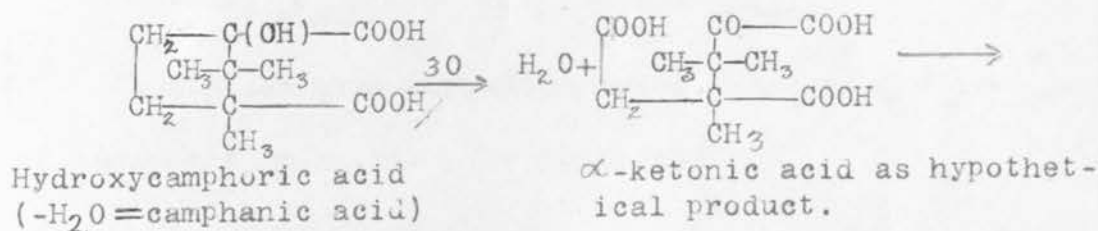
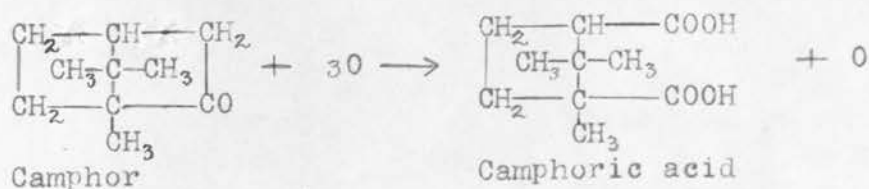


He believes that all three oxydation acids possess the same arrangement of carbon atoms and proposes the following formulas:

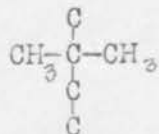


The oxydation would then go on as follows:

(13)

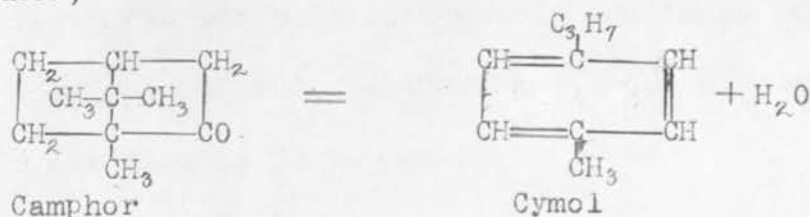


It had long been known that camphanic acid was formed from brom- camphoric acid and this formula shows how the reaction can take place by splitting off one molecule of hydrobromic acid and then through the lactone reaction giving rise to camphanic acid. Königs has shown that camphoric acid when oxydized with chromic acid yields trimethylsuccinic acid, which tends to confirm the grouping

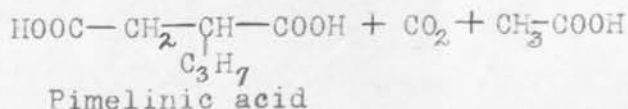
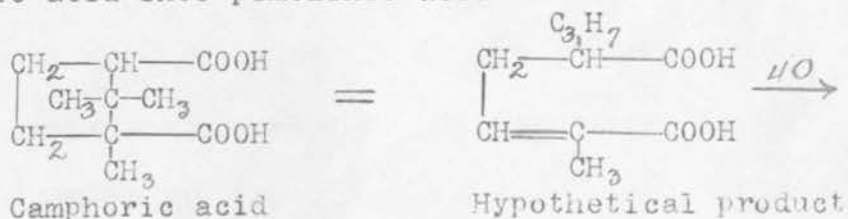


The production of cymol from camphor may take place

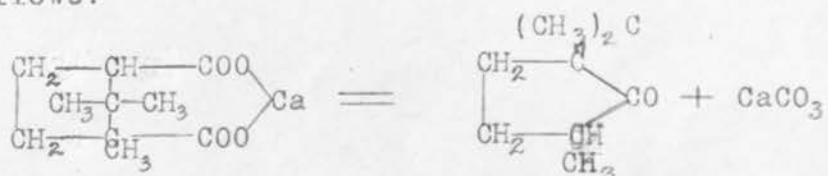
in this manner,



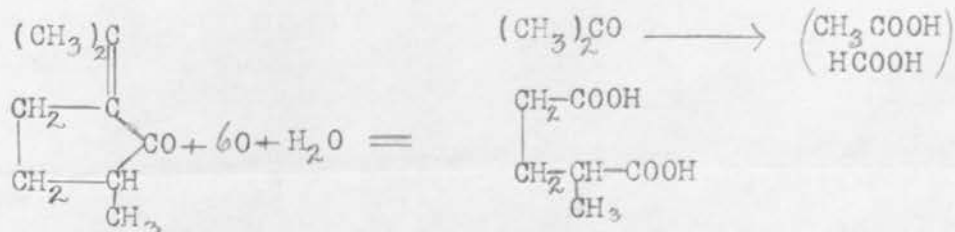
A similar transformation takes place in the changing of camphoric acid into pimelinic acid:



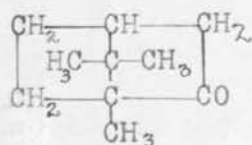
By distillation of the calcium camphorate phoron is as follows:



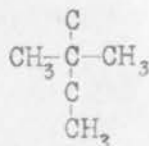
The oxydation of phoron into methyl glutaric acid, acetic acid and formic acid may be represented by,



Bredt has proven still further that among the oxydation products of camphor with nitric acid are found esters of oxalic, dimethyl malonic, succinic and trimethylsuccinic acids. In the formula for camphor



can be seen on the left side the atomic grouping $\begin{array}{l} \text{CH}_2 - \text{C} - \\ | \\ \text{CH}_2 - \text{C} - \end{array}$ which represents the grouping of succinic acid; in the middle the arrangement for dimethylmalonic acid, $\begin{array}{c} \text{C} \\ | \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\ | \\ \text{C} \\ | \\ \text{CH}_3 \end{array}$ and trimethylsuccinic acid.



Camphoroxime.

Perhaps the most satisfactory proof of the ketonic nature of camphor was furnished by Naegli, who made a very exhaustive study of just such substances as were known to be formed by the oxidation of secondary alcohols. He reasoned that if Kekule¹⁾ was correct in his theories, each of the ketones he had described ought to react with hydroxylamine to form the characteristic oxime. He succeeded in introducing an oxime group into both menthone and Japan camphor, and accordingly named them menthoneoxime and camphoroxime. To be sure this did not absolutely prove the ketonic nature of camphors, as they might be aldehydes, and the resulting hydroxylamine product an aldoxime, but the fact that borneol is changed to camphene on separation of one molecule of water, and changes from borneol to camphor by removal of two atoms of hydrogen, goes to show that camphor is a ketone rather than an aldehyde. Besides, the aldoximes readily decompose in the presence of dilute mineral acids, into hydroxylamine and the corresponding

1) Berichte, 16-493.

hydrocarbon, while Naegli found that his camphoroxime remained intact even in the presence of warm sulphuric acid.

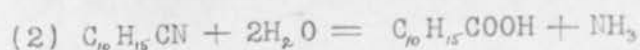
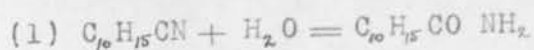
The discovery of camphoroxime gave rise to a very interesting series of new camphor derivatives. Having determined the structure of his new compound Naegli proceeded to investigate whether it would act like other oximes in forming derivatives. He made its sodium salt, $C_{10}H_{15}NO_2Na$, and also its ethyl ester, fully deciding its acid nature. In attempting to make an acetyl ester of camphoroxime by treating it with acetyl chloride he met with a very interesting reaction although the product was not what was expected. Instead of an acetyl ester there appeared an aromatic smelling liquid which corresponded to the formula $C_{10}H_{15}N$. It was plain that it was formed by the removal of a molecule of water from camphoroxime, and consequently he named it camphoroxime anhydride. He suspected that it was in reality a nitrile of an acid, but repeated attempts to saponify it failed. Instead he obtained after several hours of heating with alcoholic potash, a white crystalline sol-

id which proved to^{be} isomeric with camphoroxime. Being satisfied that they were not the same he named it isocamphoroxime.

Goldschmidt¹⁾ proved that the so-called anhydride was in reality a nitrile by causing it to combine with another molecule of hydroxylamine, and further, by obtaining after several days heating with alcoholic potash a successful saponification of the material. The reaction gave rise to an acid which has later been called campholenic acid. This compound has since been fully studied and made in a variety of ways, and many of its most important derivatives made. Goldschmidt also proved Naegli's isocamphoroxime to be the amide of campholenic acid. The only difference between the work of Naegli and Goldschmidt being that the former secured only a partial saponification while the latter succeeded in adding two molecules of water thus forming a molecule of ammonia, and one of the campholenic acid. The difference of the two reactions may be shown as follows:

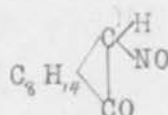
1) Berichte, 1885-1632.

(19)

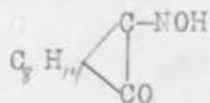


Dicamphoroxime and Isonitrosocamphor.

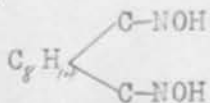
By reduction of monochloronitro camphor Cazeneuve obtained nitrocamphor which he indicated by the following formula:



and by acting upon camphoroxime with amylnitrite and sodium ethylate Claissen and Manasse obtained an isomeric solid which they represented by



and which they named isonitrosocamphor. The NOH-group present in this compound appears to be a true oxime group and upon treatment with hydroxylamine they obtained a true dicamphoroxime,



They also succeeded in splitting off the oxime group

- 1) Bulletin Soc. Chim., Serie III, 1, 558, 2-199.
- 2) Annalen, 274-73.

of isonitrosocamphor thereby forming a molecule of hydroxylamine and one molecule of camphorquinone. Indicating the two oxime groups by alpha and beta, isonitrosocamphor may be called the beta oxime of orthocamphorquinone.

Manasse¹⁾ investigated the dioxime of orthocamphorquinone and found that by treating the isonitrosocamphor directly with hydroxylamine hydrochloride either in alcoholic or in caustic soda solution, the dioxime would form. He found three varieties, two in the alcoholic and one in the caustic soda solution, melting at 181° , 270° , and 131° , respectively. The one obtained from the alkaline solution solidified again after melting at 131° , and melted at 181° , showing that it had been changed into its isomer of that melting point.

1) Berichte, 26-243.

EXPERIMENTAL PART.

There are two camphoroximes according to whether they are made from dextro- or laevo-rotatory camphor. Beckman, who carried out a very extended series of experiments on the optical properties of camphor derivatives, states that the oxime produced from dextro-rotatory camphor is strongly laevo-rotatory, while that made from the laevo-camphor is dextro-rotatory. They are alike in properties, both crystallizing in needles and melting at 115°.

Camphoroxime is best made by observing the following proportions: 10 grams of camphor are dissolved in 115 cubic centimeters of 95% alcohol; 10 grams of hydroxylamine hydrochloride added and the mixture shaken until the latter is all dissolved. The experiment is just as successful and much more rapidly carried out if the hydroxylamine hydrochloride is first dissolved in the minimum amount of water. To this mixture is added 15 grams of powdered chemically pure caustic soda, and the whole shaken with frequent warming until the latter is all dissolved.

The process may be hastened considerably without any injury to the experiment by adding from time to time a small amount of water thus hastening the solution of the alkali. The whole is then heated upon a water bath with a reflux condenser until the precipitate obtained by adding dilute sulphuric acid completely dissolves in an excess of the acid.

CAMPHOROXIMEPHTHALICACIDESTER.

With the expectation that phthalic acid anhydride would react with camphoroxime a slight excess of the former was added to a benzene solution of the oxime, and the mixture heated for several hours on the water-bath. When the solution was cooled a considerable quantity of crystals was deposited on the sides of the flask. Some of these were redissolved on further heating, while the remainder seemed insoluble even after long boiling. The benzene was evaporated and left a white residue which melted at 136° . This was purified from excess of the anhydride by treatment with water in which the camphoroximephthalicacidester is insoluble. The crystals melt sharply at $135^{\circ}-6^{\circ}$, evidently

with decomposition, as crystals may be seen to form immediately in the clear liquid. This is due to the breaking down of the new compound into phthalic acid and campholenic nitrile, which is proven by the odor of the clear liquid in the melting point tube.

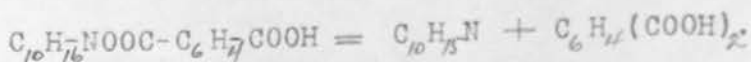
Camphor-oxime-phthalic-acid-ester may be recrystallized by dissolving in alcohol and diluting in water. It forms long needle-shaped crystals. These are readily soluble in chloroform, slightly soluble in ether, alcohol, benzol and amyl alcohol, insoluble in carbon bisulphide and water. Heating the ester in alcohol a heavy colorless liquid was produced which undoubtedly is the ethyl ester of the remaining carboxyl group of the phthalic acid.

The reactions may be indicated as follows:

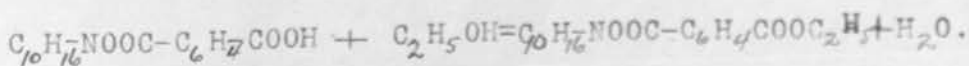
- 1) The formation of the camphoroximephthalicacidester,



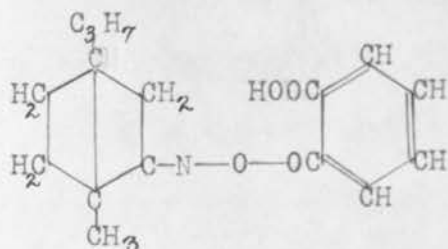
- 2) The decomposition on melting,



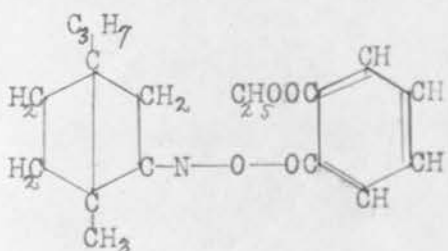
- 3) The formation of the ethyl ester,



The structural formulas may be shown as follows:



Camphoroximephthalic acid ester.



Ethylcamphoroximephthalic acid ester.

Analysis of camphoroximephthalic acid ester - $C_{18}H_{24}NO_4$.

0.1322 gm. of the substance gave 0.3319 Gm. CO_2 and
0.0851 gram H_2O .

	Calculated for $C_{18}H_{24}NO_4$	Found:
C	68.57	68.47
H	6.66	7.14

FORMYL CAMPHOROXIMES.I. Camphorparaformaldoxime, $C_{13}H_{21}NO_3$.

Two interesting compounds are formed when camphor oxime is treated with formaldehyde. If the aldehyde is fresh and contains none of the para form the camphor oxime dissolves in the water solution, but if it is boiled for some time, or exposed to sunlight until the paraformaldehyde has a chance to form, the oxime no longer dissolves but changes at once into an oily colorless liquid. That the paraformaldehyde is the cause of the reaction may be proved by obtaining some of the solid substance by evaporation of the water solution and treating it with some camphor oxime in ether solution. The oil is very soluble in ether and other organic solvents and is therefore easily separated and purified. It is not a stable compound. Allowed to stand at the ordinary temperature in a desiccator it begins to break down, giving rise to the oxime again. Kept in a cold place the decomposition goes on much more slowly.

Properties of the oily liquid:

Specific gravity 1.05

Refractive index at 23° is 1.42615.

 $[\alpha]_D = -35.77.$

Two analyses gave the following results:

I. 0.2060 gm. subst. gave 0.4918 gm. CO₂ and 0.1688 gm. H₂O.

II. 0.2265 " " " 0.5398 " " " 0.1896 " "

	Calculated for C ₃ H ₇ NO ₃ :	I	Found: II
C	65.27	65.02	64.99
H	8.78	9.102	9.3006

Determination of the Molecular Weight by lowering of the Freezing Point.

Weight of benzol taken	14.9698 gm.
Weight of oil taken	0.1310 "
Lowering of the Freezing Point	0.195 degree.
Constant for benzol	53.00

$$\text{Hence } \frac{K \times P}{d \times g} = \frac{53 \times .131 \times 100}{.195 \times 14.9698} = 237.85.$$

Calculated for C₃H₇NO₃ 239.00.

In the formula "K" represents the molecular constant for the solvent used, "p" the amount of material taken and "d" the lowering of the freezing point, "g" the amount of solvent used.

Determination of Molecular Weight

by Traube's Method.

Traube has originated a method for determining the molecular weight of a compound in which he makes use of the following formula:

$$\frac{M}{d} + S = \text{Covolume.}$$

Where "M" is the molecular weight, "d" is the density of the compound, "S" the sum of the atomic volumes of the constituents. The covolume has been found to be a constant and equal to 25.9, which he considers as the space required for the vibration of the molecule above the sum of the atomic volumes.

Calculation of the molecular weight:

C	128.7	C=9.9
H	65.1	H=3.1
N	1.5	N=1.5

O 16.5

O=5.5

Cov..... 25.9

Sum of the atomic volumes = 237.7, to which must be
-8.1 for the presence of a carbon ring of six atoms.

Therefore $S = 229.7$, but "d" is 1.05, and

Molecular Wt. found..... 241.185.

Calculated for $C_{13}H_{21}NO_3$ 239.00

II. Addition Product, Camphorformaldoxime- $C_{10}H_{16}NOCH_2OH$.

If paraformaldoxime is placed in water with some
form aldehyde and allowed to stand for some time beautiful
plates are formed which are soluble in all ordinary or-
ganic reagents, but insoluble in water. The crystals melt
sharply at $62^{\circ}-3^{\circ}$.

Analyses gave the following results:

I .1811 gm. subst. gave .4452 gm. $C O_2$ and .1647 gm. H_2O .

II .2345 " " " .5799 " " " .2042 " "

III.1913 " " " 13 c.c. N, at 23° and 739 m.m.pres.

	Calculated for	Found:		
		I	II	III
	$C_{11}H_{17}NO_2$:			
C	67.005	67.04	67.44	
H	9.64	10.10	9.68	
N	7.106			7.6

HALOGEN DERIVATIVES OF CAMPHOROXIME.

I. Camphoroxime Monochloride, $C_{10}H_{15}Cl NOH$.

With the expectation of introducing a sulphur group of some kind into the camphor molecule, camphoroxime was treated with the reddish brown sulphur dichloride. The oxime and chloride were first dissolved in ether and then slowly mixed. A reaction at once takes place throwing down an abundant white precipitate which is amorphous if precipitated rapidly but nicely crystallized in colorless needles if the chloride is added more slowly. This precipitate is perfectly insoluble in ether but soluble in alcohol, chloroform and water, but insoluble in benzol.

Analyses and tests showed conclusively that it is not a sulphur compound, as only a mere trace of sulphur

was found. One analysis gave the following results:

0.4100 gm. substance gave 0.00765 gm. BaSO_4 .

The weight of sulphur is therefore 0.00165 gm., or in per cent. would be only .002%, showing that sulphur was only present as an impurity.

The probability now remained that the substance was a chloride of camphoroxime. It gave abundant proof of the presence of chlorine. In that case there would be formed a molecule of hydrochloric acid for every atom of chlorine which enters the camphor ring. This would immediately unite with a molecule of the oxime to form the hydrochloride which is insoluble in ether. The fact that there is a mixture of substances present was proved by experiment. If the precipitate obtained is dried and the melting point taken it melts at $155^{\circ}\text{-}6^{\circ}$. If however the precipitate is first dissolved in alcohol and reprecipitated with ether, a beautifully crystallized substance is obtained which melts at 290° . It was apparent at the start that only about half of the original material could be reprecipitated from ether, and upon trial it was found that the

hydrochloride could not be so precipitated. A cheaper method of purifying the material was found in the fact that it is extremely soluble in water while the camphor oximehydrochloride is practically insoluble. If the mixture of the two substances is placed in water and immediately thrown upon a filter a very pure specimen is obtained. The water must be allowed to evaporate spontaneously as heat decomposes the substance and gives the oxime again. Upon evaporation large transparent crystals were obtained which melted at 293° . This melting also showed the material to be purer than that made by the other method, as it did not char at all now before melting while in the first case it began to char at about 200° .

The crystals examined under the microscope with polarized light proved to be biaxial in form and to belong to the orthorhombic system.

Forms Noted:

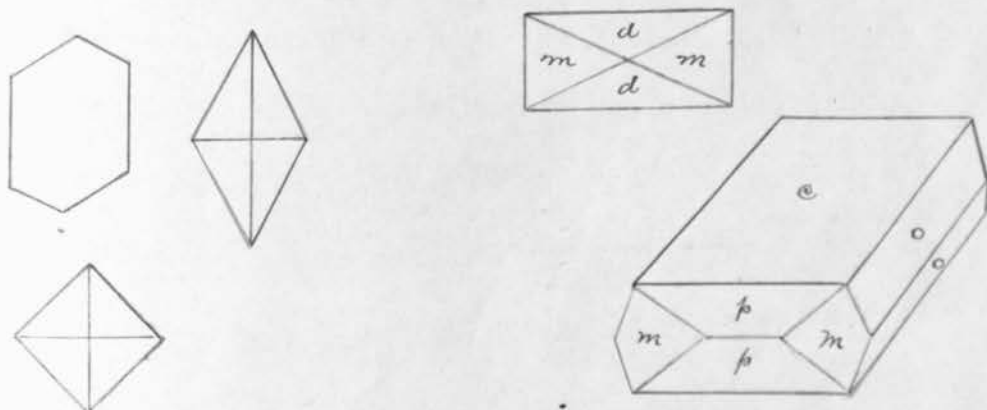
Macropinnacoid	$a : \infty b : \infty c.$
Unit Prism	$a : b : \infty c$
Unit Pyramid	$a : b : c.$

(32)

Brachydome $\propto a : b : c.$

Brachypinnacoid $\propto a : (m/b) : \propto c.$

The following drawings represent the predominant forms seen under the microscope:

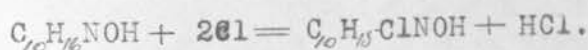


The following figures were obtained upon analysis:

I	.1737 gm. subst.	gave	.3860 gm. CO_2	and	.1494 gm. H_2O .
2.	.1148 " "	"	.2560 " "	"	.0872 " "
3.	.1188 " "	"	.087656 gm. AgCl .		
4.	.1133 " "	"	.079850 " "		

	Calculated for	I	II	III	IV
	$\text{C}_{10}\text{H}_{15}\text{ClNOH}$:				
C	59.55	60.604	60.81		
H	7.94	9.55	8.43		
Cl	17.63			17.48	18.29

The reaction may be indicated as follows:



Determination of Specific Rotation.

Weight of material taken03 gm.

Amount of solvent used 10 C.C.

Length of tube in decimeters 2.00

Rotation in the polariscope -1°

$$\text{Therefore } [\alpha]_D = \frac{a \times 100}{c \times L} = \frac{-1 \times 100}{.333 \times 2}$$

For unit length optical rotation is -75.075.

Determination of Molecular Weight by lowering of the

Freezing Point.

Weight of acetic acid used 14.7786 gm.

Weight of substance taken 0.0952 "

Lowering of the Freezing Point125

Molecular Depression for Acetic Acid 39.00.

Therefore M equals 200.99.

Calculated for $C_{10}H_{15}ClNOH$ 201.45.

Comparison has been made between the camphoroxime-hydrochloride and the new substance in order to make certain that it is not one and the same compound, as the figures obtained by the combustions may serve for the hydrochloride as well.

Camphoroximehydrochloride

Insoluble in ether,

Soluble in alcohol.

Not reprecipitated from

alcohol solution with ether. alcohol sol. with ether.

Almost insoluble in water.

Melting Point 162° .

$[\alpha]_D = -54.45.$

Camphoroxime Monochloride.

Insoluble in ether.

Soluble in alcohol.

Reprecipitated from al-

cohol sol. with ether.

Very soluble in water.

Melting Point 293° .

$[\alpha]_D = -75.075.$

By passing chlorine for a long time into a benzene solution of camphoroxime an oily liquid was obtained which does not seem to be entirely free from solid matter, but if toluol is used a higher temperature may be reached, and a clear slightly greenish yellow liquid is obtained upon evaporation. That the reaction takes place

is evidenced by the fact that a large amount of insoluble white crystals are formed in the first stages of the experiment which were proven to be the camphoroximehydrochloride. After a while these crystals again disappear. The solution passes through a series of colors such as have been noticed by other investigators on passing chlorine into various reagents. In the case of the benzene solution the color became the same as that of a strong solution of copper sulphate, but towards the completion of the experiment the color almost disappeared. The oily liquid boiled with decomposition at 135° . This decomposition gave rise to a crystalline solid, soluble in chloroform, which melted in the neighborhood of 300° , indicating the monochloride already described.

In attempting to remove the chlorine atom from the molecule both silver oxide and caustic soda solution were used. In the first case no satisfactory results were obtained as the product of the reaction always broke down giving a black product which showed the presence of silver and the absence of chlorine. The presence of silver

in the decomposed residue seems to indicate that a silver compound of some kind may have been formed, and that this gave rise upon evaporation to the oxide of silver again.

When the monochlorcamphoroxime is treated with with a caustic soda solution on the other hand, quite a different reaction takes place. When a strong solution is used the camphoroxime monochloride passes into an oily liquid which does not crystallize in water. By using a weaker solution the substance no longer turns into an oil but into a soluble white powder, which upon standing has a tendency to become soft and pasty. When a still more dilute solution of sodium hydroxide was used a powder was formed which did not change perceptibly in the air, and which when placed in water took on a beautiful crystalline form. The substance did not have a sharp melting point but began to melt at 75° and was completely melted at 90° .

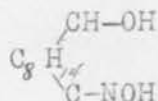
Two analyses of the material gave the following results:

I	0.2260 Gm. Subst.	gave	0.5702 gm. CO_2	and	0.1775 gm. H_2O .
II	0.1287 "	"	0.3261 "	"	0.1175 " "

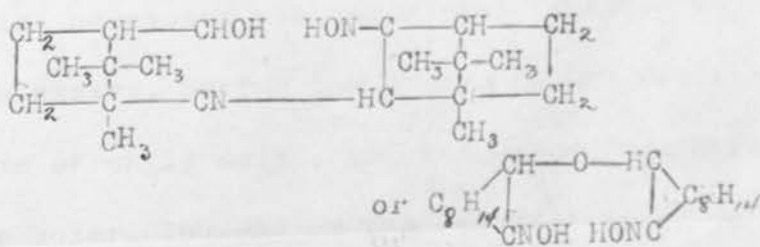
	Calculated for	Found:	
		I	II
	$C_{20}H_{32}N_2O_3$		
C	68.96	69.102	68.808
H	9.19	10.14	8.72

The reaction may be explained in the following manner

If the weak solution of caustic soda only replaces the chlorine, this compound would be formed



but the analyses do not correspond to such a formula; if however two of these molecules unite with the abstraction of one molecule of water, the new formula would correspond very well with the data obtained by analysis. The compound may then be either one containing two NOH-groups or one with one oxime group and one hydroxyl group. The structure would be either



II. Camphoroxime Monobromide.

A number of methods have been tried for the preparation of bromides of camphoroxime, but the energetic action of the bromine in heated solutions gave rise to gummy products which could not be separated to any advantage. Forster¹⁾ attempted to make alpha-bromcamphoroxime by the direct action of bromine on camphoroxime, but the attempt failed owing to the vigorous action of free bromine.

The following method was found to yield a stable and pure monobromcamphoroxime. The oxime was first dissolved in chloroform and the solution covered with a layer of water, to absorb the hydrobromic acid which is formed during the reaction. Small quantities of bromine are added from time to time, and the solution allowed to stand in the dark. It usually took about twenty-four hours for the bromine color to disappear. The amount of bromine necessary was calculated in order to avoid any large excess. During the course of the reaction the water became strongly acid, and the chloroform obtained a faint straw color. The end of the reaction could be determined

1) Forster, J. Chem. Soc., Trans. 1897-1030.

by taking a drop of the chloroform solution, and allowing it to evaporate on a watch crystal. If no crystals appeared the reaction was complete. The water was separated and the chloroform washed until it no longer gave any acid test with litmus paper moistened with water. If the chloroform is not well washed the hydrobromic acid present exerts a decomposing action upon the bromide and breaks it down forming gummy decomposition products in a short time. The chloroform was allowed to evaporate spontaneously or else in a vacuum desiccator, and a heavy oily liquid was obtained, which had a marked camphoric odor and a pale yellow color.

When kept in a desiccator this is a fairly stable compound and may be preserved for several weeks. There is a tendency to form small crystals in the oil, especially if the hydrobromic acid had not been all removed, and if it is left exposed to the air. These did not melt below 365, and were thought to be ammonium bromide. Left standing in a desiccator the crystals do not form but the odor of the campholenic nitrile becomes noticeable after some

time, and the color is changed to a dark brown and final-brownish-black.

Numerous attempts to remove the halogen were made with different hydrolytic reagents but all proved unsuccessful. During such attempts silver bromide and potassium or sodium bromide were formed but the reaction goes on irregularly, and no definite reaction is obtained. Lapworth investigated the action of hydrolytic agents upon alpha-dibromcamphor, and obtained small quantities of new products but never a theoretical yield and always accompanied with a number of gummy and oily products. The odor of the nitrile was always present.

Results of Analysis:

0.2196 gm. subst. gave 0.3918 gm. CO_2 and 0.1216 gm. H_2O .

	Calculated for $\text{C}_{10}\text{H}_{15}\text{Br NOH}$:	Found:
C	48.77	48.65
H	6.09	6.15

1) J. Chem. Society, Trans. 1899 -1134.

Determination of the Molecular Weight.

I. Weight of benzole taken 11.2506 gm.

Weight of oil taken0918 "

Lowering of the Freezing Point..... .175°

$$M = \frac{K \times p}{d \times g} = \frac{53 \times .0918}{.175 \times 11.2506} = 247.1$$

II. Weight of benzole taken 11.2506 gm.

Weight of oil taken1724 "

Lowering of the Freezing Point33°

$$M = \frac{K \times p}{d \times g} = \frac{53 \times .1724}{.33 \times 11.2506} = 246.1$$

Calculated for

 $C_{10}H_{15}Br$ NOH:

246.

Found:

I

II

247.1

246.1

Determination of the Molecular Weight from theRefractive Index.

The formula $\frac{n-1}{d}$ proposed by Dale and Gladstone has been found to hold good for a large number of compounds. In it "n" is the refractive index, "d" the density. This expression is known as the specific refractive constant, and when multiplied by the molecular weight is

known as the molecular refraction of a compound. It has been proved that the molecular refraction is additive and may be found for any compound by adding the refractive equivalents of the atoms which make up the compound. Thus the molecular refraction of $C_{10}H_{15}BrNOH$, will be the sum of the respective atomic refractive equivalents. These were taken from Vol. I of Ostwald's Lehrbuch, page 447.

Thus $C = 5$, $H = 1.3$, $O = 2.8$, $N = 4.1$, $Br = 15.3$.

Therefore $C_{10}H_{15}BrNOH = 93$.

And $M\left(\frac{n-1}{d}\right) = 93$.

Refractive Index of the oil at $20^{\circ} = 1.556414$.

Density at $20^{\circ} = 1.48$.

Hence $M\left(\frac{1.5564 - 1}{1.48}\right) = 93$.

$M = 247.4$

Calculated for
 $C_{10}H_{15}BrNOH$

246.

Found:

247.4

III. Dibrom Camphoroxime.

The first attempts to make bromine unite with the camphoroxime were made in an alcohol solution. The oxime was dissolved in alcohol and bromine water added. Upon heating this a pale yellow oily substance settled to the bottom. It was very difficult to secure large enough quantities to work with as prolonged heating turned the oil dark colored and gave indications of breaking it down.

Two analyses of the substance gave the following figures which correspond to the ethyl ester of the dibromcamphoroxime.

	Calculated for $C_{10}H_{14}Br_2NO-C_2H_5$	Found:	
		I.	II
C	40.79	40.70	40.49.
H	5.38	5.43	5.03

The ethyl ester of dibromcamphoroxime may be represented by the following formula:

