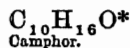


ART. IX.—*On the action of hydrated hypochlorous acid on Oil of Turpentine and Camphor*; by C. GILBERT WHEELER.

OIL of turpentine and camphor are chemically closely related, differing in composition by only a single molecule of oxygen.



The intimate relation here indicated, has been by Berthelot clearly proven to exist, he having obtained camphor from oil of turpentine by combining the latter with hydrochloric acid, separating it therefrom as camphene—isomeric with oil of turpentine—and oxydizing platinum sponge.† Camphor may thus be considered as “Oxy-camphene.” Dussart has recently claimed to have succeeded in obtaining camphor direct from oil of turpentine.‡

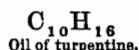
With regard to the relation of bodies to the homologous series of the fatty and aromatic acids it may be observed that where the number of molecules of carbon are the same, the members of the fatty series contain more hydrogen while those of the aromatic series contain less. Oil of turpentine, therefore, with its numerous isomerically allied bodies (terbenes), occupies a position intermediate between these two important

\* C=12. O=16.

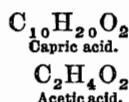
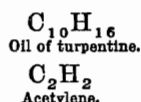
† Jahresbericht, 1858, p. 441.

‡ Zeitschrift für Chemie, 1867, 11.

groups of organic bodies, as the following example will illustrate:



That on the one side, oil of turpentine sustains the intimate relation to the aromatic series here assumed, has been by experiment abundantly illustrated. I need only to refer to the formation of terephthalic acid and nitrobenzol from oil of turpentine and the formation of cymol from camphor. The relations, however, to the fatty series of the bodies under consideration have not been thus satisfactorily demonstrated. Now oil of turpentine occupies apparently a similar position with reference to capric acid as acetylene does to acetic acid, as is herewith shown:



It appeared to me, therefore, to be a subject worthy of investigation to ascertain whether the relations above expressed could be proven by experimental research. I have for this purpose, made use of hydrated hypochlorous acid as a reagent, and have been able to obtain a substance which may be regarded as belonging to the series of the fatty acids.

If oil of turpentine (boiling point  $159^\circ$ ) is added to a dilute aqueous solution of hypochlorous acid and shaken, it at once becomes yellow, thick and heavy, and soon settles to the bottom of the vessel. Were concentrated acid employed, the mixture would rapidly become heated and other products be formed than that sought, or, under the most favorable circumstances, but very little of the new body would be obtained. The oil should be slowly added, not allowing an increase of temperature, and ceasing when on adding a fresh portion, but slight change in color is produced, or before the characteristic odor of the hypochlorous acid can no longer be readily recognized.

The heavy oil is separated from the aqueous solution by filtration. The latter contains chlorid of mercury, originating from the oxyd of that metal employed in the preparation of the hypochlorous acid, also an organic substance, which, on evaporating the solution, separated as an oil with more or less decomposition. This is the most interesting of the products of the reaction, and in order to obtain it pure from the solution it is necessary to avoid the application of a high temperature.

To effect this, a quantity of common salt is added till the solution is saturated, which is then shaken with small por-

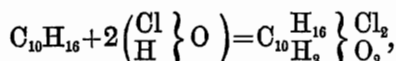
tions of ether. The ethereal extracts are united and shaken with a concentrated solution of chlorid of ammonium, which takes up all the mercury chlorid, the ether is then removed with a pipette and chlorid of calcium added in order to effect its dessication. The filtrate is distilled and at the close of the operation a current of dried air is transmitted through the residue in order to more completely remove all traces of ether. The body thus obtained is the product of the direct combination of hydrated hypochlorous acid with oil of turpentine, and on its combustion I obtained the following results:

0.3450 gm. yielded 0.6190 gm. carbonic acid and 0.2340 gm. water.  
0.2985 " " on ignition with lime, 0.3270 " AgCl.

These figures indicate the formula  $C_{10}H_{18}Cl_2O_2$ .

		Theory.			Found.
$C_{10}$	120	49.79	-	-	48.93
$H_{18}$	18	7.46	-	-	7.53
$Cl_2$	71	29.46	-	-	29.00
O	32	13.29			

This substance is therefore formed according to the following equation:



and judging from its empirical formula, might be viewed as bichlorinated capric acid; it, however, is entirely without the chemical characteristics that would appertain to such a body. We have rather here before us, the dichlorhydrin of a four-atomic alcohol, and which must beyond doubt be considered as belonging to the fatty acid series. Between this substance and that obtained by Neuhoﬀ\* from naphthalin there is the most complete analogy, as the following comparison illustrates:

$C_{10}H_{16}$   
Oil of turpentine,  
(Terpentine).  
 $C_{10}H_8$   
Naphthalin.

$C_{10}H_{18}Cl_2O_2$   
Dichlorhydrin of  
Terpen-alcohol.  
 $C_{10}H_{10}Cl_2O_2$   
Dichlorhydrin  
of Naphthalen-alcohol.

$C_{10}H_{20}O_4$   
New 4-atomic alcohol,  
(Terpen-alcohol).  
 $C_{10}H_{12}O_4$   
Naphthalin-alcohol,  
(4-atomic).

Dichlorhydrin of terpen-alcohol is a colorless, transparent, viscid substance, of a somewhat greater consistence than turpentine, completely neutral, difficultly soluble in water, but readily soluble in ether and alcohol. On heating its alcoholic solution with nitrate of silver, chlorid of silver is formed. It cannot be distilled, for before the necessary temperature is attained, decomposition commences and hydrochloric acid is given off. With nitric acid it is oxydized and yields a resinous mass.

\* Zeitschrift für Chemie, 1866.

The above mentioned, as yet unknown, terpen-alcohol I attempted to obtain by treating the dichlorhydrin with baryta; however, there appeared to result a too energetic decomposition of the substance. I further tried the action of zinc and sulphuric acid, hoping to substitute hydrogen for the chlorine of the substance, was however, unsuccessful. I was, nevertheless, able to obtain with sodium a derivative of this dichlorhydrin. If sodium is added to the etherial solution, there is formed, after some hours, much chlorid of sodium and a yellow substance settles to the bottom of the vessel. If the whole is then treated with ether and the latter evaporated, there remains a thick mass which still gives a chlorine reaction. However, on digesting that portion not taken up by the ether with alcohol, filtering the same from the insoluble chlorid of sodium, the concentrated filtrate when slightly acidulated with sulphuric acid and shaken with ether, yields, on evaporating the etherial solution, a body containing no chlorine. This is insoluble in water, but soluble in alcohol and ether. It yielded no crystalline compounds with metallic bases, and its ammonia salt decomposed on evaporation. The lead, silver and copper salts, were amorphous powders, and the isolated acid could not be obtained crystallized, but only as a brownish translucent solid. On combustion I obtained from 0.1360 grm., 0.328 grm. carbonic acid and 0.1070 grm. water, which would indicate the formula  $C_{10}H_{16}O_3$ .

		Theory.			Found.
$C_{10}$	120	65.21	-	-	65.75
$H_{16}$	16	8.69	-	-	8.75

The formation of this acid can hardly be imagined to be the result of any very simple reaction; doubtless the dichlorhydrin, on parting with its chlorine, splits up into secondary products. As the quantity obtained of this body was but small, I was unable to study its chemical relations more completely. In view, however, of what shortly follows, and referring to the same, I would propose "Hydrophoronylic acid" or "Oxy-camphinic acid" as a suitable name for this substance.

Dichlorhydrin of terpen-alcohol is, however, only obtained in small quantities when oil of turpentine and hypochlorous acid are brought into contact. The chief product is the heavy oil first alluded to. A quantity of this was dissolved in alcohol, precipitated with water, redissolved in ether, dessicated, distilled, and thus obtained pure. The results on analysis were the following:

0.270 gm. gave	0.532 $CO_2$	and	0.177 $H_2O$	=	53.74 carbon	and	7.28 hydrogen.
0.407 " "	0.800 "		0.255 "	=	53.61 "		8.92 "
0.340 " "	0.529 AgCl	=	38.36 chlorine.				

These figures lead to no simple or at all probable formula; the body was possibly a mixture of mono- and trichlorinated oil of turpentine. A mixture of equal equivalents would demand 53.99 p. c. carbon, 6.08 hydrogen and 39.93 chlorine. This oil decomposed with evolution of hydrochloric acid on heating. It is also decomposed with formation of chlorid of potassium on digesting with an alcoholic solution of potassa. If it is heated for some time with nitric acid a small quantity of a volatile substance very irritating to the eyes is formed, together with a very considerable quantity of a resinous mixture from which was extracted with warm water, oxalic acid and another acid which slowly crystallized from the solution on standing. The crystals were readily soluble in ether and alcohol, and on ignition gave forth the odor of acetic acid. Dissolved in water and acetate of lead added, a salt was precipitated, which, on analysis, yielded 66.34 p. c. lead, 0.2805 gm. of substance giving 0.2725 sulphate of lead. Malonate of lead requires 66.99 p. c. of lead. From these various data, it became evident that the heavy oily substance formed from the oil of turpentine is a mixture, only that remaining in solution in the water present, being a simple body.

As we have seen that two molecules of hydrated hypochlorous acid unite direct to oil of turpentine, it appeared to me interesting in this connection to investigate whether chloric acid is capable of being similarly added, as Carius has succeeded in doing with benzol, obtaining the acid named by him trichlorophenomalic acid.\* Carius employed a mixture of chlorate of potassa and sulphuric acid and proved that in the presence of benzol, the chloric acid is reduced to chlorous acid and the latter unites with the benzol direct. An analogous reaction appears to take place where oil of turpentine is employed. I obtained with turpentine a finely crystallized body which is perhaps the substance sought, having the formula  $C_{10}H_{18}Cl_2O_4$ . I hope to give this reaction a closer investigation.

At the outset, I referred to the intimate chemical relation existing between oil of turpentine and camphor, and with this in mind it may be interesting to investigate also the action of hypochlorous acid on camphor, a substance partaking on the one hand much of the nature of an aldehyd, and on the other, that of an alcohol. Its behavior on being treated with a solution of potassa in alcohol, splitting up into an alcohol (borneol) and an acid, resembles that of an aldehyd.† It does not, however, unite with bisulphites of the alkalies and it admits of having a molecule of hydrogen substituted for one of potassium

\* *Annalen der Chem. und Pharm.*, 1867.

† Berthelot, *Annalen Chem. und Pharm.*, ci, 94.

or sodium, as is the case with the alcohols.\* The true chemical structure of camphor must be determined by a further study of its derivatives.

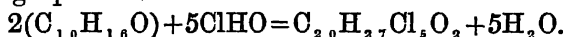
While a dilute solution of hypochlorous acid acts readily and rapidly on oil of turpentine, its action on camphor is exceedingly slow. In the first experiment I allowed camphor to remain in a weak solution of hyponitrous acid for eight days, and thereupon one day in a concentrated solution. The product of the reaction, a white, indistinctly crystallized solid, was washed with water till no acid reaction remained, dissolved in alcohol and again precipitated by diluting with water. It still contained a small quantity of an oily substance, held mechanically, and which was removed by strongly pressing between filter paper. It was again crystallized and then was submitted to an analysis.

0.3255 grm. gave 0.6035 grm. carbonic acid and 0.178 grm. water.  
0.4995 " " 0.611 " AgCl  
0.260 " " 0.382 " "

From these figures the formula  $C_2H_{27}Cl_5O_2$  may be calculated.

		Theory.			Found.	
					I.	II.
$C_{20}$	240	50.37	-	-	50.57	
$H_{27}$	27	5.66	-	-	6.07	
$Cl_5$	177.5	37.27	-	-	37.63	37.11

The formation of this substance can be explained by the following equation:



The result is a different and a much simpler one where camphor is immediately brought in contact with concentrated hypochlorous acid; it is at once transformed into a thick fluid, becomes warm, and after some time again hardens to a crystalline solid. This body is the chief product of the reaction, though a very small quantity of another organic substance is found in the solution. The crystalline substance is dissolved in alcohol, precipitated with water and thoroughly washed with cold water. It is then again repeatedly dissolved in alcohol and crystallized therefrom until obtained quite pure. On its analysis I obtained the following results:

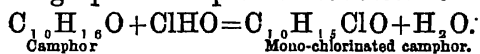
0.2320 grm. gave 0.5940 grm. carbonic acid and 0.1710 grm. water.  
0.2295 " " 0.1615 " chlorid of silver.

These figures correspond with those of simple chlorinated camphor.

		Calculated.			Found
$C_{10}$	120	64.35	-	-	64.54
$H_{15}$	15	8.07	-	-	8.18
Cl	35.5	19.03	-	-	18.70

\* Baubigny, Zeitschrift für Chemie, 1866, p. 408.

The following equation expresses the reaction:



Substitution products of this character appear in general to be the chief results of the action of the reagent here employed; addition products are formed only in small quantities. Carius obtained from benzol, monochlorinated benzol, together with a body named by him "trichlorhydrin der Phenose."\* Monochlorinated camphor has not heretofore been obtained, though Clauss has obtained products containing four and six atoms of chlorine by the action of chlorine on camphor dissolved in trichlorids of phosphorus.†

Monochlorinated camphor is a white crystalline powder, soluble in ether and alcohol, insoluble in water. Its solution in concentrated alcohol on evaporation remains for a long time of a syrupy consistence; from dilute alcohol it crystallizes more readily and in very small, imperfectly formed needles. It melts at 95° C., is decomposed, with liberation of hydrochloric acid, at 200° C., and another substance, having an agreeable odor, is sublimed over. The taste and smell of this body are similar to ordinary camphor. It is acted on with difficulty by nitric acid even when boiling; by sulphuric acid it is dissolved at ordinary temperatures and again precipitated on dilution with water. With nitrate of silver its alcoholic solution yields chlorid of silver. Heated to 120° with concentrated solution of ammonia, chlorid of ammonium is formed and a derivate soluble in water. Treated with perchlorid of phosphorus there remained, after the removal of the oxychlorid of phosphorus formed, a substance which blackened on attempting to distill a portion. Its distillation was therefore not proceeded with, but it was washed with water, dissolved in alcohol and again precipitated by dilution. The oil-like substance thus obtained soon became a magma which yielded white crystals on pressing between filter paper. The substance was probably either the body  $\text{C}_{10}\text{H}_{15}\text{Cl}_3$ , or that resulting therefrom on subtracting one atom of hydrochloric acid, viz:  $\text{C}_{10}\text{H}_{14}\text{Cl}_2$ .

A considerable quantity of monochlorinate of camphor was treated with a solution of potassa in alcohol for 6 to 8 hours. The whole thereby became brownish-red and a large quantity of chlorid of potassium was formed. On dilution with twice its volume of water a voluminous precipitate (A) was obtained. The filtrate gave no precipitate on farther addition of water, and contained the potassa salt of a new organic acid. The latter was isolated on addition of sulphuric acid, then dissolved in

\* Zeitschrift für Chemie, 1866, p. 67.

† Annal. Chem. und Pharm., cxxxvi, 323; xlv, 301.

ether, filtered, and thoroughly dried after evaporation of the ether. Its analysis yielded the following results:

0.2608 grm. gave 0.6318 grm. carbonic acid.\*

0.2496 " " 0.6040 " " and 0.1870 grm. water.

These figures correspond with the formula  $C_{10}H_{14}O_3$ .

	Calculated.					Found.	
						I.	II.
$C_{10}$	120	65.93	-	-	-	66.07	65.99
$H_{14}$	14	7.70	-	-	-		8.23

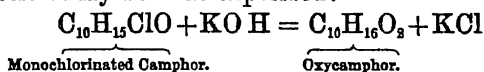
The acid was neutralized with ammonia and acetate of lead added. 0.2240 grm. of the lead compound gave 0.1180 grm. sulphate of lead = 36.21 pr. ct. lead. The formula  $C_{10}H_{13}PbO_3$ , requires 36.42 p. c. The acid is therefore monobasic and has the following rational formula:  $(C_9H_{13}O) CO.OH$ . The radical requires one molecule of hydrogen in order to become phoron, and an experiment with a small quantity, by heating with lime, made it apparent that this substance was produced as it is in like manner from some other camphor derivatives. I therefore name this body phoronylic acid. Phoronylic acid is isomeric with camphoric acid; it is a syrupy fluid, not soluble in water, readily soluble in ether and alcohol. It has but slight odor, somewhat resembling cumarin. This odor is especially marked when the substance is heated with sulphuric acid and chromate of potassa. The alkaline salts of phoronylic acid are readily soluble in water and appear not to crystallize; the ammonia salt loses its ammonia on evaporation. The salts of the heavy metals are insoluble.

The precipitate (A), mentioned in the foregoing, dissolved in alcohol, yielded on evaporation beautiful crystalline needles. Obtained pure by repeated crystallization and analyzed, the following were the results:

0.1970 grm. gave 0.5130 grm.  $CO_2$  and 0.1659 grm.  $H_2O$ , which indicate the substance  $C_{10}H_{16}O_3$ .

		Calculated.				Found.	
$C_{10}$	120	71.43	-	-	-	71.02	
$H_{16}$	16	9.52	-	-	-	9.36	
$O_3$	32	19.05	-	-	-	...	
		100.00					

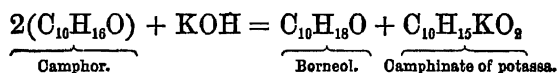
The reaction may be thus expressed:



Oxycamphor crystallizes in small white needles, is easily soluble in alcohol, insoluble in water, melts at  $137^\circ$ , may be sub-

\* The hydrogen determination met with an accident.

limed without change, volatilizes somewhat even in boiling water and resembles ordinary camphor in taste and odor. Oxycamphor is isomeric with camphinic acid discovered by Berthelot. According to that chemist, ordinary camphor on being heated with an alcoholic solution of potassa splits up into borneol and an acid which he presumed to have the composition  $C_{10}H_{16}O_2$ .\* He did not analyze the acid but explained the process of its formation as follows :



It appeared to me desirable to analyze this substance and establish its isomeric character with oxycamphor. A quantity of camphor was therefore heated with an alcoholic potassa solution in a sealed tube to  $180^\circ$  for 6 to 8 hours. On opening the tube an inflammable gas escaped. (Probable H and  $CH_4$  from decomposed alcohol.) The contents of the tube were diluted with water, the precipitated borneol and camphor filtered off and the filtrate completely neutralized with sulphuric acid. On concentrating till all the potassic sulphate had crystallized out, the mother-liquor was acidified with sulphuric acid, the precipitated camphinic acid washed with water, dissolved in ether and obtained therefrom by evaporation. The acid thus obtained corresponded completely with that described by Berthelot. It was an almost solid, "fast feste," transparent mass which, on account of its peculiar consistency, was very difficult to entirely free from moisture, and this doubtless accounts for the carbon determination in the subjoined analysis being too low. Nevertheless, there remains no doubt that the formula assigned to it is correct and that it is isomeric with oxycamphor.

The results of analysis were : 0.236 grm. substance, 0.610 grm. carbonic acid, and 0.211 grm. water.

		Calculated.			Found.
$C_{10}$	120	71.43	-	-	70.56
$H_{16}$	16	9.52	-	-	9.91
$O_2$	32	19.05	-	-	....

Camphinate of lead, dried at  $100^\circ$ , a white insoluble powder, yielded the following results on analysis :

0.1390 grm. substance gave 0.0787 grm. sulphate of lead = 38.77 p. c. lead. The theory calls for 38.26 p. c.

Camphinic acid is perhaps capable of yielding capric acid, or some body isomeric therewith, on submitting it to the action of nascent hydrogen.

A summary view of the established results of the foregoing

\* *Ann. der Chem. und Pharm.*, cxii, 364.

investigation and their closer allied chemical relations may be gathered from the following statement of formulæ.

Oil of turpentine=Camphene,  $C_{10}H_{16}$ .

Camphor =Oxycamphene,  $C_{10}H_{16}O$ .

Oxycamphor =Dioxycamphene,  $C_{10}H_{16}O_2 = C_{10}(\overset{H}{\underset{O}{(OH)}}_{15} O$

Camphinic acid,  $C_{10}H_{16}O_2 = (C_9H_{15})CO.OH$

Oxycamphinic acid (hydrophor-  
nylic acid),  $C_{10}H_{16}O_3 = (C_9H_{15}O)CO.OH$

Phoronylic acid,  $C_{10}H_{14}O_3 = (C_9H_{13}O)CO.OH$

Monochlorinated camphor,  $C_{10}H_{15}ClO$

Terpendichlorhydrine,  $C_{10}H_{18}Cl_2O_2$

In closing, I acknowledge with pleasure the valuable service in connection with the foregoing, of my assistant, Mr. Oscar Loew.

Nuremberg, June. 1867.