

III.—*Studies of the Terpenes and Allied Compounds. The Formation of Ketones by the Interaction of Camphor and Agents such as Sulphuric acid and Zinc Chloride.*

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THE interaction of camphor and sulphuric acid has been the subject of numerous investigations, commencing with that of Delalande in 1839, and evidently much time and labour has been spent in the endeavour to determine the nature of the oily product, hitherto unfortunately, as we will show, all to no purpose, and it is mainly on this account that we deem it desirable to record our observations in detail.

Chautard, in 1856, assigned the formula  $C_9H_{12}O$  to Delalande's product, terming it *camphren*. Schwanert, in 1862, altered this formula to  $C_9H_{14}O$ , and suggested that the substance was an isomeride of acetophorone. Lastly, Kachler, in 1872 (*Annalen*, **164**, 75), came to the conclusion that the "camphren" of previous workers was not a definite substance, but rather a mixture of "phorone," probably with hydrocarbons; he, however, accepted Schwauert's formula  $C_9H_{14}O$  as that of the main constituent, regarding it as the isomeride of acetophorone. It may also be mentioned that Cazeneuve has incidentally referred to "camphren," and stated that he has confirmed the formula attributed to it.

It is needless to enter into a fuller account of previous work, as covering references are to be found in Kachler's paper, especially as the results are negatived by us.

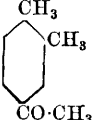
In the course of an investigation, commenced in 1877, of the

products of the action of various dehydrating agents on camphor, an account of which was published by one of us in conjunction with Dr. A. K. Miller in 1883 (*Ber.*, **23**, 2255), the "camphren" prepared in accordance with Schwanert's directions was compared with a product obtained, together with hydrocarbons, on carefully distilling camphor with dehydrated zinc chloride; the conclusion arrived at was that the two products were practically identical, but it was evident that they were not uniform substances; all attempts to separate pure substances from them by repeated fractional distillation were, however, unsuccessful.

The experience gained during recent years that crystalline compounds are so often obtained by the interaction of phenylhydrazine and ketonic compounds rendered it desirable again to attempt the resolution of "camphren," and the results now to be described afford further striking testimony of the extreme value of phenylhydrazine as an analytical agent.

Briefly stated, our results are as follows:—

Besides camphor, which cannot be entirely got rid of owing to the fact that it is less sensitive to the action of sulphuric acid than are the products of change, the so-called "camphren" contains at least two oxygenated compounds: one of these is the acetylorthoxylene of the

formula ; the other is apparently the constituent to which

the crude oil owes its pleasant, marked peppermint-like odour, resembling that of camphorone prepared by distilling calcium camphorate, and on this account, and as it yields the same oxidation product as camphorone, viz.,  $\alpha$ -methylglutaric acid, but boils at a higher temperature (about 20°), we think that possibly it is the next homologue of camphorone. Unfortunately, we have not hitherto succeeded in obtaining any crystalline derivative of this latter constituent of the oil; we are therefore continuing to study it.

The work has been mainly done with material prepared from camphor and sulphuric acid, but we have isolated acetylorthoxylene from the zinc chloride product which, as before said, in its general properties is identical with that obtained by means of sulphuric acid; a quantity of the material prepared by Miller and one of us from camphor and zinc chloride being available was used for the purpose of the comparison.

The production, undoubtedly in considerable quantity, in such a manner of *acetylorthoxylene* from camphor is of extreme interest and

of no slight theoretical importance; while reserving the discussion of the question for a subsequent communication, we would point out that it appears to afford further evidence antagonistic to the view that camphor bears a very simple relation to cymene (parisopropylbenzene), a view which one of us has over and over again called in question.

#### *Preparation of "camphren."*

In the first instance, following Schwanert's directions, we heated a solution of camphor in four times its weight of ordinary oil of vitriol on the water-bath; after some time, the mixture darkened in colour and sulphur dioxide was evolved, the evolution of gas becoming more rapid as action proceeded; after heating during about six hours, the dark solution was allowed to cool, then mixed with about two volumes of water and subjected to distillation in a current of steam as long as any oil passed over.

The product was a yellow oil; the yield, however, was but small—equal to only about one-fourth the weight of the camphor taken, a large proportion of the camphor being converted into non-volatile, brittle, carbonaceous matter; a considerable quantity of unchanged camphor was also present in the oily product. At the outset of the investigation, it therefore became necessary to devise a better method of preparing "camphren," and, with this object in view, various experiments were instituted.

In the first place, instead of using ordinary oil of vitriol, the camphor was dissolved in a mixture of 4 parts of the concentrated acid with 1 part of water; when this solution was heated in boiling water, no visible action took place for a long time, but after 10 to 12 hours, sulphur dioxide began to be evolved, the solution darkening very considerably; after heating during about 20 hours, the product was isolated in the manner described above. The quantity of oil obtained was not only very small, but it was found to contain an even larger quantity of camphor than that produced by following Schwanert's directions.

The effect of heating a solution of camphor in 4 parts of concentrated sulphuric acid and 1 part of water at temperatures above 100° was next tried; at 107°, action set in after a short time, sulphur dioxide being evolved, the mixture darkening as before. The quantity of crude oil produced under these conditions seemed to depend to a considerable extent on the duration of the heating, but was never more than 50 to 60 per cent. of the camphor taken.

After many trials, which it is unnecessary to describe, the following method was adopted as the least unsatisfactory:—A mixture of 200 grams of camphor with 800 grams of concentrated sulph-

uric acid, contained in a large flask, was quickly heated on a sand-bath to 105—110°; as soon as the temperature had risen to about 105°, action set in, the solution rapidly darkening, sulphur dioxide being copiously evolved. It was necessary at this stage to heat most carefully, so that the temperature of the mixture, as shown by a thermometer immersed therein, did not rise much above 110°, as otherwise the action gradually became more and more energetic, the mixture frothing over, the only product under such circumstances being a black, porous, carbonaceous mass. After keeping the mixture at 105—110° during 50 to 60 minutes, the flask was taken from the sand-bath and placed aside to cool; the black solution was then mixed with about 2 vols. of water, and distilled with steam; the oily distillate was washed with dilute soda to free it from attached acid, and dried by means of calcium chloride. The yield of crude product was about 140—150 grams, or 70—75 per cent. of the camphor taken, only a comparatively small quantity of camphor being converted into carbonaceous matter.

The yellow oil prepared in the manner described was specifically lighter than water, and had a peculiar peppermint-like odour, quite different from that of camphor. When distilled from an ordinary distilling flask under atmospheric pressure, the thermometer at once rose to about 210°, and almost the whole passed over between this temperature and 245°; on collecting the distillate in fractions at intervals of about 5°, it was noticeable that the lowest boiling portions had an unpleasant odour, due, doubtless, to the presence of some sulphur compound. The several fractions were liquid, unless distillation was very slowly conducted, in which case more or less camphor crystallised from the fractions collected below 220—225°; the fractions collected at higher temperatures gave no such deposit, but when again distilled they usually afforded fractions from which camphor separated on cooling.

The fact that the crude oil contains camphor had been previously recognised by Schwanert, who recommended heating the oil at a temperature just below its boiling point in a stream of hydrogen as the best means of getting rid of this impurity; on trying this method, it was found to be not only very tedious, but also unsatisfactory in other respects, the camphor being very incompletely expelled, even after prolonged heating. It seemed not improbable that renewed treatment with sulphuric acid would be a satisfactory method of getting rid of the camphor, and, therefore, the crude oil was heated with sulphuric acid under the conditions last described. This treatment, however, proved to be absolutely useless, as not only was a considerable quantity of the oil converted into carbonaceous matter, but the portions passing over on distillation with steam appeared to be as

rich in camphor as before. Several other means, such as fractional distillation with steam and fractional precipitation by water of the solution of the oil in cold concentrated sulphuric acid, were tried, in the hope of obtaining an oil free from camphor, but unsuccessfully, and it therefore became necessary to resort to fractional distillation.

By employing a long fractionating column (without glass beads), and carrying on the distillation very slowly, it was found to be possible, by repeated fractionation, to separate the crude oil into camphor and a yellow oil boiling above  $220^{\circ}$  under ordinary atmospheric pressure; during this process, the oil darkened in colour, and one or more of its constituents underwent slight decomposition, a small quantity of water being formed, not noticeable at the time of distillation, but at once observed on redistilling any of the liquid fractions. The portions of the oil boiling after repeated fractionation above  $220^{\circ}$  still contained camphor, which, apparently, could not be entirely separated by fractional distillation; on continuing the process, employing a long column as before, it was found to be possible, after several operations, to separate the oil into a portion boiling at about  $220$ — $236^{\circ}$  and a residue boiling above  $236^{\circ}$ .

This residue, on distillation from an ordinary distilling flask, began to boil at about  $236^{\circ}$ , the thermometer slowly rising to about  $250^{\circ}$ ; at this temperature only a relatively very small quantity of a thick, brown oil of undetermined nature remained in the flask.

The distillate collected between  $236^{\circ}$  and  $250^{\circ}$ , although evidently a mixture, could not apparently be resolved into its constituents by continued fractional distillation; it was found, however, that on warming portions of this distillate with phenylhydrazine and glacial acetic acid, a deep red solution was formed from which crystals could be obtained, and the more readily the higher the boiling point of the oil which was treated; it was also found that the constituent of the oil affording the crystalline product could be regenerated from the latter without difficulty. These observations rendered it possible to separate from the mixture a pure substance which was ultimately recognised as acetylorthoxylene [ $\text{Me} : \text{Me} : \text{Ac} = 1 : 2 : 4$ ].

*Acetylorthoxylenehydrazone*,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CMe}\cdot\text{N}_2\text{HPh}$ .

This compound was prepared in large quantities from the portion of the oil produced in the manner above described boiling at  $236$ — $250^{\circ}$ . For this purpose, the oil (150 grams) was mixed with phenylhydrazine (108 grams) and acetic acid (about 50 grams) was added to the mixture; interaction very readily took place, the solution becoming hot, the colour at the same time changing to dark brownish-red. After adding a little alcohol (about 50 grams) and stirring

well, the mixture was kept in a cool place during about 24 hours, at the end of which time a considerable quantity of dark brownish-red crystals had separated from the liquid: this product was separated by filtration and purified by two or three crystallisations from alcohol, from which it was deposited in flat, pale yellow plates or prisms.

Two different samples of the compound, which had been repeatedly recrystallised and then quickly dried at 80°, were analysed with the following results:—

Sample A.	I.	0.2026 gram	gave	22.05 c.c.	N <sub>2</sub> at 19°	and	740 mm.
„	B.	0.2360	„	23.85	„	18°	„
„	III.	0.2254	„	22.3	„	9°	„

	Calculated for	Found.		
	C <sub>10</sub> H <sub>12</sub> .N <sub>2</sub> HPh.	I.	II.	III.
N . . . . .	11.8 p. c.	12.4	12.0	12.2 p. c.

The hydrazone crystallised well, and was easily obtained in an almost pure condition; no carbon and hydrogen determinations were made because of the unstable character of the substance. Although, when freshly crystallised, it was almost colourless, when kept for a short time, even in the dark and in a closed tube, it became pinkish-red or brown, and began to decompose; it could, however, be kept under alcohol for days without undergoing any appreciable decomposition, although the supernatant solution soon became brownish-red. It was readily soluble in cold acetone, benzene, hot glacial acetic acid and boiling alcohol, but only moderately easily in boiling light petroleum; it crystallised well from boiling 80 per cent. alcohol, from which it separated on cooling in almost colourless, transparent plates. When quickly heated, it melted completely at 112°, being at the same time decomposed. The hydrazone was readily acted on by a hot alcoholic solution of ferric chloride, and converted into nitrogen, acetylorthoxylene and decomposition products of phenylhydrazine; it was also readily hydrolysed by cold concentrated muriatic acid into acetylorthoxylene and phenylhydrazine hydrochloride. It dissolved in cold concentrated sulphuric acid, with development of heat, giving a yellowish-green solution, from which acetylorthoxylene separated as an oil on the addition of water.

The quantity of hydrazone obtained from the oil varied considerably, depending to a great extent on the care with which the oil had been fractionated; working with large quantities (150—200 grams), and employing portions of the oil boiling at 236—250°, the yield of purified hydrazone was rather more than half the weight of the oil taken; when the oil contained substances boiling below 236°, the

yield was diminished. The reason of this is that, even after careful fractionation, the oil is a mixture of at least three substances : namely, camphor, acetylorthoxylene and another constituent to be referred to later on in the paper. The mother liquors from the crystalline hydrazone contained a large quantity of a thick, dark red oil mainly produced by the interaction of the other compounds and phenylhydrazine ; this doubtless prevents the crystallisation of a portion of the acetylorthoxylenehydrazone.

*Acetylorthoxylene*,  $C_6H_2Me_2 \cdot CO \cdot CH_3$  [Me : Me : Ac = 1 : 2 : 4].

When the preparation of a crystalline, although very unstable, hydrazone from the oily product of the action of sulphuric acid on camphor was first effected, its reconversion into the ketone from which it had been formed was at first accomplished in the following way :—The purified hydrazone was dissolved in boiling alcohol, and treated with a hot concentrated alcoholic solution of ferric chloride ; a vigorous action at once set in, and therefore it was necessary to add the ferric chloride cautiously to prevent the mixture from frothing over owing to the rapid evolution of nitrogen. As soon as no further effervescence took place on the addition of a fresh quantity of ferric chloride, the mixture was distilled with steam ; when most of the alcohol had passed over, the distillate gradually became turbid, owing to the separation of a colourless oil, and as the alcohol in the receiver became more and more dilute, a considerable quantity of oil was precipitated. The process was interrupted as soon as oil ceased to pass over, and, after cooling, the oil was separated with the aid of a funnel, and dried with calcium chloride. On distilling the oil under ordinary atmospheric pressure, it began to boil at about  $80^\circ$ , and between this temperature and  $170^\circ$  about 35 per cent. (decomposition products of phenylhydrazine) passed over ; the thermometer then immediately rose to about  $245^\circ$ , the remainder of the oil distilling constantly at  $245\text{--}247^\circ$ , and leaving only a trace of a brown residue.

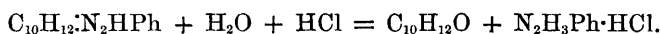
As the liquid boiling at  $245\text{--}247^\circ$  seemed to undergo slight decomposition with liberation of water when distilled under ordinary atmospheric pressure, it was carefully dried and then redistilled under a pressure of 310 mm. ; the portion boiling constantly at  $212\cdot5\text{--}213^\circ$ , which formed about 90 per cent. of the whole, was collected separately and analysed, with the following results :—

I.	0.1628	gram	gave	0.4826	gram	$CO_2$	and	0.1192	gram	$H_2O$ .
II.	0.1458	„	„	0.4324	„	„	„	0.1069	„	„

	Calculated for C <sub>10</sub> H <sub>12</sub> O.	Found.	
		I.	II.
C.....	81.08 p. c.	80.84	80.88 p. c.
H.....	8.11 „	8.13	8.14 „
O.....	10.81 „	11.03	10.98 „

The compound obtained in this way was a colourless, highly refractive, mobile oil, having a pleasant odour, resembling that of coumarone rather than that of peppermint; it boiled at 212.5—213° under a pressure of 310 mm., and at 246—247° under a pressure of 760 mm., the observations being made in both cases with a small Zincke thermometer. It was readily converted by phenylhydrazine into a crystalline hydrazone, identical with the substance prepared from the crude oil made by heating camphor with sulphuric acid; it also gave a crystalline hydroxime on treatment with hydroxylamine. It did not combine with sodium hydrogen sulphite. The proof of the identity of this product from camphor with the 1 : 2 : 4-acetylorthoxylene recently prepared by Claus is given later in the paper.

In preparing large quantities of the ketone from its hydrazone, the method just described has certain disadvantages; in the first place, the presence of so large a quantity of alcohol in the steam distillate, no doubt, prevents the complete separation of the oil, unless a large volume of water be added; and, in the second place, the whole of the phenylhydrazine is lost, and its decomposition products become mixed with the ketone. On trying to improve on the earlier method, it was found that the hydrazone was readily hydrolysed by concentrated muriatic acid, interaction taking place in accordance with the equation



As it is not only possible, by working in this way, to recover almost the whole of the phenylhydrazine, but also to obtain a more nearly pure crude product, we made use of this method in all the later preparations, and proceeded as follows:—The freshly crystallised, alcohol-moist hydrazone (100—150 grams) was placed in a large flask, and about 300—350 c.c. of concentrated muriatic acid was added to it; on shaking, the pale yellow hydrazone acquired a bright green colour, and in a very short time the contents of the flask became so solid that agitation was no longer possible; the colour then slowly changed to canary-yellow. After a short time, water having been added, the ketone was separated from the aqueous solution of phenylhydrazine hydrochloride by distilling with steam; the phenylhydrazine salt in the residue was mixed with only a very small quantity of resinous impurity, and could easily be isolated in a clean condition by the



ordinary method. The ketone prepared in this way was almost pure, distilling under ordinary atmospheric pressure at 245·5—247°, only a trace passing over below and above these limits; it was indistinguishable from the compound obtained by decomposing the hydrazone with ferric chloride.

Analyses of the purified compound gave the following results:—

- I. 0·1485 gram gave 0·4413 gram CO<sub>2</sub> and 0·1074 gram H<sub>2</sub>O.  
 II. 0·1546            "            0·4584            "            0·1137            "

	Calculated for C <sub>10</sub> H <sub>12</sub> O.	Found.	
		I.	II.
C.....	81·08 p. c.	81·04	80·86 p. c.
H.....	8·11    "	8·03	8·17    "
O.....	10·81   "	10·93	10·97   "

The quantity of acetylorthoxylene obtained from 100 grams of the original oil collected between 236° and 250° was, on the average, about 30 grams.

*Acetylorthoxylenehydroxime*, C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub>·CMe·NOH.

In order to obtain further evidence as to the nature of the ketone prepared from camphor, it was submitted to the action of hydroxylamine, and was thus converted into a hydroxime which was subsequently recognised as identical with that prepared by Claus from acetylorthoxylene.

In preparing the hydroxime, an alcoholic solution of the purified ketone was treated with a slight excess of hydroxylamine hydrochloride and a large excess of potash, separately dissolved in dilute alcohol before admixture; the mixture was kept for about 24 hours at the ordinary temperature. From concentrated solutions, the product was partially deposited in crystals, but dilute solutions remained clear; in either case, on mixing the solution with dilute muriatic acid, a crystalline precipitate was obtained, which was well washed with water and dried on biscuit ware. The crude product was practically pure, and the yield theoretical.

A large number of analyses of this compound were made, in order to definitely establish the composition of the ketone; for this purpose, the crude product was crystallised twice from alcohol and carefully dried at 70°.

	Substance.	CO <sub>2</sub> .	H <sub>2</sub> O.
I.....	0·1761	0·4733	0·1284
II.....	0·1817	0·4899	0·1296
III.....	0·1432	0·3870	0·1066
IV.....	0·1708	0·4608	0·1260
V.....	0·1404	0·3790	0·1040
VI.....	0·1794	0·4824	0·1279

	Substance.	N <sub>2</sub> .	t.	Bar.
VII.....	0·2154	15·4 c.c.	12°	756 mm.
VIII.....	0·1710	12·95 „	20°	740 „

	Calculated for C <sub>10</sub> H <sub>12</sub> ·NOH.	Found.			p. c.
		I.	II.	III.	
C .....	73·62	73·30	73·53	73·64	p. c.
H .....	7·97 „	8·10	7·92	8·27	„
N .....	8·58 „	—	—	—	„

	Found.					p. c.
	IV.	V.	VI.	VII.	VIII.	
C .....	73·58	73·62	73·33	—	—	p. c.
H .....	8·19	8·22	7·92	—	—	„
N .....	—	—	—	8·6	8·6	„

These results prove beyond doubt that the hydroxime has the composition C<sub>10</sub>H<sub>13</sub>NO. In the earlier analyses, for some cause not discovered, the carbon determinations gave results about one-half per cent. too low, although the substance used seemed to be pure; on this account, a number of analyses are quoted which would otherwise have been superfluous.

The acetylorthoxylenehydroxime prepared from camphor crystallised from dilute alcohol in beautiful, colourless, lustrous plates; from dilute acetic acid in slender prisms; and from boiling water, in which it was only very sparingly soluble, in slender filaments; when a cold solution of the hydroxime in dilute alcohol was allowed to evaporate spontaneously, the hydroxime was deposited in moderately thick, prismatic forms, sometimes an inch in length.

It fused at 84·5—85°, and was readily soluble in most ordinary solvents, except water and light petroleum; it also freely dissolved in a concentrated solution of sodium hydroxide and in concentrated muriatic acid. When heated in small quantities under ordinary atmospheric pressure, it distilled without appreciable decomposition; it was readily hydrolysed by warm muriatic acid, the ketone being regenerated.

According to the previous description given by Claus, acetylorthoxylene melts at 89—90° (uncorr.); notwithstanding this considerable difference between our observations and his, there is no doubt that the products from the two sources are identical, as will be shown later in the paper.

#### *Acetylorthoxyleneacetoxime*, C<sub>10</sub>H<sub>12</sub>·NOAc.

To prepare its acetate, the above described hydroxime was dissolved in excess of acetic chloride, the solution boiled for a few

minutes, then allowed to cool, and the acetic chloride partially evaporated in a desiccator over potash; if the boiling were continued for any length of time, the solution darkened in colour and the product was not easily obtained in a colourless condition. On adding light petroleum to the concentrated acetic chloride solution, the acetate was deposited after a short time in almost colourless crystals, and was easily purified by recrystallisation from boiling light petroleum.

The analyses of the compound so prepared gave the following results:—

I.	0.1781 gram	gave	0.4598 gram	CO <sub>2</sub>	and	0.1191 gram	H <sub>2</sub> O.
II.	0.1748	„	0.4485	„		0.1143	„
III.	0.1789	„	10.8 c.c.	N <sub>2</sub>	measured at	15°	and 750 mm.
IV.	0.2406	„	14.8	„		14°	„ 745 „
V.	0.2674	„	16.2	„		14°	„ 750 „

	Calculated for C <sub>12</sub> H <sub>16</sub> NO <sub>2</sub> .	Found.					p. c.
		I.	II.	III.	IV.	V.	
C	70.24 p. c.	70.41	70.00	—	—	—	p. c.
H	7.31 „	7.43	7.26	—	—	—	„
N	6.83 „	—	—	7.07	7.19	7.12	„

The acetylorthoxylyleneacetoxime separated from light petroleum in ill-defined colourless crystals which melted at 71—72°. It dissolved freely in alcohol, benzene and most of the ordinary organic solvents, except cold light petroleum. When warmed with dilute soda, it was quickly reconverted into the hydroxime.

*Intramolecular change of acetylorthoxylylenehydroxime.*

It has been shown by Meyer and Warrington (*Ber.* **20**, 500) that certain hydroximes readily undergo intramolecular change under the influence of acetic chloride, being converted into substituted amides or substituted amines, in accordance with the general equation



these products are readily hydrolysed, yielding primary amines and monocarboxylic acids. Beckmann (*Ber.*, **19**, 988; **20**, 1507, 2580) has shown that a similar change can be readily brought about by treating the hydroximes with mineral acids, or with phosphorus pentachloride and water successively. At the time when the nature of the ketone from camphor had not been elucidated it was clearly important to study the action of the agents above referred to on the hydroxime prepared from the ketone, it being probable that if it

proved to be convertible into a substituted amide, the investigation of the acid and amine produced by the hydrolysis of this amide would throw some light on the constitution of the ketone.

A solution of the purified hydroxime (about 5 grams) in dry ether having been cooled in a freezing mixture, a small quantity of phosphorus pentachloride was added; on shaking, a colourless solid—probably the hydrochloride of the hydroxime—separated from the solution, but the phosphorus pentachloride was only very slowly dissolved. This being the case, the vessel was removed from the freezing mixture for a short time in order to hasten the action, the temperature of the solution being kept below  $10^{\circ}$ ; on continued shaking, the colourless solid gradually passed into solution, the phosphorus pentachloride being also dissolved. As soon as no further action took place on adding a fresh quantity of pentachloride, the ethereal solution was shaken with ice-cold water, dried, and evaporated; the yellow, oily residue slowly solidified on keeping, and, after having been washed with a little dilute ammonia, as it showed an acid action, it was recrystallised from hot dilute methyl alcohol, from which it separated on cooling in colourless needles.

The compound obtained in this way melted at about  $95^{\circ}$ , was insoluble in water, and contained nitrogen; it was not further examined as in the meantime the constitution of the ketone had been determined, but, as will be shown later in the paper, it is in all probability an acetylxylylidine of the constitution  $C_6H_3Me_2 \cdot NHAc$  [Me : Me : NHAc = 1 : 2 : 4].

*Bromacetylorthoxylylene*,  $C_6H_2BrMe_2 \cdot CO \cdot CH_3$ .

In order to ascertain whether the ketone obtained from camphor was a saturated compound, its behaviour with bromine was investigated. On adding to a solution of the purified ketone in chloroform (about 2 parts), cooled to  $-16^{\circ}$ , a few drops of a chloroform solution of bromine, the liquid immediately assumed the colour of bromine, so that at this temperature no action took place; when, however, the solution was allowed to rise in temperature, the reddish-brown coloration soon disappeared, but no hydrogen bromide was evolved. On now continuing the addition of the chloroform solution of bromine to the liquid kept at about  $0^{\circ}$ , a yellowish-red solid was gradually deposited, and, by the time that one molecular proportion of bromine had been added the contents of the flask had become almost solid; on removing the flask from the freezing mixture and placing it aside, the solid product soon began to pass into solution, while hydrogen bromide was evolved in large quantities. It was evident, therefore, that the solid product was an un-

stable additive compound, which decomposed at the ordinary temperature.

As soon as the evolution of hydrogen bromide was at an end the clear chloroform solution was washed with dilute sodium carbonate and water successively, and dried with calcium chloride; on evaporating the chloroform, a dark-green oil was obtained.

This oil was cooled to about  $-10^{\circ}$ , mixed with a little light petroleum, and a few crystals, obtained in the manner described below, were placed in the solution; after a short time, crystallisation commenced and a large quantity of a blue or slate-coloured powder was deposited. This substance was separated by filtration, washed with a little light petroleum, dried on biscuit ware, and then recrystallised from boiling light petroleum, with addition of animal charcoal.

The colourless crystals of the bromo-derivative obtained in this way were kept for some time over sulphuric acid, and then analysed by Carius' method, with the following results:—

- I. 0.4000 gram gave 0.3324 gram AgBr.  
 II. 0.2327 „ „ 0.1944 „ „

	Calculated for $C_{10}H_{11}BrO$ .	Found.	
		I.	II.
Br .....	35.24 p. c.	35.36	35.54 p. c.

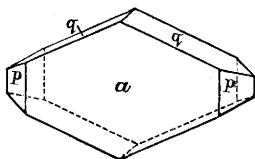
The substance is, therefore, a monobromo-substitution product of the ketone, and its formation under the circumstances above described is evidence of the saturated character of the ketone.

It separated from boiling light petroleum in lustrous, colourless, ill-defined plates, but when crystallisation took place slowly it was deposited in well-defined, flat, hexagonal plates, and in short, compact prisms; it crystallised from warm dilute alcohol in beautiful long needles. It melted at  $63-64^{\circ}$ , and distilled with only very slight decomposition under the ordinary atmospheric pressure, when heated in small quantities, the vapours evolved being extremely irritating when inhaled; it was only very sparingly soluble in boiling water, but dissolved freely in cold chloroform, acetone, benzene, acetic acid and hot alcohol, also in cold, concentrated sulphuric acid forming a greenish-yellow liquid. When a dilute alcoholic solution of the bromo-derivative was warmed with silver nitrate, a yellow precipitate was at first produced, but on continued heating the mixture turned black. On warming a small quantity of the bromoketone with phenylhydrazine, a violent action was observed; in glacial acetic acid solution combination took place almost immediately on warming, but, as the product seemed to be an oil, it was not further examined.

The quantity of purified bromacetylorthoxylene obtained under the

conditions described above was about 12 grams from 11 grams of the ketone. The mother liquors from the crystalline product yielded on evaporation about 5 grams of a green oil, from which, on long keeping, a few well-defined crystals, melting at 63—64°, were deposited; these crystals of bromacetylorthoxylene were examined by Mr. W. J. Pope, who describes them as follows:—

“The substance crystallises in six-sided plates of great brilliancy. The pinacoid  $a\{100\}$  is the largest form exhibited by the crystals, but this, like the other forms present, is considerably corroded. The form  $q\{011\}$  is ordinarily small and dull; the prism  $p\{110\}$  is still smaller but gives somewhat better reflections. Traces of the pinacoid  $c\{001\}$  are frequently observed, but no measurements could be obtained from the faces, which were also badly corroded. In consequence of the poor character of the faces, the measurements given below can only be regarded as approximate. The extinction through  $a\{100\}$  is parallel to the edge  $ap$ .



“Crystalline System. Monosymmetric.

$$a : b : c = 0.957 : 1 : 0.461.$$

$$\beta = 83^\circ 21'.$$

“Forms present:—

$$\begin{aligned} a & \dots \{100\} \dots \infty P \infty \\ p & \dots \{110\} \dots \infty P \\ q & \dots \{011\} \dots R \infty \end{aligned}$$

	Angle.	Number of observations.	Limits.	Mean.	Calculated.
$ap$	100 : 110	9	42° 47' — 44° 7'	43° 26'	43° 32'
$pp$	110 : 110	8	92 20 — 93 12	92 55	—
$qq$	011 : 011	11	48 4 — 50 21	49 12	—
$qq$	011 : 011	6	129 41 — 131 40	130 20	130 48
$aq$	100 : 011	9	83 9 — 84 18	83 58	—
$aq$	100 : 011	4	95 23 — 96 58	96 32	96 2"

Attempts were made to obtain the additive compound, already referred to, in a pure condition, but without success. When the cold chloroform solution was quickly filtered before the evolution of hydrogen bromide commenced, a considerable quantity of a yellowish-red substance remained on the filter; this, however, was very unstable,

and underwent decomposition even when quickly dried on biscuit ware placed in a desiccator, melting to a yellowish oil, hydrogen bromide being evolved. This oil solidified after some time to a mass of crystals melting at 63—64°, evidently identical with the bromo-derivative just described; the crystals obtained in this way were those sown in the above mentioned petroleum solution.

*Bromacetylorthoxylenehydroxime*,  $C_6H_2BrMe_2 \cdot CMe \cdot NOH$ .

This compound was easily prepared in the following manner:—The purified bromoketone was dissolved in warm, dilute alcohol, and treated with a concentrated aqueous solution of excess of hydroxylamine hydrochloride; after gently warming to dissolve any precipitate that was formed, the solution was placed aside and allowed to cool; after about two hours, the mixture was again heated to about 60°, and then kept at the ordinary temperature for two days. The crystals of the hydroxime which were gradually deposited were separated by filtration, dried in the air, and recrystallised from a mixture of benzene and light petroleum with addition of animal charcoal.

A bromine determination, made by Carius' method with a sample of the dried compound, gave the following result:—

0.1801 gram gave 0.1374 gram AgBr.

	Calculated for $C_{10}H_{11}Br \cdot NOH$ .	Found.
Br . . . . .	33.05 per cent.	32.51 per cent.

This hydroxime crystallised from hot dilute alcohol, and from boiling light petroleum in very long, colourless needles melting at 109—110°, and dissolved freely in cold chloroform, benzene, alcohol, and glacial acetic acid, but was only moderately easily soluble in boiling light petroleum; it seemed to be insoluble in cold concentrated muriatic acid, and also in cold soda, but it dissolved in concentrated sulphuric acid yielding a colourless solution.

The method of preparation given above must be strictly adhered to in order to obtain a good yield of the purified hydroxime. When the alcoholic solution of the bromoketone was boiled for some time with hydroxylamine hydrochloride and then mixed with water, an oily precipitate was produced which soon became crystalline; this product seemed, however, to be a mixture of two substances, possibly the two modifications of the hydroxime, one of which was readily, the other only sparingly, soluble in benzene. When the bromoketone was treated with excess of hydroxylamine in alkaline alcoholic solution in the usual manner, a dirty, gum-like, yellow substance was produced.

*Oxidation of acetylorthozylene.*

The experiments made up to this time having shown that the ketone obtained from camphor was a saturated compound of the composition  $C_{10}H_{12}O$ , its behaviour with oxidising agents was next studied; it was soon found that, by suitable treatment with nitric acid, well-defined oxidation products could be obtained, the process being carried out as follows:—

The purified ketone, about 24 grams, was placed in a large flask provided with a reflux condenser, and mixed with about 150 c.c. of a mixture of equal volumes of water and nitric acid ( $d = 1.4$ ); apparently no action took place at the ordinary temperature, even when stronger acid was used but, on boiling the liquid, oxides of nitrogen were evolved. After heating for some hours, the partially exhausted acid was decanted from the undissolved oil, a fresh quantity of acid of the same strength as before was added, and the mixture boiled again, this process being repeated from time to time. As oxidation went on, the oil became less mobile and gradually changed to a yellow, butter-like mass, which in its turn was converted into a yellowish, granular powder. As soon as this change was complete and particles of oil were no longer visible, the solution—from which oxides of nitrogen were still being rapidly evolved—was decanted from the solid product, and the latter well washed with water; the nitric acid liquors, from which on cooling a small quantity of a yellow substance was deposited, were then largely diluted with water, filtered, the solid residue washed with water, and added to the main portion of the oxidation product; the total weight of the yellow powder obtained in this way when dried at  $100^\circ$  was about 23 grams.

This oxidation product was dissolved in sodium carbonate, the solution boiled with animal charcoal to free it from traces of oil, filtered, and acidified with muriatic acid; the precipitate was then separated by filtration, well washed with cold water, and dried. On repeatedly extracting the finely-divided substance with boiling chloroform, an almost colourless powder remained undissolved, a crystalline acid passing into solution; the relative quantities of these two products seemed to depend to a considerable extent on the manner in which oxidation had been carried out, but generally speaking the insoluble acid formed rather more than half the crude mixture.

*Paraxylic acid*,  $C_6H_3Me_2COOH$  [Me : Me : COOH = 1 : 2 : 4].

On evaporating the filtered chloroform extract obtained in the manner just described, a crystalline acid remained which was easily



purified by recrystallisation, first from boiling benzene, and then from a mixture of chloroform and light petroleum; analyses of the purified compound, dried at 100°, gave the following results:—

I. 0.1614 gram	gave 0.4250 gram CO <sub>2</sub>	and 0.0980 gram H <sub>2</sub> O.
II. 0.1702	„ 0.4488	„ „ 0.1016
III. 0.2002	„ 0.5264	„ „ 0.1194

	Calculated for C <sub>9</sub> H <sub>10</sub> O <sub>2</sub> .	Found.		
		I.	II.	III.
C .....	72.0 p. c.	71.81	71.91	71.70 p. c.
H .....	6.6 „	6.75	6.56	6.62 „
O .....	21.4 „	21.44	21.53	21.68 „

The melting point of this acid was 161—162°; a solution of its sodium salt containing excess of sodium carbonate did not decolorise potassium permanganate.

The silver salt of the acid, prepared in the usual way, crystallised from boiling water in colourless, slender needles, which formed beautiful arborescent aggregates:—

0.3090 gram dried at 100° gave 0.1290 gram Ag.

	Calculated for C <sub>9</sub> H <sub>9</sub> O <sub>2</sub> Ag.	Found.
Ag.....	41.95 per cent.	41.74 per cent.

It was evident from these analyses that the oxidation product was a monocarboxylic acid of the composition C<sub>9</sub>H<sub>10</sub>O<sub>2</sub>; on referring to the literature, it appeared that an acid of this composition, and melting at 163°, had been previously obtained by Fittig and Laubinger (*Annalen*, 151, 269) by oxidising pseudocumene with dilute nitric acid: from the description of the properties of this acid we were at once led to suppose it to be identical with the compound obtained from the ketone, and soon succeeded in proving this to be the case.

The acid prepared from the ketone, like that described by Fittig and Laubinger, was almost insoluble in cold, and only very sparingly soluble in boiling water, but dissolved freely in alcohol, from which it crystallised in microscopic prisms. Fittig and Laubinger gave 163° as the melting point of this acid; the acid obtained from the ketone melted at 161—162°, so that the difference was very small and probably one of observation only.

In order to obtain further evidence the calcium salt was prepared and analysed, paraxylic acid, according to Fittig and Laubinger, being a well-defined salt of the composition (C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>)<sub>2</sub>Ca + 3½H<sub>2</sub>O. The salt was easily obtained by boiling the purified acid with water and excess of calcium carbonate, and then filtering the hot solution; on cooling, it

was deposited in long, colourless needles which were separated by filtration and dried on biscuit ware.

Analyses of the air-dried salt gave the following results :—

- I. 0.3131 gram heated at 150—155° lost 0.0490 gram.  
 0.2641 gram of anhydrous salt gave 0.1048 gram  $\text{CaSO}_4$ .  
 II. 0.2797 gram heated at 150—155° lost 0.0428 gram.  
 0.2369 gram of anhydrous salt gave 0.0948 gram  $\text{CaSO}_4$ .

	Calculated for $(\text{C}_9\text{H}_9\text{O}_5)_2\text{Ca} + 3\frac{1}{2}\text{H}_2\text{O}$ .	Found.	
		I.	II.
$\text{H}_2\text{O}$ .....	15.71 p. c.	15.65	15.30 p. c.
Ca .....	11.83 „	11.67	11.77 „

The identity of the acids from the two sources being established, it is unnecessary to fully describe the properties of the compound obtained from the ketone, although perhaps one fact in connection with its silver salt may be mentioned. When this was gently heated in a covered porcelain crucible, the inside of the lid became covered with a yellowish, waxy sublimate, which from its melting point and other properties was found to be paraxylic acid; the acid seemed, however, in some, but not in all cases, to be in an unstable crystalline form, as, when the sublimate was scraped off the lid with a spatula, a sudden and considerable increase in bulk was observed and the waxy mass broke up into microscopic crystals.

#### *Xylidinic Acid*, $\text{C}_6\text{H}_3\text{Me}(\text{COOH})_2$ .

The colourless powder which remained after repeatedly extracting the crude oxidation product of the ketone with boiling chloroform (see above) was dissolved in alcohol, and reprecipitated from the filtered solution with chloroform; this process having been repeated in order to free it completely from paraxylic acid, it was well washed with boiling chloroform and finally recrystallised from hot dilute alcohol.

Analyses of two samples of the colourless, amorphous powder, purified in this way, and dried at 100°, gave the following results :—

- I. 0.1671 gram gave 0.3662 gram  $\text{CO}_2$  and 0.0688 gram  $\text{H}_2\text{O}$ .  
 II. 0.1805 „ „ 0.3992 „ „ 0.0763 „ „

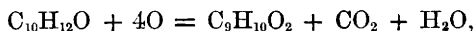
	Calculated for $\text{C}_9\text{H}_3\text{O}_4$ .	Found.	
		I.	II.
C .....	60.00 p. c.	59.77	60.31 p. c.
H .....	4.44 „	4.57	4.69 „
O .....	35.55 „	35.66	35.00 „

The purified acid did not melt at  $330^{\circ}$ , and its solution in sodium carbonate solution was unaffected by potassium permanganate.

The most probable explanation of the formation of an acid of the composition  $C_9H_8O_4$  in the manner described was that it was produced by the oxidation of some of the paraxylic acid, in which case it would be a methylphthalic acid; although no experiments were made with the direct object of proving this view to be correct, there is no doubt that the acid obtained was identical with the so-called  $\beta$ -xylidinic acid [ $COOH : COOH : Me = 1 : 3 : 4$ ], which was first obtained by Jacobsen (*Ber.*, **14**, 2112), by oxidising isoxylic acid with potassium permanganate, and more recently by Claus (*J. pr. Chem.* [2], **42**, 508) by the oxidation of paracymyl methyl ketone.

*Constitution of the ketone obtained from camphor.*

The formation of paraxylic acid in the manner described above practically settled the question of the constitution of the ketone obtained from camphor: the oxidation of a ketone of the composition  $C_{10}H_{12}O$  to paraxylic acid being expressed by the equation



it was obvious that a methyl group in the ketone had been displaced by hydroxyl, that is to say, that an acetyl had been converted into a carboxyl group; consequently the ketone had the constitution  $C_6H_3Me_2Ac$  [ $Me : Me : Ac = 1 : 2 : 4$ ]. On referring to the literature, it appeared that a ketone of this constitution and some of its derivatives had been recently described by Claus (*J. pr. Chem.*, **41**, 396), who had prepared it by treating orthoxylene with acetic chloride in presence of aluminium chloride. On comparing the properties of the substances described by Claus with those of the compounds prepared by us, the evidence of the identity of the two series of compounds was found to be insufficient, as the following table will show:—

Claus.

Ketone, $C_{10}H_{12}O$ . . . . .	B. p. $243^{\circ}$ uncorr.).
Hydroxime, $C_{10}H_{12}:NOH$ . . . . .	M. p. $89^{\circ}90^{\circ}$ * (uncorr.).
Hydrazone, $C_{10}H_{12}:N_2HPh$ . . . . .	„ $113^{\circ}$ .

Armstrong and Kipping.

Ketone, $C_{10}H_{12}O$ . . . . .	B. p. $246-247^{\circ}$ (760 mm.; uncorr.).
Hydroxime, $C_{10}H_{12}:NOH$ . . . . .	M. p. $84.5-85.5$ (uncorr.).
Hydrazone, $C_{10}H_{12}:N_2HPh$ . . . . .	„ about $112^{\circ}$ (uncorr.).

The difference of  $3-4^{\circ}$  in the boiling point of the ketone did not

\* In a private communication we received from Claus, the melting point given was  $88-89^{\circ}$ .

seem to be a matter of much importance, as the observations were probably made under different conditions; the difference of about  $1^{\circ}$  in the observed melting points of the hydrazone was also disregarded, as it was almost impossible, owing to the instability of the compound and the fact that it melted with decomposition, to hope for perfect agreement. The hydroxime, on the other hand, was stable in the air, formed well-defined crystals, and was easily obtained in a pure condition, so that a difference of  $4\frac{1}{2}^{\circ}$  in the observed melting points could not very easily be accounted for.

We tried in vain to raise the melting point of our preparation; a sample of the purified substance, melting at  $84.5$ — $85.5^{\circ}$ , was recrystallised from dilute alcohol, light petroleum, dilute acetic acid and water successively, but the melting point remained unchanged.

It became necessary, therefore, to obtain additional facts before the question of identity could be satisfactorily settled.

Claus (*loc. cit.*) having described a crystalline condensation product melting at  $113^{\circ}$  which he obtained by treating acetylorthoxylene with hydrogen chloride, we first studied the behaviour, under like conditions, of the ketone obtained from camphor. On passing hydrogen chloride into a few grams of the ketone obtained from camphor, the yellow oil first turned wine-red and then dark brown, and gradually became less and less mobile; after passing the gas for about four hours, the product was mixed with water, the mixture boiled for some time to expel unchanged ketone, and the water decanted from the brown, insoluble oil; on adding a little alcohol, the oil slowly solidified, and after several recrystallisations from dilute alcohol and from benzene, it was obtained in pale yellow plates and prisms, melting at  $111$ — $112^{\circ}$ .

We next proceeded to synthesise acetylorthoxylene in the manner described by Claus, and obtained a yellowish oil, boiling at  $246$ — $247^{\circ}$ , which had the very characteristic odour of the ketone prepared from camphor. A portion of this oil was treated with phenylhydrazine in glacial acetic acid solution; the hydrazone obtained melted at the same temperature, and was identical in appearance and properties with the compound previously prepared from the camphor ketone; both compounds crystallised in flat plates or prisms, which showed straight extinction in polarised light. Another portion of the oil prepared from orthoxylene was treated with hydroxylamine; the hydroxime thus produced melted, after recrystallisation, at  $84.5$ — $85.5^{\circ}$ , and was indistinguishable from that obtained from the camphor ketone; on warming a portion of the hydroxime with acetic chloride, a crystalline acetyl derivative was obtained, melting at  $71$ — $72^{\circ}$ , and identical with that obtained from the hydroxime of the camphor ketone.

Finally, we were able, through the kindness of Professor Claus, who sent us a sample, to directly compare the hydroxime of acetylortho-xylene prepared in his laboratory with the compound obtained from the camphor ketone; the two substances melted at the same temperature ( $84\cdot5$ — $85\cdot5^\circ$ ) when suspended on the same thermometer, and showed the same behaviour in every other respect.

One point only remains to be mentioned with regard to the question of identity; the compound melting at  $95^\circ$  which was obtained by treating the hydroxime of the ketone with phosphorus pentachloride (see p. 86) melted at the same temperature and was evidently identical with acetylxylydine [ $\text{Me} : \text{Me} : \text{NHAc} = 1 : 2 : 4$ ], which Claus informs us he has prepared from the hydroxime of acetylortho-xylene under different conditions.

These facts prove conclusively that the ketone  $\text{C}_{10}\text{H}_{12}\text{O}$  produced by the action of sulphuric acid on camphor has the constitution assigned to it above.

*Further investigation of "camphren."*

It has already been stated that the crude oil formed by the action of sulphuric acid on camphor consists of at least three substances, but only two of these, namely, camphor and acetyl-xylene, had been isolated; it was therefore desirable to continue the investigation of the crude oil, with the object, more especially, of isolating the compound which imparts such a characteristic peppermint-like odour to the mixture.

For this purpose we first turned our attention to the red oil which remains in the mother liquors from the crystalline acetylortho-xylene-hydrazone (see p. 81); quantitative experiments having indicated that the red oil is itself a hydrazone, we endeavoured to prepare the ketone from it by methods similar to those employed in the case of the crystalline hydrazone. When the red oil was treated with ferric chloride in boiling alcoholic solution, effervescence, due, doubtless, to the liberation of nitrogen, set in, and the mixture darkened; on distilling with steam, a relatively small quantity of a yellow oil collected in the receiver, a very large quantity of dark, resinous matter remaining in the flask. The oil was found to have only a slight odour of peppermint and to contain a considerable quantity of acetylortho-xylene, which was identified by means of its hydroxime. Since this method failed to give the desired result, we next tried to hydrolyse the red oil with muriatic acid; excepting a small quantity of tarry matter, it readily dissolved in the concentrated acid, yielding a deep, reddish-brown solution, which, after keeping for some time, remained clear on adding water; when, however, the acid solution was neu-

tralised with sodium carbonate, a dirty, yellowish solid was precipitated. Many endeavours were made to purify this solid substance, but without success; it separated from solvents in the form of a dark yellow or brown oil, and underwent change so readily, probably in consequence of oxidation, that we were unable to examine it satisfactorily.

These experiments having proved unsuccessful, we again attempted a separation of the constituents of the crude "camphren" by fractional distillation, but after repeated trials, were obliged to abandon the attempt as hopeless; although, by working in the usual way, we often succeeded in collecting a large quantity of a liquid passing over, say, between 220° and 225°, on redistillation, it began to boil considerably below 220°, and the thermometer rose to about 240° before the whole had distilled. We were unsuccessful in obtaining any appreciable quantity of oil boiling below 200°, from which it would seem that the characteristic peppermint-like smell of "camphren" is not due to the presence of camphorophorone or camphorone, which, according to Koenigs and Eppens (*Ber.*, 25, 260), boils at 195—200° under 715 mm. pressure. We also endeavoured to obtain the crystalline tribromo-derivative of camphorophorone, described by Koenigs and Eppens, by treating "camphren" with bromine; although these attempts failed, they cannot be regarded as affording satisfactory evidence of the absence of camphorophorone.

*Oxidation of "camphren" with nitric acid.*—To obtain further information as to the nature of the other constituents of "camphren," it became necessary to resort to indirect methods. Having already characterised the acids produced by the oxidation of pure acetylorthoxylene with nitric acid (see pp. 90—93), it appeared desirable to ascertain whether well-defined oxidation products were not obtainable from the other constituents of the crude oil. A sample of the oil collected between 225° and 235°, that is to say, freed as far as possible from camphor and acetylorthoxylene, was boiled with about 30 volumes of a mixture of nitric acid ( $d = 1.3$ ) with an equal bulk of water; dense, ruddy fumes were evolved, most of the oil gradually passing into solution, the remainder being converted into a yellowish solid. The latter was separated by filtration and was found to consist of xylidinic acid and paraxylic acid, doubtless formed by the oxidation of acetylorthoxylene still present in the oil oxidised. The nitric acid solution was evaporated on the water-bath, the residue taken up with water, and the solution evaporated again, this treatment being continued until the nitric acid was completely expelled; a thick, yellow oil then remained which slowly deposited a small quantity of a crystalline substance when kept in a cool place; the mixture was then stirred up with a little ether, the crystals separated by filtration, washed with ether, and

dried on biscuit ware. The compound obtained in this way crystallised in colourless prisms, melting at about  $100^{\circ}$ , and was freely soluble in water, giving an acid solution; it was proved to be oxalic acid. The ethereal solution of the oil separated from the oxalic acid, was evaporated and kept for a long time over sulphuric acid, but as it did not crystallise and could not be distilled, it was not further examined.

*Oxidation of "camphren" with potassium permanganate.*—Camphor, as is well known, is only very slowly oxidised by potassium permanganate in neutral or in acid solution even at  $100^{\circ}$ ; experiments showed that pure acetylorthoxylene was also stable under the conditions mentioned, whereas crude "camphren" was readily oxidised. These facts served to suggest a method of obtaining oxidation products of the oil having a peppermint-like smell. About 75 grams of oil collected between  $225^{\circ}$  and  $235^{\circ}$ , 30 grams of concentrated sulphuric acid and 150 c.c. of water were placed in a large bottle, and a cold, saturated, aqueous solution of potassium permanganate was gradually added to the mixture with constant shaking; the pink colour immediately disappeared, and, as heat was developed to a slight extent, the bottle was cooled under the tap from time to time; the process was stopped after adding in this way about 150 grams of potassium permanganate and sufficient dilute sulphuric acid to keep the solution acid, although even more permanganate would have been reduced. The filtered solution was concentrated on the water-bath until crystals began to separate, then strongly acidified with dilute sulphuric acid, and extracted 10 times with ether; the dried ethereal solution gave on evaporation about 20 grams of a yellow oil, which soon solidified to a mass of crystals. This substance was spread on biscuit ware to free it from traces of oil and then crystallised twice from hot chloroform, from which it separated in colourless, ill-defined masses, melting at  $77-78^{\circ}$ .

Analyses of the compound gave the following results:—

I. 0.1603 gram gave 0.2851 gram  $\text{CO}_2$  and 0.1030 gram  $\text{H}_2\text{O}$ .

II. 0.1651           "           0.2974           "           0.1012           "

	Calculated for $\text{C}_6\text{H}_{10}\text{O}_4$ .	Found.	
		I.	II.
C .....	49.31	48.50	49.12 p. c.
H .....	6.85	7.14	6.81   "
O .....	43.84	44.36	44.07   "

The compound was an acid; it readily dissolved in ammonia, and on adding silver nitrate to the neutral solution, a colourless silver salt was precipitated; this salt was separated, well washed with cold water, and dried, first on biscuit ware and then at  $100^{\circ}$ ; it seemed to

be amorphous, only sparingly soluble in boiling water, and comparatively very stable.

0.4445 gram gave 0.2667 gram Ag.

	Calculated for $C_6H_9O_4Ag_2$ .	Found.
Ag.....	59.93 per cent.	60.00 per cent.

The melting point and other properties of the acid at once led us to suspect its identity with the  $\alpha$ -methylglutaric acid prepared by Wislicenus and Limpach by the decomposition of the ethereal salt produced by the interaction of ethylic  $\beta$ -iodopropionate and ethylic sodiomethylacetoacetate. Just about the time when we were engaged in settling this question, Koenigs and Eppens (*loc. cit.*) published a short account of some experiments on camphorophorone, the ketone of the composition  $C_9H_{14}O$  obtained by the dry distillation of calcium camphorate. They stated that, on oxidation with potassium permanganate, camphorophorone yields an  $\alpha$ -methylglutaric acid which they proved by direct comparison to be identical with Wislicenus and Limpach's acid, at the same time giving a very complete account of the properties of the compound.

On comparing Koenigs and Eppens' description with the properties of the acid obtained by us, there was agreement as to melting point and solubility, and a neutral solution of our acid gave precipitates with mercurous nitrate and copper sulphate, but not with lead acetate, calcium chloride and cadmium sulphate, a behaviour which was in accordance with Koenigs and Eppens' statements. One fact, however, seemed for a short time to point to the two acids not being identical, namely an apparent difference in the properties of their mercuric salts; a neutral solution of Koenigs and Eppens' acid was stated to give no precipitate with mercuric chloride, whereas a neutral solution of the acid prepared from "camphren" gave a very considerable precipitate. This difference in behaviour, however, was simply due to a difference in conditions; we used a neutral solution of the ammonium salt, they a neutral solution of the barium salt, and the reason that a precipitate is not produced in the latter case is because the mercuric salt is readily soluble in presence of barium chloride (or calcium chloride). Through the kindness of Dr. Koenigs, we were able to satisfactorily establish the identity of the acids from the two sources by direct comparison.

It may be noted that Kachler (*Annalen*, **164**, 83 and 89) seems to have obtained  $\alpha$ -methylglutaric acid by the oxidation of "camphren" with nitric acid and with chromic acid; his statements regarding the properties of the compound, however, are too meagre to decide the question.



The theoretical interpretation of the results recorded in this communication will be discussed in a subsequent paper.

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