in composition with the expressed oil of pumpkin seed examined by us.[1]

II. *The "Press-cake."*—This material was extracted with hot alcohol, and in the resulting extract the presence of the following constituents was determined: (1) A quantity of fatty oil, corresponding to about 6 per cent. of the weight of the entire seed, and agreeing closely in character with that obtained by expression; (2) soluble protein products; (3) a quantity of sugar; (4) resinous material, amounting to about 0.3 per cent. of the weight of the entire seed. From the resin there were isolated a very small amount of a phytosterol (m. p. 158–159°), and a new alcohol, designated *cucurbitol*, $C_{24}H_{40}O_4$ (m. p. 260°), which yields an acetyl derivative melting at 150°. Cucurbitol appears to be closely related to two other crystalline alcohols recently isolated in these laboratories, namely, *grindelol*, $C_{23}H_{38}O_4$ (m. p. 256–257°), from *Grindelia camporum*, which yields an acetyl derivative melting at 161°, and *ipurganol*, $C_{21}H_{31}O_4$ (m. p. 222–225°), from jalap resin, which yields an acetyl derivative melting at 166–167°. These three alcohols are evidently members of a homologous series, which is represented by the general formula $C_nH_{2n-8}O_4$.

III. *The Shells.*—These amounted to 48.7 per cent. of the weight of the entire seed. They contained a quantity of fatty oil, which was similar in character to that obtained from the kernels by expression, but, in addition to the fatty acids obtained from the latter, a small amount of arachidic acid was isolated. The resinous material contained in the shells corresponded to about 0.3 per cent. of the weight of the entire seed, and from it, besides a mixture of fatty acids, very small quantities of a phytosterol (m. p. 138–140°) and *cucurbitol*, $C_{24}H_{40}O_4$, were separated. It was observed that these shells, like those of the pumpkin seed, contain traces of copper.

In order to ascertain whether the resin obtained from watermelon seed possesses any physiological activity, some tests were kindly conducted for us by Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories. The resin, both from the kernels and the shells of the seed, was administered to a dog in amounts of one gram each, but no obvious effect was produced, and it may therefore be considered quite innocuous.

THE CONSTITUTION OF RETENE AND ITS DERIVATIVES.

BY JOHN E. BUCHER.

Received January 13, 1910.

In the early part of the work in this laboratory on the condensation of aromatic propiolic acids to derivatives of 1-phenyl-2,3-naphthalene-

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[1] THIS JOURNAL, 32, 358.

dicarboxylic acid,[1] much difficulty was experienced in determining the structure of the latter compounds. They could be transformed into carboxylic acids of diphenyl, diphenyleneketone and fluorene. A comparatively small number of such acids are described in the literature and in some cases the structure given is evidently uncertain or else incorrect. They did not aid materially in determining the structure of the naphthalene products. Later in the work, very efficient methods for determining the nature of the products under investigation were found. These methods were found equally applicable for determining the constitution of the derivatives of diphenyl, diphenyleneketone and fluorene, as well as the substances of which these are oxidation products.

It was found, for instance, that the constitution of retene could be shown very easily by applying three of these methods.[2] The first method used was that of oxidizing substances in pyridine solution with potassium permanganate. The second depends on the fact that diphenyleneketonecarboxylic acids are very easily oxidized to benzene polycarboxylic acids by alkaline potassium permanganate, if the oxidation is finished by means of fuming nitric acid, aided by the catalytic action of manganese nitrate. The third depends on the fact that when diphenyleneketonecarboxylic acids are heated with potassium hydroxide, the ring breaks in such a way as to have the carboxyl groups as far apart as possible.

Retene, $C_{18}H_{18}$, was examined early in the work, hoping that it would be of service in connection with the above investigation. It is designated as 8-methyl-5-isopropylphenanthrene (I) in such standard works as those of Beilstein and V. von Richter. The numerous derivatives are also assigned corresponding structural formulas, in nearly all cases, without even a question mark, as is shown in the example of reteneketone in Richter's "Lexikon der Kohlenstoffverbindungen."

On looking up the original work of Bamberger and Hooker,[3] it was seen that there was no justification for this distribution of the two substituting groups. They showed, in their very careful research, that retene is a methylisopropylphenanthrene but they were not able to determine the position of the two groups. They state positively that they did not prove that the groups are in the para (5,8-) position or even that they are both united to the same benzene nucleus. They thought one group to be in the ortho (8-) position, however. The diphenyleneketonedicarboxylic acid (V) obtained from retene does not yield an anhydride easily. When this acid is heated with potassium hydroxide it yields a diphenyltricarboxylic acid. On page 114, they state that this acid yields a fluorescein, thus showing that the groups are in the ortho position. On

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[1] THIS JOURNAL, 30, 1244 (1908).

[2] *Ibid.*, 32, 219 (1910).

[3] *Ann.*, 229, 114 (1885).

page 161, they describe the same acid as not changing in any way *even at* 270°. They, as well as nearly all of those who used this argument, evidently overlooked this contradiction. Even if an acid (VI) not splitting out water were formed quantitatively, it would still be possible that the groups were in the ortho position originally. Failure to consider the possibility of isomeric acids has led to uncertainty in other cases in assigning structural formulas to derivatives of diphenyl, diphenyleneketone and other substances of this kind. Since there are *twenty-eight* isomers possible, considering only two rings, in the case of retene, it is evident that the formula given in the literature has no value. The idea of getting substances of known structure from this hydrocarbon was therefore abandoned for a time.

A little later it was pointed out by Fortner[1] that the formula of retene must be incorrect. He synthesized a 2-diphenyleneketonecarboxylic acid which was found to be identical with one obtained from retene by Bamberger and Hooker. This showed that one of the groups in retene must be in position 2- but he was not able to determine which one.

Schultze[2] in working on resin-oils, showed that they contain hydrogenated retenes. He showed that these could be transformed into retene and also that they could be oxidized to *1,2,4-benzenetricarboxylic acid.* This observation proves that the two groups cannot be on the same benzene ring. The same observation had also been made by earlier observers, only one might question whether their compounds were pure enough to be used for work on the constitution of retene.

Lux[3] also investigated the constitution of retene. By fusion of reteneketone with potassium hydroxide, he obtained two methylisopropyldiphenylcarboxylic acids. One of these acids did not esterify easily and he concluded that it must contain two substituting groups in the ortho positions to the carboxyl group. This was used to show that in retene one group must be in the meta position (8-) compared with the diphenyl. He was not able to determine whether this group was methyl or isopropyl. As a result of the work of Fortner, Schultze, Lux and others, it follows that the formula (I) of Bamberger and Hooker cannot be correct but that retene probably has a structure represented either by formula II or III.

In addition to these, Easterfield and Bagley have advocated the formula with the methyl group in position 8- and the isopropyl group in position 6-. It will be shown in the latter part of this paper in discussing the structure of abietic acid (VII), that some of the evidence upon which they base this formula is really the strongest evidence which can be cited against it.

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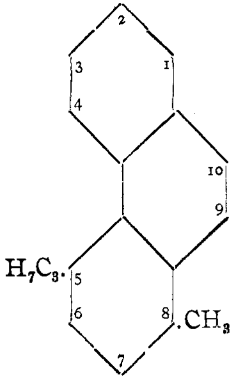
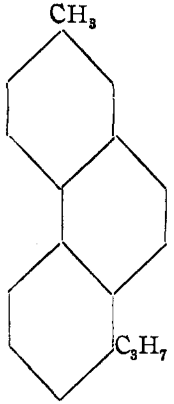
[1] *Monatsh. Chem.*, **29**, 763 (1904).

[2] *Ann.*, **359**, 132 (1908).

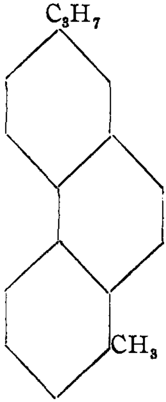
[3] *Monatsh. Chem.*, **35**, 452 (1908).



I.



II.

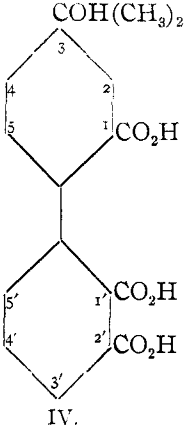


III.

In our study of the oxidation of organic substances in pyridine solution in this laboratory, we obtained compounds which give a perfectly satisfactory solution of this problem—the properties of the oxyisopropyldiphenyltricarboxylic acid obtained in the following manner showing the position of the methyl group in retene.

Ten grams of retenequinone are dissolved in 50 cc. of pyridine and 25 cc. of water in a three-liter flask, provided with a reflux condenser. The flask is heated on the water bath and in the course of half an hour 60 grams of finely powdered potassium permanganate are added in about six portions. The flask is shaken vigorously during the process and more water is added, as needed, to keep the contents in a pasty condition. The total quantity of water present at the end of the experiment should be about 100 cc. The heating and shaking were continued until the permanganate was all reduced. The whole operation required about one hour. The pyridine was then recovered by distilling it with a current of steam until the odor had disappeared. The oxides of manganese were then removed by filtration and 1.1 grams of unchanged retenequinone recovered from them. The warm filtrate was then oxidized with 10 grams of potassium permanganate to complete the process. When the color had disappeared, the solution was filtered, made nearly neutral with sulphuric acid and concentrated to a small bulk to remove the potassium sulphate. It was then acidified and extracted with ether. On distilling off the ether, a mixture of acids was left in the form of a sirup. After the addition of a small quantity of water, the solution was boiled *in vacuo* until the odor of ether disappeared. It was then allowed to evaporate spontaneously nearly to dryness. On taking up the acids with a little warm water, one sparingly soluble acid could be separated from the other very soluble acids. After crystallizing from water, 2.2 grams were obtained.

The acid titrated for a tribasic acid with a molecular weight of 345. The theory for an hydroxyisopropyldiphenyltricarboxylic acid (IV) is 344.

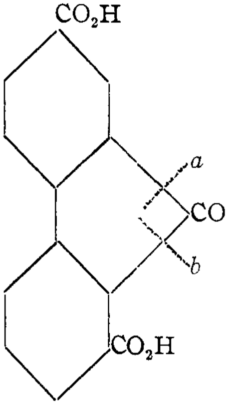


IV.

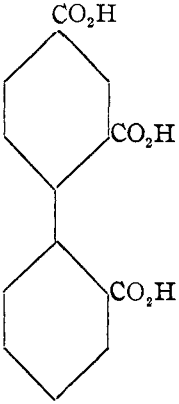
The acid loses water easily upon heating, leaving a residue which is still soluble in sodium carbonate. This shows the acid to be tribasic. The formation from retenequinone shows the position of groups 1- and 1′-. The formation of water on heating shows another carboxyl group in an adjacent ortho position (2′-). As the isopropyl residue remains in the compound, it is certain that group 2′- must have come from the methyl group. It follows from this that the methyl group must be in position 8- in retene. This excludes formula II and shows that formula III for an 8-methyl-2-isopropylphenanthrene must represent the structure of retene.

This experiment also yields other important evidence. On further oxidation the oxyisopropyl acid (IV) yields the corresponding tetrabasic acid which is easily soluble in water and gives diphenyl for the hydrocarbon. This tetrabasic acid, on heating, gave off water but the residue dissolved in sodium carbonate with effervescence. The acid, therefore, does not contain a carboxyl group in position 2 (formula IV). Also, a small quantity of *1,2,3-benzenetricarboxylic acid* was obtained—proving that in retene the groups must be united to different rings. These products alone are sufficient to determine the general structure of retene—the only point left open in formula III being whether the isopropyl group is in position 2, 3 or 4. There can be no doubt that the other acids which are formed in this one oxidation experiment will enable us to tell which of these three possibilities is the true one.

However, it was thought easier to oxidize the diphenyleneketone dicarboxylic acid (V) which Bamberger and Hooker obtained from retene by oxidation.



V.



VI.

Bamberger and Hooker state that this acid is oxidized to oxalic acid by potassium permanganate. This view is misleading, however, as comparatively small quantities of oxalic acid are formed. It has been shown that acids of this type are oxidized very readily to the corresponding benzenepolycarboxylic acids.[1] One would expect this particular acid to break up at *a* and *b*, thus yielding *two* isomeric benzenetricarboxylic acids.

Accordingly, one gram of this yellow ketonic acid was oxidized with potassium permanganate in the usual way. After filtering off the oxides of manganese, the solution was concentrated, acidified and extracted with ether. The sirupy solution of acids was heated in an evaporating dish over the water bath to expel the last traces of ether. Fuming nitric acid and a crystal of manganese nitrate were then added. Brisk effervescence, due to the oxidation of oxalic acid and probably some —$CO.CO_2H$ groups, took place at once and a white solid acid separated. The solution was evaporated to dryness and the acid washed with fuming nitric acid and then recrystallized from water. The acid separated in clear massive crystals, which are characteristic of 1,2,3-benzenetricarboxylic acid. It titrated for a molecular weight of 246 and lost 14.45 per cent. of water at 100°. Theory for 1,2,3-$C_6H_3(CO_2H)_3.2H_2O$; $M = 246$, $H_2O = 14.63$ per cent. The water of crystallization serves to distinguish it from the isomeric 1,2,4-benzenetricarboxylic acid which occurs in the filtrate and separates at ordinary temperatures without water of crystallization. The crystals of the latter acid are also quite different so there was no trouble in recognizing it. Both gave excellent yields of benzene for the hydrocarbon.

The isolation of both these acids limits the structure of retene, at once, to one group in position 8- and the other group in either position 2- or

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[1] This Journal, 32, 220 (1910).

3-. It also excludes Bamberger and Hooker's formula, which would necessitate the formation of 1,2,3,4-benzenetetracarboxylic acid and phthalic acid. Taken in connection with the above oxidation in pyridine solution the only question left open is whether the isopropyl group in formula III is in position 2- or 3-.

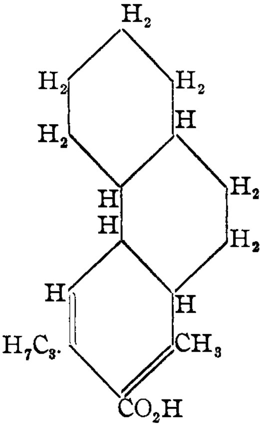
The oxidation of the diphenyleneketonedicarboxylic acid (V) was also effected in the following way. Heating this acid with potassium hydroxide should lead to the formation of the acid represented by formula VI, the ring breaking at *b*. The acid obtained in this way did not split out water upon heating, confirming the view that the statement made by Bamberger and Hooker on page 161 in their article is correct and that the structure they suggest on page 114 is incorrect. This 1,3,2'-diphenyltricarboxylic acid was then dissolved in 5 parts of fuming nitric acid, the solution being boiled ten minutes in the water bath. It was then evaporated to dryness in a casserole, taken up in hot water and reduced with sodium amalgam. The oxidation was then carried on exactly as in the preceding experiment, except that concentrated nitric acid was used instead of fuming acid in the final treatment with nitric acid and manganese nitrate. This avoids the danger of getting nitro acids. As expected, this experiment gave a small quantity of meta-phthalic acid and a large quantity of 1,2,4-benzenetricarboxylic acid. The latter acid contained no water of crystallization, titrated for a molecular weight of 212 and gave a good yield of benzene for the hydrocarbon. These results are in thorough accord with those obtained by the direct oxidation of the yellow ketonic acid (V).

On oxidizing reteneketone, Bamberger and Hooker obtained a mixture of the diphenyleneketonedicarboxylic acid (V) and the corresponding hydroxyisopropyldiphenyleneketonemonocarboxylic acid. We have shown that this mixture can be used in the above experiments instead of the pure dibasic acid—thus avoiding a very tedious process of purification. As there is no danger of ambiguous results, this mixture was also used in the following experiment: It was heated with potassium hydroxide at 218° to break up the ketone ring and form the corresponding acid derivatives of diphenyl. The resulting acids were reduced with hydriodic acid at 200° in the hope of reducing the hydroxyisopropyl group to the isopropyl group. The hydrocarbon was then prepared in the usual way. One would expect the oil thus obtained to be a mixture of diphenyl (from acid V), and of isopropyldiphenyl. This mixture was oxidized in pyridine solution with potassium permanganate exactly in the way described above for retenequinone. After the oxides of manganese and neutral matter had been removed, the alkaline solution was acidified and extracted with ether. The acid thus obtained was 3-diphenylcarboxylic acid. This completes the evidence for the constitution of retene by showing that the isopropyl group is in position 2- as represented in formula III. As this evidence, based especially on the formation of the two isomeric benzenetricarboxylic acids, 3-hydroxyisopropyl-1,1′,2′-diphenyltricarboxylic acid and 3-diphenylcarboxylic acid *directly from retene,* is independent of all previous work we now have very strong evidence that the above structure must be correct.

The constitution of retene having been established, it is now an easy matter to correct the various structural formulas of the retene derivatives which appear in the literature. This includes compounds of diphenyl, diphenyleneketone, fluorene, reteneketone, retenequinone, etc.

Many important natural products are hydrogenated derivatives of retene. This is true especially of resin and resin oil derived from the *Coniferae* as is shown by many investigations, among which may be mentioned that of Schultze.[1] The mineral resin fichtelite, $C_{18}H_{32}$, is a completely reduced retene. It is therefore tetradecahydro-8-methyl-2-isopropylphenanthrene. The resin left from the distillation of turpentine is said to consist very largely of abietic acid. This acid is claimed to be a decahydroretenecarboxylic acid $C_{18}H_{27}.CO_2H$ and it is therefore not surprising that its hydrocarbon, $C_{18}H_{28}$ should occur in resin oil.

That abietic acid has the above constitution was apparently shown by Easterfield and Bagley[2] who succeeded in converting it into retene and also into dehydrofichtelite $C_{18}H_{30}$. As the acid has a low esterification velocity, they conclude that it is a diortho-substitution product. The formula of Bamberger and Hooker (I) for retene does not allow such a structure and they consider it incorrect in consequence. They then change the isopropyl group to position 6- and write the formula as follows (VII).



VII.

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[1] *Ann.*, 359, 129 (1908).

[2] *J. Chem. Soc.*, 85, 1238 (1904).

Their formula would make retene an 8-methyl-6-isopropylphenanthrene. They offer no better evidence for their formula than Bamberger and Hooker did for formula I. They state that the formula is in accordance with the oxidation products, 1,2,4-benzenetricarboxylic- and metaphthalic acids! The very formation of these acids, however, is conclusive evidence against the formula, for such a compound would not yield the above acids. Their assumption is also shown to be untenable by the work described in this paper. It does explain the low esterification velocity of the acid, but many other arrangements would do just as well.

It may be pointed out that the formula (III), which has now been proved for retene, has *one* position (1-) diortho-substituted and if abietic acid is really a carboxyl derivative, the acid group might be in this position. The very extensive literature is so contradictory that one can not rely on it to decide this point. Some consider the abietic acid to be a dihydroxy derivative and others even question the composition, $C_{19}H_{28}O_2$, of the acid.

The wide bearing of the work, on retene, on natural products is still further shown by the suggestion of Neuberg and Rauchwerger that cholesterol is related to abietic acid and may therefore contain a reduced retene nucleus.

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THE COLORED SALTS OF SCHIFF'S BASES.

III. THE SALTS OF BASES FORMED BY CONDENSING *m*-AMINODIMETHYLANILINE AND *m*-AMINODIETHYLANILINE WITH AROMATIC ALDEHYDES.

BY F. J. MOORE.

Received January 19, 1910.

It has already been shown in previous papers[1] that benzylidene compounds of the general type,

when treated with acids in non-aqueous solvents, add successively two molecules of the latter, and that the salts containing one molecule of acid differ markedly in color from those containing two molecules. The former are, for the most part, dark red, while the latter are light yellow, the free bases themselves varying from a light cream color to orange. For this behavior three possible explanations have been suggested. For a detailed discussion of these, the reader must be referred to the papers mentioned. Here it will be sufficient to sum them up briefly as follows:

The first ascribes the difference in the color of the salts to the position of that nitrogen atom selected by the first molecule of acid. The second

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[1] THIS JOURNAL, 30, 394 and 1001.