The above samples have all been gray irons. White iron it was thought, on account of its low silicon and absence of graphitic carbon, would not lend itself as readily to oxidation; but samples of white irons, treated in the same way, were oxidized as completely and in the same time as gray.

SAMPLE OF WHITE IRON.

	Per cent. sulphur.	Per cent. sulphur.	Per cent. sulphur.
Bamber's method	0.431	0.432	0.429
Oxidation in basic mixture	0.432	0.430	0.430

This method could no doubt be worked to advantage, using a stream of oxygen and combustion tube. The method does away with the precipitation of the sulphur in the presence of the ferric salt, and the time required for a determination is about that required for the determination of sulphur in coke.

LABORATORY OF THE E. & G. BROOKE IRON CO.,
BIRDSBORO, PA.

THE CONSTITUTION OF CAMPHENE.[1]

BY F. D. DODGE.

Received April 17, 1902.

THE constitution of camphene is as yet an unsettled point in the chemistry of the terpene series. The objections to the Bredt formula[2] have been stated by Semmler[3] and others, but no satisfactory substitute has been suggested.

As a result of some experiments with the reaction of Bertram and Walbaum,[4] the addition of acetic acid, in presence of mineral acids, I have been led to a somewhat different conception of the camphene molecule.

Camphene and pinene yield the acetates of isoborneol and terpineol, respectively. As regards other terpenes, but little appears to have been published, and I have made the following experiments.

1. *Pinene*, from American turpentine (sp. gr. 0.867. $\alpha_D = + 11°$). 50 cc. with 100 cc. pure acetic acid, containing 1 per cent. sulphuric acid, allowed to stand at 15°-20° for five days. Quantitative saponification showed 43 per cent. terpineol acetate.

---

[1] Read before the New York Section of the American Chemical Society, February 7, 1902.

[2] *Ber. d. chem. Ges.*, (1893), p. 3056.

[3] *Ibid.*, (1900), p. 3421.

[4] *J. prakt. Chem.*, **49**, 1.

2. *Camphene* (by Reychler's method from pinyl chloride), after six days, product contained 77 per cent. isobornyl acetate.

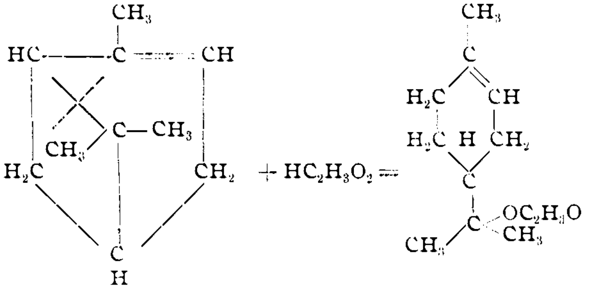
3. *Limonene* (α_D = + 100°. Sp. gr. = 0.847), after five days, α_D = 0°, product showed 4 per cent. of acetate. On distillation, about 50 per cent. of a terpene mixture was obtained, containing principally terpinene.

4. *Terpinolene* (from terpineol by oxalic acid), after six days, 11 per cent. acetate formed.

5. *Terpinene* (from limonene), after six days, 8 per cent. acetate.

It is to be noted that the bornylene of Wagner, to which must probably be assigned the camphene formula of Bredt, also does not combine with acetic acid under these conditions, which fact was utilized by Wagner to separate it from camphene.[1]

Pinene and camphene are thus sharply differentiated from the other terpenes. The acetic reaction is not obtained (or but to a limited extent) with any singly or doubly unsaturated terpene, except in the case of pinene. But in pinene, the double bond is not attacked, but the 4-ring is opened, producing a terpineol derivative.



Pinene. Terpineol acetate.

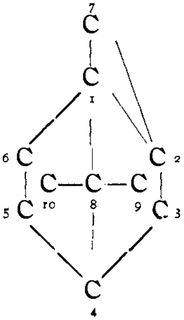
The possibility now suggests itself, that in camphene we may have, not a double bond, but a 4-ring (or possibly a 3-ring) which is readily opened, yielding the ester of isoborneol.

The close relations of camphene, isoborneol, and camphor indicate with great probability that camphene contains the camphor nucleus, in which case there are but two possibilities of such additional ring-formation.

---

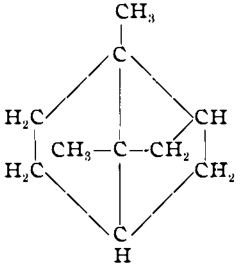
[1] *Ber. d. chem. Ges.*, (1900), p. 2121.

1. A 3-ring between C_1, C_2, and C_7.



A study of the spacial relations as shown by the tetrahedral models leads to the conclusion that such a structure is improbable. This assumption would also lead to a formula for camphenilone, which is identical with that established for the fenchocamphorone of Wallach.[1] These two compounds are, however, certainly not identical, and the C_1, C_2, C_7 ring hypothesis is hence untenable.

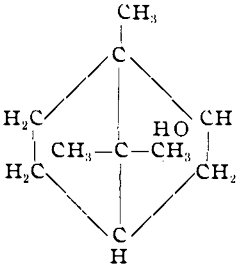
2. A 4-ring, C_1, C_2, C_9, C_8, leads to the formula



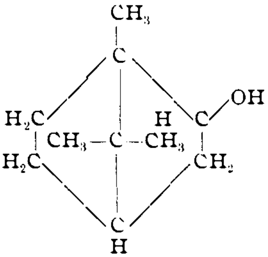
which, I believe, best explains the properties and reactions of camphene.

As in the case of pinene, we have here a 4-atom ring, readily opened under the influence of acids, yet differing from pinene in one respect. When the 4-ring of pinene is separated, the molecule is rearranged in more stable forms either of the terpineol or camphor series, and reversion to pinene is impossible. In camphene, the atoms composing the 4-ring are, as it were, held in position by the stable 5- and 6-ring nucleus, and the 4-ring may be opened and closed *ad libitum; i. e.,* we can pass from camphene to isoborneol, and the reverse at will. To isoborneol must be assigned the cis-configuration, while borneol is represented by the trans-form.

[1] *Ann. Chem.* (Liebig), **300**, 294; **302**, 371; **315**, 273.



Isoborneol.

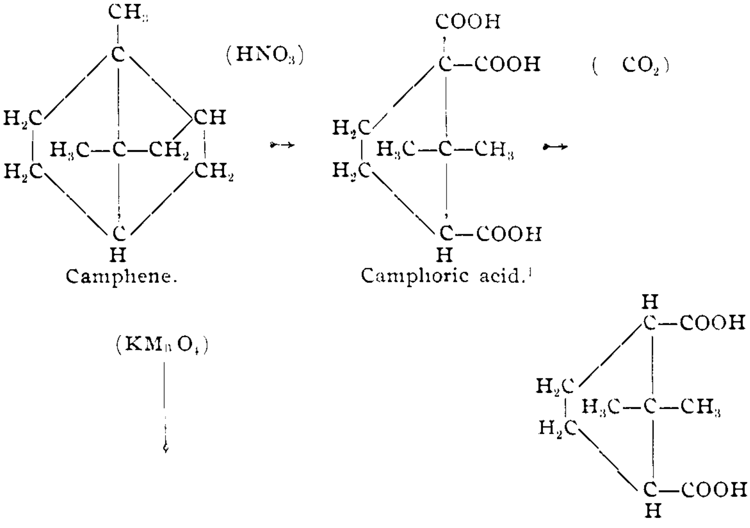


Borneol.

The greater reactivity of isoborneol is due to the proximity of the hydroxyl to the C_9 methyl group, and the differences in properties of the cis-chloride (isobornyl chloride, camphene hydrochloride) and the trans-chloride (bornyl chloride, pinyl chloride) are similarly explained.

According to this hypothesis, camphene is a saturated molecule, *i. e.*, contains no double bond. In fact there appears to be very little reason to consider it unsaturated. The difficult oxidation by permanganate, the action of bromine, etc., and many other reactions show that camphene is differently constituted from the typical unsaturated terpenes.

The new formula explains very satisfactorily the various oxidation products of camphene. Thus, we have:



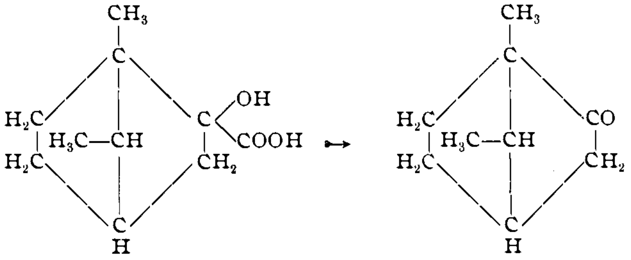
Camphene.

Camphoric acid.[1]

Apo-camphoric acid.

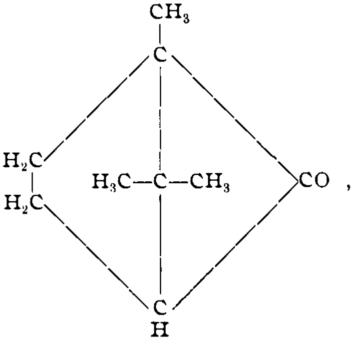
---

[1] *J. Chem. Soc.* (1891), p. 648.

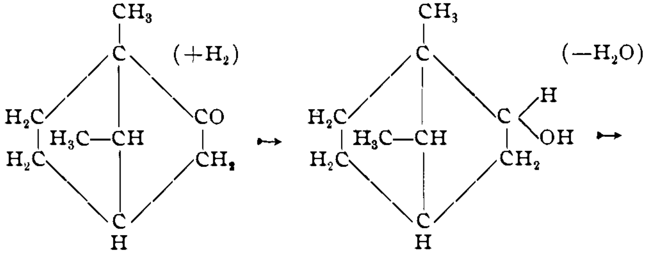


Camphenylic acid.[1] Camphenilone.

Camphenilone, $C_9H_{14}O$, here appears as a true lower homologue of camphor, which it strikingly resembles. Jagelki's formula,[2]



is improbable, because it assumes an oxidized 4-carbon ring, which is known to be an unstable arrangement, and it leads further to very improbable formulas for dehydrocamphenylic acid, and camphenilene. The new formula presents no serious difficulties. Thus:

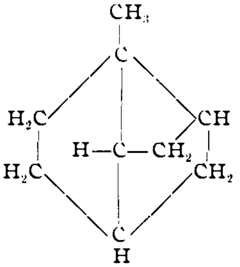


Camphenilone. Camphenilol.

---

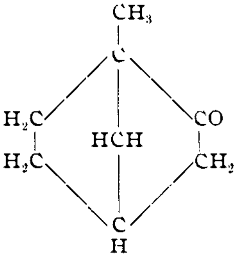
[1] *Chem. Centrbl.*, (1897), I, p. 1056.

[2] *Ber. d. chem. Ges.*, (1899), p. 1498.

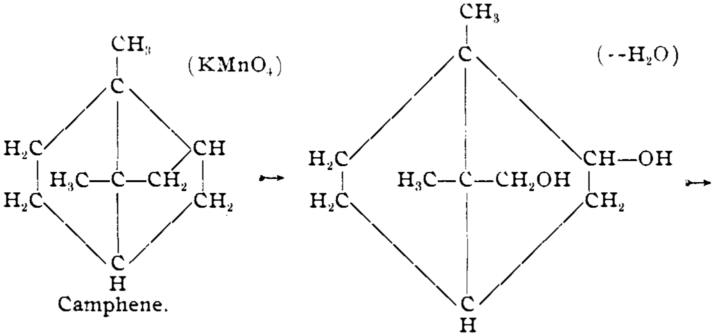


Camphenilene.

These reactions are exactly analogous to the formation of camphene from camphor, and if the hypothesis is correct, it should be possible to put camphenilene through further transformations, leading finally to the second lower homologue of camphor:



Wagner's camphene glycol[1] and its reactions may be shown as follows:

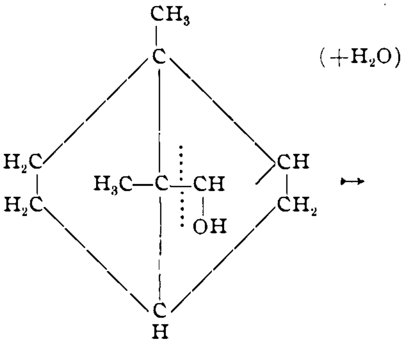


Camphene.

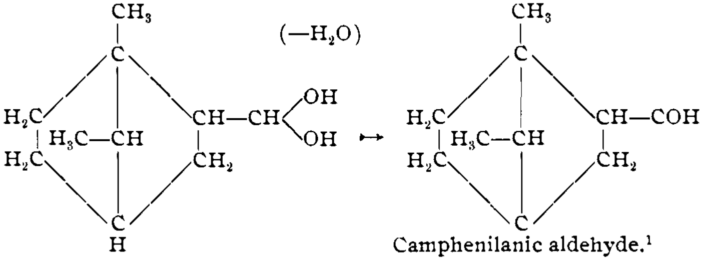
Glycol, or 9-hydroxy-isoborneol.

---

[1] *Ber. d. chem. Ges.*, (1890), p. 2311.



9-Hydroxycamphene.



Camphenilanic aldehyde.[1]

Further oxidation then leads to camphenilanic acid, camphenylic acid, and camphenilone.

As regards the other oxidation products mentioned by Jagelki (*l. c.*), it is unnecessary to discuss them in detail. Blaise,[2] who has examined and repeated some of Jagelki's work, arrives at rather different results. He concludes that the former's camphenilone formula cannot possibly be correct, and that this compound does not contain the trimethylcyclopentene ring characteristic of the camphor series. This deduction is entirely in harmony with the formulas here suggested.

A few other points in connection with the camphene formula remain to be mentioned.

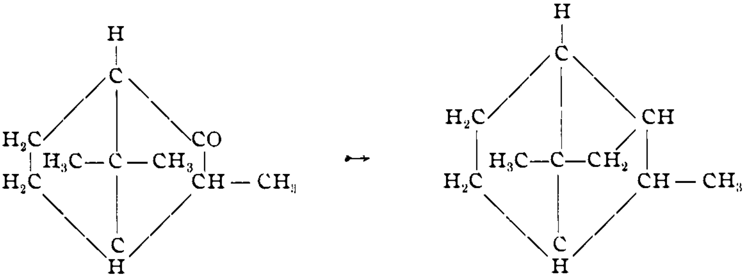
It has been shown[3] that fenchene behaves, with acetic acid, like camphene, and we are led to an analogous formula:

---

[1] *Chem. Ztg.*, (1896), p. 842. *Ber. d. chem. Ges.*, (1899), p. 1498.

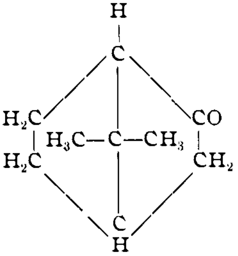
[2] *Compt. rend.*, **129**, 886.

[3] Schimmel & Co.: *Chem. Centrbl.*, (1898) II., p. 985.



Fenchone. Fenchene (?).

But, fenchocamphorone has, most probably, the structure.



Fenchocamphorone.

and its formation from this fenchene is hard to explain. Wallach,[1] however, has recently shown that ordinary fenchene is a mixture of at least three compounds, and Kondakow and Lutschinin[2] have reached a similar conclusion. The conditions in the fenchone series appear to be complex, and further experiment is necessary.

The characteristic feature of the new camphene formula is the connection between C_2 and C_9. Now the symmetry of the camphor nucleus shows that if such a connection is possible, a similar one may occur between C_3 and C_9.

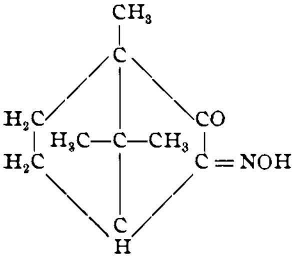
In fact a compound is known, which I believe is best represented by such a formula. This is the camphenone of Angeli[3] whose formation may be shown thus:

---

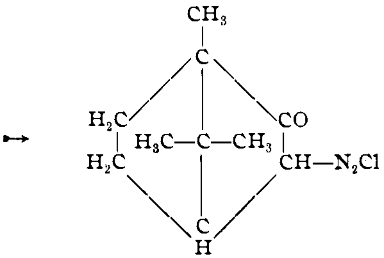
[1] *Ann. Chem.* (Liebig), **302**, 371 ; **315**, 273.

[2] *Chem. Ztg.*, **25**, 131.

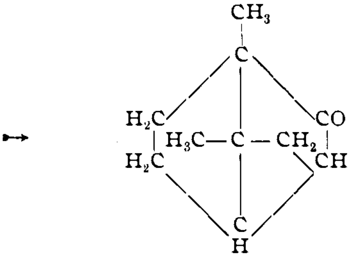
[3] *Gazz. chim. ital.*, **23**, (II.) 351 ; **24**, (II.) 318.



Isonitrosocamphor.

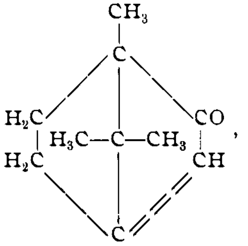


Diazocamphor, HCl.



Camphenone (?).

Angeli proposed the formula



but the tetrahedral models show that this structure is highly improbable. Harries and Matfus[1] have further found that camphenone does not show the hydroxylamine reaction characteristic of $\alpha\beta$-unsaturated ketones.

I would add, finally, that camphenilone, if correctly formulated above, should yield isonitroso and oxy-methylene derivatives which are improbable if Jagelki's formula is true. These reactions are under investigation.

NEW YORK, February, 1902.

---

[1] *Ber. d. chem. Ges.*, **32**, 1340.