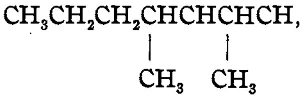
and dried over potassium carbonate, the ether was then distilled off and the residue consisting of the nonylene fractionated. The yield was twenty grams of hydrocarbon boiling at 132–133°.

Calculated for C_9H_{18}: C, 85.71; H, 14.29
Found: C, 85.29; H, 14.22.

Properties: Colorless liquid boiling at 132–133°.

Miscible with all the common organic solvents. Immiscible with water. Decolorizes bromine in chloroform solution. It has an odor like that of petroleum.

2,4-Dimethylheptane,  $CH_3CH_2CH_2\underset{\underset{CH_3}{|}}{CH}CH\underset{\underset{CH_3}{|}}{CH}CH$, was made from the nonylene by reducing it by Sabatier and Senderens' method of passing the vapor of the nonylene with an excess of hydrogen over freshly reduced nickel at 160–180°, after the manner of the reduction of 2-methyl-5-metheneheptane to 2,5-dimethylheptane described in the preceding paper. The nonane was then carefully fractionated with a fifth degree thermometer until five grams were obtained boiling at 132.9–133°.

Calculated for C_9H_{20}: C, 84.37; H, 15.63
Found: C, 84.28; H, 15.92

Properties: Colorless liquid boiling at 132.9–133° at 752 millimeters pressure. It is miscible in the common organic solvents. Does not decolorize bromine in chloroform. Odor of petroleum. Sp. gr. is 0.7206 at 15° compared to water at 15°. The index of refraction was determined with a Pulfrich refractometer N_D (25°) = 1.4014.

CAMBRIDGE, MASS.,
October, 1911.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. VIII. CAMPHONOLIC ACID AND CAMPHONOLOLACTONE.

BY WILLIAM A. NOYES, E. E. GORSLINE AND R. S. POTTER.

Received November 23, 1911.

Three lactones are known which correspond to three hydroxy acids which retain the tertiary carboxyl of camphoric acid. These are:

1. Campholactone, obtained by Fitting and Woringer[1] in distilling lauronolic acid and formed when lauronolic acid is warmed with dilute acids.

2. Isocampholactone, first obtained in an impure condition by one of us[2] in decomposing aminolauronic acid,

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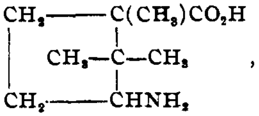
[1] *Ann.*, 227, 10.

[2] *Am. Chem. J.*, 17, 432; 32, 290.

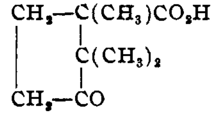


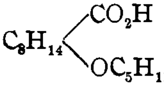
with nitrous acid and later obtained by Bredt[1] by decomposing the nitroso derivative of the anhydride of aminolauronic acid with sodium hydroxide.

3. Camphonololactone[2] corresponding to a hydroxy acid formed along with the hydroxy acid of isocampholactone in decomposing the nitroso derivative of aminolauronic acid with sodium hydroxide.[3]

4. In addition to the three hydroxy acids corresponding to the three lactones a hydroxy acid called hydroxylauronic acid,[4] which has not been converted into a lactone, has been obtained by the decomposition of the ethyl ester of aminolauronic acid by nitrous acid. The same acid, apparently, is one of the products of the decomposition of the nitroso derivative of the anhydride of aminolauronic acid with sodium hydroxide.[5] Hydroxylauronic acid has been obtained only as a viscous liquid and the evidence that it is a single, definit compound and not a mixture of two or more hydroxy acids is not very satisfactory.

While structural formulas for some of these lactones and hydroxy acids are to be found in the literature, the formulas which have been given rest on very slender evidence. In the hope of securing more satisfactory evidence for the structure of some one of these acids we undertook, three years ago, the reduction of camphononic acid,



The structure of this acid was demonstrated very conclusively by Lapworth and Lenton.[6] After several months of work and many futile attempts, we finally obtained the *amyl ether of camphonolic acid*,  $C_8H_{14}\left\langle\begin{matrix}CO_2H\\OC_5H_{11}\end{matrix}\right.$, by reducing the camphononic acid with amyl alcohol and sodium. About that time a brief note was published by Bredt[7] in which he stated that he had effected the desired reduction by electrolytic means. Our own work in this line was, accordingly, discontinued. More recently we have undertaken a careful study of the products obtained by the decomposition

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[1] *Ber.*, 35, 1991.

[2] This name is suggested by Professor Bredt in a private communication.

[3] Noyes and Taveau, *Am. Chem. J.*, 35, 385.

[4] *Am. Chem. J.*, 18, 687. THIS JOURNAL, 31, 278.

[5] *Am. Chem. J.*, 32, 289; 35, 385.

[6] *J. Chem. Soc.*, 79, 1284.

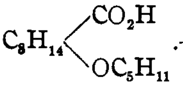
[7] *Ann.*, 366, 1.

of the nitroso derivative of the anhydride of aminolauronic acid with sodium hydroxide. Among these products Taveau[1] found a lactone melting at 164–165° which gave a hydroxy acid melting at 189.5°.[2] By comparing the properties of this acid and lactone with those of a sample of the *cis*-camphonolic acid and camphonololactone obtained by the reduction of camphononic acid, very kindly sent us by Professor Bredt, we have established the identity of the two substances. We have also oxidized our hydroxy acid to camphononic acid. These compounds must, therefore, have the structures

Experimental Part.

Camphononic acid was prepared by the method of Lapworth and Lenton,[3] somewhat modified. Camphanamide (19.7 g.) was dissolved in 10% sodium hydroxide by boiling for a short time. The solution was cooled to 0° and 120 cc. of a solution of 5.4 cc. of bromine in 120 cc. of cold sodium hydroxide (10%) was added. The mixture was allowed to stand 1 1/2 hours at room temperature, was heated for 4 hours on the water bath and was again allowed to stand over night. On the addition of an excess of hydrochloric acid the camphononic acid was precipitated and was filtered off after thorough cooling. It was crystallized from carbon tetrachloride and from water. The yield was about 10 grams but the reaction seems to be very sensitive to slight changes in the conditions. The purified camphononic acid melts at 229–230°; Lapworth and Lenton give the melting point as 228°. In a solution containing 2.4 g. in 100 cc. of benzene $[\alpha]_D = 17.8°$ at 27.5°. In a solution containing 3 g. in 100 cc. of alcohol $[\alpha]_D = -3.9°$.

Reduction of Camphononic Acid. Amyl Ether of Camphonolic Acid,



$C_8H_{14}\begin{cases}CO_2H\\OC_5H_{11}\end{cases}$.—Four grams of sodium were placed in a flask connected with an upright condenser, ten cc. of amyl alcohol were added through the condenser and then, gradually, 4 grams of camphononic acid dissolved in 20 cc. of amyl alcohol. More alcohol was added as necessary and the boiling continued till all of the sodium had disappeared. The amyl alcohol was distilled with steam, indifferent substances were removed with ether and the reduction product obtained by extracting with ether after acidifying with hydrochloric acid. The acid obtained was a viscous,

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[1] *Am. Chem. J.*, 35, 385.

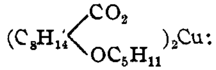
[2] The values given in the experimental part of this paper are probably more accurate.

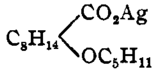
[3] *J. Chem. Soc.*, 79, 1233.

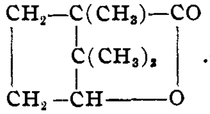
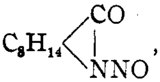
yellow oil which distilled at 222–223° under a pressure of 40 mm. The analyses indicate that it was mixed with a little unchanged camphononic acid, from which it could not be separated by distillation, but taken with the analyses of salts given below, they leave no doubt as to the character of the compound:

Calculated for $C_{14}H_{26}O_3$: C, 69.4 ; H, 10.7.
Found: C, 68.3, 68.2, 68.5; H, 9.8, 9.9, 10.2.
68.7, 69.3 ; 10.1, 10.0.

The calcium salt was prepared by boiling a solution of the acid in dilute alcohol with calcium carbonate. From this solution the copper and silver salts were prepared by precipitation. The analyses gave:

Calculated for  $\left(C_8H_{14}\begin{matrix}CO_2\\OC_5H_{11}\end{matrix}\right)_2Cu$: Cu, 11.5; found, 11.4%.

Calculated for  $C_8H_{14}\begin{matrix}CO_2Ag\\OC_5H_{11}\end{matrix}$: Ag, 30.9; found, 31.3%.

Cis-camphonololactone,  .—As stated above, this lactone has been prepared by Bredt by the electrolytic reduction of camphononic acid.[1] Taveau obtained[2] it by decomposing the nitroso derivative of the anhydride of aminolauronic acid,  $C_8H_{14}\begin{matrix}CO\\|\\NNO\end{matrix}$, by boiling it with a 10 per cent. solution of sodium hydroxide. We have prepared it again in a similar manner, using 37.5 cc. of a 33 per cent. solution of sodium hydroxide to 25 grams of the nitroso compound and shaking the mixture for some hours. The bottle containing the mixture was set upright in cold water, to keep it cool, and provided with a stopper bearing a tube which allowed of the escape of the nitrogen which is evolved. The decomposition is very slow at first, owing to the very difficult solubility of the nitroso compound. After some laurolene has been formed, however, it proceeds more rapidly. When the decomposition was nearly complete a second portion of sodium hydroxide and the nitroso compound was added and after some time a third portion. In subsequent decompositions some of the previous mixture was added to hasten the start of the reaction.

After separating the laurolene the mixture of acids formed was precipitated with sulfuric acid and taken up and extracted with ether. The isocampholactone was separated by dissolving the acids in sodium or potassium carbonate and these acids after precipitation a second time were subjected to fractional distillation under the low pressure obtained by a

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[1] *Ann.*, 366, 1.

[2] *Am. Chem. J.*, 35, 385.

Geryk pump. The lactone obtained was about 4 per cent. of the weight of the nitroso compound which was decomposed. We find the melting point of the lactone one or two degrees higher than that given by Taveau and four or five degrees higher than that of the lactone kindly sent us by Professor Bredt, but the following table of comparisons leaves no doubt as to the identity of the compounds:

CIS-CAMPHONOLOLACTONE.

	From nitroso compound. Noyes and Potter.	Mixture.	From reduction of camphononic acid, Bredt.
Melting point.............	165°–167°	163°–165°	161°
$[\alpha]_D$ in alcohol............	—20.2°		—16.8°
(0.05 g. in 1 cc.)..........	at 28°		at 30°
$[\alpha]_D$ in alcohol............	—22.3°		
(0.1 g. in 1 cc.)...........	at 26°		

CIS-CAMPHONOLIC ACID.

	From nitroso compound.	Mixture.	From reduction of camphononic acid. Bredt.
Melting point.............	202°–203°	201°–202°	201°
$[\alpha]_D$ in alcohol............	+29.2°		+29.7°
(0.1 g. in 1 cc.)...........	at 28°		at 30°

	Lactone from nitroso compound.	Mixture.	From our hydroxy acid.
Melting point.............	165°–167°	165°–167°	165°–167°
$[\alpha]_D$ in alcohol............	—20.2°		—19.8°
(0.05 g. in 1 cc.)..........	at 28°		at 28°

Taveau[1] gives the melting point of his hydroxy acid as 189.5°. Professor Bredt[2] gives the melting point of his acid as 197–198°. The differences are doubtless due to differences in the rate of heating, as the acid is rapidly transformed into the lactone at its melting point or below and slow heating may depress the melting point many degrees. Our thermometer was checked by testing it in boiling paratoluidine and found correct. The melting points were made with an Anschütz thermometer, and there was no stem correction required.

The hydroxy acid was easily converted back to the lactone by heating for fifteen minutes at 255°. The conversion is practically quantitative and the rotation of the regenerated lactone is almost identical with that of the original, indicating that no molecular rearrangement has occurred in the process.

Camphononic Acid from Cis-Camphonolic Acid.—Five-tenths of a gram of camphonolic acid was mixed with 3 cc. of Beckmann's chromic acid mixture[3] (twice the theoretical amount) and allowed to stand over night. Two cubic centimeters of dilute sulfuric acid (1 : 1 by vol.) were added and the mixture allowed to stand again for 24 hours. The solution was

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[1] *Am. Chem. J.*, **35**, 386.

[2] *Ann.*, **366**, 2.

[3] *Ibid.*, **250**, 325.

diluted, extracted with ether and the camphononic acid was crystallized by dissolving in benzene, evaporating in a test tube on the water bath till crystallization began and adding an equal volume of petroleum ether. The following comparisons with the camphononic acid from camphanamide (see above) establish its identity:

CAMPHONONIC ACID.

	From camphanamide by Lapworth's method.	Mixture.	From our hydroxy acid by oxidation.
Melting point	229°–230°	227°–228°	227–228°
$[\alpha]_D$ in benzene	+17.8°		+17.0°
(0.024 g. in 1 cc.)	at 27.5°		at 27.5°
$[\alpha]_D$ in alcohol	—3.9°		—3.9°
(0.02 g. in 1 cc.)	at 28°		at 29°

Conclusions.

1. The lactone obtained by Taveau by the decomposition of the nitroso derivative of the anhydride of aminolauronic acid with sodium hydroxide is identical with cis-camphonololactone obtained by Bredt by the reduction of camphononic acid and the corresponding hydroxy acids, camphonolic acid, are also identical.

2. Camphonolic acid has been oxidized to camphononic acid, establishing more completely that this acid contains the hydroxyl group in the same position as the secondary carboxyl of camphoric acid.

3. The amyl ether of camphonolic acid, $C_8H_{14}(OC_5H_{11})CO_2H$, and its copper and silver salts have been prepared. The free acid is a viscous liquid.

4. Cis-camphonololactone melts at 165–167°; $[\alpha]_D$ in alcohol (0.05 g. in 1 cc.) at 28° is —20.2° or at 26° (0.1 g. in 1 cc.) it is —22.3°.

Cis-camphonolic acid melts at 202–203° when rapidly heated; $[\alpha]_D$ in alcohol (0.1 g. in 1 cc.) at 28° is +29.2°.

Camphononic acid melts at 229–230°; $[\alpha]_D$ in benzene (0.024 g. in 1 cc.) at 27.5° is +17.8°; $[\alpha]$ in alcohol (0.02 g. in 1 cc.) at 28° is —3.9°.

URBANA, ILLINOIS.

THE ROLE OF OXIDASES IN THE FORMATION OF CERTAIN CONSTITUENTS OF ESSENTIAL OILS.

[PART I.]

BY BENJAMIN T. BROOKS.

Received October 20, 1911.

The work described in the present paper was undertaken with the object of throwing some light on the manner in which ketones and aldehydes are formed in certain essential oils.

In the study of the essential oil of *Michelia champaca* L.[1] it was noted that an energetic oxidase was present in the flowers, and on investigating

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[1] Brooks, THIS JOURNAL, 33, 1763 (1911).