

with a small quantity of bone-black gave a 40% yield of a pure white crystalline product melting at 165.5°.

0.052 g. of acid required 24.8 cc. NaOH 0.0210 *N*. Neutral equivalent found = 100. Theory, 97. Subst., 0.1424; CO₂, 0.3220; H₂O, 0.0644. Required for C₁₀H₁₀O₄: C, 61.85%; H, 5.19%. Found: 61.67%, 5.03%.

This data proves that the oxidation product is *o*-carboxyhydrocinnamic acid.

An attempt was made to oxidize the dihydroxy acid obtained from the dibromide of Δ^1 -dihydronaphthoic acid-2 to the keto hydroxy compound (m. p. 119–120°). This was, however, not successful, although some *o*-carboxyhydrocinnamic acid was obtained, which serves to demonstrate the structure of the dihydroxy acid.

Summary.

1. The missing isomeric dihydro- β -naphthoic acid has been prepared by rearrangement of both Δ^3 -dihydronaphthoic acid-2 and Δ^2 -dihydronaphthoic acid-2 and its identity as a chemical individual has been established.

2. The structures of the three isomeric dihydro acids have been demonstrated through the reactions of the corresponding dibromides.

3. The structure of Δ^1 -dihydronaphthoic acid-2 (the new isomer) has been conclusively established by means of oxidation reactions.

URBANA, ILL.

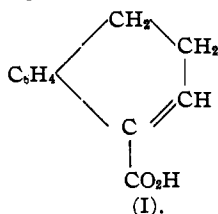
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF ILLINOIS.]

THE STRUCTURE OF THE DIHYDRO- α -NAPHTHOIC ACIDS.

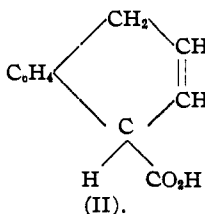
BY OLIVER KAMM AND HARRY BRUCE McCLUGAGE.¹

Received December 18, 1915.

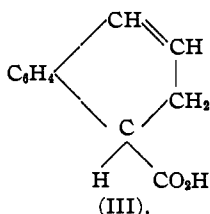
Three dihydro- α -naphthoic acids having the unsaturated linkage in the ring carrying the carboxyl group are theoretically possible, *viz.*:



Δ^1 -Dihydronaphthoic acid-1.



Δ^2 -Dihydronaphthoic acid-1.



Δ^3 -Dihydronaphthoic acid-1.

Of the above acids, two have previously been prepared although the structure of only one of them has been conclusively established. In the present paper additional evidence is presented in favor of the struc-

¹ From a thesis presented to the Faculty of the University of Illinois in partial fulfillment of the requirements for the degree of Bachelor of Arts (McClugage, 1915).

tures of the two known isomers. Although we have not yet succeeded in synthesizing the third isomeric acid, it seems desirable to publish our results at the present time because of the fact that the reactions used for the demonstration of structures in the α -naphthoic acid series are exactly analogous to those used by Derick and Kamm¹ in the beta series. This evidence, together with the analogy found in the benzoic acid series, furnishes strong proof that the reactions outlined below may be used for the demonstration of structure of these unsaturated acids.

The reduction products of the naphthoic acids were studied almost simultaneously by Sowinski² and by Baeyer and Schoder,³ who prepared two of the dihydro acids. The labile acid (so named because of the ease of its rearrangement into the higher melting stable isomer) was prepared by the direct reduction of α -naphthoic acid with sodium amalgam. The stable isomer was obtained by boiling the labile acid in aqueous sodium hydroxide solution.

The evidence in favor of Structure I (Δ^1 -dihydronaphthoic acid-1) for the stable dihydro acid is based mainly upon the fact that by its oxidation Baeyer and Schoder were able to obtain an acid melting at 165°, which agrees with the melting point of *o*-carboxyhydrocinnamic acid. To the above evidence must be added the generalization presented by Baeyer: In a rearrangement of a labile acid under the influence of an alkali the double union shifts toward the carboxyl group.

The labile dihydro acid may therefore have either of the two remaining structures. Meyer and Jacobson⁴ state that either Structure II or III may be the correct one for this acid, but from the data available they have not attempted to differentiate between these two formulas. Sowinski,⁵ without conclusive evidence in his favor, has presented Formula III, while Bethmann,⁶ who has measured the ionization constants of the dihydro acids, also presented a Δ^3 -structure for one of the isomers. Baeyer,⁷ on the other hand, is inclined in favor of Structure II. The evidence advanced in this paper agrees with the views of Baeyer.

The labile dihydro acid has been resolved into its optically active components by Pickard and Neville.⁸ This is, however, not a demonstration of the structure of the acid since both Δ^2 -dihydronaphthoic acid-1 and Δ^3 -dihydronaphthoic acid-1 possess asymmetric molecules. Consequently Pickard and Neville have attempted to decide between the

¹ Preceding article in THIS JOURNAL.

² *Ber.*, 24, 2354 (1891).

³ *Ann.*, 266, 169 (1891).

⁴ "Lehrbuch der Organischen Chemie," 1903, Vol. 2, Pt. 2, p. 446.

⁵ *Loc. cit.*, p. 2360.

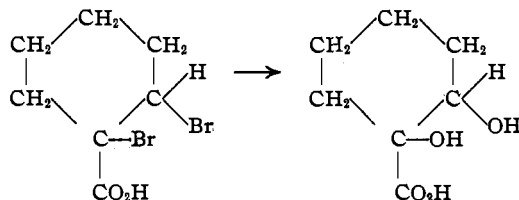
⁶ *Z. physik. Chem.*, 5, 400 (1890).

⁷ *Loc. cit.*, p. 173.

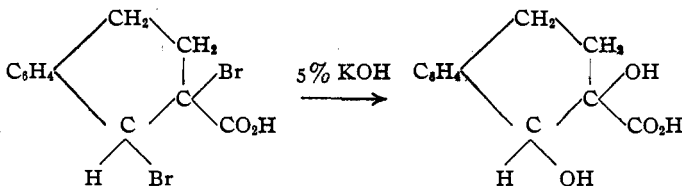
⁸ *J. Chem. Soc.*, 87, 1763 (1905).

two possible formulas by studying the speed of rearrangement of the labile into the stable isomer. For this purpose, the *d*-form of the labile acid was used, since it was possible to follow the rearrangement into the inactive stable isomer by means of polarimetric measurements. They state in their conclusions that it is some additional evidence in favor of the Δ^2 -constitution that the measurements of the velocity of the transformation into the Δ^1 -acid show the rearrangement to be unimolecular, but that it must be remembered that what is measured may be the velocity of the slower of two successive changes. This, therefore, was not advanced as a final proof of the structure of the labile acid.

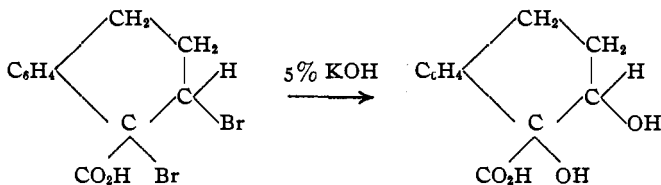
In the present work the evidence in favor of the structures of these dihydro acids is based upon the reactions of the corresponding dibromides with cold, dilute, aqueous solutions of alkalis. When the dibromide of Δ^1 -tetrahydro benzoic acid was treated with dilute alkali solution, Aschan¹ found that the two bromine atoms were replaced by hydroxyl groups.



Similarly, it was found² that the bromide of Δ^1 -dihydronaphthoic acid-2 reacts in an exactly analogous manner.



An exact analogy was found to exist between the above reactions and that of the dibromide of the stable dihydro- α -naphthoic acid, since the latter was converted into the dihydroxy acid upon treatment with a five per cent. potassium hydroxide solution. No evidence was obtained of the formation of α -naphthoic acid which, because of its slight solubility

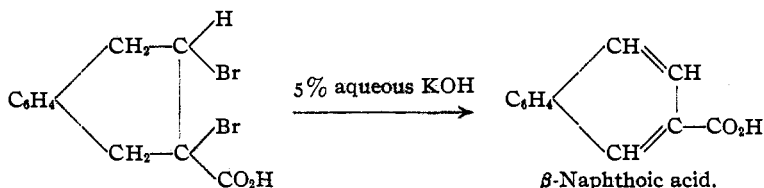


¹ *Ann.*, 271, 281 (1893).

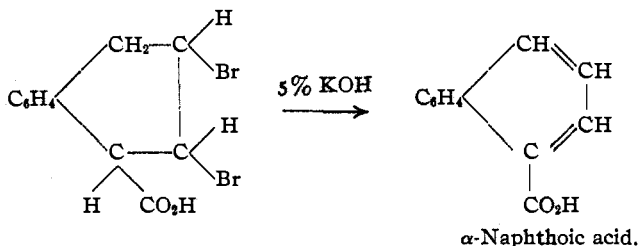
² Derick and Kamm, *Loc. cit.*

in water, would have been detected even in traces. This is, therefore, an argument in favor of the Δ^1 -structure.

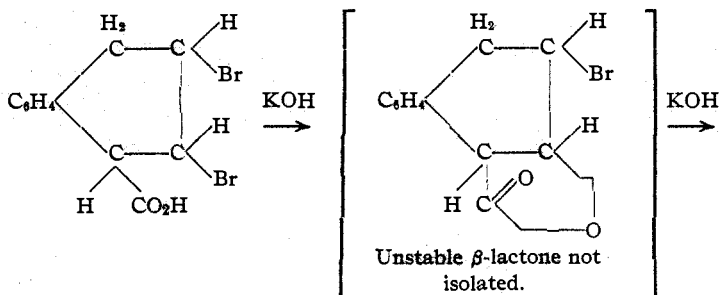
If the labile dihydro acid possesses Structure II above, we are able to predict the reactions of its dibromide by analogy to previously observed reactions. For example, in the case of the dibromide of Δ^2 -dihydro-naphthoic acid-2, the reaction forming β -naphthoic acid is almost quantitative.¹



By analogy one would predict that the dibromide of the dihydro- α -naphthoic acid possessing Structure II would react in the following analogous manner:

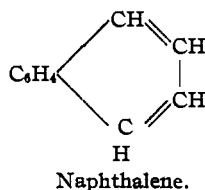


When the dibromide of the labile acid was treated in the cold with dilute aqueous potassium hydroxide solution, an exceptionally good yield of α -naphthoic acid was obtained. This reaction is not quite quantitative, due to the formation of a trace of naphthalene, according to the following reactions:²



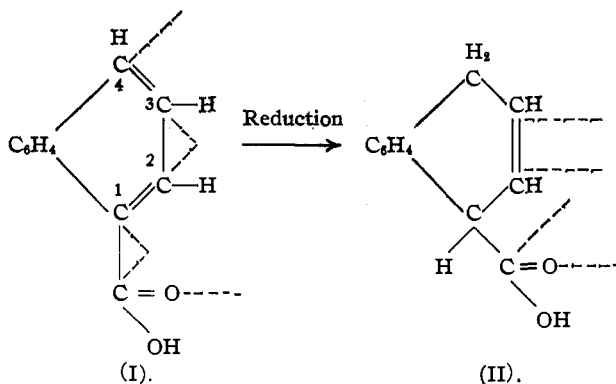
¹ See the preceding article on the structure of the dihydro- β -naphthoic acids.

² This side reaction, as will be shown in the experimental part of this paper, explains the conflicting data (Baeyer and Schoder *vs.* Sowinski) concerning the reaction of this bromide with dilute alkali.



The formation of α -naphthoic acid from the dibromide of the labile acid has been reported by Schoder, who conducted his experiment with the use of warm alcoholic potash, conditions under which the dibromide of the stable acid also yielded α -naphthoic acid.¹ In the present work, however, conditions were similar to those referred to above in the β -naphthoic acid series, conditions under which the bromide of Δ^1 -dihydronaphthoic acid-1 yielded no α -naphthoic acid.

From the above data we conclude that Structure II is the correct one for the labile dihydro acid. Additional evidence in favor of this formula is offered by Thiele's Partial Valence Theory,² which predicts the first dihydro- α -naphthoic acid formed by reduction to be the Δ^2 -isomer. According to Thiele's view, the formulas for α -naphthoic acid and its first reduction product would be represented as follows:



Since the valence on carbon 4 (Formula I) would be only partly conjugated with the phenyl ring, the formula predicts that the first two hydrogen atoms would add in the 1,4 positions, the double union shifting to the 2,3 position. Exact analogies to the above reaction have been reported by Baeyer in the reduction of terephthalic acid, $\Delta^{1,2}$ -dihydroterephthalic acid, and others; in fact some of the strongest evidence in favor of the Thiele views are to be found throughout the classical work of Baeyer on the "Constitution of Benzene."³

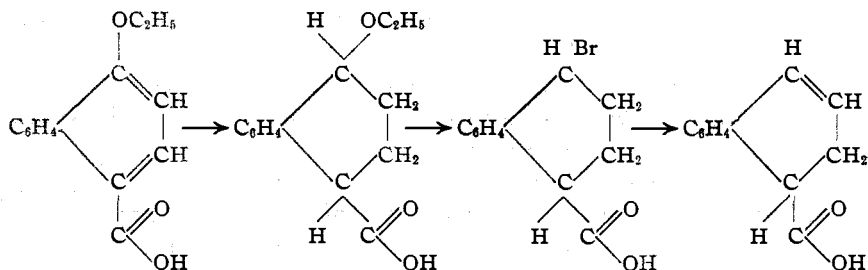
¹ *Ann.*, 266, 183 (1891).

² *Ibid.*, 306, 125 (1899).

³ For brief discussions see Cohen's "Organic Chemistry for Advanced Students," 1910, pp. 448-456; Henrich "Theorien der Organischen Chemie," 1912, pp. 36 and 64.

The product obtained by the rearrangement of the labile isomer (Δ^2 -acid) is Δ^1 -dihydronaphthoic acid-1. We have examined the products of rearrangement in the hope of being able to isolate at least traces of the Δ^3 -acid. Up to the present time, however, this search has not been successful.

An attempt was also made to synthesize the third isomeric dihydro acid (Δ^3 -dihydronaphthoic acid-1). The method chosen for this synthesis is illustrated by the following series of reactions:



When the 1,4-ethoxy naphthoic acid was treated in hot solution with sodium amalgam, the reduction was carried to completion but the ethoxy group was also replaced by a hydrogen atom, tetrahydro- α -naphthoic acid being the product obtained. It is hoped that by reduction in the cold this elimination of the ethoxy group can be prevented.

A similar observation has been reported by Einhorn and Lumsden,¹ who found that *o*-ethoxy benzoic acid when reduced yields hexahydrobenzoic acid in place of the desired ethoxy derivative.

Experimental Part.

The Preparation of α -Naphthoic Acid.—This acid was prepared through the nitrile, the latter having been prepared from α -naphthylamine by the Sandmeyer reaction. The nitrile, together with some naphthol, was separated by means of steam distillation. The distillate was treated with alkali and the nitrile removed by ether extraction.

In the hydrolysis of the nitrile the reaction was carried to the intermediate amide stage by using a solution of alcoholic potash prepared from 99% alcohol. The amide partly crystallized out from the alcohol solution and the remainder was obtained by dilution with water. The melting point was found to be 205° and did not change on further recrystallization.²

Hydrolysis to the acid stage was accomplished by boiling either the nitrile or the amide with a mixture of equal volumes of water, glacial acetic acid and sulfuric acid (sp. gr. 1.84) for about one hour. The acid was ob-

¹ *Ann.*, 286, 264 (1895).

² The melting points given in this paper refer to capillary melting points, corrected for stem exposure. The corrections were usually negligible since calibrated Anschütz thermometers were used.

obtained by pouring the above hydrolysis mixture into cold water. The product was almost colorless and after one crystallization from 30% acetic, was found to melt at 162°. This melting point checked exactly with the one obtained from the purified Kahlbaum product. The yield was less than 20% of the theoretical.

α -Naphthoic acid was also prepared from the bromide of Δ^2 -dihydro-naphthoic acid-1 by the method described in one of the following sections. The melting point of this product after one crystallization from dilute acetic acid was found to be 161°, but a second purification raised the value to 162°.

Preparation of the Labile Dihydro- α -naphthoic Acid.— α -Naphthoic acid was reduced with sodium amalgam, a stream of carbon dioxide being passed into the solution to neutralize the free alkali, as directed by Baeyer and Schoder.¹ For a 10 g. portion of the acid, 200 g. of 3% sodium amalgam were used. At a temperature of about 10°, the reduction to dihydro acid was complete in about thirty minutes, as was indicated by the permanganate test.

The dihydro acid, isolated and purified according to the method given by the above authors, was found to melt sharply at 86°. Because of this variation from the reported value 91°, and in the hope that some Δ^3 -dihydro-naphthoic acid-1 had been formed as one of the products in the reduction, we have taken special precautions in the purification of the product.

The acid obtained from the reduction of two 10 g. portions of α -naphthoic acid and including the product obtained from the mother liquors by ether extraction, was divided by fractional precipitation² into nine approximately equal fractions. A final fraction (0.6 g. in weight) was obtained by means of ether extraction. With the exception of the first fraction, which was slightly colored, all fractions were pure white. Fractions 2 to 9 all melted at 83–4° and after one crystallization from petroleum ether melted at about 85°. The fraction obtained by ether extraction melted two degrees lower.

Since the labile acid is the most soluble acid in this series, and since it also possesses the largest ionization constant, we would in the case of fractional precipitation of a mixture find it in highest purity in the end fractions. Consequently we have re-purified separately Fraction No. 2 and Fraction No. 9, by four successive recrystallizations from petroleum ether.

Fraction No. 2. M. p.	Fraction No. 9. M. p.
1..... 84°	1..... 84°
2..... 85.5°	2..... 85.5°
3..... 86°	3..... 86°
4..... 86°	4..... 86.5°

¹ *Loc. cit.*

² See preceding article for other applications of this method.

After one recrystallization from dilute acetone the melting point 86.5° was not changed. Immediately following the above observations the thermometers used were tested out both at the boiling points of pure benzene and of water and found to be accurate.

The question therefore arises: Is the above acid, which was purified more highly than has been reported previously, identical with the acid (m. p. 91°) prepared by Baeyer and Schoder?

A sensitive criterion of the purity of this acid is rendered available by a measurement of its ionization constant. Fortunately, Bethmann¹ has measured the ionization constants of these acids, using in his work the samples prepared by Schoder. Unfortunately, however, he does not report the melting points of the acids and does not state whether the samples received any additional purification.

Ionization Constants of the Dihydro- α -Naphthoic Acids.—The ionization constants of both the labile and the stable dihydro- α -naphthoic acids were determined in aqueous solution at a temperature of 25° . The details of the conductivity work will be presented in a subsequent paper from this laboratory. In the calculation of the constants the value for the conductivity at infinite dilution ($\lambda_0 = 376$) was calculated from the Ostwald rule.² In the following tables

C = concentration of the acid.

λ = equivalent conductance at 25° at the concentration C, uncorrected for the conductivity of the water used.

K = ionization constant calculated according to the equation

$$K = \frac{C\lambda^2}{\lambda_0(\lambda_0 - \lambda)}$$

TABLE I.—LABILE ACID.

Δ^2 -Dihydronaphthoic acid-1.

M. p. 86.5° . Water used = 0.84×10^{-6} .

C.	λ .	$K_a^{25^{\circ}}$.
0.004 N	59.02	11.69×10^{-5}
0.002 N	80.30	11.60×10^{-5}
0.001 N	107.80	11.52×10^{-5}
0.0005 N	141.85	11.43×10^{-5}

TABLE II.—STABLE ACID.

Δ^1 -Dihydronaphthoic acid-1.

M. p. 121.5° . Water used = 0.65×10^{-6} .

C.	λ .	$K_a^{25^{\circ}}$.
0.001 N	92.19	7.96×10^{-5}
0.0005 N	122.66	7.90×10^{-5}
0.00025 N	159.47	7.81×10^{-5}

The values given by Bethmann, uncorrected for changes in units, are as follows:

$K_a^{25^{\circ}}$ Labile dihydro- α -naphthoic acid = 11.4×10^{-5} ;

$K_a^{25^{\circ}}$ Stable dihydro- α -naphthoic acid = 8.1×10^{-5} .

The agreement with the values found in the present work is satisfactory enough to demonstrate that the acids were practically identical with those studied by Baeyer and Schoder.

¹ *Z. physik. Chem.*, 5, 399 (1890).

² See Lunden's "Affinitätsmessungen an Schwachen Säuren und Basen," p. 9.

Preparation of the Stable Dihydro- α -naphthoic Acid.—In the preparation of this acid by the rearrangement of the labile dihydro acid it is not necessary to boil the latter with dilute alkali for several hours. We find that a thirty-minute treatment with boiling 5% aqueous potassium hydroxide solution is sufficient to secure a complete rearrangement. Since the melting point of this acid was found to differ from the reported value the method of purification is mentioned here in detail.

Baeyer and Schoder¹ state that the crude acid melts at 115° before and 125° after recrystallization. The solvents used were water and ethyl acetate.

In the present work the acid was purified as follows:

(a) The acid obtained by rearrangement was precipitated in fractions, each fraction melting at about 120°, thus showing the product to be free from the labile isomer since the latter would appear in the end fractions.

(b) Each individual fraction was then recrystallized from ethyl acetate, and the melting points found to be 121°.

(c) The above fractions melting at 121° were then converted into the bromide, the latter purified, and the free dihydro acid recovered and crystallized from dilute acetic acid. The melting point was still 121°.

(d) This acid recovered from the dibromide was then subjected to fractional precipitation with the following results:

No. of fraction.....	1	2	3	4	5
Melting point.....	120°	121°	121°	121°	121°

(e) Fractions 2 to 5 were combined and recrystallized successively from dilute acetic acid, dilute acetone and finally from low-boiling ligroin. M. p. 121.5°.

The ionization constant of this acid (m. p. 121.5°) has been measured as a test of its purity, the result being given in Table II (p. 426).

Preparation of the Dibromides.—Five grams of the labile acid were dissolved in 10 cc. of chloroform and a solution of 5 grams of bromine, diluted with about 5 cc. chloroform added gradually. Decolorization of the bromine was rapid and since the solution was kept cold the evolution of hydrobromic acid was very slight. The bromine addition product is in this case soluble in chloroform and therefore it was necessary to precipitate it by the addition of several volumes of petroleum ether. The derivative separated at first in the form of an oil which upon manipulation with a stirring rod was converted into a finely divided white crystalline solid, which was filtered off and washed with ligroin. The yield was 6.5 g. and the m. p. 125°, although the latter value was slightly raised upon subsequent purification.

The bromide of the stable dihydro acid was prepared in a similar manner, except that because of the fact that it is only slightly soluble in chloro-

¹ *Ann.*, 266, 181 (1891).

form it could be isolated exactly as described for the bromides of the three dihydro acids in the β -naphthoic acid series. The theoretical amount of bromine was dissolved in 5 cc. chloroform and the solution added gradually to a cold solution of 5 grams of the stable dihydro acid dissolved in 20 cc. chloroform. The bromine color was destroyed less rapidly than in the preceding experiment. After the solution had been standing in a dark place for about fifteen minutes the bromide had separated almost completely. The cream colored solid was filtered off and washed with a small quantity of chloroform. The final product was almost pure white and melted at 151° with decomposition. The yield was 7.6 grams.

Decomposition with Alkali of the Dibromide of the Labile Acid.—

When the dibromide derived from the labile dihydro- α -naphthoic acid was treated with dilute alkali (5% aqueous potassium hydroxide solution was used) it dissolved completely to give a clear solution. After about one minute, however, the solution became slightly turbid, due to the separation of a small amount of naphthalene. This product was filtered off and its melting point found to be 79° . From the filtrate, an 85% yield of pure α -naphthoic acid was obtained.¹ The melting point of the product after one crystallization from dilute acetic acid was 161° . The above data probably explains the discrepancies between the observations of Sowinski and those of Baeyer and Schoder, since the former states that the dibromide is not completely soluble in alkali, while the latter disagree with this statement and claim that a clear solution in alkali is obtained.

The rate of decomposition of the dibromide with 5% aqueous potassium hydroxide solution at room temperature (about 25°) is extremely rapid as is indicated by the following table. A weighed quantity of the dibromide was dissolved in a known volume of standardized alkali and 1 cc. portions withdrawn at definite time intervals, the excess of alkali being determined by adding a known excess of standard acid and titrating back to color (using phenolphthalein) with standard alkali. Table III shows that most of the dibromide is decomposed during the first five minutes and that the decomposition is complete after fifteen minutes. The total amount of alkali used corresponded very closely with the theoretical amount for the elimination of two molecules of hydrobromic acid. The correction for the amount of alkali neutralized by the carboxyl group has, of course, been applied to the figures given in Table III:

TABLE III.

Total time of reaction.....	0	5	15	30 min.
No. of cc. of 0.01 <i>N</i> KOH required.....	0.0	22.4	35.6	35.6 cc.

¹ Sowinski's statement that a mono bromo derivative of a dihydro acid is obtained under these conditions was not confirmed since it was found, by conducting the experiment with a standard alkali solution, that exactly two molecules of hydrobromic acid were eliminated. It is probable that Sowinski obtained a mixture of dibromo acid, α -naphthoic acid, and the mono bromo derivative.

From the dibromide, the original dihydro acid was recovered by means of glacial acetic acid and zinc dust. By use of the same method Schoder obtained a product melting at 85° .

Decomposition with Alkali of the Dibromide of the Stable Acid.—Three grams of the dibromide were dissolved in 60 cc. of approximately 5% aqueous potassium hydroxide solution. The liquid soon assumed a light purple color which in the course of one-half hour changed to a wine-red. Upon acidification, the color of the solution changed to yellow. The colored product is acidic in nature for it may be extracted with ether only after the alkaline solution has been acidified. It was separated from the dihydroxy derivative described below, by means of its greater solubility in ether.

The acid solution was extracted repeatedly with ether; extractions 1 and 2 were set aside because of the presence of the colored impurity mentioned above, while extractions 3 to 10 were combined, dried with anhydrous sodium sulfate, and the ether evaporated for the isolation of any water soluble acid present. The acid crystallized from the ether solution, after partial evaporation of the latter, in the form of white plates. (Melting point 175° *d.*) The acid is only sparingly soluble in ether but very soluble in water, which agrees with the properties of a hydroxy acid. Its aqueous solution does not reduce potassium permanganate solution instantly, as is the case with the unsaturated acids. Its neutral equivalent was determined with the following results:

0.0381 g. of substance required 8.80 cc. of 0.0207 *N* NaOH. Neutral equivalent found = 209. Theory for $C_{11}H_{12}O_4$ = 208.

Subst., 0.1476; CO_2 , 0.3364; H_2O , 0.0782.

Theory for $C_{11}H_{12}O_4$: C, 63.46%; H, 5.77%. Found: 62.15%, 5.88%.

The rate of decomposition of the dibromide of the stable dihydro acid was also followed by titration as was described above for the labile isomer. The quantity of alkali used again corresponded closely with the theoretical amount required for the elimination of two molecules of hydrobromic acid, and it was again found that most of the decomposition took place during the first five minutes.

Reduction of 1,4-Ethoxynaphthoic Acid.¹—Five grams of this acid were reduced in hot alkaline solution using 3% sodium amalgam, a stream of carbon dioxide being passed into the solution. The first portion of amalgam (200 g.) reacted quickly, indicating that reduction was taking place. When a small portion of the solution was treated with several drops of dilute potassium permanganate solution instantaneous decolorization took place, indicating partial reduction of the ethoxy acid, since the original product was stable toward permanganate. The total amount

¹ The preparation and proof of structure of this acid will be presented in a later paper from this laboratory.

of 3% amalgam required to complete the reduction was 1200 g. An acid was isolated which was quite stable toward permanganate, as would be expected of a tetrahydro acid. The melting point without special purification was found to be 81°, slightly lower than that of tetrahydro- α -naphthoic acid. Results of the titration for the neutral equivalent were as follows:

0.1390 and 0.0916 g. acid = 9.35 and 6.20 cc. 0.085 *N* alkali. Neutral equivalent found (1) 175 and (2) 174.

The above neutral equivalents agree with the theoretical value (176) for tetrahydro- α -naphthoic acid, indicating that the ethoxy group had been eliminated in the process of reduction.

URBANA, ILL.

ZINGIBEROL—A NEW SESQUITERPENE ALCOHOL OCCURRING IN THE ESSENTIAL OIL OF GINGER.

By BENJAMIN T. BROOKS.

Received November 18, 1915.

It is a well-known fact that the distilled oil of ginger, *Zingiber officinal* Roscoe, possesses the characteristic aroma of ginger. The odor is not intense, but is very persistent, recalling sandal wood oil in this respect. Gildemeister and Hoffman¹ state "Only a few of the important constituents of ginger oil are known; of the substances which give it the characteristic odor nothing is known."

In the course of an examination of ginger oil which had been freed of terpenes and sesquiterpenes, the author isolated and identified citral, methyl heptenone, nonylaldehyde, linalool, *d*-borneol, acetic and caprylic acids, combined as esters, a trace of a phenol which was probably chavicol though not positively identified, cineol and also a sesquiterpene alcohol, C₁₅H₂₆O, which evidently bears the same relation to the sesquiterpene, zingiberene, as santalol does to santalene, and since it imparts to ginger oil the peculiar persistent, though mild, ginger odor, I have called it *zingiberol*. Although all of the constituents of ginger oil contribute something to the composite odor of the fresh root, the alcohol zingiberol is the only one of them possessing the peculiarly characteristic fragrance of ginger.

It should, perhaps, be pointed out that ginger oil does not produce the sharp pepper-like sensation when introduced into the mouth that is produced by the fresh root, and that the so-called "gingerol" claimed by Garnett and Greier² to have been isolated by them has no existence in fact. The latter authors did not characterize their gingerol further than that it probably was a phenol and possessed a sharp stinging taste. Fol-

¹ Gildemeister and Hoffman, "Die Aetherische Oele," Leipsig, 2, 292 (1913).

² *Chem. Zentr.*, 1907, II, 924; 1909, II, 1593.