(4) From the above facts the conclusion is drawn that the heavy high boiling fractions of petroleum contain homologs of benzene, or hydrocarbons containing the benzene nucleus.

(5) The high boiling residues from the decomposition of phenyl paraffin are highly fluorescent, which supports the theory advanced in an earlier paper that the fluorescence of petroleum oils is due to the presence of complex hydrocarbons related to benzene.

PITTSBURGH, PA.

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

THE STRUCTURE OF THE DIHYDRO-β-NAPHTHOIC ACIDS.

BY C. G. DERICK AND OLIVER KAMM.[1]

Received December 18, 1915.

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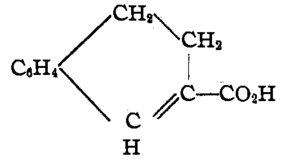
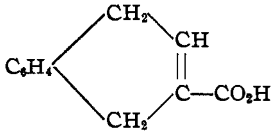
I. Introduction.

Three dihydro-β-naphthoic acids which have an unsaturated linkage in the ring carrying the carboxyl group are theoretically possible, their structures being represented as follows:



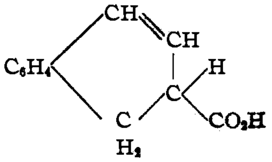
(I).

Δ¹-Dihydronaphthoic acid-2.[2]



(II).

Δ²-Dihydronaphthoic acid-2.



(III).

Δ³-Dihydronaphthoic acid-2.

Of the above acids, two have previously been prepared and the structure of one of them has been definitely demonstrated. In the present work, which was carried out in connection with a study of the correlation of ionization and structure, the third isomeric acid has been prepared and demonstrations of the structures of the three isomers have been developed.

By the reduction of β-naphthoic acid with sodium amalgam, Sowinski[3] obtained two of the isomeric acids represented above. This work is also

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[1] Presented at the Cincinnati meeting (1914) of the American Chemical Society. From a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Illinois (Kamm, 1915).

[2] The nomenclature used is that given in Meyer and Jacobson's "Lehrbuch der Organischen Chemie," 1903, Vol. 2, Pt. 2, p. 446.

[3] *Ber.*, 24, 2354–2363 (1891).

reported by Baeyer and Besemfelder,[1] who obtained the acids in a higher state of purity. By reduction with sodium amalgam in the cold a mixture consisting chiefly of the labile acid (so-called because of the ease of its rearrangment into the higher-melting stable isomer) was obtained, while reduction in hot solution yielded chiefly the stable acid. The mixture obtained in either case was separated, due to the different solubilities of the two isomers in water.

Structure III (above) has been assigned by Baeyer and Besemfelder to the labile acid not only because of the ease of its rearrangement into the stable isomer but also because they found that with bromine it formed an unstable dibromide which decomposed spontaneously into a monobromolactone. This indicates that a bromine atom was initially present in the gamma position with respect to the carboxyl group which is possible only in the case of the dibromide derived from Structure III. The same acid, because of the asymmetry of its molecule, should be capable of existing in two optically active components, and that such is the case has been shown by Pickard and Yates[2] who have prepared *d*-Δ^3-dihydronaphthoic acid-2. This is a further confirmation of the structure of the labile acid since the two other isomers represent symmetrical structures.

The stable dihydro acid obtained by rearrangement of the labile acid must therefore possess one of the two remaining structures (I or II above). Baeyer,[3] as well as Meyer and Jacobson,[4] from the data at hand have not attempted to differentiate between the two possible structures. Formula II has been suggested by Besemfelder[5] as the most probable structure because of the ease with which β-naphthoic acid is formed when the corresponding dibromide is digested with alcoholic potash. Under similar conditions, however, the monobromolactone derived from the labile dihydro acid also yielded β-naphthoic acid. It is therefore evident that the behavior of its dibromide with alkali is an unsafe criterion for the assignment of the structure of the stable acid unless the dibromides of both the Δ^1 and Δ^2 dihydro acids have been treated in this manner. This is now possible, for in the present work the third isomeric dihydro acid has been prepared. The dibromide of Baeyer's labile dihydro acid has also been prepared and found to be fairly stable, not undergoing spontaneous decomposition as reported. It is therefore possible to study side by side the reactions of the dibromides of the three isomers. The structure of the new dihydro acid has, however, been demonstrated independently by means of its oxidation products.

[1] *Ann.*, **266**, 187–202 (1891).

[2] *J. Chem. Soc.*, **95**, 1011–1015 (1909); *Chem. Zentr.*, [2] **1909**, p. 445.

[3] *Ann.*, **266**, 174 (1891).

[4] *Loc. cit.*

[5] *Ann.*, 266, 198 (1891).

II. The Third Isomeric Dihydro-β-naphthoic Acid.

When the stable dihydro acid (m. p. 161°) is treated with water and an excess of barium hydroxide in a sealed tube at a temperature of 160–180°, the third isomeric acid is formed. Its melting point after purification is found to be 118.5° (cor.). The same product may be obtained from the labile isomer, although in some cases it is found contaminated with the 161° stable acid, indicating that the rearrangement has taken place with the formation of the latter as an intermediate product.

We might suggest Structure I as that of the new acid on the basis of this rearrangement, since we would expect the acid having the unsaturated union in intimate relation to both the carboxyl group and to the phenyl ring to be the most stable toward rearrangement. This has already been stated by Baeyer, who has suggested the possibility of preparing the third isomer by a method analogous to the one used.

The method of preparation of the 118° acid (Δ^1) suggests that the same object might be accomplished by means of a strenuous treatment with concentrated potassium hydroxide solution at ordinary pressures and such was actually found to be the case. When either the labile or the Δ^2 stable acid is boiled with a solution of potassium hydroxide (1 : 2) for about eight hours, a 75% yield of the third isomer is obtained. It is separated from any unchanged acid and from the small amount of β-naphthoic acid formed by oxidation by means of fractional precipitation. It is obtained in a higher state of purity from its dibromide.

The 118° acid is analogous to the other stable acid ($\cdot\Delta^2$) and to Δ^1 unsaturated acids in general in its behavior. It is attacked instantaneously by potassium permanganate and with an excess is destroyed. In the cold it adds bromine slowly. It was characterized by means of its dibromide and its amide as well as by analysis and a determination of its neutral equivalent. Additional tests of its homogeneity as a pure chemical individual are discussed in the experimental part of this paper.

III. Proof of the Atomic Linkage Structures of the Three Dihydro-β-naphthoic Acids from the Chemical Behavior of Their Respective Dibromides.

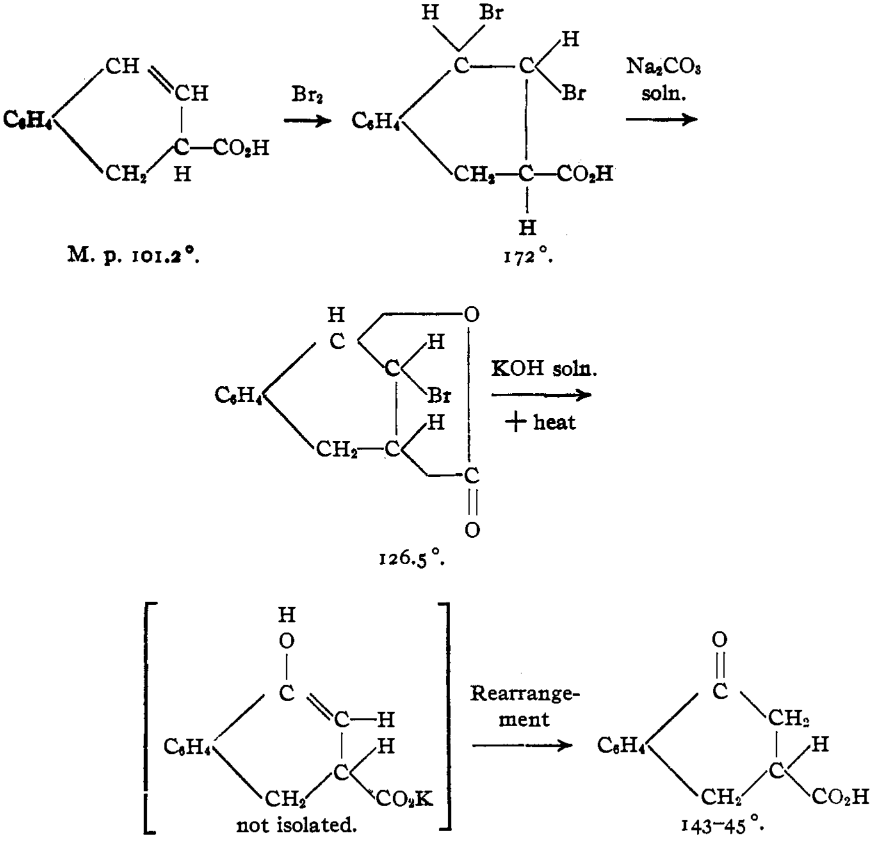
As already mentioned, Baeyer and Besemfelder were able to prepare the dibromide of only one dihydro acid, the dibromide of the labile acid undergoing spontaneous decomposition with the evolution of hydrobromic acid. By using a somewhat different procedure the dibromides of all three isomers may be prepared without meeting any of the difficulties encountered by previous investigators. The dihydronaphthoic acids are all very soluble in chloroform while their dibromo derivatives are not. The method used was to dissolve the acid in chloroform and to add the calculated amount of bromine also dissolved in chloroform, keeping the mixture cold. Under these conditions the dibromo derivatives separate out in the form of white crystals.

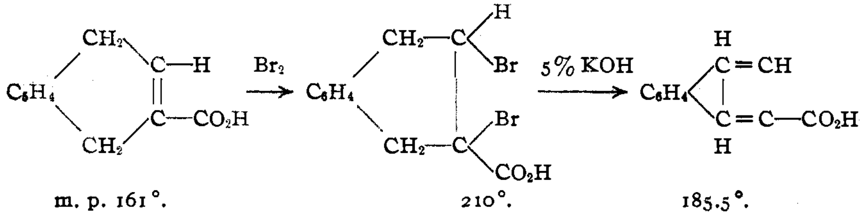
The melting points of the acids and of the corresponding dibromides are as follows:

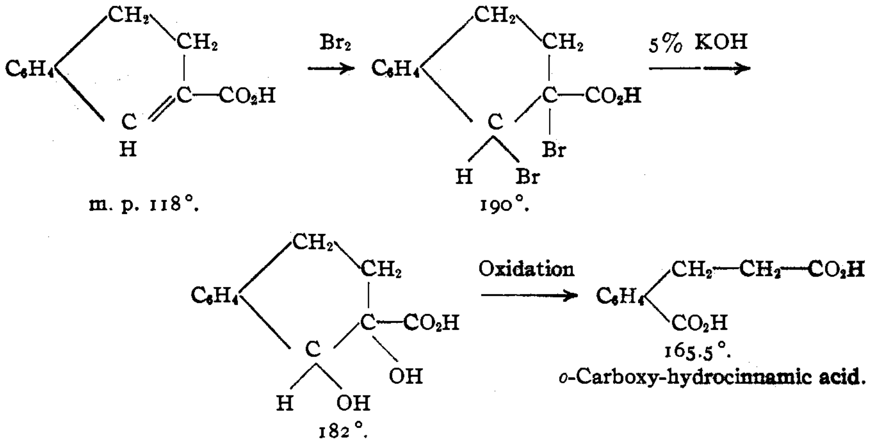
TABLE I.

	M. p.	M. p. of dibromide.
Labile Δ^3 acid	101.2°	172° with decomp.
Stable Δ^1 acid	118°	190° with decomp.
Stable Δ^2 acid	161°	210° with decomp.

Behavior of the Dibromides with Alkalis.—The three dibromides react in so characteristic a manner with dilute alkalis that this behavior may be used as a demonstration of the structure of the dibromides themselves and therefore of the corresponding unsaturated acids. In these decompositions it is unnecessary to use boiling alcoholic potash, in fact the best results are usually obtained with a cold 10% aqueous solution of sodium carbonate. The reactions observed are as follows:







The dibromide of the labile dihydro acid (Δ^3) when treated with sodium carbonate solution at first dissolves completely. Soon, however, a turbidity is observed and after a few minutes the monobromolactone separates. The dibromide of the stable (Δ^2) isomer dissolves readily in dilute alkali to a clear solution, although it is decomposed rapidly and almost quantitatively into β-naphthoic acid. This decomposition takes place even at a temperature of 0° (although more slowly), no color changes being apparent. The dibromide of the 118° acid (Δ^1), on the other hand, undergoes the characteristic reactions observed when an α,β-dibromo acid is treated with alkali. If the solution is warmed, a deep blue color develops slowly, but finally disappears, a yellow solution remaining. At the same time a trace of an indifferent substance separates, due probably to the decomposition of an unstable β-lactone.[1] No trace of β-naphthoic acid is formed, the main product being the dihydroxy acid represented above. Its formation is analogous to the decomposition of α,β-dibromohexahydrobenzoic acid observed by Aschan.[2] Independent evidence of the structure of this dihydroxy derivative and therefore of the Δ^1-dihydro acid itself is offered by the oxidation of the dihydroxy acid to *o*-carboxy-hydrocinnamic acid of known structure.

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[1] The reactions of dibromocinnamic acid may be taken as an example. Nef *Ann.*, 308, 267 (1899); Fittig-Kast, *Ann.*, 206, 33 (1881).

[2] *Ann.*, 271, 281 (1893).

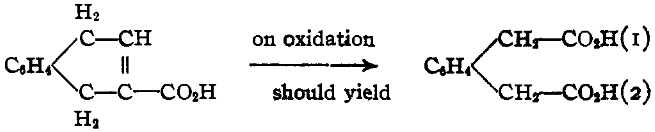
The reactions of the dibromides outlined above demonstrate that the three dihydro acids described are distinct chemical individuals. The results confirm the conclusions of Baeyer and Besemfelder in regard to the structure of the labile dihydronaphthoic acid (Structure III). Moreover, since the structure of this acid is known, and since we have prepared the third isomeric acid and its dibromide and made a study of the decomposition products of the latter, we may now accept the reactions of the dibromide of the stable (161°) acid as conclusive evidence that Structure II is correct, while Structure I should be given to the new isomer (118° acid). Independent evidence in regard to the structure of the latter is, however, presented below.

More recently it has been found[1] that the dibromides of the dihydro-α-naphthoic acids react in an exactly analogous manner to that observed in the β-naphthoic acid series. This evidence can be used on the one hand to demonstrate the structures of the corresponding dihydro-α-naphthoic acids, and on the other is additional evidence in favor of the use of the reactions of these dibromides for the demonstration of structure.

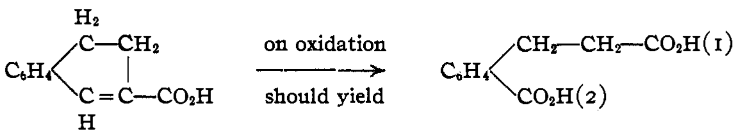
IV. Proof of the Atomic Linking Structure of the Third Dihydro-β-naphthoic Acid by Oxidation.

Although the reactions of the dibromides present satisfactory evidence in favor of the structures of the corresponding dihydro acids, it was considered advisable to demonstrate the structure of the new isomer in an entirely independent manner. The method chosen was that of oxidation.

Meyer and Jacobson[2] state that the stable acid of Baeyer has either Structure I or Structure II below.



(I).



(II).

For this demonstration of structure by means of oxidation reactions, the new isomeric acid Δ¹-dihydronaphthoic acid-2 was used, the oxidizing agent being alkaline potassium permanganate. Using this method,

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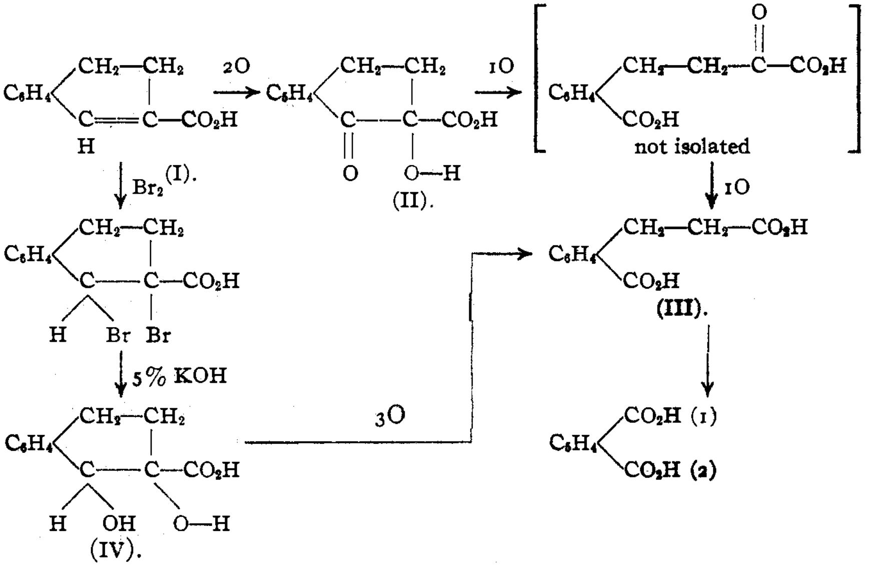
[1] Kamm and McClugage. See the following article in THIS JOURNAL.

[2] *Loc. cit.*

Baeyer and Shroder[1] had succeeded in demonstrating the structure of Δ^1-dihydronaphthoic acid-1, since upon oxidation *o*-carboxyhydrocinnamic acid was obtained. The β-isomer under examination should yield the same final product, and such was found to be the case. It was necessary, however, to apply very radical changes to the Baeyer method, since the first attempts always yielded products contaminated with large amounts of phthalic acid. The modified method adopted was to carry on the oxidation in steps, using the theoretical amounts of permanganate.

The reactions observed were as follows:



The keto-hydroxy acid (II) was obtained in 50–60% yield, and from it pure *o*-carboxyhydrocinnamic acid (III) was obtained in 40% yield. The latter product was also obtained from the dihydroxy acid (IV).

The structures of the three theoretically possible dihydro-β-naphthoic acids have thus been definitely established by analytical methods, and a study of the correlation of ionization and structure in this series may now be made.

V. A Correlation of Structure and Odor.

An interesting correlation between chemical structure and odor was noticed during the course of this study. When the amides of the various naphthoic acids, discussed in this paper, were prepared, it was noted that of the three dihydro-β-naphthoic acids, only the two stable isomers gave amides which possessed a very marked cinnamon-like odor. This was especially noticed in the case of the new isomer, Δ^1-dihydronaphthoic acid-2. Accordingly, the amide of cinnamic acid was prepared and was

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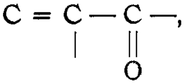
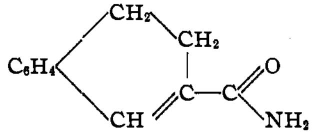
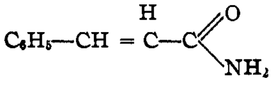
[1] *Ann.*, 266, 176 (1891).

found to possess an identical odor. This cinnamon-like odor is known to be characteristic of the side-chain linkage  $>C = \underset{|}{C} - \underset{\overset{\|}{O}}{C} -$, as was learned from cinnamic aldehyde. The analogy in structure is apparent.



Amide of Δ^1-dihydronaphthoic acid-2.



Amide of cinnamic acid.

The melting points of the amides prepared in this work are given in Table II. The amide of cinnamic acid is included since the literature gave the widely varying values 141.5° and 147°.

TABLE II.

Acid.	M. p.	M. p. of amide.	Acid.	M. p.	M. p. of amide.
Beta-naphthoic	185°	195°	Stable dihydro-naphthoic	118°	155°
Tetrahydro-naphthoic	96°	137°	Stable dihydro-naphthoic	161°	168°
Labile dihydro-naphthoic	101.2°	140–50°	Cinnamic	133°	148°

VI. Experimental Part.

The Preparation of β-Naphthoic Acid.—This acid was prepared using the Sandmeyer reaction,[1] starting with a pure grade of β-naphthyl amine. The nitrile was distilled with steam and hydrolyzed as outlined below. This method yielded an exceptionally pure grade of β-naphthoic acid, which after one crystallization from dilute acetic acid melted at 185°. The yield was, however, less than 20% of the theoretical. For the preparation of large amounts of the acid, the following method was found to be more satisfactory: β-Naphthalene sulfonic acid was prepared in the usual manner by treating naphthalene with concentrated sulfuric acid at 180°. The β-sulfonic acid was separated as the calcium salt,[2] recrystallized from water and then converted into the sodium salt. The yield of the latter was 625 grams from one kilo of naphthalene. A more convenient, more rapid, and more efficient method for preparing the pure β-sulfonic acid has recently been published by Witt.[3] Naphthalene is sulfonated by heating it for a few minutes at 160°. The clear homogeneous liquid is poured into water, small amounts of sulfone and unchanged naphthalene separated, and the acid solution evaporated to a smaller bulk. The β-isomer crystallizes out as the tri-hydrate and is obtained pure after a recrystallization from 10% hydrochloric acid. The separation of the two isomeric sulfonic acids through their calcium salts is therefore unnecessary.

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[1] Gattermann, "Practical Methods of Organic Chemistry," eleventh edition (translated, 1914), p. 248.

[2] *Ber.*, 3, 196 and 710; Gattermann, *Loc. cit.*, p. 291.

[3] *Ber.*, 48, 751–753 (1915).

The nitrile was prepared in the usual manner by subjecting to dry distillation the sodium salt intimately mixed with an equal weight of potassium ferrocyanide. The yield of crude nitrile was 120 g. from 625 g. of sodium sulfonate, but can be improved by conducting the dry distillation under diminished pressure, or by distilling the mixture in small quantities. The yield of naphthoic acid from hydrolysis of 120 g. of nitrile was 100 g. The method was materially improved in the following manner: In the dry distillation with potassium ferrocyanide, the yield is exceptionally poor if the calcium sulfonate is fused directly. If, however, potassium cyanide is used, the calcium salt itself may be substituted, without converting it into the more fusible sodium salt. 40 g. of calcium sulfonate mixed with an equal weight of potassium cyanide and distilled in four portions yielded 18 g. of crude nitrile from which an almost equal weight of crude naphthoic acid was obtained.

The nitrile was hydrolyzed as directed by Baeyer and Besemfelder,[1] using a mixture of equal volumes of concentrated sulfuric acid, glacial acetic acid and water. The material, which Baeyer and Besemfelder report as insoluble in sodium carbonates solution should, however, not be discarded as directed but should be boiled with 20% KOH solution, thus increasing the yield of the acid. This insoluble material consists largely of the amide. A sample of the nitrile which had been purified by distillation was found to saponify more smoothly. It was in this case easily possible to stop the hydrolysis at the amide stage. The crude β-naphthoic acid was precipitated as the barium salt from a dilute hot solution of its sodium salt by means of barium chloride solution. The free acid was recovered by recrystallization from 30 to 50% acetic acid, treated with bone-black, and purified by fractional crystallization. The pure acid melted[2] at 185.5°. Its amide (m. p. 195°) was prepared using one mol of phosphorus pentachloride and decomposing the acyl halide with ammonia water. It was also obtained (m. p. 194°) in the hydrolysis of the nitrile as mentioned above.

The Reduction of β-Naphthoic Acid.—The reduction with 3% sodium amalgam in the cold, a stream of CO_2 being passed into the solution to neutralize the free alkali, yielded a mixture consisting of 75% labile dihydro and about 25% stable Δ^2 dihydro acids. Reduction in hot solution yielded the same two acids except in different proportions, 40% and 60%, respectively. The labile isomer obtained by reduction in hot solution, however, contains appreciable amounts of the tetrahydro acid, from which it is separated only with difficulty. The methods of reduc-

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[1] *Ann.*, 266, 187 (1891).

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

tion and the use of fractional precipitation as described by Baeyer and Besemfelder have been found satisfactory. The advantages of the method of fractional precipitation over that of fractional crystallization for the separation of mixtures of these isomeric acids should be further emphasized. The most soluble isomer is usually also the one having the largest ionization constant, and consequently the separation is unusually effective. The use of too concentrated solutions should, however, be avoided since this will result in the occlusion of the salt by the precipitated acid. The melting points of the acids have either been found to be as reported by Baeyer or slightly higher. Only in the case of the labile isomer was a lower value observed than that reported previously. Since the acid was to be used for conductivity measurements, it became necessary to investigate this point carefully. The melting point found was 101.2°, whereas the reported value is 104°.

Preparation of the Labile Dihydro-β-naphthoic Acid and the Separation of Isomers by Means of Fractional Precipitation.—A typical reduction will be described here. Ten grams of pure β-naphthoic acid were dissolved in a small amount of dilute potassium hydroxide solution and the solution diluted to 100 cc. The latter was then cooled to 5°, a steady stream of carbon dioxide passed into it and 150 g. of crushed 3% sodium amalgam added at one time. Small portions (0.5 cc.) of the solution were withdrawn at ten-minute intervals and tested with potassium permanganate.[1] The reduction was complete in forty minutes. The sodium carbonate solution was separated from the mercury, a few pieces of ice added, and the free dihydro acids precipitated with hydrochloric acid. The precipitate, which consists of white crystals, was dissolved in very dilute potassium hydroxide solution (100–150 cc.) and the dihydro acids precipitated in fractions, using approximately normal hydrochloric acid, adding the latter slowly from a pipet. The ten fractions obtained were almost equal in weight (approximately 1 g. each); the first three consisted of cream-colored flakes, while the others were more granular (typical of the labile isomer) and were pure white.

No. of fraction.	M. p. before recrystallization.		No. of fraction.	M. p. before recrystallization.	
1	155–57°	Stable dihydro acid	6	101°	
2	154–56°		7	100°	Recrystallized from 30% acetic acid, m. p. 101.0° Labile isomer
3	152–54°		8	100.5°	
4	103.5°	Mixture of labile and stable acids	9	100.5°	
5	101.5°		10	100°	

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[1] The dihydro acids are oxidized under these conditions while β-naphthoic acid is not. The permanganate is added until a permanent color is obtained, a small amount of sodium sulfite then added and the solution acidified. If the reduction is incomplete the sparingly soluble naphthoic acid will precipitate.

Fractions 7 and 8, after recrystallization, were again subjected to fractional precipitation and shown to be homogeneous.

REFRACTIONATION OF FRACTIONS 7 AND 8.

No.	M. p.	No.	M. p.
1a	100.2°	*4a*	100.8°
2a	100.8°	*5a*	100.6°
3a	100.8°	*6a*	100.6°

Fraction 3*a* was recrystallized from dilute acetic acid. The product consisted of pure white needles melting at 101.1°.

REFRACTIONATION OF FRACTION 4 (M. P. 103.5°).

No.	M. p.		No.	M. p.	
1*b*	155–56°	Stable isomer	5*b*	101°	Labile isomer
2*b*	154–56°		6*b*	101°	
3*b*	140–50°	Mixture	7*b*	101°	
4*b*	102–3°		8*b*	100.8°	

Refractionation of Fractions 7 and 8 shows that they are not further purified by a second fractional precipitation. Fraction 4 falls intermediate between the fractions of the stable isomer (m. p. 161°) and the lower melting labile isomer. The results of the refractionation of this one gram fraction illustrates the effectiveness of the method. Fraction 9 was completely destroyed with an excess of potassium permanganate in alkaline solution and an examination of this solution failed to show the presence of tetrahydronaphthoic acid.

Several grams of the dihydro acid (101°) were then converted into the dibromide by the method outlined below. From the pure dibromide, the original dihydro acid was recovered by the action of zinc dust in acetic acid solution. The recovered acid was crystallized from dilute acetic acid and melted at 101°. It was again subjected to fractional precipitation and again shown to be homogeneous. The maximum melting point was 101.2° and was not changed when the acid was recrystallized from low-boiling ligroin.

Rearrangement of the Dihydro-β-naphthoic Acids.

Rearrangement with Barium Hydroxide at 160°.—Two grams of the labile acid (Δ^3-dihydronaphthoic acid-2) were heated with an excess of barium hydroxide (10 g. + 40 cc. water) in a sealed tube at a temperature of 160° for about six hours. When the tube was opened, a distinct naphthalene-like odor was noticed, although decomposition with the loss of carbon dioxide was only slight. The barium salt of an acid was isolated. It was recrystallized from water and the free acid recovered. The latter melted at 118° and appeared to be a pure compound since its melting point was unchanged on subsequent purification from various solvents.

0.1470 g. required 11.00 cc. 0.0764 *N* KOH. Neut. equiv. = 175. Theory for a dihydro acid = 174.

The results are different from those obtained by Baeyer,[1] who prepared a stable isomer melting at 160° by boiling the labile acid in potassium hydroxide solution under atmospheric pressure.

The first experiment was then repeated, the acid being purified not by recrystallization of its barium salt but by means of fractional precipitation. It was found to be homogeneous since each fraction melted within the range of 115–117° and all fractions melted at 118° after additional purification.

In a later experiment, however, Baeyer's stable acid (m. p. 161°) was obtained in addition to the 118° product. It was found to be less soluble in water than the latter, and hence the two acids could be partly separated by means of fractional precipitation. The 161° acid is, however, obtained best by the direct reduction of β-naphthoic acid in hot solution, when it is obtained together with the labile isomer from which it may be separated more readily.

The stable acid (161°, now known to be Δ^2-dihydronaphthoic acid-2) was also treated with barium hydroxide under high pressure as had been the case with the labile isomer. Here also the new acid (m. p. 118°) was obtained in addition to some unchanged product. The following diagram will represent the changes involved:

$$101.2^\circ\text{ isomer} \xrightarrow[\text{or Ba(OH)}_2+\text{heat}]{\text{KOH}+\text{heat}} 161^\circ\text{ isomer} \xrightarrow[\substack{\text{or Con. KOH with}\\ \text{prolonged heating}}]{\text{Ba(OH)}_2\text{ at }160\text{–}80^\circ} 118^\circ\text{ isomer}$$

Both experiments were repeated using potassium hydroxide solution in place of barium hydroxide. The results were identical with those reported above. Variations in temperature and in the time of heating have also been used, but the results are similar to those given above and details will not be repeated here.

Rearrangement under Atmospheric Pressure.—The rearrangement of the labile and stable acids using potassium hydroxide solution at atmospheric pressure was also investigated. Three grams of the labile isomer (m. p. 101°) were boiled under a reflux condenser with 10% potassium hydroxide solution for abour one hour. The mixture of acids obtained was separated by fractional precipitation and found to consist of almost equal quantities of the stable isomer (161°) and unchanged labile acid. The 118° isomer was not observed. This confirms the results reported by Baeyer and Besemfelder. It should be noted, however, that the amount of β-naphthoic acid formed during this rearrangement, due to the oxidation of the stable isomer by the oxygen of the air is almost negligible. Baeyer's statement[2] that the rearrangement is not a

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[1] *Ann.*, **266**, 192 (1891).

[2] *Loc. cit.*, p. 192.

smooth one may be explained better by the following experiments: Thirteen grams of the labile isomer (m. p. 101°) which had been prepared and purified as described above were heated for four hours in a more concentrated potassium hydroxide solution than had been used in the previous experiment. (50 g. KOH dissolved in 100 cc. H_2O). Fractional precipitation yielded the fractions indicated below. It will be noted that the first four fractions consist chiefly of the stable isomer (161°) but appear to be less pure than the corresponding acid prepared by heating the labile isomer with more dilute potassium hydroxide solution. These low melting points are not due to admixture with β-naphthoic acid as Baeyer supposed, but are accounted for by the presence of the 118° isomer which is only slightly more soluble than the 161° isomer. Fractions 6 and 7 give evidences of the presence of the new isomer (118°) while the remaining fractions consist of unchanged labile acid. Fractions 1 to 7 were combined and again boiled with 1 : 2 KOH for four hours. In the same manner, Fractions 8 to 13 were combined and boiled with 1 : 2 KOH for eight hours. The second column of melting points represents the fractions obtained after the second treatment with concentrated potassium hydroxide, while the last column gives the melting points of the fractions after recrystallization from acetic acid.

No.	M. p.	No.	M. p.	Recrystallized from 30% acetic acid.
1	145–50°	1*a*	114–15°	..
2	145–50°	2*a*	114–15°	115.5°
3	145–47°	3*a*	114°	115.5°
4	140–45°	4*a*	114°	114.5°
5	124–27°	5*a*	114°	114.5°
6	117°	6*a*	101°	..
7	116°	..	....	..
8	100°	1*b*	113–14°	..
9	99°	2*b*	113–14°	115.5°
10	99°	3*b*	113–14°	115°
11	100°	4*b*	113–14°	115°
12	100°	5*b*	112°	115°
13	99°	6*b*	107–10°	112°
	...	7*b*	95–100°	110°

Fractions 2*b* to 5*b* were converted into the barium salt, the latter was recrystallized and the free acids recovered (m. p. 116°).

These results show that both the labile and the stable isomers may be rearranged almost completely into the new isomeric acid (m. p. 118°), the rearrangement of the labile isomer proceeding through the intermediate so-called stable isomer (161°). It is apparent also that the new isomer is contaminated with a less soluble impurity from which it is not completely separated by means of fractional precipitation or by recrystallization.

Comparative conductivity measurements on the 116° sample obtained above and the purer 118° acid obtained by the barium hydroxide treatment, showed no difference in conductivity between the two samples. The impurity present in the 116° sample must therefore be the stable isomer (161°) which is less soluble, or extremely small amounts of the more highly ionized β-naphthoic acid. This problem was investigated quantitatively and it was found that the impurity corresponded to only 2% of the total weight of the 116° sample.

Purification of the 118° Isomer through the Dibromide.—Five grams of the 115–16° sample were converted into the dibromide, using the method outlined below. From the dibromide, the dihydro acid was recovered and found to melt at 118°. This recovered product was subjected to fractional precipitation and shown to be homogeneous. The maximum melting point of the 118° acid after recrystallization from ligroin was 118.5°. The chloroform mother liquors from the precipitation of the dibromide were allowed to evaporate spontaneously to one-half volume and a second smaller group of dibromide recovered. The chloroform filtrate was extracted with dilute alkali to remove the last traces of the dibromides as well as any unchanged dihydro acids together with naphthoic acid. From this alkaline extract, 0.10 g. of β-naphthoic acid was recovered. This might have been present in the 116° sample as such or it may have been formed from the action of alkali upon small amounts of the dibromide of the stable (161°) isomer. This separation of traces of 161° acid from the 118° isomer was repeated with known mixtures, and found satisfactory. These reactions are described in detail below, in addition to other tests showing the 118° acid to be a pure chemical individual and not a eutectic mixture.

Δ^1-Dihydronaphthoic Acid-2 (118° Isomer).—The structure of this isomer is demonstrated below. A brief description of the acid together with some additional tests which have shown it to be a distinct chemical individual will be given here.

Analysis of 118° acid:

Subst. 0.1798; CO_2, 0.4982; H_2O, 0.0923. Calc. for $C_{11}H_{10}O_2$: C, 75.8; H, 5.79. Found: C, 75.6; H, 5.75.

The analysis, the determination of the neutral equivalent given above, and the fact that the acid forms a dibromide, together with the analysis of the latter (below) proves that we are dealing with a dihydronaphthoic acid. To this we may add that the original acid, unchanged in melting point, is recovered from its dibromide as well as from its amide after purification of these derivatives. This would not be the case if we were dealing with a mixture. The 118° isomer is oxidized instantaneously by potassium permanganate in alkaline solution as is the case with other unsaturated acids. Five grams of the pure acid were dissolved in very dilute potassium hydroxide solution adding just enough alkali to dissolve the acid completely. The acid was then oxidized in the cold by the addition of 10 g. of potassium permanganate dissolved in 300 cc. water, the oxidizing agent being added slowly in the cold. After filtering off the MnO_2, the solution was evaporated on the water bath to a smaller bulk (50–100 cc.). Upon acidification of the clear, light yellow solution with mineral acid, no precipitate was obtained, showing the absence of both naphthoic acid and tetrahydronaphthoic acid. From the acidified solution some phthalic acid was obtained by ether extraction.

When a solution of several grams of the new isomer in chloroform was treated with bromine in chloroform, it was found that addition did not take place rapidly since even the first drop of bromine solution decolorized slowly. This is characteristic of stable acids in general, and is a definite proof that the labile acid (Δ^3-dihydronaphthoic acid-2) from which the new isomer had been prepared is absent, since the latter decolorizes bromine instantaneously. The reactions of the dibromides of the three isomers, however, give even more conclusive proof than that above. The evidence from this source is presented in one of the following sections.

Finally, known mixtures of the 118° isomer with the 101° isomer, the 161° isomer and with β-naphthoic acid, respectively, were prepared and it was found possible to secure fairly satisfactory separations by means of fractional precipitation.

The 118° isomer crystallizes from dilute acetic acid or from dilute alcohol in clusters of radiating needles. Its degree of solubility in water, dilute acetic acid, ligroin, etc., is intermediate between that of the two other isomers. Preliminary measurements of the ionization constant of the 118° isomer have indicated that the value for this constant is very close to 3.0×10^{-5} at 25° in aqueous solution.

Solubility in Water of the 161° and 118° Isomers.—The stable acid (161°) described by Sowinski[1] and by Baeyer[1] is more stable toward melting point, solubility and ionization than is the new isomer described above. Toward rearrangement, however, the 118° acid is the most stable isomer under the conditions discussed above. These measures of stability are not necessarily contradictory since they are determined under widely varying conditions. The solubilities of the two isomers in pure water at various temperatures were determined and it was found that the solubility curves do not intersect in the range examined. This solubility data is given in the following table. In order to make direct comparison possible, the results are expressed in terms of 10 cc. of the saturated solution. The amounts actually titrated were larger and at the lower temperatures amounted to 50 cc. The temperature coefficient

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[1] *Loc. cit.*

of solubility for the two isomers is almost identical for the range 0° to 97°. This explains the difficulty found in completely separating these two acids.

TABLE III.

Temp.	No. of cc. saturated solution.	No. of cc. 0.01 N $Ba(OH)_2$ solution used.	
		118° isomer.	161° isomer.
96–97°	10.00	20.1	10.5
90°	10.00	14.6	8.0
80°	10.00	9.3	4.68
71–72°	10.00	6.7	3.48
55–56°	10.00	2.89	1.45
40°	10.00	1.34	0.69
20°	10.00	0.56	0.34
0°	10.00	0.39	0.19

Preparation of the Amides.—The amides of the three dihydro acids and of the tetrahydro acid were prepared as directed under the section dealing with β-naphthoic acid. To test out the method for unsaturated acids, the amide of cinnamic acid was prepared. The melting points have been given in Table II.

Preparation of the Dibromides.—The method used was similar to that recommended by Nef[1] for the preparation of the dibromide of cinnamic acid. Three grams of the 118° isomer are dissolved in 10 cc. chloroform. To the clear, colorless solution there are added slowly 3 g. of bromine dissolved in 5 cc. of chloroform, the solution being kept cold. (Besemfelder[2] used almost 100% excess bromine.) The sparingly soluble dibromide begins to separate out after fifteen minutes. The mixture is, however, allowed to remain in a dark place for two hours, after which only a faint bromine color remains; it is then filtered, using a suction filter and the crystals washed with 10 cc. chloroform. White crystals melting at 190°. Yield, 5 g. For the determination of the melting point and for the analysis, a product which had been precipitated from a more dilute chloroform solution was used.

Subst., 0.1956; AgBr, 0.2219. Calc. for $C_{11}H_{10}O_2Br_2$: Br, 47.9%. Found: 48.2%.

The dibromides of the labile (101°) acid and of the stable (161°) acid were prepared in an analogous manner; in each case the dibromides were found to be less soluble in chloroform than the corresponding acids and for this reason they were readily obtained pure. Their melting points have been given in Table I. No difficulty was found in preparing the dibromide of the labile acid since it did not decompose spontaneously as reported by Baeyer and Besemfelder. Its analysis is as follows:

Subst., 0.2449; AgBr, 0.2755. Calc. for $C_{11}H_{10}O_2Br_2$: Br, 47.9%. Found: 47.8%.

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[1] *Ann.*, 308, 267 (1899).

[2] *Loc. cit.*, pp. 190 and 194.

Reactions with Alkalis of the Three Isomeric Dibromides.—The dibromide of the labile acid (Δ^3-dihydronaphthoic acid-2) dissolves completely in 5% sodium carbonate solution. Soon, however, the clear solution becomes turbid and a precipitate is formed which increases rapidly. The product formed was found to be the monobromolactone already described by Baeyer. One gram of the bromide yielded 0.6 g. (80%) of the lactone. The melting point after recrystallization was 126°. The fact that the initial product dissolves completely in dilute sodium carbonate, proves that the lactone is not present as a contamination of the dibromide. When this lactone was boiled with 20% potassium hydroxide solution, it dissolved slowly and remained in solution after cooling. The following day the solution was acidified, an acid being thrown down which melted after one crystallization from water at 143–45° and whose solubility in water is 1.5 g. per liter. From the method of preparation, this product was suspected of being a keto acid. This agrees with its neutral equivalent, its analyses and with the fact that it readily forms a semicarbazone. (M. p. 266° decomp.) It is fairly stable toward the action of potassium permanganate in the cold.

0.0977 g. acid required 6.85 cc. KOH solution 0.0764 *N*.

Neutral equivalent = 187. Theoretical for keto acid = 190.

Subst., 0.0772; CO_2, 0.1964; H_2O, 0.0367. Required for $C_{11}H_{10}O_3$: C, 69.47%; H, 5.31%. Found: 69.36%, 5.28%.

The dibromide of the 161° stable acid (Δ^2-dihydronaphthoic acid-2), when dissolved in 5% sodium carbonate solution or in 5% potassium hydroxide solution, decomposed smoothly, with the loss of two molecules of hydrobromic acid, into β-naphthoic acid. Boiling the bromide with alcoholic potassium hydroxide solution is unnecessary since the decomposition proceeds rapidly in aqueous solution even at 0°. From 0.4 g. of bromide, 0.19 g. (90%) of pure β-naphthoic acid was obtained. This reaction agrees[1] with that observed when the dibromide of Δ^2-dihydronaphthoic acid-1 is treated with alkali.

The bromide of the 118° isomer (Δ^1-dihydronaphthoic acid-2) was treated with cold 5% aqueous potassium hydroxide and the decomposition of the product followed by drawing off small portions of the solution at intervals. It was found that most of the bromide decomposed during the first minute, and that the reaction was complete in less than fifteen minutes. The color changes described previously take place on warming the solution, but titration showed that no additional amount of alkali was required. The trace of indifferent substance already mentioned in the theoretical part of this paper was separated by ether extraction from alkaline solution. It was a liquid possessing a fragrant odor and still contained bromine. Because of the small quantity formed in the reaction, it was not further examined.

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[1] Kamm and McClugage, THIS JOURNAL, **38**, 419 (1916).

The main product formed is a dihydroxy acid. Because of the great solubility of the latter, it was separated from the acidified solution by repeated ether extractions. The fact that its solubility in ether is not great necessitates ten to fifteen extractions. It separates from the ether in white plates. From 3 g. of the dibromide, 1.2 g. (65%) of the dihydroxy acid was isolated. M. p. 182°.

0.0370 g. required 6.15 cc. $Ba(OH)_2$ solution 0.0281 *N*. Neutral equivalent found, 214. Theory, 208. Subst., 0.0780; CO_2, 0.1808; H_2O, 0.0415. Theory for $C_{11}H_{12}O_4$: C, 63.46%; H, 5.82%. Found: 63.20%, 5.91%.

The structure of this dihydroxy acid is further demonstrated by the fact that under the conditions outlined below, it was oxidized to *o*-carboxyhydrocinnamic acid of known structure.

The reaction observed in the decomposition of the bromide of Δ^1-dihydronaphthoic acid-2 agrees with that of the bromides of Δ^1-tetrahydrobenzoic acid and of Δ^1-dihydronaphthoic acid-1.

Purity of the Dibromides.—The reactions described above and also in the theoretical part of this paper may be used to test the purity of a given dibromide, in the following manner: The dibromide of Δ^3-dihydronaphthoic acid-2 is decomposed into the monobromolactone as described, and the latter separated by ether extraction. No acid is precipitated upon acidification of the alkaline solution. This shows that no trace of the dibromide of Δ^2-dihydronaphthoic acid-2 could have been present since the latter decomposes almost quantitatively under these conditions into the extremely insoluble β-naphthoic acid. Similarly, the dibromide of Δ^1-dihydronaphthoic acid-2 does not yield a trace of β-naphthoic acid. Neither could the monobromolactone of the Δ^3-isomer be detected. Hence the dibromide of the Δ^1-isomer must be free from the other two isomers.

Recovery of Dihydro Acids from the Bromides.—The three dihydro acids may be recovered from the corresponding bromides by treating the latter with zinc dust in glacial acetic acid. This method was found efficient as a means of purification and as a proof of the homogeneity of a given acid. This has already been described in detail in the section on the preparation of the labile dihydro-β-naphthoic acid.

Oxidation of Δ^1-Dihydronaphthoic Acid-2. Proof of Structure.—The method used by Besemfelder[1] in attempting to isolate a definite oxidation product from the Δ^2-isomer was the addition of potassium permanganate in excess until a permanent color was obtained. Consequently a large excess of permanganate was used (17 g. for 4 g. of the dihydro acid). In the present work, the following modification was adopted: The calculated amount of potassium permanganate was added slowly

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[1] *Loc. cit.*

to the ice-cold solution of dihydro acid dissolved in a very dilute alkali. In spite of these precautions, the only definite product isolated in several preliminary oxidations was *o*-phthalic acid or a mixture of acids consisting chiefly of the latter. The method finally used was to carry on the oxidation in steps using about the theoretical amount (or 10% excess) of the oxidizing agent necessary to carry the oxidation to a given stage.

Five grams of the 118° acid are dissolved in 75 cc. water containing 3 g. KOH and the solution cooled with ice. For the oxidation, 6 g. of $KMnO_4$ dissolved in 500 cc. water are added slowly during a period of about one hour, the solutions being kept cold. Finally, the mixture is warmed on the water bath to coagulate the manganese dioxide. The latter is filtered off, using suction, and the filtrate evaporated down to about 100 cc. The yellow solution is then again filtered if necessary and acidified. After standing overnight, the oxidation product will have separated in the form of radiating clusters. An additional yield is obtained by ether extraction, bringing the total to 50–60% of theory. One recrystallization from water and treatment with bone-black yields a white product melting at 119–120°. In comparison with the dihydro acid from which it is derived, it is very soluble in water. The oxidation was repeated several times in the attempt to isolate the intermediate dihydroxy acid, but uniformly the results outlined above were obtained.

0.0462 g. acid required 10.50 cc. NaOH 0.0210 *N*. Neutral equivalent found = 210. Subst., 0.1054; CO_2, 0.2340; H_2O, 0.0566. Required for $C_{11}H_{10}O_4$: C, 64.04%; H, 4.90%; for $C_{11}H_{10}O_4 + H_2O$: C, 58.9%; H, 5.40%. Found: 60.5%, 5.98%.

This product is believed to be the keto hydroxy acid or its hydrate indicated in the theoretical part of this paper. The titration value is not conclusive except that it shows that we are not dealing with the predicted dibasic keto-acid which would have a neutral equivalent of only 111. In a case of this kind, the titration is more conclusive than is the elementary analysis. The above product is suspected of being the keto hydroxy acid with water of crystallization. The neutral equivalent of a sample soon after crystallization, having been dried on a clay plate for one hour, gave a value of 230. The initial product had been standing for several days. Several unsuccessful attempts were made to prepare a semicarbazone.[1]

The keto-hydroxy acid may be further oxidized to *o*-carboxy hydrocinnamic acid under the conditions outlined above (5 g. acid require 5 g. $KMnO_4$). In this case it is noticed that the permanganate is not decolorized as rapidly as in the oxidation of unsaturated acids. The oxidation product is isolated as in the previous experiments, and is obtained almost pure, melting at 164°. One recrystallization and treatment

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[1] Discussion of steric hindrance in semicarbazone formation. Kötz and Michels, *Ann.*, 350, 208–9 (1906).

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; CO_2, 0.3220; H_2O, 0.0644. Required for $C_{10}H_{10}O_4$: 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.

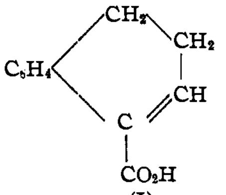
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY, UNIVERSITY OF ILLINOIS.]

THE STRUCTURE OF THE DIHYDRO-α-NAPHTHOIC ACIDS.

BY OLIVER KAMM AND HARRY BRUCE McCLUGAGE.[1]

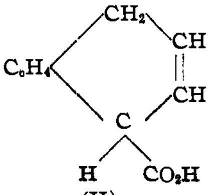
Received December 18, 1915.

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



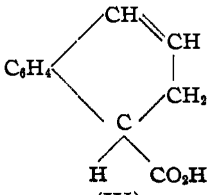
(I).

Δ^1-Dihydronaphthoic acid-1.



(II).

Δ^2-Dihydronaphthoic acid-1.



(III).

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-

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