A STUDY OF THE MOLECULAR STRUCTURE OF THE ACID $C_{10}H_{16}O_3$ FROM NEPETA CATARIA, L

A thesis submitted to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

by

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Acknowledgments

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Historical Introduction

The first mention of catnip in the United States appears to be that of Carver[1] who describes catmint (Nepeta Cataria, L.) in his travels through the interior parts of North America, 1766-68, as a plant with a woody root, divided into several branches, sending forth a stalk about three feet high, with leaves like those of the nettle or betony, having a strong smell of mint and a biting acrid taste. The flowers he describes as of a faint purple or whitish colour.

Catnip is a perennial labiate[2], indigenous to Europe and Asia. It was imported from Europe into the United States[3], where it now grows commonly near dwellings, from Canada and Minnesota in the north to Virginia and Arkansas in the south.

Pater[4] who has made attempts to cultivate Nepeta Cataria, L., concludes from his experiments that the plant is a biennial, not a perennial. He first raised the plants from seeds in a hot-bed, and after five weeks planted them out in the open. In spite of the very dry weather, the seedlings grew up quickly, and gave two cuts. The following year his Nepeta plantation again made a fine and abundant growth. The third year the plants ceased to grow.

Richter[5] maintains that the Nepeta species originally belonged to the Mediterranean flora, the word "Nepeta" being connected with the town Nepete[6] in Etruria, now

Tuscany, Italy. "Cataria", meaning pertaining to cat, is derived from "catus", the Latin for "cat".

Carver[7] claims that the plant is called catmint, because it is said, that cats have an antipathy to it, and will not let it grow. Our present notion concerning catnip and animals of the cat family is contrary to that of Carver. Instead of showing an aversion or repugnance for the catnip, we are quite generally agreed that it is a fondness which the cat manifests for the plant, either in the fresh or dried condition.

A. K. Fisher[8], at one time in charge of Economic Investigations, is credited with the discovery that animals of the cat family, other than the house cat (The house cat has long been associated with this plant, for as early as 1648 we find recorded in Bp. Hall Select Th. 51, "The dog when he is stomach sick can go to his proper grass, the cat to her "nep". Tryon[9], Way to Health, 1683, says, "They purge their nauseous Stomachs by eating of Grass, as Cats do theirs by eating of the Herb Nipp".[10]) are attracted by the herb. To quote from the Literary Digest: "Walking through the National Zoo, with a sprig of catnip in his pocket, he noticed that a mountain lion woke up when he passed by, and that a tiger next door, reputed to be dangerous, seemed to be courting his friendship. It minced up to the bars and tried to follow him. Fisher tossed the catnip over the fence. The tiger purred, sniffed and rolled

over on it, licked the fur where it had touched, located the sprig on the floor, pounced upon it and finally ate it". Fisher reported this singular conduct to the United States Biological Survey, and an investigation was begun to determine whether the plant could be used effectively as bait for beasts of prey of the cat family.

According to the United States Department of Agriculture [11], the volatile oil mixed with petrolatum makes a successful bait and has been extensively used in many of the western states for trapping mountain lion, bobcats, lynx, and other destructive members of the cat family.

Nepeta Cataria is known by a number of synonyms in the different languages. Among the various language equivalents are: (See next page)

Latin	English	German	French	Italian	Spanish
Nepeta Cataria	Catnep		Cataire [12] Chataire [15]	Catara [13]	Catera [14]
Mentha felina [16]	Catnip [17] Catmint [19] Catrup [20] Cat's wort [21] Fieldmint [22] Nep [23] Neppe [24] Nip	Katzen-minze	Menthe de chats [18]		
		Katzen-melisse [25] Stein-minze [26] Marien-nessel [27] Katzen-kraut [28]	Herb aux chats [29]		

Medicinally catnip has never gained much importance, although it has been used, usually as the infusion, as a carminative, stimulant, tonic, diaphoretic and emmenagogue.[30] The first reference found to its use as a drug dates back for almost four centuries.[31] In Kellybuch Hom. Apoth., 1561, we find recorded: "He that hath a feruent cough, let him take nepps, that cattle delite in".

The dried leaves and tops were official in four revisions of the United States Pharmacopoeia, viz., the 1840, 1850, 1860, and 1870 (U.S.P. II-V). It was again taken up by the National Formulary in 1916, being official in the last two revisions (N.F. IV and V).

1. Lloyd Lib. Bull. Rep. Series No. 5 (1907), 519.
2. Lyons, Plant Names, Scientific and Popular, 259.
3. Henkel, U.S.Dept. of Ag. Bull. No. 219; Report Schimmel & Co., April, 1912, 149.
4. Ber. Schimmel & Co., 1925, 42
5. Pharm. Ztg. 70, 1485 (1925); Report Schimmel & Co., 1926, 17.
6. Gray's Manual of Botany, 8th. ed., 1889, 416.
7. See ref. 1.
8. Science Service's Daily Science News Bulletin; Lit. Digest 97, 20 (June 30, 1923).
9. Murray's Eng. Dict.
10. ibid.
11. Oil Paint and Drug Reporter 104, No. 24, 38 (1928); Report Schimmel & Co., 1924, 14.
12. See ref. 8
13. Wood & Bache, U.S.Disp. 18th. ed., 1601.
14. ibid.
15. See ref. 8
16. Anthony, Med. & Sur. Jour. (Surg. Gen. Lib. Ind. Cat.).
17. See Ref. 8
18. Stille, Maisch, Caspari, Maj.Disp. 5th. ed., 424.
19. See Ref. 8.
20. ibid.
21. ibid.
21. ibid.
22. See ref. 9.
23. ibid.
24. ibid.
25. Real-Enzyklopoedie der Gesamten Pharmazie.
26. ibid.
27. ibid.
28. See ref. 18.
29. ibid.
30. Maisch, Organic Materia Medica, 290.
31. See ref. 9.

Previous Chemical Investigation

Gillispie[1], in 1889, appears to have been the first to publish an analysis of the plant. From his investigations he reports to have found 0.3 % of volatile oil, small quantities of fixed oil, a crystalline wax, 5.80 % mucilage, 12.62 % of dextrin and glucose, 1.30 % cane sugar, 35.44 % cellulose, 18.50 % ash, and small quantities of a bitter principle. This last named constituent was partly removed from the drug by ether, but alcohol was found to be the best solvent. On removing the alcohol, dissolving the residue in water, agitating the aqueous solution with ether and evaporating the ethereal solution he obtained a semi-crystalline substance which possessed a very bitter taste and an acid reaction. This substance did not reduce Fehling's Solution either before or after boiling with acid and gave none of the reactions of the alkaloids. Gillispie concluded that this compound is probably an organic acid.

No doubt, as a result of this investigation, Maisch[2], in 1895, records among other constituents of Nepeta Cataria, a bitter principle (crystalline, soluble in ether, acid reaction, not a glucoside) ; and Ruaby, Bliss and Ballard[3], in 1930, list a bitter acid as one of the constituents of catnip.

Liotta[4] has studied the volatile oil of Nepeta Cataria, L.,of the Sicilian valleys where it grows plentifully in the neighborhood of Scaletta. He reports that the oil dis-

tilled from the entire dry plant has a yellowish-brown color, but the fresh leaves distilled separately yield an almost colorless oil. According to Lietta[5] the catmint oils of Sicily contain considerable quantities of carvacrol, an alcohol to which he has given the name of "nepetol", and traces of pulegone and thymol.

Klein[6] also gives thymol and carvacrol as constituents of the oil from the leaves of Nepeta Cataria, L. The Fluckiger Test[7] was applied to the catnip oils distilled in our laboratory during the summer of 1934 and the summer of 1935. The oils of 1934 were very readily soluble in chloroform and gave the very slightest trace of color, while the 1935 oils were less soluble in chloroform and gave not the slightest trace of color.

From the distillation of the dried herb of Klausenberg, Pater[8] obtained 0.18 % of a heavy green oil, smelling remarkably like lemons (B.P. 215°-225° C). When the young sheets were distilled they yielded a pleasantly scented water, very like rose water.

Gildemeister[9] describes catnip oil as having a minty and camphor-like odor that is not pleasant.

The work on catnip oil at the University of Wisconsin was started by E. R. Miller[10] while chemist at the Wisconsin Pharmaceutical Experiment Station. He distilled a considerable quantity of catnip oil during 1915-16. A preliminary determination of the saponification value, which turned

out very high, caused him to suspect the presence of a lactone. Klein[11] records among the unnamed lactones, a lactone $C_{10}H_{16}O_2$, as found in Nepeta Cataria, L.

Kremers[12] first isolated the crystalline substance under consideration and showed that eighty-five percent of the oil was soluble in aqueous alkali from which solution the dissolved substance could be precipitated by acid. The oily precipitate crystallized upon standing.

R. M. Hixon[13] in 1928 examined the non-lactone constituents of the oil. The peculiar catnip odor was shown to reside in a small amount of an acetic ester of an alcohol.

O. A. Heath[14], in 1922, attempted the first investigation at the University of Wisconsin, of the so-called lactone obtained from catnip oil. This investigation was continued by the writer in 1933.

1. Gillispie, Henry R., Am. Jour. of Pharm. 61, 558 (1889).
2. Maisch, John M., A Manual of Organic Materia Medica, 280.
3. Rusby, Bliss and Ballard, Properties and Uses of Drugs, 528.
4. Report Schimmel & Co., 1924, 14.
5. ibid., 1926, 17.
6. Klein, Handbuch der Pflanzenanalyse, Vol. 2.
7. Jour. Am. Pharm. Ass. 17, 524 (1928).
8. Ber. Schimmel & Co., 1925, 42.
9. Die Aeth. Oele, 2ed., Vol. III, 453.
10. Jour. Am. Pharm. Ass., 11, 96 (1922).
11. Klein, l.c., Vol. 3, 860.
12. Unpublished results.
13. See ref. 10.
14. Unpublished results.

Material

Some of the catnip from which the so-called lactone under investigation was obtained was grown in the gardens of the Wisconsin Pharmaceutical Experiment Station under the direction of Professor Riethmann. That distilled by Miller was wild catnip gathered from the vicinity of Madison, Wisconsin. The fresh plant was harvested at the time of flowering and immediately steam distilled. The volatile oil thus obtained was a light amber color.

The so-called lactone was obtained from this volatile oil by shaking out with successive portions of a ten per-cent solution of aqueous sodium hydroxide and subsequent precipitation with diluted hydrochloric acid. Joseph B. Semb[1] during the winter of 1933-34, prepared some of the crystalline compound investigated by the writer. Semb combined all the various catnip oils which had accumulated since 1928 and isolated the compound as stated above. He recrystallized it from a mixture of acetone, alcohol and ether. The writer prepared the compound from the oils distilled during the summer of 1934 and of 1935. It was recrystallized from a mixture of ether and petroleum ether. Many attempts were made to recrystallize the compound from various single solvents and combinations of solvents. The combination of the two named above were found to be by far the best. The compound is very soluble in ether and but slightly soluble in petroleum ether. Consequently it was

first dissolved in the least amount of ether and then petroleum ether was added. The mixture was set aside in a cool place. The following day large handsome crystals resembling rock candy had separated out.

The writer also obtained considerable quantities of the compound from the thick, viscous, dark colored mother liquids left after Senb had removed the compound as previously stated. The mother liquid was warmed on the water bath with a thirty percent aqueous solution of sodium bisulphite. Upon cooling, the reaction mixture separated into two layers, an oily layer, less viscous than the original oil, formed the upper layer, while the lower aqueous layer contained white needle-like crystals. The oily layer was carefully removed. The crystalline material was filtered from the aqueous layer, washed with ether, recrystallized from water and again washed with ether. These needles which melt at 95-96° C are identical with the sodium bisulphite addition product obtained from the so-called lactone itself (See p. 35), as indicated by the mixed melting point and a sulphur determination which checks with that of the latter.

The so-called lactone was regenerated from this bisulphite addition product by decomposing with hydrochloric acid. The compound which crystallizes very slowly from the acid solution was recrystallized from an ether - petroleum ether solution.

This so-called lactone is a white crystalline compound.

When first prepared it is practically odorless but upon standing it developes a somewhat penetrating acid-like odor (the odor becoming more pronounced , especially after standing during the summer season), and a very bitter taste. This compound is presumably the bitter principle isolated by Gillispie and recorded by Maisch, and the bitter acid listed by Rusby, Bliss and Ballard.

1. Unpublished results.

Chemical Study of the Acid

The writer in May, 1935, took a sample of the crystals to Dr. A. N. Winchell, Professor of Geology, who kindly made a crystalographic study of the compound and records the following observation: "The crystals ..... are optically negative and biaxial with an optic angle of about 45°. A plate normal to the acute bisectrix shows extinctions from I inclined at a small angle (10° I) to the striations and cleavage. The crystals are probably monoclinic. A plate normal to the obtuse bisectrix shows parallel extinctions with the optic plane normal to the cleavage."

The melting point found is from 71° - 72° C.and the boiling point under atmospheric pressure (boils with decomposition, giving off water) is from 250° to 254° C.u.c. When distilled under reduced pressure (1 to 2 mm.),no constant boiling point was obtained. Neither the distillate collected nor the residue left in the distillation flask again crystallized but remained as heavy syrupy liquids even after long standing.

The specific gravity is slightly greater than that of water, being 1.222 at 25° C.

The compound is optically active. With absolute alcohol as the solvent the writer obtained the following optical rotation from a freshly prepared solution: $(\alpha)_D^{24^\circ} = +38^\circ 36'$

After the solution had stood for two days the optical rotation was again taken, yielding results slightly lower than those of the freshly prepared solution: $[\alpha]_D^{25^\circ}$ = + 36° 26'. The solution was now set aside for almost three months when the optical rotation was again taken and found to be very much lower, viz., $[\alpha]_D^{22.5^\circ}$ = + 8° 0'.

Heath[1] reports the following specific rotation: With chloroform as the solvent he obtained $[\alpha]_D^{20^\circ}$ = + 39° 96', and with absolute alcohol as the solvent he obtained $[\alpha]_D^{20^\circ}$ = + 39° 14'. Boiling for two hours under a reflux condenser did not materially change the angle of rotation.

The compound is insoluble in water and dilute acid. It is soluble in dilute aqueous sodium hydroxide and is not precipitated when the solution is saturated with carbon dioxide[2] (phenols are soluble in alkali but are precipitated upon saturating the solution with carbon dioxide). It dissolves slowly with a slight cloudiness in sodium acid carbonate[2] (phenols are insoluble in sodium bicarbonate while weak carboxylic acids, not negatively substituted, are soluble). It is insoluble in an aqueous solution of sodium formate[2] (weak carboxylic acids, not negatively substituted, are insoluble in sodium formate while strong carboxylic acids are soluble in this reagent).

The compound is more or less soluble in most commonly used organic solvents, such as chloroform, carbon tetrachloride, methyl alcohol, ethyl alcohol, ether, carbon disulphide, acetone, etc. The following results were obtained,

at room temperature, for the solvents given below:

Solvent	Grams of compound	Grams of solvent
Methyl alcohol 1)	303.0	100
Acetic acid 1)	189.0	"
Acetone 1)	180.0	"
Ethyl alcohol	175.0	"
Dioxane	125.76	"
Chloroform	118.75	"
Toluene	65.0	"
Carbon tetrachloride 1)	50.0	"
Carbon disulphide	13.0	"
Heptane 1)	0.358	"

Note: The chloroform and carbon tetrachloride solutions of the compound upon standing slowly give off hydrogen chloride. The melting point of the compound left after evaporating the solvent, chloroform, was lower (64°-65°C) than that of the original compound. The writer was unable to again obtain the compound in a crystalline form from the carbon tetrachloride solution, for upon evaporation of the solvent a thick, dark, syrupy liquid remained. The product left after evaporation of the ethyl alcohol has a lower melting point, is darker in color than the original

compound, and has a somewhat fruity odor. The crystals obtained after evaporating the carbon disulphide, the dioxane, and the toluene, respectively, melt at the same temperature as the original compound.

Elementary analysis:

A quantitative determination of carbon and hydrogen was made by the semi-micro combustion method, which is a modification of Pregl's micro method of analysis. O. A. Gisvold [3] reports the following results:

	Wt. of sample	Wt. of carbon dioxide	Wt. of water
1.	0.0611 Gm.	0.1460 Gm.	0.0477 Gm.
2.	0.0566 "	0.1356 "	0.0442 "
3.	0.0736 "	0.1762 "	0.0576 "

	Carbon	Hydrogen	Oxygen (by difference)
1.	65.16 %	8.75 %	26.11 %
2.	65.31 "	8.75 "	25.94 "
3.	65.28 "	8.75 "	25.97 "
Average:	65.25 "	8.74 "	26.00 "

By the same method the writer obtained the following results:

	Wt. of sample	Wt. of carbon dioxide	Wt. of water
1.	0.0524 Gm.	0.1254 Gm.	0.0414 Gm.
2.	0.0556 "	0.1328 "	0.0434 "

	Carbon	Hydrogen	Oxygen (by difference)
1.	65.26 %	8.83 %	25.91 %
2.	65.14 "	8.73 "	26.13 "
Average:	65.20 "	8.78 "	26.02 "

The above analyses seem to indicate a molecular formula of $C_{10}H_{16}O_3$ " a molecular weight of 184.

Calculated for $C_{10}H_{16}O_3$:	C 65.17 %	H 8.76 %	
Found :	C 65.25 "	H 8.74 "	
	65.20 "	8.78 "	

Molecular weight determination:

A molecular weight determination by the camphor method[4] gave results indicating a molecular weight of 184 to 187.

Heath[5] reports the following: " By the boiling point method a result was obtained that indicated a molecular weight of the compound as being 185 to 190. Acetone, alcohol and benzol were the solvents used. The freezing point method for acetic acid and benzol were not at all

reliable. The organic combustions of the several addition products indicated a compound having a molecular weight of approximately 187 to 188".

Water of crystallization:

The moisture was determined by the xylene method [6], using ten grams of compound, which after refluxing for several hours yielded no moisture. After evaporation of the xylene a heavy syrupy liquid remained. This did not again crystallize even after standing for several months.

Neutralization equivalent [7] and acid number [8]:

A weighed sample of the crystals was dissolved in ten cubic centimeters of neutral alcohol and titrated with standard potassium hydroxide solution (0.1226) using phenolphthalein as indicator. The following neutralization equivalent and acid numbers were obtained:

	Neut. Eq.	Acid No.
1.	188.6	297.47
2.	187.8	298.74
3.	188.3	297.86
Average:	188.2	298.03

Two samples were titrated as above, using the same

base but thymol blue as indicator. The following results were obtained:

	Neut. Eq.	Acid No.
1.	187.3	299.48
2.	187.6	299.09
Average:	187.4	299.27

The neutralization equivalent was again taken of a fraction of the compound which had stood for more than a year. Standard potassium hydroxide (0.0916) and phenolphthalein indicator were used, giving the results tabulated below:

	Neut. Eq.	Acid No.
1.	185.8	301.8
2.	186.8	300.3
3.	186.4	300.9
Average:	186.3	301.0

As seen from the above results, the neutralization equivalent seems to indicate a slightly higher molecular weight (average - 187.3) than that computed from the results of the elementary analysis (184.1).

Saponification equivalent [9] and saponification number [10]:

The saponification equivalent was determined by dissolving an accurately weighed sample of the acid in ten cubic centimeters of neutral alcohol and refluxing for thirty minutes with forty cubic centimeters of standard sodium hydroxide. The reaction mixture was allowed to cool and the excess alkali titrated with standard hydrochloric acid, using phenolphthalein as indicator.

	Sap. Eq.	Sap. No.
1.	159.1	352.5
2.	161.4	347.4
3.	162.5	345.1
Average:	161.0	348.3

Salt forming properties:

a). Sodium salt - The sodium salt was prepared by dissolving the acid in dilute sodium hydroxide and neutralizing to phenolphthalein. The solution was allowed to evaporate at room temperature, the residue washed with ether and dried in a vacuum desiccator. This salt did not crystallize when first prepared but remained more or less syrupy. However, after standing in a desiccator over calcium chloride for over a year, it has become more or less crystalline and continues to remain so after being

removed from the desiccator and allowed to stand in room atmosphere.

b). Potassium salt - The potassium salt was prepared as described under the sodium salt above. This salt is ether soluble and has not crystallized after long standing in a desiccator over calcium chloride, but continues to remain more or less syrupy.

c). Silver salt - The silver salt was prepared by precipitating a solution of the sodium salt (prepared by neutralizing the acid to phenolphthalein with aqueous sodium hydroxide) with an aqueous solution of silver nitrate. The heavy white amorphous precipitate was filtered from the solution on a suction filter, washed with water, alcohol and ether, and dried to constant weight in a vacuum desiccator. A gravimetric determination of the silver in the salt gave the following results:

	Wt. of sample	Wt. of silver	Percent of silver
1.	1.2286 Gm.	0.4614 Gm.	37.55 %
2.	1.3480 "	0.5046 "	37.57 "
3.	1.3878 "	0.5199 "	37.47 "
Average:			37.54 "

Calculated for a compound $C_{10}H_{15}O_3Ag$ - 37.07 "

d). Barium salt - The barium salt was prepared by adding an alcoholic solution of the acid to an aqueous solution of barium carbonate and warming for several hours on the water bath. The excess barium carbonate was filtered off, the filtrate evaporated on the water bath, the residue washed with ether and dried in a vacuum desiccator. The product was not crystalline. The percent of barium was determined by precipitating as barium sulphate. The results were as follows:

	Wt. of sample	Wt. of Barium sulphate	Percent of Barium
1.	0.3940 Gm.	0.1494 Gm.	22.33 %
2.	0.5470 "	0.2006 "	21.57 "
3.	0.2850 "	0.1078 "	22.25 "
Average:			22.05 "

Calculated for a compound $(C_{10}H_{15}O_5)_2Ba$ 27.27 "

e). Lead salt - The lead salt was prepared by precipitating a solution of the sodium salt with an aqueous solution of lead acetate. A heavy white amorphous precipitate was obtained. This was thoroughly washed with water, alcohol and ether and dried to constant weight in a vacuum desiccator. The percent of lead was determined according

to the method of Fresenius[11], yielding the results tabulated below:

	Wt. of sample	Wt. of lead oxide	Percent of lead
1.	0.7654 Gm.	0.3626 Gm.	44.03 %
2.	0.6796 "	0.3180 "	45.37 "
Average:			43.70 "
Calculated for a compound $(C_{10}H_{15}S_2O)_2Pb$			34.13 "

f). Rubidium and caesium salts - Both the rubidium and caesium salts were prepared by adding an alcoholic solution of the acid to an aqueous solution of rubidium and caesium carbonate respectively. Neither of these gave crystalline salts, but remained as heavy syrups after spontaneous evaporation of the solvent, washing with alcohol and ether, and drying in a desiccator.

g). Piperidine salt - Two grams of the crystalline acid were dissolved in about 25 cc. of benzene and 1.1 cc. of piperidine were added. The solution became turbid at once but no immediate precipitate formed. The solution was set aside and the solvent allowed to evaporate spontaneously. After many days colorless crystals with a piperidine-like odor separated. These were filtered off and recrystallized

from ethyl alcohol. This compound is water soluble, melting at 98°- 99° C.

If to an alcoholic solution of this compound, a few drops of platinic chloride T. S. are added, an immediate yellow crystalline precipitate separates out.

The percent of nitrogen in the above piperidine salt determined by the Kjeldahl method gave the following results:

	Wt. of sample	Wt. of nitrogen	Percent of nitrogen
1.	0.2872 Gm.	0.01814015 Gm.	6.31 %
2.	0.3214 "	0.02025651 "	6.45 %
Average:			6.38 %

Calculated for a compound $C_{10}H_{16}O_3 \cdot C_5H_{11}N$ - 5.80 %

The above results seem to indicate that one molecule of each substance was involved in the reaction.

When the heavy syrupy liquid from which Semb had removed the so-called lactone was treated with piperidine and the solution taken up in water, a heavy oily material separated out. The aqueous layer was separated from this oily material and set aside. After standing for some time a crystalline material separated which was identical with the piperidine salt of the acid. (These crystals are very hard to purify from the adhering oily material).

b). Para-toluidine salt - Two grams of the acid were dissolved in about 20 cc. of benzene. One and two-tenths grams of p-toluidine were likewise dissolved in about 20 cc. of benzene. The benzene solution of the p-toluidine was slowly added to the benzene solution of the acid with constant shaking. The mixture remained clear for several minutes after which it first became turbid and then a white crystalline precipitate settled out. This was filtered off on a suction filter and thoroughly washed with benzene. It was immediately recrystallized from ethyl alcohol, thoroughly washed with alcohol and ether and dried over phosphorous pentoxide. Melting point, 134° - 135° C.

This compound is insoluble in water and dilute acid. It dissolves slowly in dilute alkali. The compound is very unstable. If allowed to stand in the atmosphere over night it changes to a thick yellow paste. If kept over phosphorous pentoxide it decomposes a little more slowly.

The percent of nitrogen determined by the Kjeldahl method gave the following results:

	Wt. of sample	Wt. of nitrogen	Percent of nitrogen
1.	0.4078 Gm.	0.0179 Gm.	4.39 %
2.	0.2178 "	0.0090 "	4.14 "
Average:			4.26 "

Calculated for a compound $C_{10}H_{16}O_3 \cdot C_7H_9N$ - 4.80 "

A reaction carried out exactly as described above except that phenylhydrazine was substituted for the p-toluidine gave an immediate turbidity but no crystalline product could be obtained.

i). Other salts - Two gram samples of the acid, each likewise dissolved in benzene, were treated with the calculated amounts for one molecule reaction of aniline, n-butylamine, and pyridine respectively. Although the solutions all showed a turbidity, none of these yielded crystalline derivatives. The aniline compound is a dark tar like liquid with a pleasant odor. The n-butylamine compound is a straw colored liquid while the pyridine derivative is a thick colorless syrupy liquid.

Ester forming properties:

a). p-bromophenacyl ester[12] - The p-bromophenacyl ester was prepared by refluxing for thirty minutes, one gram of the sodium salt of the acid with one gram of p-bromophenacyl bromide in alcoholic solution. A heavy yellow resinous material and a flaky substance separated upon cooling. The supernatant liquid containing the flaky precipitate was decanted from the resinous material which settled to the bottom of the flask. The solid precipitate was filtered off and twice recrystallized from a hydro-

alcoholic solution, yielding a slightly yellow colored pleasant smelling compound melting between 127° to 134°C. The percent of bromine determined by the Stepanoff method gave the following results:

	Wt. of sample	Wt. of silver bromide	Percent of bromine
1.	0.1160 Gm.	0.64810 Gm.	30.47 %
2.	0.1140 "	0.60754 "	30.14 "
Average:			30.30 "

Calculated for a compound $C_{10}H_{15}O_3 \cdot CO\,CH_2\,C_6H_4\,Br$ - 20.97 "

Calculated for a compound $C_{10}H_{15}O_3 \cdot (CO\,CH_2\,C_6H_4\,Br)_2$ - 27.56 "

b). P-nitrobenzyl ester[12] - The p-nitrobenzyl ester was prepared yielding an orange colored oily product.

Amide formation with thionyl chloride[13]:

One gram of the acid was heated very slowly under a reflux condenser with 5 cc. of thionyl chloride from fifteen to thirty minutes. The reaction mixture was cooled and carefully poured into 15 cc. of concentrated ammonium hydroxide. The product was a heavy oily liquid. Attempts to crystallize it were unsuccessful. (When the acid was added to the

thionyl chloride it dissolved immediately with a very vigorous reaction).

Anilide [13]:

One gram of aniline, 0.5 gram of the sodium salt of the acid, and 0.5 cc. of concentrated hydrochloric acid were mixed in a dry test tube and heated under the reflux condenser for about an hour. The reaction mixture was diluted with 15 cc. of water and cooled in a beaker of ice. A thick pasty mass was obtained. Attempts to crystallise the compound were unsuccessful.

Toluide [13]:

The same reaction as described for the anilide above was carried out using one gram of p-toluidine instead of the aniline. The reaction product likewise was a thick pasty mass which could not be crystallised.

Evidence of a carbonyl group in the molecule:

a). Iodoform reaction [14] - If to a solution of a few small crystals of the acid in dilute aqueous sodium hydroxide, a solution of iodine in potassium iodide is added drop by drop, a fine yellow precipitate results. This

melts at 119° C.(melting point of iodoform) and the mixed melting point with iodoform is also 119° C. At times the iodoform comes down very readily in the cold and at other times the reaction was obtained with difficulty.

An attempt to isolate the acid formed from the reaction mixture was unsuccessful.

b). Reaction with sodium bisulphite - The acid was warmed on the water bath with a thirty percent aqueous solution of sodium bisulphite. Upon cooling, an immediate white needle-like precipitate settled out. This was recrystallized twice from water and thoroughly washed with ether, yielding beautiful shining white needles, melting at 95°-96° C. The percent of sulphur in this compound was determined according to the method of Rosean and Woodward[15] giving the results tabulated below:

	Wt. of sample	Wt. of sulphur	Percent of sulphur
1.	0.2618 Gm.	0.0276740 Gm.	10.5 %
2.	0.2484 "	0.0277288 "	11.1 "
3.	0.3044 "	0.0327430 "	10.7 "
Average:			10.8 "

Calculated for a compound $C_{10}H_{16}O_3 \cdot Na \times SO_3$ - 11.18 "

These results seem to indicate that but one molecule of the acid reacts with one molecule of sodium bisulphite.

The original compound is again regenerated from the bisulphite addition product when the latter is decomposed with sodium carbonate and the solution acidified with hydrochloric acid, or when decomposed with hydrochloric acid directly.

e). Reaction with semicarbazide - The semicarbazone was prepared by dissolving 2 grams of semicarbazide hydrochloride in 10 cc. of water. Ten cubic centimeters of a 10 percent solution of sodium hydroxide were added. One gram of the acid was added to this solution. The acid went into solution. The mixture was set aside until the following day when it was acidified with diluted hydrochloric acid. A white crystalline precipitate separated out at once. This compound after recrystallization from a hydroalcoholic solution, melted at 160°- 161° C. The compound is practically insoluble in benzene and ether.

f). Reaction with thiosemicarbazide - The thiosemicarbazone was prepared by heating on the water bath for thirty minutes, a mixture of 2 grams of the acid plus 3 grams of thiosemicarbazide hydrochlorides in 40 cc. of diluted acetic acid (32 cc. of glacial acetic acid plus 8 cc. of water). After cooling, the solution was diluted

with water until it became slightly turbid. It was then set aside to crystallize. The following day the crystalline compound which had separated from the solution was filtered off, thoroughly washed with water, dried, and recrystallized from benzene. The thiosemicarbazone crystallizes from this solvent in the form of beautiful white needles melting at 180° - 185° C. A yield of one and one-tenth grams was obtained from the first precipitate.

The percent of nitrogen determined by the Kjeldahl method gave the following results:

	Wt. of sample	Wt. of nitrogen	Percent of nitrogen
1.	0.2482 Gm.	0.03410174 Gm.	13.73 %
2.	0.2530 "	0.03730933 "	14.74 "
Average:			14.23 "

Calculated for a thiosemicarbazone $C_{10}H_{16}N_4OS_2$ = 16.33 "

e). Reaction with hydroxylamine - An oxime was prepared by dissolving 5 grams of the acid in a solution of 12.5 grams of hydroxylamine hydrochloride in 30 to 40 cc. of water to which 50 cc. of a 10 percent sodium hydroxide solution had been added (Kamm, p. 172). Enough alcohol was added to dissolve the acid. The mixture which was perfectly clear was set aside until the following day when it was

acidified with diluted hydrochloric acid. A slightly yellow colored crystalline precipitate came down immediately. This was thoroughly washed with water and dried. Melting point of the oxime is 134°- 135°C. A yield of four grams was obtained.

The percent of nitrogen determined by the Kjeldahl method yielded the following results:

	Wt. of sample	Wt. of nitrogen	Percent of nitrogen
1.	0.2854 Gm.	0.0254919 Gm.	8.93 %
2.	0.2458 "	0.0212719 "	8.65 "
Average:			8.79 "

Calculated for an oxime $C_{10}H_{16}O_2NOH$:- 7.03 "

The Beckmann Rearrangement [16] for ketoximes has been attempted on the above oxime in order to obtain first the amide and then the corresponding acid. No successful results have been obtained.

f). Reaction with phenylhydrazine - Numerous attempts have been made to prepare a phenylhydrazone ,but thus far a crystalline compound has not been obtained. A reaction is apparent ,but the reaction product is a more or less gummy compound.

Saturation of the acid:

a). Iodine number - The iodine number as determined by the Hanus method gave zero results as indicated below:

	Wt. of sample	Titration of sample	Titration of blank
1.	0.7914 Gm.	29.2 cc.	29.3 cc.
2.	0.9782 "	29.3 "	29.4 "
3.	0.7310 "	29.4 "	29.5 "

b). Thiocyanogen number - The thiocyanogen number was determined, also giving zero results.

c). Addition of bromine - When a solution of bromine in carbontetrachloride is slowly added to a solution of the acid in the same solvent, the solution is not decolorized. However, when this solution is exposed to sunlight, vapors of hydrogen bromide are given off. A bromine determination of this compound gave practically zero results.

Reaction with Fehling's Solution:

The acid does not reduce Fehling's Solution either before or after boiling with mineral acid.

Tests for phenolic and enolic hydroxyl group:

a). Reaction with ferric chloride[17] - When a drop of ferric chloride test solution is added to a very dilute aqueous solution (about one-tenth percent) of the acid, it gives no color reaction. Neither does the same test applied to a dilute alcoholic solution of the acid give a color test.

b). Reaction with alcoholic bromine[18] - The acid was dissolved in absolute alcohol. To this mixture a drop of an alcoholic bromine solution was added. The solution was not decolorized. (See also, Addition of bromine).

Test for alkoxyl group:

Four determinations for alkoxyl groups were made by the Zeisel method[19] giving zero results.

Reaction with metallic sodium:

The so-called lactone was dissolved in dry benzene. To this solution small clean cut pieces of metallic sodium were added until no more reaction was apparent. The compound reacts quite readily yielding a sort of gelatinous precipitate. The benzene solution containing the precipitate was carefully decanted from the remaining unreacted

sodium and the solvent allowed to evaporate spontaneously leaving a gelatinous precipitate (resembling moistened tragacanth) which hardened more or less after long standing.

The same reaction as described above was carried out using anhydrous ether which had been dried over metallic sodium instead of the dry benzene. In this case an immediate white precipitate separated. This precipitate, when filtered from the solution and placed on a watch glass, liquifies.

The above described precipitate was refluxed with p-bromophenacyl bromide in alcoholic solution for thirty minutes. The reaction mixture was cooled and slightly diluted with water. No immediate precipitate formed but upon standing for many days white rosette-like crystals melting between 120°-130° C. separated from the solution.

Reaction with phosphorus pentachloride:

When to a few crystals of the acid contained in a dry test tube a small amount of phosphorus pentachloride is added, a very vigorous reaction takes place. The resulting mixture becomes an emerald green if allowed to stand for a day - Upon longer standing the green color deepens.

If the reaction mixture is poured on a watch glass to solidify, pressed on a clay plate to remove the phosphorus

oxychloride, and then added to a concentrated solution of ammonia water, no crystalline amide is obtained.[20]

Alkaline hydrolysis:

From 3 to 4 grams of the acid were refluxed for forty-five minutes with 30 to 40 cc. of 25 percent sodium hydroxide. The alkaline solution was then distilled. No volatile alcohol was obtained. The alkaline solution was cooled and shaken out with ether. No residue was left after evaporation of the ethereal solution. The solution was now acidified with diluted sulphuric acid. An oily precipitate which came to the surface of the liquid settled out. The oily liquid was separated from the aqueous liquid by means of a separatory funnel. The oily liquid was taken up in ether, the ethereal solution washed with water, dilute alkali and again with water. It was dried over sodium sulphate. Upon evaporation of the solvent from two to three grams of a yellow syrupy liquid remained. This liquid does not again crystallize even after long standing. The aqueous acidified liquid from which the oily liquid had been separated was shaken out once with a small amount of ether. It was again distilled, yielding a distillate that was neutral to litmus, phenolphthalein and methyl orange.

Reaction with ammonia gas:

a). When ammonia gas is passed through a solution of the acid in anhydrous ether, two products are obtained. Product I is a white crystalline compound, presumably a di-nitrogen compound, while product II is a heavy amber colored syrupy liquid containing but one atom of nitrogen as shown by the nitrogen determination.

Ten grams of the acid were dissolved in about one-hundred and fifty cubic centimeters of anhydrous ether and dry ammonia gas passed through the solution for several hours. A heavy, white, salt-like precipitate separated immediately. The flask with the reaction product was set aside until the following day. The precipitate had settled to the bottom of the flask as a heavy resinous material. The supernatant ether was decanted and the residue taken up in alcohol, in which solvent it was readily soluble. After standing for several days a small amount of a white crystalline (I) material separated. This was filtered off and the filtrate evaporated, first on the water bath and finally in a vacuum desiccator. A thick, syrupy, amber-colored liquid remained. When a small amount of ether was now added to this in an attempt to wash the material, it all went into solution. However, when an excess of ether was added the solution became turbid and more of the white crystalline material separated out. This was again filtered off and the filtrate evaporated and washed with ether as before until

no more crystalline material could be obtained.

The various crystalline precipitates (I) were combined, thoroughly washed with alcohol and ether, and dried over calcium chloride. The compound melts with decomposition at 239° - 240° C.u.c. This compound is insoluble in water and ether, but is soluble in dilute hydrochloric acid and dilute potassium hydroxide. When a small amount of this material is treated with twenty-five percent sodium hydroxide in the cold in a test tube fitted with a cork into which is fastened a piece of moistened red litmus paper, the paper slowly turns blue. The compound readily gives off ammonia when heated in a test tube with dilute alkali (as indicated by the odor of ammonia and a test with moistened red litmus paper).

A nitrogen determination of the above compound by the Kjeldahl method gave the following results:

	Wt. of sample	Wt. of nitrogen	Percent of nitrogen
1.	0.2726 Gm.	0.03038769 Gm.	11.14 %
2.	0.1600 "	0.01806379 "	11.28 "
Average:			11.21 "

Calculated for a compound $C_{10}H_{16}O_3 \cdot NH_3$ - 6.96 "

Calculated for a compound $C_{10}H_{16}O_3(NH_3)_2$ - 12.84 "

The alcoholic ethereal filtrate from which precipitate I had been separated was again evaporated on the water bath and dried in a vacuum desiccator until all traces of the solvent had disappeared. A thick amber colored syrupy liquid (II) again remained. The yield of this compound is about eight grams as compared with about one gram of the crystalline (I) compound.

Compound II (the syrupy liquid) is insoluble in dilute hydrochloric acid (does not dissolve in the acid solution even upon boiling) and dilute sodium hydroxide respectively. It also gives off ammonia when treated with twenty-five percent sodium hydroxide in the cold as described above under compound I. It gives off ammonia readily when heated in a test tube with dilute alkali.

A nitrogen determination of this compound (II), also by the Kjeldahl method, gave the results indicated below:

	Wt. of sample	Wt. of nitrogen	Percent of nitrogen
1.	0.8106 Gm.	0.054280188 Gm.	6.68 %
2.	1.1794 "	0.076826482 "	6.46 "
Average:			6.57 "

Calculated for a compound $C_{10}H_{16}O_3 . NH_3$ = 6.96 "

Product II (the syrupy amber-colored liquid) was again taken up in anhydrous ether and dry ammonia gas again passed through the solution for almost an hour in an attempt to

see whether more of the crystalline product, I, could be obtained. No white crystalline substance separated as there did when the reaction was carried out for the first time with the crystalline catnip compound, but the solution became turbid and a heavy amber colored liquid separated. The ethereal solution was again decanted from the resinous material and set aside. The resinous material was again taken up in alcohol.

After the ethereal solution had stood for many days, a very few small crystals separated. There was not enough precipitate to recrystallize. It was dried on a porous plate. Melting point of compound is 145° - 150° C.c.c.

No solid or crystalline substance separated from the alcoholic solution this time, not even after several months. The ethereal solution from which the small amount of crystalline material had been separated, was combined with the alcoholic solution, the solvent evaporated on the water bath, and the residue dried over phosphorus pentoxide. The heavy syrupy liquid remaining resembled that obtained the first time.

A nitrogen determination was again made giving the results tabulated below:

	Wt. of sample	Wt. of nitrogen	Percent of nitrogen
1.	0.5802 Gm.	0.0385647 Gm.	6.64 %
2.	0.4888 "	0.0323126 "	6.61 "

Average:

First determination 6.62 %

The compound apparently had not taken on any more of nitrogen. 6.57 "

When the above compound is dissolved in alcohol and a few drops of platinic chloride T. S. are added a crystalline precipitate comes down after standing for several days.

b). A similar reaction was carried out as described under "a" above but in this case absolute alcohol was used as the solvent instead of anhydrous ether. When the dry ammonia gas was passed through this solution, no immediate precipitate separated as under "a", but the reaction mixture turned a deep yellow. The mixture was set aside. After standing for eight or nine days, a crystalline material began to deposite in the bottom of the flask. This was filtered off, washed with alcohol and ether and dried. It also melts with decomposition at 240° C. u.c.

A nitrogen determination of this compound by the Kjeldahl method gave results which check with the crystalline compound under "a" as shown below:

	Wt. of sample	Wt. of nitrogen	Percent of nitrogen
1.	0.3222 Gm.	0.0394953 Gm.	12.25 %
2.	0.2595 "	0.0291496 "	11.22 "
Average :			11.73 "

Crystalline compound from ether solution - 11.21 %

The alcoholic filtrate from which the crystalline compound had been separated, upon evaporation of the solvent, also left a thick, viscous, syrupy, amber-colored residue.

c). Five grams of the acid were treated exactly as described under "a", also using anhydrous ether as the solvent, but instead of allowing the reaction mixture to remain at room temperature, the flask containing the reaction mixture was well stoppered and placed in a frigidaire as soon as the passage of the ammonia gas was stopped. It remained at this cold temperature for about five weeks after which it was removed from the frigidaire. The appearance of the white precipitate which had separated out at the time the ammonia gas was first passed into the solution had not changed as far as could be observed. However, after standing at room temperature for several hours it too settled to the bottom of the flask as a thick yellow resinous liquid. The supernatant ethereal solution was decanted and the resinous material taken up in alcohol in which solvent it was readily soluble.

The decanted ethereal solution was allowed to evaporate spontaneously. Upon evaporation of the solvent a white crystalline compound remained. This was carefully and thoroughly washed with ether and dried over calcium chloride.

Melting point, 122° C. The compound is insoluble in water, ether, dilute alkali, but is soluble in dilute acid. When treated with 25 percent sodium hydroxide in the solid in a test tube stoppered with a cork into which is fastened a piece of moistened red litmus paper, the paper turns blue very slowly. When heated in a test tube with dilute alkali, ammonia is given off and oily droplets settle out of the solution.

The resinous material which was taken up in alcohol began to deposit a crystalline material after standing for several days. These crystals were filtered off, washed with ether and alcohol, and dried over calcium chloride. The compound melts with decomposition at 240°- 242° C. u.c. It gives off ammonia under the same conditions as described above.

Reaction with aqueous ammonium hydroxide:

When the compound is refluxed with aqueous ammonium hydroxide two different nitrogen containing compounds are also obtained, the one a crystalline compound (I) and the other also a deep amber-colored , syrupy liquid(II).

Ten grams of the acid were refluxed for one hour with aqueous ammonium hydroxide. No immediate precipitate formed but the solution became a deep yellow. The reaction mixture was set aside in a well stoppered Erlenmeyer flask. After

standing for many days a precipitate (I) settled out. This was filtered from the solution and recrystallized from ethyl alcohol. The melting point is 195° - 196° C. u.c. The compound is insoluble in dilute alkali, dilute acid and dissolves but slowly in cold concentrated sulphuric acid. It does not give off ammonia, nor does it go into solution when heated in a test tube with dilute alkali.

The percent of nitrogen determined by the Kjeldahl method was as follows:

	Wt. of sample	Wt. of nitrogen	Percent of nitrogen
1.	0.1710 Gm.	0.0269431 Gm.	15.76 %
2.	0.1940 "	0.0299588 "	15.44 "
Average:			15.60 "

Calculated for a compound $C_{10}H_{16}O_3(NH)_2$ - 12.84 "

Less than one gram of this compound was obtained.

The filtrate from which the above described precipitate was removed was evaporated on the water bath, and the residue again refluxed with fresh ammonium hydroxide. No more solid material separated. The solution was again evaporated on the water bath leaving a thick, amber-colored, syrupy liquid (II) which was thoroughly washed with water and ether and dried in a vacuum desiccator. The residue has a slight piperidine-like odor when warm. It is insoluble in water, dilute acid and dilute alkali. It gives off ammonia

under the same conditions as the compound described on page 49 .

The percent of nitrogen found in the above compound by the Kjeldahl method was:

	Wt. of sample	Wt. of nitrogen	Percent of nitrogen
1.	0.5632 Gm.	0.03578714 Gm.	6.29 %
2.	0.2638 "	0.01882173 "	7.13 "
Average:			6.71 "

Calculated for a compound $C_{10}H_{16}S_3O$, NH - 6.96 "

The yield of this compound was about six grams as compared with less than one gram of the solid compound.

When the above product is dissolved in alcohol and a few drops of platinic chloride T. S. are added, a crystalline precipitate comes down very slowly.

When a few drops of this compound are boiled with dilute sulphuric acid in a test tube, a pine chip which is placed in the solution is colored red [21] . (Ber. 19, 46 (1886), "Die gebildeten Pyrollabkoemmlinge zeigen alle eine charakteristische Reaction. Sie faerben beim Kochen mit verduennten Mineralsaeuren einen Fichtenspahn intensiv roth".)

Reaction with acetyl chloride:

Three grams of the acid were treated with an excess (8 cc.) of acetyl chloride in the cold. The reaction mixture became slightly warm and vapors of hydrogen chloride were seen to escape when moist air was passed over the flask. These vapors turned moistened blue litmus paper red. The reaction mixture was allowed to stand for several hours (being slightly warmed toward the end of the reaction). It was then poured into distilled water, a heavy syrupy liquid settling to the bottom of the beaker. After thoroughly washing with water, the syrupy liquid was taken up in 30 to 40 cubic centimeters of toluene in an attempt to crystallize the compound from this solvent. The solution was set aside on the lower shelf of an ice box where it remained for several months. No precipitate separated from the solution.

The flask containing the reaction product was removed from the ice box and the solvent allowed to evaporate spontaneously. The residue was again a thick syrupy liquid, slightly darker in color than the product when first taken up in the toluene. When an attempt was made to wash this syrupy liquid with a small amount of dilute alkali, an immediate white fluffy precipitate settled out. This precipitate was filtered from the solution, thoroughly washed with water, and recrystallized from ethyl alcohol. The white fluffy compound which burns with a smoky flame,

leaving no residue, melts at 138° - 139° C. This compound still retains the very bitter taste of the original but the taste develops far more slowly. It is insoluble in water, dilute alkali, and dilute acid. It is ether soluble. It does not decolorize bromine in carbontetrachloride, is not oxidized by alkaline permanganate, and does not appear to react with metallic sodium in dry benzene.

An attempt was made to determine the saponification equivalent but no consistent results were obtained.

An elementary analysis of the compound was also attempted but the results were not consistent.

The alkaline solution from which the above described precipitate had been removed, together with the first aqueous washings of the precipitate, was acidified with diluted hydrochloric acid. The solution became turbid but no precipitate formed. After standing at room temperature for several days, a heavy syrupy liquid began settling out of the solution. This was separated from the aqueous layer by means of a separatory funnel, washed with water, taken up in ether, the ethereal solution again washed with water, and finally dried over anhydrous sodium sulphate. The solvent was evaporated and the residue dried over phosphorus pentoxide. The compound is insoluble in water and dilute acid. It gives a turbid solution with dilute alkali.

The neutralization equivalent and acid number were determined, using phenolphthalein as indicator.

	Neut. Eq.	Acid No.
1.	139.0	403.5
2.	139.8	401.0
3.	139.8	402.1
Average:	139.4	402.2

When the solutions from the above neutralizations were combined and evaporated on the water bath, a small amount of the solid compound melting at 137° - 138° C. separated.

Two grams of the compound were treated exactly as described above, but in the second experiment the reaction product was allowed to stand at room temperature after being taken up in the toluene solution. No crystalline nor syrupy precipitate separated even after several months. The solvent was spontaneously evaporated, leaving a thick syrupy liquid which was washed, first with dilute alkali, and then with water. The residue was taken up in ether, the ethereal solution washed with water and dried over sodium sulphate. After evaporation of the solvent the residue was dried over phosphorus pentoxide.

The product is a deep yellow colored syrupy liquid with a pleasant odor. It is insoluble in water, dilute acid, and gives a turbid solution with alkali.

The neutralization equivalent and acid number, using phenolphthalein as indicator, gave the follwoing results:

	Neut. Eq	Acid No.
1.	144.2	388.9
2.	144.7	387.7
3.	144.4	388.5
Average:	144.4	388.5

When the above solutions were combined and evaporated on the water bath, a small amount of the solid compound melting at 137° - 138° C.was also obtained.

A determination of the saponification equivalent and saponification value yielded the following results:

	Sap. Eq.	Sap. value
1.	116.2	483.1
2.	116.8	481.2
3.	116.3	483.1
Average:	116.8	483.1

The saponification equivalent and the saponification value for a compound $C_{10}H_{15}O_3 + CO(CH_3)_2$ are 113 and 495.2, respectively.

Reaction with acetic anhydride:

Three grams of the acid were refluxed for one and one-hours with an excess of acetic anhydride. After cooling,

the reaction mixture was poured into fifty cubic centimeters of distilled water and warmed on the water bath for a few minutes. A heavy liquid settled to the bottom of the flask. Upon cooling, the aqueous solution was decanted and the residue again warmed with fifty cubic centimeters of water. This was again decanted when cold and the residue washed several times with cold water. It was then taken up in ether and the ethereal solution washed first with dilute alkali and again with water. After drying over sodium sulphate, the solvent was evaporated and the residue dried over phosphorus pentoxide.

The product is a thick viscous colorless liquid, insoluble in water, dilute acid and dilute alkali. It does not decolorize bromine in carbon tetrachloride.

When dissolved in alcohol and rapidly titrated with 0.1299 sodium hydroxide, it is practically neutral to phenolphthalein. However, upon standing, more and more alkali can be added.

A determination of the saponification equivalent and saponification value gave the following results:

	Sap. Eq.	Sap. value
1.	144.8	390.9
2.	146.4	382.9
Average:	145.6	386.9

Oxidation:

a). Potassium permanganate oxidation - Several oxidation experiments of the acid with potassium permanganate were made under slightly different conditions. In every case, crystalline and liquid products were obtained. The solid products all appear to be different (all have different melting points and solubilities) while two of the liquid products appear to be the same.

1. Permanganate oxidation in neutral solution.

Ten grams of the acid, finely pulverized, were placed into a two liter flask in about 800 cc. of distilled water. A two percent solution of potassium permanganate was slowly run into this from a separatory funnel. The reaction mixture was constantly agitated. The solution was immediately decolorized and became slightly warm. The permanganate was added until a permanent pink color remained. The reaction mixture was set aside until the following day when the clear supernatant liquid was filtered from the precipitated manganese dioxide. The manganese dioxide was refluxed with alcohol and ether respectively. After evaporation of the respective solvents, no residue remained.

The clear liquid from which the manganese dioxide had been removed was now acidified with diluted sulphuric acid. The solution became turbid but no immediate precipitate separated. The solution was set aside for several days during which time a white crystalline compound (I) settled

out very slowly. Precipitate I was filtered off and the solution again set aside. After standing for some few days, more of the crystalline compound settled out. This was again filtered off and combined with the first precipitate. The filtrate was set aside in an evaporating dish and allowed to evaporate spontaneously. No more of the solid compound separated. However, after several days a yellow syrupy liquid began to settle out of the solution. When the solution had become fairly well concentrated, the yellow liquid precipitate (II) was separated from the aqueous layer by means of a separatory funnel. It was thoroughly washed with water, taken up in ether, the ethereal solution again washed with water and dilute alkali (about 0.5 %) and dried over anhydrous sodium sulphate. After evaporation of the solvent the residue was dried over phosphorus pentoxide.

Product I (crystalline precipitate) - The solid or crystalline precipitate was recrystallized twice from ethyl alcohol. Melting point, 212° - 213° C. u.c. This compound of which the yield was less than one gram, is insoluble in water, dilute acid, dilute alkali, and ether. It is soluble in cold concentrated sulphuric acid. It still retains the bitter taste of the original compound but the taste develops far more slowly than with the original.

Product II (syrupy liquid precipitate) - This compound is insoluble in water and dilute acid, but is soluble in dilute alkali.

B. Permanganate in alkaline solution.

a. At ordinary temperature - Ten grams of the acid were dissolved in three to fifo percent aqueous potassium hydroxide. A two percent aqueous solution of potassium permanganate was run into the alkaline solution, drop by drop, from a separatory funnel while the reaction mixture was constantly agitated. The reaction mixture became slightly warm. The permanganate solution was added until the pink color was no longer discharged. The solution was now set aside until the following day when the precipitated manganese dioxide was filtered off, leaving a clear alkaline solution.

The clear alkaline solution was distilled, yielding no volatile alcohol. After cooling it was shaken out with ether, the ethereal solution washed with water, dried over sodium sulphate, and the solvent evaporated. No residue was obtained. The solution was then acidified with diluted sulphuric acid. It turned slightly cloudy but no precipitate formed. However, upon slightly warming, a flocculant white precipitate came down. This was filtered off and the filtrate was distilled. About one-hundred and fifty cubic centimeters of distillate were collected. While the distillate was acid to litmus and phenolphthalein, a determination of the Du Claux[2)] number gave practically zero results, i.e., neither the original ten cubic centimeters nor the three successive ten cubic centimeter portions collected required

more than three tenths of one cubic centimeter of 0.0943 sodium hydroxide for neutralization. The distillate was returned to the original solution and the combined liquids shaken out with ether, the ethereal solution thoroughly washed with water and dilute alkali, and dried over sodium sulphate. The solvent was evaporated leaving a thick syrupy residue (II) which was dried over phosphorus pentoxide.

Product I (crystalline compound) - This compound is insoluble in water, dilute acid and dilute alkali, melting point 228° C.u.c. When refluxed with alcoholic alkali, the compound hydrolyses, although no consistent saponification results were obtained.

Product II (liquid precipitate) - This compound is insoluble in water and dilute acid, neither does it dissolve readily in dilute alkali. However, when dissolved in alcohol a neutralization equivalent and acid number were determined, using phenolphthalein as indicator. The following results were obtained:

	Neut. Eq.	Acid No.
1.	115.8	492.6
2.	113.7	493.1
3.	114.5	489.6
Average:	114.0	491.7

The above solutions were combined and precipitated

with aqueous silver nitrate, the silver salt thoroughly washed with water, alcohol and ether, and dried to constant weight over phosphorus pentoxide. A gravimetric determination of the silver in the salt gave the following results:

	Wt. of sample	Wt. of silver	Percent of silver
1.	0.4202 Gm.	0.2150 Gm.	51.1 %
2.	0.4346 "	0.2222 "	51.1 "
3.	0.3794 "	0.1934 "	50.9 "
Average:			51.03 %

Calculated for a compound whose molecular weight is 114.0 - 48.84 %

The molecular weight of the compound as calculated from the percent of silver in the silver salt is - (107.88 ÷ 0.5103) - 107.88 = 103.52.

The sodium salt of the above compound II was prepared by neutralizing with sodium hydroxide to phenolphthalein, evaporating the solution on the water bath and washing the residue with alcohol and ether. (The alcoholic and ethereal washings after evaporation left a viscous yellow residue). The salt which was still highly colored and non-crystalline was ground up in mortar with ether and the ethereal solution decanted. This process was repeated many times until the residue after drying appeared fairly white and clean. The silver salt was again prepared yielding results which

agree fairly well with those obtained from the first determination:

	Wt. of sample	Wt. of silver	Percent of silver
1.	0.4514 Gm.	0.2324 Gm.	51.48 %
2.	0.5548 "	0.2876 "	51.85 "
3.	0.5074 "	0.2616 "	51.55 "
Average:			51.56 "
First determination:			51.03 "

Both the p-bromophenacyl ester and the p-nitrobenzyl ester were prepared. In each case an oily product was obtained.

b). At a temperature between 50° to 60° C. - Twenty grams of the acid were oxidized exactly as described under (a) above until the pink color was no longer discharged. After this point the reaction mixture was warmed on the water bath between 50° and 60° C and more permanganate solution was slowly added. The solution was more slowly decolorized from this point. The manganese dioxide was filtered from the clear supernatant alkaline solution. The filtrate was again distilled, yielding no volatile alcohol. After cooling it was again shaken out with ether, the ethereal solution evaporated, leaving no residue. The alkaline solution was now concentrated on the water bath

to a small volume, cooled and acidified with diluted sulphuric acid. Upon acidification the solution gave off carbon dioxide very abundantly as indicated by an effervescence and a turbidity produced when the gas was passed into a solution of lime water.

A crystalline precipitate (I) separated from the solution almost at once. This was filtered off and purified by recrystallization from a hydrochloric solution. The yield was about two and one-half grams.

The filtrate (acidified solution) was distilled, yielding a distillate that was acid to litmus. Several hundred cubic centimeters were collected and the Du Claux value determined. This time the distillate contained a far larger percent of acid than that obtained under (a) above. The Du Claux value found was :

Original 10 cc. portion required 3.0 cc. of alkali
First 10 cc. portion required 8.1 cc. of alkali
Second 10 cc. portion required 8.8 cc. of alkali
Third 10 cc. portion required 8.8 cc. of alkali

Du Claux number :

1. 7.0
2. 7.3
3. 7.3

This agrees fairly close with the Du Claux constant of acetic acid [23] (6.8, 7.1, 7.4).

The entire distillate was now neutralized with potas-

sium hydroxide and evaporated on the water bath leaving a brown semi-crystalline residue, insoluble in ether but soluble in an excess of alcohol. The alcoholic solution upon filtration removed some of the brown material, although the solution was still highly colored. The alcoholic filtrate after evaporation at room temperature was dried over phosphorus pentoxide. About one and seven-tenths grams of crystals were obtained.

The above crystals are deliquescent when exposed to the air (potassium acetate[24] - " it is very deliquescent when exposed to the air").

When a few small crystals are placed in a test tube with a few drops of ethyl alcohol to which is added a drop of concentrated sulphuric acid and the solution slightly warmed, odors of ethyl acetate are evolved (test for acetic acid and acetates[25]).

When a few of the crystals are dissolved in water (about 1cc.) and a drop of ferric chloride T.S.is added, a deep red color is produced. This color is destroyed upon the addition of mineral acid (test for acetates[25]).

The p-bromophenacyl ester was prepared, yielding an ester melting at 85° C.(melting point of the p-bromophenacyl ester of acetic acid is 85° C.[26]).

The residue, i.e. the acidified solution, was now shaken out with ether, the ethereal solution washed with water and dilute alkali, dried over sodium sulphate and the solvent evaporated. There remained a thick syrupy residue

(II) which was dried over phosphorus pentoxide. A yield of about seven grams was obtained, practically all of which was shaken out with the first 50 cc. of ether.

Product I (crystalline compound) - This compound is insoluble in water and dilute acid but is soluble in dilute alkali, melting point 250° - 251° C. u.c.

The following neutralization equivalent was obtained:

	Neut. Eq.
1.	155.6
2.	155.5
Average:	155.55

The silver salt of the above acid yielded the following percent of silver:

	Wt. of sample	Wt. of silver	Percent of silver
1.	0.1826 Gm.	0.0836 Gm.	45.78 %
2.	0.1858 "	0.0856 "	46.06 "
Average:			45.92 "

Calculated for a monocarboxylic acid whose molecular weight is 155.6 - 41.11 %

The molecular weight as calculated from the percent of silver in the silver salt is - (107.88 ÷ 0.4592) - 107.88 = 124.87.

Product II (liquid residue) - This product is insoluble in water and dilute acid but is soluble in dilute alkali. It still retains the very bitter taste of the original acid.

The neutralization equivalent and acid number were determined:

	Neut. Eq.	Acid No.
1.	112.0	500.5
2.	111.3	503.7
3.	112.8	499.6
Average:	111.8	501.8
Product II under (a)	114.0	491.7

The silver salt of this acid gave the following percent of silver:

	Wt. of sample	Wt. of silver	Percent of silver
1.	0.4190 Gm.	0.2162 Gm.	51.3 %
2.	0.3904 "	0.2002 "	51.2 "
3.	0.3882 "	0.1992 "	51.3 "
Average:			51.26 %
Product II under (a)		51.03 and	51.56 "

While the neutralization equivalent and the acid number do not agree as closely, the silver salt agrees fairly close with the same product under (a).

Product II was again dissolved in dilute aqueous potassium hydroxide and further oxidized with a two per-cent permanganate solution. The reaction was carried out exactly as described above under (b). When the clear filtrate from which the manganese dioxide had been removed, was acidified this time no more of the crystalline precipitate was obtained. However, the solution effervesced very strongly upon acidification. When the acidified solution was distilled this time a greenish-blue liquid separated. Upon cooling, this insoluble liquid which formed the upper layer, was separated from the lower aqueous layer and purified as previously described. The residue was a heavy syrupy liquid resembling the original product.

A silver salt was again prepared yielding results which agree with the determination before further oxidation:

	Wt. of sample	Wt. of silver	Percent of silver
1.	0.4324 Gm.	0.2234 Gm.	51.66 %
2.	0.4088 "	0.2082 "	51.92 "
3.	0.3336 "	0.1684 "	51.47 "
Average:			51.68 "
First determination:			51.26 "

b). Chromic acid oxidation[24] - Ten grams of the acid were oxidized as follows: Sixty cubic centimeters of dis-

tilled water, 28 grams of potassium dichromate, and 10 grams of the finely pulverized acid were placed into a 500 cc. round bottom flask. Forty cubic centimeters of concentrated sulphuric acid were slowly added, with constant shaking, to this solution. The reaction mixture which became very warm, was cooled. After the mixture had ceased to become warm from the heat of the reaction, it was carefully heated under a reflux condenser for about two hours.

When moistened blue litmus paper was held in the mouth of the condenser it turned red very rapidly, although there were no vapors visible. When this gas was passed into a solution of calcium hydroxide an immediate white precipitate formed (indicating carbon dioxide).

The reaction mixture was cooled and then poured into 100 cc. of distilled water. A pasty mass separated. This solidified after standing for a short time. The solidified mass (I) was filtered off and the filtrate distilled, yielding a distillate (II) which was acid to litmus.

About 150 cc. of the distillate were collected and the Du Claux constant determined. The following results which indicate acetic acid were obtained:

Titration of original 10 cc. portion - 9 cc. alkali
Titration of first 10 cc. portion - 6 cc. alkali
Titration of second 10 cc. portion - 6.4 cc. alkali
Titration of third 10 cc. portion - 6.7 cc. alkali

Du Claux constant:

Unknown acid	Acetic acid
6.6	6.8
7.1	7.1
7.4	7.4

The entire distillate was now neutralized with sodium hydroxide and the solution evaporated to dryness on the water bath. The residue which was fairly white and clean (there was no brown color or impurity as in the case of the permanganate oxidation) was washed with ether and re-crystallized from ethyl alcohol.

These crystals are not deliquescent when exposed to the air.

When a drop of ferric chloride T.S. solution is added to an aqueous solution of the crystals, a red color is produced. This color is destroyed by the addition of mineral acid.(See p. 65).

When a few crystals are placed in a test tube with a few drops of ethyl alcohol to which is added a drop of concentrated sulphuric acid and the solution slightly warmed, odors of ethyl acetate are evolved (See p. 65).

Product I (solidified mass) - The solid precipitate was purified by warming on the water bath with 30 cc. of five percent sulphuric acid. This solid material upon warming again became a pasty mass which crystallized when cooled.

The crystalline material was separated from the acid solution on a suction filter, dissolved in 80 cc. of five percent sodium hydroxide and the solution filtered. The filtrate was poured into 150 cc. of ten percent sulphuric acid. The compound crystallizes very slowly from the acid solution in the form of white salt-like crystals. The precipitated crystals were filtered off, several crops of crystals being collected. The compound was further purified by again dissolving in sodium hydroxide and precipitating with sulphuric acid.

The above compound is soluble in water, very soluble in alcohol, ether, benzene and chloroform. It is insoluble in dilute acid but is soluble in dilute alkali. It no longer possesses the bitter taste of the original acid but has a decided sour taste.

The first crop of crystalline compound obtained melts, after purification, at 80° C. The following neutralization equivalent and acid number were obtained with phenolphthalein indicator:

	Neut. Eq.	Acid No.
1.	106.8	526.4
2.	106.4	527.1
Average:	106.45	526.7

The above solutions were combined and precipitated with aqueous silver nitrate. The silver salt contained the

following percent of silver:

	Wt. of sample	Wt. of silver	Percent of silver
1.	0.1220 Gm.	0.0584 Gm.	47.6 %
2.	0.1438 "	0.0700 "	48.6 "
Average:			48.1 "

Calculated for a monocarboxylic acid, whose molecular weight is 106.45 - 50.58 %

A second crop of crystals were collected and purified as above. The melting point was but one degree higher than that of the first. The neutralization equivalent was slightly lower:

	Neut. Eq.	Acid No.
1.	102.9	544.9
2.	104.1	538.6
Average:	103.5	550.6

The percent of silver in the silver salt was found to be higher than that of the first:

	Wt. of sample	Wt. of silver	Percent of silver
1.	0.2419 Gm.	0.1262 Gm.	52.17 %
2.	0.1888 "	0.0946 "	51.75 "
Average:			51.96 "

the above acid is higher than that of the comparable permanganate oxidation product as shown by the results below:

	Wt. of sample	Wt. of silver	Percent of silver
1.	0.1400 Gm.	0.0744 Gm.	53.14 %
2.	0.1704 "	0.0906 "	53.18 "
3.	0.2170 "	0.1144 "	52.71 "
Average:			53.00 "
Silver content of comparable permanganate oxidation product:			51.26 "

e). Nitric acid oxidation: - Several nitric acid oxidation experiments were attempted under different conditions.

When oxidized with dilute nitric acid, with slight warming, only a viscous brown syrupy liquid was obtained.

With concentrated nitric acid under certain conditions two products, a solid and a liquid, were obtained.

Ten grams of the acid were treated with an excess of concentrated nitric acid in a liter round bottom flask. While the acid readily goes into solution, no reaction is apparent in the cold. The reaction mixture was slightly warmed on the water bath until brown fumes were seen to escape. After the mixture had ceased to boil from the heat of the reaction, it was warmed for a short time on the water bath.

After cooling, the yellow syrupy residue was poured into distilled water and set aside in a crystallizing dish. About one gram of a crystalline water soluble, ether insoluble, compound, melting point, 100-102° C., was obtained. This compound has a decided sour taste.

The liquid product is a thick yellow syrup of which not more than three to four grams were obtained.

Reduction:

a). Catalytic hydrogenation - The original acid, hydrogenated by Professor Homer Adkins under different conditions, yielded two reduction products which have been designated as reduction products A and B.

Reduction product A - Reduction product A is the first reduction product obtained from the catalytic (Ni or Cu-Cr-oxide) hydrogenation of the acid under conditions employed to reduce ketones, viz., 125 - 150° C.

This first reduction product is a limpid liquid with a somewhat minty odor.

The boiling point under 8mm. pressure is 112-115° C.; under atmospheric pressure the compound boils without decomposition at 272° C.a.c. (The original acid boils with decomposition at 250-254° C.a.c.

The compound is also optically active but the optical rotation is much lower than that of the original acid, being $(\alpha)_D^{25^\circ}$ = + 14° 21'. (The optical rotation of the original acid is slightly more than + 58°).

The compound is insoluble in water, dilute acid and dilute alkali. (The original compound is alkali soluble).

The compound does not decolorise bromine in carbon-tetrachloride.

The compound does not form a sodium bisulphite addition product. (The original acid readily forms a sodium bisulphite addition product).

The compound reacts very slowly with metallic sodium

in dry benzene (the original acid reacts far more readily under the same conditions) yielding a more or less gelatinous residue. When two to three grams of the compound were treated with metallic sodium in dry benzene, the benzene solution decanted from the unreacted sodium after several days, and the solvent evaporated, a gelatinous residue remained. This dried to a more or less solid mass after a time. It was thoroughly rubbed in a mortar with ether and the ethereal washings decanted, leaving a fairly white crystalline product. Attempts were made to prepare both the p-toluidide and the p-bromophenacyl derivatives from this compound, but neither one yielded crystalline derivatives.

The compound reacts very slightly with phosphorus pentachloride.(The original reacts very readily with this reagent).

A determination of the saponification equivalent and the saponification value yielded results slightly lower than those obtained for the original acid:

	Sap. Eq.	Sap. Value
1.	158.2	354.54
2.	153.1	366.39
3.	155.5	360.73
Average:	155.6	360.55
Original acid:	161.0	348.5

Calculated for a compound $C_{10}H_{16}O_2$ - 168.0

Elementary analysis of the compound by Glavold gave the following results:

	Wt. of sample	Wt. of carbon dioxide	Wt. of water
1.	0.0780 Gm.	0.2048 Gm.	0.0702 Gm.
2.	0.0740 "	0.1951 "	0.0674 "
3.	0.0602 "	0.1584 "	0.0510 "

	Carbon	Hydrogen	Oxygen (by difference)
1.	71.60 %	10.07 %	18.33 %
2.	71.89 "	10.19 "	17.92 "
3.	71.75 "	9.65 "	18.60 "
Average:	71.75 "	9.97 %	18.45 "

Calculated for a compound $C_{10}H_{16}O_2$ -

C 71.42 % H 9.52 %

Reduction product E - Reduction product E is a second reduction product obtained by Professor Adkins with the same catalyst at a temperature of 250 °C., conditions favorable to the reduction of a lactone.

This second reduction product is a slightly lemon colored, viscous glycerine-like liquid.

The boiling point under 8 mm. pressure is 140-145° C.

The compound is insoluble in water, dilute acid and dilute alkali.

This compound gives a more vigorous reaction with metallic sodium in dry benzene than the original acid.

The compound reacts very vigorously with phosphorus pentachloride.

Gisvold reports the following elementary analysis of the compound:

	Wt. of sample	Wt. of carbon dioxide	Wt. of water
1.	0.0641 Gm.	0.1634 Gm.	0.0586 Gm.
2.	0.1006 "	00.2557 "	0.1046 "
3.	0.0670 "	0.1699 "	0.0604 "
4.	0.0725 "	0.1865 "	0.0718 "

	Carbon	Hydrogen	Oxygen (by difference)
1.	69.60 %	10.23 %	20.17 %
2.	69.65 "	11.13 "	19.22 "
3.	69.17 "	10.09 "	20.74 "
4.	70.27 "	11.11 "	18.62 "
Average:	69.67 "	10.64 "	19.69 "

Calculated for a compound $C_{10}H_{20}O$ -

C 69.70 % H 11.71 %

Reduction with metallic sodium in absolute alcohol:

Fifteen grams of the acid were dissolved in 500 cc. of absolute alcohol in a two liter round bottom flask and the flask placed under a reflux condenser. From 10 to 15 grams of metallic sodium, cut into small pieces, were slowly added through the condenser (the operation required from three to four hours).

The reaction mixture which became fairly hot from the heat of the reaction, turned a deep yellow in color. It was allowed to stand over night. The following day it was diluted with twice its volume of distilled water and the solvent evaporated on the water bath. A highly brown colored residue remained.

The residue was refluxed with about 100 cc. of alcohol and filtered while hot. This extraction was repeated four or five times. The alcohol extracted practically all of the colored substance.

The alcoholic filtrates were combined and evaporated on the water bath, yielding an alkaline residue. This residue was now taken up in from 200 to 300 cc. of distilled water.

A small part of the above aqueous liquid was acidified with diluted sulphuric acid. A dark brown resinous precipitate was formed.

The remainder of the aqueous liquid was exactly neutralized with diluted nitric acid and fractionally precipitated with aqueous silver nitrate. Four fractions

of the silver salt, all of which were very dark in color, were thus obtained.

A gravimetric determination of the silver in the four fractions yielded the following results:

	Fraction I	Fraction II	Fraction III	Fraction IV
1.	36.38 %	45.92 %	48.84 %	50.74 %
2.	36.08 "	46.07 "	48.76 "	50.72 "
3.	38.24 "	47.20 "	49.04 "	50.71 "
Av:	37.56 "	46.39 "	48.78 "	50.72 "

1. Unpublished notes on catnip lactone.
2. Kamm, O., Qualitative Organic Analysis, 2nd. ed. (1932), 261.
3. Unpublished results.
4. Kamm, l.c., 131.
5. Unpublished results.
6. Jenkins & Dukes, Qualitative Pharmaceutical Chemistry, 229.
7. Kamm, l.c., 151.
8. U.S.P.X., 427.
9. Kamm, l.c., 156.
10. U.S.P.X., 457.
11. C.R. Fresenius, Instruction in Qualitative Chemical Analysis, 297.
12. Kamm, l.c., 179.
13. Shriner & Fuson, Identification of Organic Compounds, 144.
14. Kamm, l.c., 149.
15. Jour. Chem. Soc., 2357 (1932).
16. Ber. 30, 503 (1897).
17. Kamm, l.c., 150.
18. Klein, Handbuch der Pflanzenanalyse, Vol. I, 205.
19. Kamm, l.c., 206.
20. Kamm, l.c., 152.
21. Knorr, Ber. 19, 46 (1886).
22. Kamm, l.c., 152.
23. Ibid., 153.
24. U.S.P.X., 295.
25. Ibid., 440
26. Kamm, l.c., 179
27. Shriner & Fuson, Id c., 139.

Distillation

As previously stated, (See p. 19) when the acid is distilled under atmospheric pressure it boils with decomposition at 250-254° C.u.c.

From 5 to 10 grams of the acid were carefully distilled in a 50 cc. distillation falsk, the distillate being collected in a similar flask. The distillate separated into two layers, an upper light yellow limpid liquid layer with a characteristic penetrating minty odor, and a lower aqueous layer. No gas could be detected.

A second distillation was made with an attempt to measure the quantity of water given off. Twelve grams of the acid were placed into a 250 cc. distillation flask which had a 12 to 16 inch side arm fractionating column. A small condenser was attached to the small tube near the top of the fractionating column . One thermometer was placed in the distillation flask while a second thermometer was placed in the top of the fractionating column. The distillate was collected in a graduated cylinder.

The distillation was started with a gentle heat which was gradually increased. Decomposition was indicated by white vapors and bumping. Water slowly distilled over, a little more than 0.8 Cm. was collected (it was difficult to get all the water droplets out of the condenser). The calculated quantity of water given off by 12 grams of the acid if one molecule is eliminated, is about 1.1 grams.

The heating was continued for almost two hours , very little oil coming over (the few drops that did distill over also formed the upper layer of the distillate). The lower thermometer registered 270° C. while the upper one registered from 80-90° C. The distillation was now stopped and the light yellow liquid in the distillation flask was cooled after which it was transferred to a 50 cc. distillation flask. The liquid now distilled over very readily with no more decomposition around 250° C.

The distillate is a light yellow limpid liquid with a penetrating minty odor, resembling peppermint oil. It is neutral to litmus. When the oil, dissolved in neutral alcohol, is rapidly titrated with standard alkali, it is practically neutral to phenolphthalein. However, it has a fading end point and more and more alkali can be added over a period of several days until a permanent pink color remains.

A determination of the saponification equivalent and saponification number gave the results indicated below:

	Sap. Eq.	Sap. No.
1.	191.8	291.77
2.	191.7	293.67
Average:	191.75	292.72
Original acid:	141.0	348.3

When a few drops of the distillate are dissolved in

carbon tetrachloride and a five percent bromine solution of carbon tetrachloride is slowly added, the solution is readily decolorized. (The original acid does not decolorize bromine in carbon tetrachloride).

The distillate still shows evidence of a carbonyl group as indicated by the formation of a phenylhydrazone, semicarbazone, thiosemicarbazone and oxime. However, all of these are formed ~~the~~ more slowly and all have different melting points than the corresponding derivatives obtained from the original acid.

a). Phenylhydrazone - The phenylhydrazone [1] was prepared by dissolving the oil in alcohol, adding water up to the point of turbidity and then adding an equal quantity of phenylhydrazine. A yellow needle-like derivative is precipitated. The hydrazone recrystallized from a hydroalcoholic solution melts at 174° C. u.c. (No crystalline phenylhydrazone was obtained from the original acid).

A nitrogen determination of the above hydrazone by the Kjeldahl method yielded the following results:

	Wt. of sample	Wt. of nitrogen	Percent of nitrogen
1.	0.2026 Gm.	0.02596 Gm.	12.81 %
2.	0.2252 "	0.02613 "	11.60 "
Average:			12.2 "

Calculated for a phenylhydrazone $C_{10}H_{16}O_2 \cdot NHC_6H_5$ - 10.21 "

b). Semicarbazone - (See p. 36 for prep.) The semicarbazone, recrystallised from a hydroalcoholic solution, melts at 163-164° C. u.c. That of the original acid melts at 160-161° C. u.c.

c). Thiosemicarbazone - (See p. 36 for prep.) The thiosemicarbazone recrystallised from alcohol in the from of beautiful white scales melts at 165° C. u.c. This compound is insoluble in benzene while the thiosemicarbazone obtained from the original acid is soluble in the latter solvent from which it crystallises in the from of white needles melting at 180-185° C. u.c.

d). Oxime - (See p. 37 for prep.) This oxime crystallises from the acidified solution very slowly, taking almost a week to come out, while the oxime of the original acid precipitates immediately upon acidifying the reaction mixture. The melting point of the above oxime is 83-84° C. while that of the original acid is 134-135° C.

The four derivatives here described were obtained from both of the above distillation liquids.

1. Kamm, l.c.,155.

Non-alkali Soluble Fraction of Catnip Oil

The 1934 and 1935 catnip oils were obtained from the steam distillation of the above ground portion of the plant which was harvested during the latter part of July and the early part of August. The material consisted in part of catnip grown in the gardens of the Wisconsin Pharmaceutical Experiment Station under the direction of Professor W. O. Richtmann, and in part of wild flowering herb gathered from this vicinity.

The 1934 oils were distilled by O. A. Gisvold while the 1935 oils were distilled by P. J. Jannke.

The 1934 oils consisted of the following three lots:

1. 70 Gm.
2. 135 "
3. 93 "

All of the above fractions were very dark brown in color and had strong penetrating odors.

The 1935 oils also consisted of three lots:

1.	858 Gm.	Sp. G.		1.8750
2.	142 "	"	"	1.335
3.	181 "	"	"	1.359

Lot two consisted of first distillate and cohobated oil while lot three consisted entirely of cohobated oil. These oils had the characteristic catnip oder and were much lighter in color than the 1934 oils.

The three fractions of the 1934 oils were combined

and shaken out separately with alkali as described on page 15. The first fraction of the 1935 oils was shaken out separately while the last two fractions were combined and shaken out together.

The non-alkali soluble fractions of both the 1934 and 1935 oils were now combined and subjected to steam distillation. About 38 grams of a bluish-green oil with a peppermint-like odor were obtained.

Sp. G. 22° = 0.9087; (Hixon[1] reports d_{25} = 0.900).

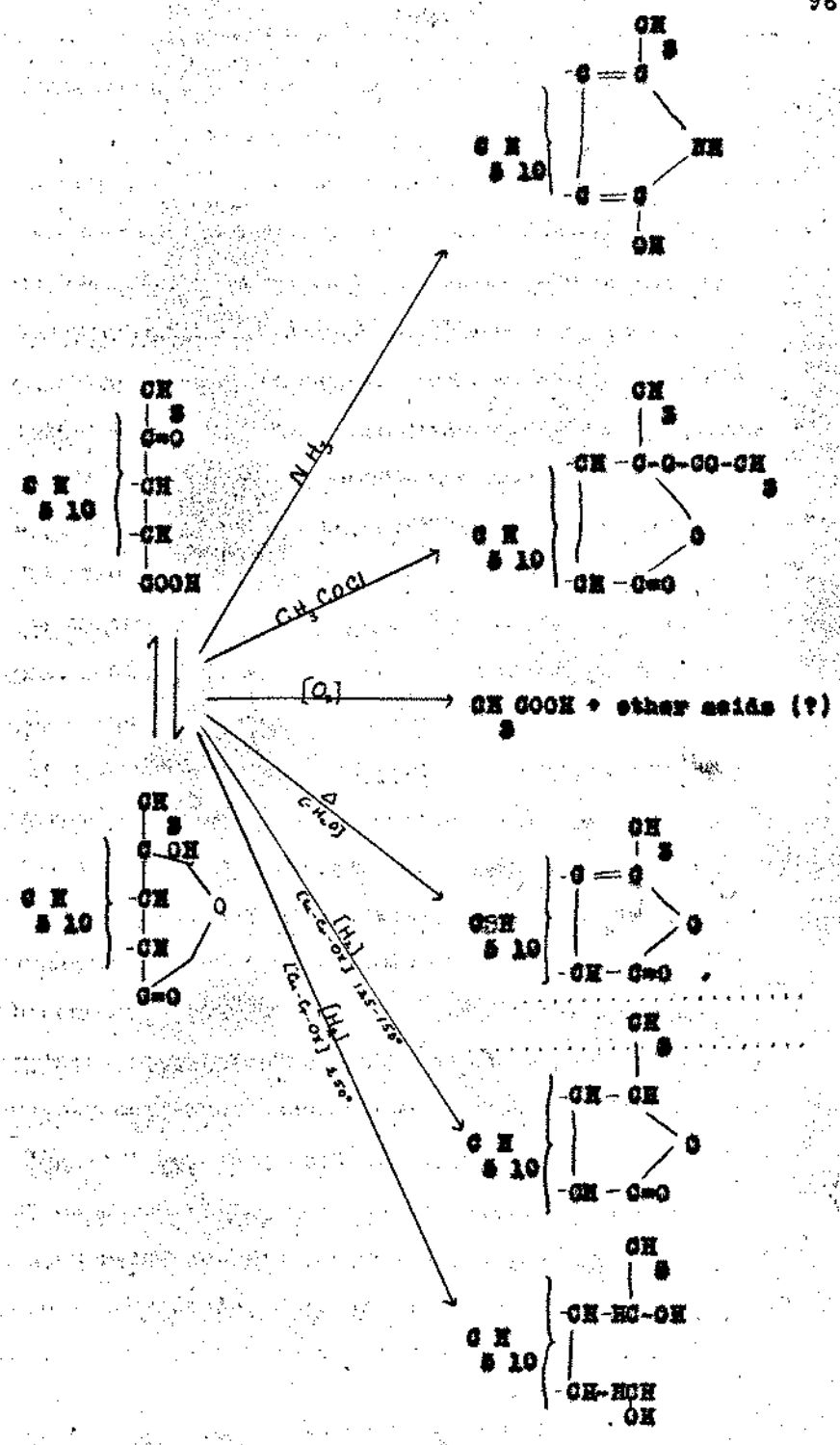
$(\alpha)_D^{22^{\circ}}$ = -9° 8.6'; (Hixon[1] reports $(\alpha)_D^{22.5^{\circ}}$ = -14.6°)

No constant boiling point was obtained. The oil appears to separate into three fractions. Fraction I came over between 160-175° C; fraction II between 230-240° C; fraction III leaves light yellow residue which remained in the distillation flask.

Saponification number, 81 (average); (Hixon[1] reports 84).

Saponification after acetylation, 134(average); (Hixon[1] reports 84).

1. Jour. Am. Pharm. Ass., 11, 96 (1922).


NH3
C6H5COCl
[O]
Δ (C4H8O)
[H] (Cu-Cr-Ox) 185-195°
[H] (Cu-Cr-Ox) 250°