TABLE I.—MIXTURES OF KNOWN COMPOSITION.

			Vacuum distillation.					
No.	Ester content. %.	Wt. sample. G.	Pressure. Mm.	Temp. of distn. of bulk.	Time. Hrs.	Ester found. %.	Ester found. % theoretical.	Ester found × 1.28.
34	2.50	100	3	31.0°	4	1.97	78.8	2.52
38	2.00	100	3	36.0°	$3^{1}/_{2}$	1.58	79.0	2.02
66	1.00	100	3	..	$4^{1}/_{2}$	0.77	77.0	0.99
67	1.00	200	..	..	6	0.79	79.0	1.01

TABLE II.—NATURAL LEMON OILS.

No.	Aldehyde content. % citral.	Wt. sample. G.	Vac. distn. Hours.	Ester found. %.	Corrected ester content. %.	Ratio esters to aldehydes.
54001	5.4	100	$3^{3}/_{4}$	1.32	1.69	0.31
54001	5.4	100	4	1.36	1.74	0.32
53933	4.9	100	$4^{1}/_{3}$	1.05	1.34	0.27
53933	4.9	100	$2^{3}/_{4}$	1.08	1.38	0.28
53955	4.8	100	$4^{1}/_{2}$	0.99	1.27	0.26
53955	4.8	100	$3^{1}/_{2}$	0.97	1.24	0.26

TABLE III.—"TERPENELESS" LEMON EXTRACTS.

No.	Wt. sample. G.	Vol. distillate. Cc.	Ester found. %.	Corrected ester content. %.
75	400	700	0.11	0.14
79	400	600	0.07	0.09
80	400	600	0.08	0.10

Summary.

The following method, in brief, is suggested for the determination of the volatile saponifiable matter, calculated as linalyl acetate, contained in citrus oils. The terpene fraction is distilled *in vacuo* from a large, say, 100 g. sample, and the remaining volatile oil removed by steam distillation. The aldehydes in the steam distillate are condensed with semicarbazide hydrochloride and the esters determined in the presence of the semicarbazone by saponification with KOH. The process is applicable to the corresponding extracts by distilling off all the readily volatile matter and treating this exactly as the steam distillate obtained in the examination of the oils. The manipulation described in the text should be adhered to.

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A STUDY OF THE CHEMICAL AND PHYSICAL PROPERTIES OF OILS DISTILLED FROM THE VARIOUS PARTS OF THE PLANT ACORUS CALAMUS, L.

BY G. A. RUSSELL.[1]

Received August 3, 1915.

Acorus calamus, L., (Family Araceae) is found in the moderate zones of all the countries in the northern hemisphere, being indigenous to the

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[1] Published by permission of the Secretary of Agriculture.

eastern half of North America, and found as far north as Nova Scotia. It grows usually in low, wet and boggy places. In the drug market it is known under the name of "calamus," the marketable portion of the plant being the unpeeled rhizome.

The cultivation of calamus is reported to have been conducted in Poland in the thirteenth century, and in Germany in the sixteenth century.[1] Clusius is reported as having cultivated calamus in 1574 from a root received from Asia Minor. He distributed the plant to other botanists in Belgium, Germany and France, from which latter place it was introduced into England in 1596, and there grown by Gerard. During the later centuries its cultivation has not been carried on to any great extent, the supply coming from natural sources.

Distillation of the oil of calamus has been carried on practically from the time the plant was first cultivated, mention of the distilled oil being found in the price ordinance of Frankfurt in 1582 and in the Dispensatorium Noricum in 1589.[2] A chemical examination of the oil was first reported by Wendel in 1718. Since then other investigators have from time to time reported on the volatile oil. These investigators do not give the origin of the oils examined, but they probably came from plants collected in the wild state.

During the seasons of 1913 and 1914 a small quantity of calamus was grown on upland soil at Madison, Wis. The plants flourished, and at the close of the season of 1914 they were dug and the various parts distilled with steam. The aerial parts were distilled while yet green and fresh. The rhizomes and roots were first air dried, then separated and distilled. The fresh aerial parts yielded on distillation 0.123% oil, the dried rhizomes 0.638%, and the dried roots 2.50%. In addition to these, a small quantity of air-dried rhizomes from Bell, Md., was distilled, and also a small quantity of dry rhizomes obtained in the open market. The former yielded 0.95% oil, and the latter 1.493%. The yield of oil from rhizomes, as heretofore reported, is greater than in any of the above. No doubt freshly dried rhizomes from plants grown in their natural habitat yield more oil than those which have laid in stock for some time. Compared with what has heretofore been reported, the yield of oil from the rhizomes purchased in the open market is low, the age of the samples probably accounting for the low percentage. The yield of oil from rhizomes grown on upland at both Madison, Wis., and Bell, Md., is much lower than any hitherto reported. These low yields are probably due to the fact that the plant was taken from its natural habitat and grown in entirely new environments.

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[1] Bentley and Trimen, "Medicinal Plants," 4, 279 (1880).

[2] Gildemeister and Hoffmann, "The Volatile Oils," 1900, p. 301. Translated by Edward Kremers.

Physical Appearance of the Oils.—The oil from the fresh tops of calamus was straw yellow in color, with a pleasing aromatic camphor-like odor, and an acrid, spicy, somewhat bitter taste. The oil from the rhizomes grown at Madison, Wis., was light reddish brown in color. The odor was aromatic, somewhat camphoraceous, resembling the odor of the freshly dug rhizomes, and the taste acrid and bitter. The oil from the roots was golden yellow in color with a pleasant aromatic camphor-like odor and a pungent, bitter, acrid taste. The oil obtained from the rhizomes grown at Bell was similar in all respects to that produced at Madison, Wis. The oil from the rhizomes obtained in the open market was brownish yellow in color, with a pungent, somewhat aromatic and slightly camphoraceous odor, and a pungent, bitter taste.

Physical Constants of the Oils.—The usual physical constants, density, specific rotation, and index of refraction, were determined. The results are tabulated in Table I.

TABLE I.

Physical Constants of Oils from Acorus Calamus.					Chemical Constants.			
Part distilled.	Geographic source.	Density at 23°.	$[\alpha]_D$ at 23°.	n_D at 23°.	Acid number.	Ester number.	Saponification number.	Acetylization number.
Tops	Madison, Wis.	0.9509	+12.2	1.5035	None	12.6	.....	53.05
Rhizomes	Madison, Wis.	0.9547	+21.7	1.4990	None	15.5	.....	38.40
Roots	Madison, Wis.	0.9491	+18.7	1.5065	None	23.7	.....	42.10
Rhizomes	Bell, Md.	0.9938	....	1.5140	8.15[1]	55.3	63.45	.....
Rhizomes	Open market	0.9945	....	1.5080	5.75[1]	42.5	48.25	.....

From the density figures little comparison can be drawn as to the constituents of the oils; the range being between 0.9 and 1.0 indicates a mixture of terpenes and possibly some oxygen derivatives. The high specific gravity of the oils from the rhizomes grown at Bell and those obtained in the open market is partially due to age, the constant having been determined eight weeks after distilling.

All parts of the plant yield oils with dextrorotatory properties. Being optically active, all these oils must contain some compound, or compounds, with asymmetric carbon atoms. Owing to the small amounts of oil obtained from the other rhizomes distilled, an observation could not be made of their rotation.

The index of refraction of the oils from all parts of the plant lies within a very small range. All the oils have a low index of refraction, indicating the absence of compounds containing double bonds.

Solubility of the Oils.—Oil from the fresh aerial part of calamus was found to be soluble in 90% alcohol with turbidity in 5 volumes or over; soluble in 18 volumes of 70% alcohol and clear in excess.

Oil from the rhizomes grown at Madison was soluble in all proportions of both 90 and 70% alcohol.

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[1] Determined eight weeks after distilling.

Oil from the roots grown at Madison was soluble in 6 volumes of 90% alcohol, and clear in excess, also soluble in 40 volumes of 70% alcohol and clear in excess.

Since terpenes and sesquiterpenes decrease the solubility, and oxygenated compounds increase the solubility of an oil in alcohol, a comparison of the oils from the various parts of the plant is made possible. The oil from the rhizomes was very soluble in 90% alcohol, that from the tops less soluble, and that from the roots still less soluble. This characteristic of the oils indicates that a greater portion of terpenes or sesquiterpenes is present in the oil from the roots than in either the oil from the tops or rhizomes, while of the latter two the oil from the tops contains the greater amount of terpenes or sesquiterpenes. The same characteristics are manifested when the various oils are dissolved in 70% alcohol. The high solubility of the oil from the rhizomes, and the lower solubility of the oils from the tops and roots, is also probably due in part to the larger amounts of oxygenated compounds present in the oil from the rhizomes than in either of the other oils used in comparison.

Chemical Constants of the Oils.—In determining the chemical constants the usual methods were employed and the usual determinations made. The results are tabulated in Table I.

No free acids were found in the freshly distilled oils from the various parts of the plant. An index to the rapidity with which free acids are formed in the oil from the rhizome is found in the acid numbers of the two oils from the rhizomes grown at Bell, Md., and those secured in the open market, respectively.

Esters are found in all parts of the plant, as indicated by the values found. The greatest amount is found in the roots, the least in the tops. This would indicate that esters are formed more rapidly in that part of the plant furthest removed from air and light. That the ester value increases with storage is shown by the numbers obtained in the oils from the rhizomes grown at Bell and from those obtained in the open market.

In determining the acetyl value, the method as outlined in Gildemeister and Hoffmann[1] was followed. Alcohols are present in all the parts of the plant, being in greatest abundance in the tops and least in the rhizomes. This is made known by the saponification number found after acetylization, which in these oils is greatest in the oil from the tops. The values found point to the probability of the production of alcohols in those parts of the plant where the greatest activity is taking place, namely, the tops and roots.

Tests for Phenols and Aldehydes in the Oils.—A qualitative test for phenols gave negative results in all the oils, as did a quantitative test. The latter was made by shaking 5 cc. of oil with a 5% solution of sodium

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[1] *Loc. cit.*

hydroxide and allowing the mixture to stand for 25 hours. No diminution could be noted in the volume of oil. The alkaline solution was then run off, acidified with sulfuric acid, and distilled with steam. The distillate tested with ferric chloride gave negative results in all the oils from the various parts of the plant. It is concluded, therefore, that no phenols are present in these oils.

A qualitative test for aldehydes by means of Schiff's reagent gave positive results in all the oils. In all cases 2 cc. of the reagent were used and one drop of oil. From the density of the color produced, an approximate comparison can be made of the amounts of aldehyde present. Oil from the tops gave the deepest coloration, followed by that from the rhizomes and roots, in the order stated. From this qualitative test it may be inferred that the production of aldehydes is greatest in the part of the plant exposed to the action of sun and air and that this production diminishes as these factors are more or less shut off.

Combined Acids in the Oils.—Owing to the small amounts of oils available for investigation, this determination was made on the oil just previous to fractionation. The oils were saponified with alcoholic potassium hydroxide, water added and the whole heated on a water bath until the alcohol was expelled. The oil which separates out was removed, and the aqueous alkaline solution shaken out with ether to remove any adhering oil. The alkaline solution was then evaporated on a water bath to a small volume, treated with an excess of sulfuric acid and distilled with steam. The distillate was tested for acidity with litmus paper and, where any oily globules separated, these were removed by shaking out with ether, the ether evaporated and the insoluble acids thus obtained neutralized with 0.02 *N* potassium hydroxide and precipitated with 0.1 *N* silver nitrate.

All the oils contain small amounts of soluble and insoluble acids in combination. The odor of the distillates was quite pronounced, but not extremely disagreeable, indicating that the acids were of comparatively low carbon content. An attempt to produce stable silver salts of the acids from the oils of the rhizomes and roots failed, although every precaution was taken to prevent immediate reduction. The oil from the tops was found to contain a soluble acid, butyric acid, and an insoluble acid, heptoic (Oenanthylic) acid.

Silver butyrate requires 55.3% Ag. Found 56.73%.
Silver heptoate requires 45.5% Ag. Found 44.89%.

Fractionation of the Oils.—The saponified oils were fractionated under 14 mm. pressure. Fractionation was carried on in a three-bulb Ladenburg flask and the heat was so regulated that the oils all distilled with approximately the same rapidity. Seven fractions were obtained from each oil. The small amounts of oil available and the small fractions obtained, made it impossible to refractionate the fractions and precluded the chemical examination of the fractions obtained. The fractions as obtained and their physical constants are tabulated in Tables II, III, and IV, and indicated graphically in Fig. 1.

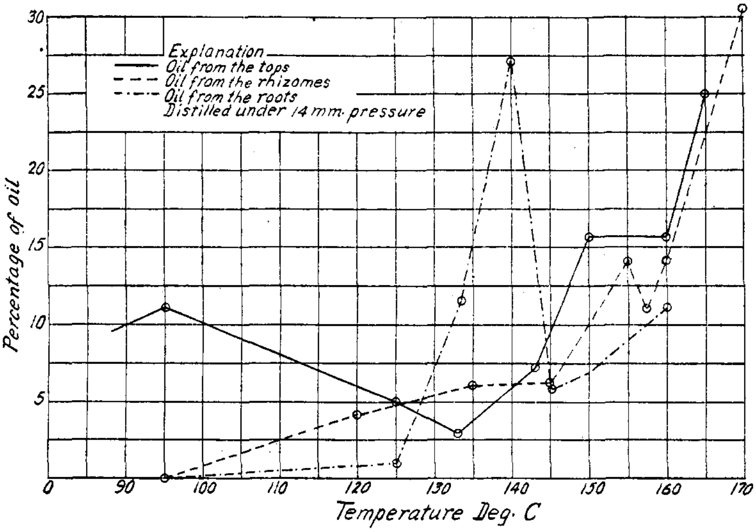

Fig. 1.—Fractionation curves of oils from the tops, rhizomes and roots of *Acorus Calamus.*

TABLE II.

Fractionation of the Saponified Oil from the Tops of Acorus Calamus.

Fraction.	Temperature.	% distilled.	Color.	Odor.	Density at 23°.	$[\alpha]_D$ at 23°.	N_D at 23°.
1	[1] to 95°	11.60	Water white	Limonene-like	0.8544	...	1.4898
2	95–125°	5.12	Water white	Limonene-like	0.9198	...	1.4950
3	125–133°	3.10	Water white	Camphoraceous			
4	133–143°	7.07	Water white	Camphoraceous, slightly disagreeable	0.9452	...	1.5024
5	143–150°	16.72	Very pale straw, yellow	Decomp. odor	0.9695	+6.1	1.5128
6	150–160°	16.17	Pale yellow	Decomp. odor, more pronounced	1.00880	+7.3	1.5240
7	160–165°	24.93	Yellow	Decomp. odor, very pronounced	1.0317	+7.7	1.5292
8	Over 165°	15.26	Deep reddish brown	Disagreeable	....	...	....

At 165° decomposition took place in the distilling flask marked by a sudden decrease in temperature. The constituents of this oil are extremely high boiling, about 25%, boiling above 160° at the pressure of 14 mm. The indications point to a large amount of sesquiterpenes present in this oil.

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[1] The oil begins to distil at 60°.

TABLE III.

Fractionation of the Saponified Oil from the Rhizomes of Acorus Calamus.

Fraction.	Temperature.	% distilled.	Color.	Odor.	Density at 23°.	$[\alpha]_D$ at 23°.	N_D at 23°.
1	[1] to 120°	4.17	Very pale straw yellow	Limonene-like	0.9272	....	1.4793
2	120–135°	6.00	Very pale straw yellow	Camphoraceous	0.9381	+16.3	1.4870
3	135–145°	6.13	Very pale straw yellow	Somewhat disagreeable, decomp. odor	0.9420	+10.4	1.4938
4	145–155°	14.30	Pale straw yellow	Rather disagreeable, decomposed odor	0.9480	+4.3	1.5032
5	155–157°	10.95	Straw yellow	Rather disagreeable, decomposed odor	0.9585	+2.0	1.5055
6	157–160°	14.03	Straw yellow	Rather disagreeable, decomposed odor	0.9670	inactive	1.5072
7	160–170°	30.42	Greenish yellow	Rather disagreeable, decomposed odor	0.9883	—3.2	1.5112
8	Over 170°	13.93	Deep reddish brown	Decomp. odor	....	....	....

At 170° sudden decrease in the temperature marked a decomposition change taking place in the distilling flask. The oil is composed chiefly of high boiling constituents, probably sesquiterpenes, or closely related products.

In fraction two the greatest portion of the oil came over between 130–135°.

In fraction three the greatest portion of the oil came over between 135–140°.

In fraction four the greatest portion of the oil came over between 145–150°.

TABLE IV.

Fractionation of the Saponified Oil from the Roots of Acorus Calamus.

Fraction.	Temperature.	% distilled.	Color.	Odor.	Density at 23°.	$[\alpha]_D$ at 23°.	N_D at 23°.
1	[1] to 125°	0.918	Water white	Camphoraceous	....	....	1.5000
2	125–135°	10.97	Light straw	Borneol-like	0.9336	+24.1	1.5000
3	133–137°	21.25	Light straw	Camphoraceous	0.9346	+17.6	1.5038
4	137–140°	27.09	Light straw	Camphoraceous	0.9381	+19.1	1.5045
5	140–145°	5.79	Light straw	Camphoraceous	0.9443	+19.9	1.5060
6	145–150°	6.82	Light lemon	Decomp. odor	0.9503	+19.4	1.5082
7	150–160°	11.40	Lemon yellow	Decomp. odor	0.9710	+11.1	1.5130
8	Above 160°	15.75	Deep reddish brown	Disagreeable decomposed odor	....	....	....

At 160° decomposition takes place in the distilling flask marked by a sudden decrease in temperature.

The major portion of this oil distils below 140° and its composition is probably more or less terpenic in character.

Summary.

Acorus calamus cultivated on upland soil yields less oil than that grown in its natural habitat. All parts of the plant contain oil, the roots having the largest percentage.

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[1] The oil begins to distil at 95°.

The oils obtained by steam distillation from the various parts of the plant, namely, aerial, rhizome, and roots, possess varying physical and chemical constants. The results of fractionation of these oils indicate that the components of each are present in varying amounts, also that these components vary to some extent.

Further work on the composition of these oils will be undertaken when larger supplies of oil are obtainable.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL COLLEGE.]

THE ACTION OF TRIOXYMETHYLENE ON *p*-XYLENE IN THE PRESENCE OF ALUMINUM CHLORIDE.

BY RALPH C. HUSTON AND DWIGHT T. EWING.

Received July 26, 1915.

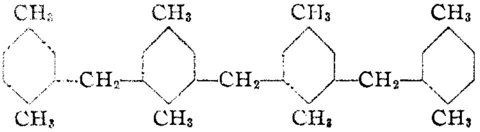
Frankforter and Kokatnur,[1] as a result of their study of the action of trioxymethylene on benzene, toluene, *o*-xylene and mesitylene, in the presence of aluminum chloride, conclude that four benzene nuclei react with a molecule of trioxymethylene to form diphenylmethane, and anthracene or their homologues, hydrogen being liberated in the reaction.

$$4C_6H_6 + (CH_2O)_3 + AlCl_3 = CH_2(C_6H_5)_2 + C_{14}H_{10} + 3H_2O + AlCl_3 + H_2.$$

In connection with other work on *p*-xylene which is being carried on in this laboratory an investigation of the behavior of this compound with trioxymethylene and aluminum chloride has been made.

The conditions of experiment were practically the same as those described by Frankforter and Kokatnur (see Experimental Part). From the resulting mixture, besides some unchanged xylene and a little toluene,

(I).



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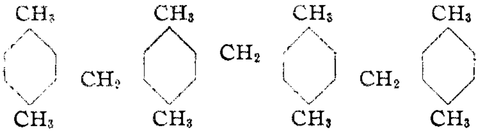

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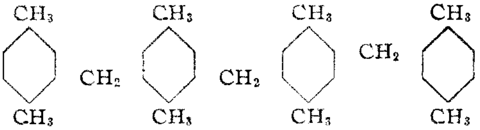

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[1] THIS JOURNAL, 36, 1529 (1914).