two elements are converted by air into the pentoxides, much more readily than was to be expected from the statements in the literature.

The experiments were made by dissolving the organic compound in dilute alcohol, adding the arsenious or antimonious oxide and boiling the mixture for a number of hours, in a reflux apparatus. The condenser employed consisted of an ordinary quill tube, about 18 inches in length. At the completion of the experiment the liquid always possessed a distinct odor of alcohol. The oxides were employed in varying proportion and the presence of the organic compounds, other than alcohol, appeared to exert little if any effect on the results. Arsenious oxide (0.5 gram), after being boiled during 26.5 hours, with 95 per cent. alcohol (3 cc.) and water (5 cc.), was found to have been converted completely into arsenic acid. Similar results were obtained with antimonious oxide.

It is, perhaps, hardly necessary to say that the arsenious and antimonious oxides employed were free from the higher oxides. The experiments described in this note were carried out, at my suggestion, by Mr. Volney A. Ray. J. BISHOP TINGLE.

MCMASTER UNIVERSITY, TORONTO, CANADA.

CHAMPACA OIL.

BY BENJAMIN T. BROOKS.

Received August 12, 1911.

From time to time small samples of so-called champaca oil have reached Europe but in most cases these samples have had an uncertain origin and, moreover, European chemists have never had a sufficient quantity of the oil for thorough investigation.

True champaca oil, prepared from the flowers of *Michelia champaca* L., should not be confused with "champaca wood oil," distilled from the wood of *Bulnesia sarmienta* Lor. The sesquiterpene alcohol champacol, or guaiol, which is characteristic of the latter oil does not occur in true champaca oil.

There are at least four species of *Michelia*, which are well known in the Indo-Malay region, of which *Michelia champaca* L. is probably the best known.

Michelia champaca L. is a tree which attains a great size in certain localities. The author has seen specimens of this tree in the Royal Botanical Gardens at Peradeniya, Ceylon, which were over three feet in diameter and the curator, Mr. H. F. McMillan states that they sometimes reach even greater dimensions. With proper care the tree can be cultivated from either seed or cuttings. Marcottage is not a success with this species, though good results are thus obtained with *Michelia longifolia* L. The flowering season ordinarily lasts from the middle of June to about the middle part of October. The young trees bear flowers abundantly in the fourth year from seed. According to a recent bulletin of the firm Roure-Bertrand Fils[1] the perfume from Philippine champaca is stronger and sweeter than that of the Singapore, Penang, Colombo or Peradeniya flowers, apparently resembling Philippine ylang-ylang oil in this respect.

The fragrance of the white flowers of *Michelia longifolia* L. is altogether different from the flowers of "yellow champaca" or *M. champaca* L., and, as will be shown in the experimental part of this paper, the two oils have no constituents in common.

Michelia fuscata is a very small tree or shrub. According to Mr. H. F. McMillan, of Peradeniya, the flowers of this shrub are the most fragrant of any flower growing in Ceylon. At present these flowers are not available in sufficient quantity for a study of their essential oil.

Michelia nilagirica is a mountain species, the flowers of which are also fragrant but their odor is not as delicate as champaca.

Schimmel & Company[2] reported benzoic acid as occurring in a sample of champaca oil examined by them, but from the rest of their description this sample probably contained ylang-ylang oil. In 1907 the same chemists[3] described a champaca oil which was stated to have been prepared by distilling a mixture of the white (*M. longifolia*) and the yellow flowers (*M. champaca*). This oil contained linalool to the extent of 60 per cent. It also contained methyleugenol and an ester of methylethylacetic acid. I have found these substances in the oil from "white champaca" but altogether absent from the essential oil of the yellow flowers.

Bacon[4] recently examined an authentic oil prepared in Manila from champaca flowers and showed the presence of isoeugenol, to the extent of 3 per cent. of the oil.

In the oil prepared from champaca flowers, yield 0.37 per cent., I have shown the presence of phenylethyl alcohol, cineole, isoeugenol, benzyl alcohol, benzaldehyde, benzoic and acetic acids. The oil is fluorescent, probably owing to the presence of a small quantity of methylanthranilate.

The constants of two specimens of the oil are as follows:

	I.	II.
Specific gravity $\frac{30^\circ}{30^\circ}$	0.9040	0.9107
Refractive index, $\frac{30^\circ}{D}$	1.4640	1.4688
Ester number	124.0	146.0
Ester number after acetylating	....	199

The chemical examination of champaca oil is rendered unusually difficult by the ease with which the oil resinifies. Treatment with sodium bisulfite slightly diminishes the tendency to form resin.

---

[1] *Bulletin of Roure-Bertrand Fils*, **1**, 26 (1909).

[2] *Semi-annual Report*, **1**, 11 (1897).

[3] *Ibid.*, **2**, 33 (1907).

[4] *Philipp. J. Sci.*, (*A*) **5**, 257 (1910).

The two most important constituents of champaca oil thus far determined are phenylethyl alcohol and cineole. The fine quality of champaca perfume is due largely to the presence of phenylethyl alcohol, which occurs both free and as an ester.

The importance of this alcohol in German oil of roses has recently been shown by Walbaum and Stephan[1] and Soden and Rojahn.[2] Benzoic acid and benzaldehyde are apparently only minor constituents and may result from the oxidation of benzyl alcohol, since an energetic oxidizing enzyme is present in the flowers. The presence of this oxidase also makes it quite probable that traces of the highly aromatic aldehyde, phenylacetaldehyde, are also present in the oil. Walbaum and Stephan conclude that traces of this aldehyde are present in German rose oil.

On standing, champaca oil deposits a comparatively large amount of a crystallin compound melting at 165–166°. This substance is a ketone. The presence of the oxidation products of benzyl alcohol and the crystallin ketone in champaca flowers, together with the oxidizing enzyme, is of some theoretical interest as showing how aldehydes, ketones and other oxidation products, found in many essential oils, may be formed. The tendency of benzyl alcohol slowly to form benzaldehyde by oxidation in the air is well-known but its oxidation almost certainly would be accelerated by an oxidase such as occurs in champaca flowers. Thus valerian root[3] and vanilla[4] owe the development of their characteristic odoriferous compounds to the activity of oxidizing enzymes. Work by the author with Dr. Arthur Koch, in Göttingen, now in the course of completion, has shown the presence of oxidizing enzymes in many other plants yielding essential oils which contain large per cents. of aldehydes or ketones.

The crystallin ketone in champaca flowers was first studied by Bacon[5] who showed that its empirical formula is $C_{16}H_{20}O_5$ and that it forms a crystallin phenylhydrazone and semicarbazone.

The substance is optically active. In alcohol solution it shows the rotation $[\alpha]_D^{30^\circ} = -82.5^\circ$. The compound reacts quantitatively with two molecules of sodium hydrogen sulfite forming a sulfonic acid salt, from which it is impossible to regenerate the original ketone in the usual manner. Since Knoevenagel has shown this behavior to be a property of the group $—HC{=}CH—CO$ it may be concluded that this group is present in the champaca ketone.

The ketone reacts with one molecule only of phenylhydrazine forming a beautiful, crystallin phenylhydrazone having the formula $C_{16}H_{20}O_4$ =

---

[1] *Ber.*, **33**, 2304 (1900).

[2] *Ibid.*, **33**, 1720 (1900).

[3] Carle, *J. Pharm.*, [4] **12**, 148.

[4] Lecomte, *Compt. rend.*, **133**, 745.

[5] *Philipp. J. Sci.*, (*A*) **5**, 257 (1910).

$N.NHC_6H_5$ and melting sharply at 161°. No hydroxyl groups are present. The remaining four oxygen atoms in the molecule are bound as an ester of succinic acid. One carboxyl group of the latter is combined as the ethyl ester and the other is bound to a hypothetical ketone alcohol, which according to the empirical formula given by Bacon must be $C_{10}H_{12}O_2$. All attempts to obtain this latter compound, by splitting the molecule, were in vain, resulting under the most favorable conditions, in a light yellow oil having an odor somewhat resembling carvone, which polymerized in a few minutes to a stiff, glassy resin. As shown by Bacon the ketone itself polymerizes with great ease, particularly when gently warmed in solution in benzene. The ease with which resinification takes place in champaca oil itself, suggests the presence of structurally related compounds.

Since the substances isolated by me from the essential oil of *Michelia champaca* L. are entirely different from those isolated by Schimmel & Company[1] from oil distilled from the yellow and white flowers, a study of the oil prepared from the latter flowers has been made. The same compounds were identified in this oil as Schimmel & Company found in the champaca oil studied by them, namely linalool, the methyl or ethyl ester of methylethylacetic acid and methyleugenol. This oil showed no fluorescence at all. This property in Schimmel's oil was perhaps due to the presence of some of the oil from the yellow flowers. Extraction of the white flowers yields none of the crystallin ketone obtained from the yellow flowers.

This oil possesses an intensely sweet, fruity odor which is altogether different from the fragrance of the yellow flowers. Its constants are as follows:

Specific gravity $\frac{30°}{30°}$	0.897
Ester number	180
Refractive index	1.4470

The oil was too dark for a polariscope reading to be taken. The low refractive index is undoubtedly caused by the methylethylacetic ester.

The white flowers also contain an energetic oxidizing enzyme.

Experimental.[2]

The rapidity with which champaca flowers darken in color after picking, particularly if they are slightly bruised, is much like the behavior of gardenia flowers in this respect. According to Bertrand the latter flowers contain an oxidizing enzyme similar to laccase. Champaca flowers were therefore investigated for oxidases. When the flowers are

---

[1] *Loc. cit.*

[2] Some of the experiments are here only briefly outlined as they are given in more detail in a recent article by the author on Philippine essential oils, *Philipp. J. Sci.*, (*A*) 6 (1911).

bruised under water an aqueous solution is obtained, which begins to turn brown the instant it is exposed to the air, the color gradually extending deeper into the solution. By preparing the aqueous extract under a layer of ligroin or paraffin oil a light yellow solution is obtained, which turns tincture of guaiac resin blue directly. Since this is a rather common property of plant extracts, the color reaction with α-naphthol and *p*-phenylenediamine was tried and positive results obtained. By heating the solution a few minutes on a steam bath the activity of the enzyme is entirely destroyed, none of the color reactions being given by the heated extract.

The oil was examined for aldehydes by shaking out with sodium bisulfite in the usual manner. From 40 grams of oil, one year old at the time of investigation, 2.1 grams of oil were extracted by bisulfite. When treated in very dilute alcohol solution with phenylhydrazine this portion gave a small quantity of crystallin benzaldehyde phenylhydrazone, which after recrystallizing from methyl alcohol melted at 154–156°. The greater part of this aldehyde fraction consisted of an oil having an odor closely resembling methylheptenone. The semicarbazones were not separated in a state of purity sufficient for positive identification of the latter compound.

Walbaum and Stephan have shown that phenylethyl alcohol is quite soluble in 30 per cent. alcohol, and since the presence of this aromatic compound was suspected in champaca oil the method proposed by them was followed. As it was desirable to know whether or not a comparatively large amount of the free alcohol was present in the original oil, 40 grams of champaca oil, previously extracted with bisulfite, were shaken out with 250 cc. of 30 per cent. ethyl alcohol. Most of the ethyl alcohol was distilled from the extract, using a condensing column, and the remaining mixture extracted with ether. In this way 2.6 grams of oil were obtained, which had a very sweet, agreeable odor and when two drops were acetylated with acetyl chloride and subsequently washed with a little sodium carbonate solution, the characteristic rose fragrance of phenylethylacetate was produced. The remaining oil was therefore dried in a little ether with potassium carbonate, and distilled. About 1.8 grams distilled between 215° and 225°, the boiling point of pure phenylethyl alcohol being 220°. This fraction was treated with phenylisocyanate and the characteristic phenylurethane of phenylethyl alcohol was obtained, which after recrystallizing from methyl alcohol melted sharply at 79.5°. Free phenylethyl alcohol is therefore present in champaca oil.

Attempts were made, with small quantities of the oil, to distil it with steam and also in a vacuum of 18 mm. but in each case a large part of the oil was converted into resin.

Therefore 75 grams of oil, which had been treated with bisulfite to remove all aldehydes, were treated with a slight excess of potassium hydroxide in aldehyde-free ethyl alcohol and the solution allowed to stand 24 hours. Part of the alcohol was then distilled *in vacuo*, the alkaline solution largely diluted with water, *slightly* acidified with sulfuric acid and the mixture extracted six times with petroleum ether. After distilling the petroleum ether, the resulting oil was distilled with steam. In this experiment 25 grams of oil were recovered. In other saponifications with small amounts of oil a *larger* per cent. of the oil was resinified. The viscous, resinous matter obtained by me is apparently identical with the viscous acid mixture obtained by Bacon,[1] who was unable to distil anything from it without decomposition, even *in vacuo*.

The oil, purified by distillation with steam, was shaken out with 3 per cent. sodium hydroxide, the alkaline solution slightly acidified and extracted with ether. The phenol thus obtained, weight 1.4 grams, smelled strongly of isoeugenol. Its benzoyl compound melted at 103°.

After removal of the phenol the oil was distilled at ordinary pressure up to 220°. The fraction boiling from 173 to 178° consisted of almost pure cineole, which compound was identified by making the characteristic compound with iodole, melting point 112°.

When a few drops of an essential oil are shaken up with a little hot water the odor of the more volatil constituents becomes much more pronounced. In the case of champaca oil the odor of cineole becomes quite strong when treated in this way. In my opinion cineole is one of the compounds which give to champaca its peculiar character.

The presence of a relatively small amount of benzyl alcohol was shown by oxidizing 0.5 gram of the fraction boiling from 200 to 210° with a little chromic acid mixture, distilling a little of the solution and precipitating benzaldehyde phenylhydrazone from the aqueous distillate. No evidence that linalool was present in this fraction was obtained. A small portion boiling from 198 to 200° gave no citral on oxidation. All the fractions between the cineole and phenylethyl alcohol fractions were quite small.

The fraction boiling from 210 to 220° was examined for phenylethyl alcohol as before. Acetylating a few drops gave the odor of aromatic phenylethyl acetate and oxidation of 2.0 grams with a small quantity of chromic acid mixture gave phenylacetic acid, which after crystallizing from dilute methyl alcohol melted sharply at 76°. Phenylethyl alcohol is therefore present in champaca oil as an ester and in the free state.

The aqueous acid solution was neutralized, concentrated and acidified with dilute sulfuric acid. Extraction with ether gave 0.5 gram benzoic acid, which after recrystallizing from hot dilute alcohol melted sharply at 120°. Distilling the aqueous solution with steam gave acetic acid,

---

[1] *Loc. cit.*

identified by making the silver salt from the neutralized, concentrated distillate. Analysis of the silver salt gave 64.5 per cent. silver; calculated for silver acetate, 64.4 per cent.

The Essential Oil from Michelia longifolia.

Schimmel & Company[1] state that the oil sent to them in 1907 was obtained by distillation in a yield of 0.0125 per cent. By extracting the white flowers with a suitable solvent and removing the oil from the essence concrete with dilute alcohol, a yield of approximately 0.08 per cent. was obtained. Thus prepared, the oil was dark green in color and showed no fluorescence.

Twenty grams of this oil were saponified by a slight excess of caustic potash in aldehyde-free alcohol. Considerable resin was formed in this case, also. A neutral fraction weighing 9.3 grams was obtained, which was distilled at 16 mm. pressure. The following fractions were obtained: 80–90°, 3.8 grams; 90–98°, 2.0 grams; 98–110°, 1.0 gram; residue, 1.0 gram. The first and second fractions were united and treated with phthalic anhydride in benzene but no primary alcohols were obtained. Since the odor of the fraction was very suggestive of linalool it was oxidized with chromic acid mixture to citral, which was identified by making its α-naphthocinchonic acid compound, melting point 198–199°. The third fraction appeared to consist of a mixture of the second and fourth fractions. The fourth fraction, weight 1.0 gram, had a specific gravity of about 1.09 and showed the refractive index $n^{30°}_{D} = 1.5130$. Its odor was very suggestive of methyleugenol. Oxidation with potassium permanganate in the cold gave about 0.15 gram of veratric acid, melting point 179–180°.

No phenolic substances were identified with certainty although a trace of a phenolic substance is present, the odor of which closely resembled thymol.

After all the neutral and phenolic substances had been removed from the original solution it was concentrated to about 15 cc., acidified with dilute sulfuric acid and extracted with ether. The acids thus extracted were neutralized with a dilute sodium carbonate solution, purified by adding a little calcium acetate, filtered and the silver salt precipitated from the filtrate. The silver salt thus obtained gave on analysis 52.0 per cent. silver; calculated for $C_5H_9O_2Ag$, 51.4 per cent. The odor of the original oil is almost entirely due to the methyl or ethyl ester of this acid.

Champaca Ketone.

The crystallin ketone which is deposited by champaca oil is best purified by recrystallization from chloroform and ligroin. When quite pure it is entirely odorless and colorless. An alcoholic solution of the

Semi-annual Report, 2, 33 (1907).

compound deposits large four-sided plates, the acute angles of which are 64°. The crystals possess two optical extinctions parallel to the axes of symmetry. A solution of the substance in chloroform yields large, six-sided plates, while precipitation with ligroin or ether yields the shortened, four-sided plates.

One gram of the ketone dissolved in 15 cc. of alcohol showed in a 10 cc. tube an optical rotation of —5.5°, $[\alpha]_D = 82.5°$.

The substance melts at 165–166°, but polymerizes rapidly at this temperature, yielding an amorphous substance which melts with decomposition at 335–340°. About 0.3 gram of the pure ketone was heated in an oil bath at 170° until thoroughly softened. After cooling, the addition of chloroform readily extracted the unchanged substance, which could be recrystallized. There remained about 0.2 gram of insoluble amorphous material, which could not be dissolved, the substance slowly absorbing the solvent and thereby being converted into a tough, gelatinous mass.

Twenty grams of the ketone were dissolved in a mixture of benzene and alcohol and shaken in a shaking machine for 4 hours with a concentrated solution of sodium bisulfite. At the end of this time the benzene layer was evaporated and 0.2 gram amorphous substance was obtained. The ketone had therefore passed quantitatively into the bisulfite solution. On treating the bisulfite solution with sodium carbonate, nothing separated, even on warming, as is usually the case. A small test portion yielded nothing on making strongly alkaline with sodium hydroxide. Extraction of the alkaline solution with chloroform yielded nothing.

When the neutralized, aqueous sulfite solution was evaporated on the steam bath, a heavy viscous layer finally separated from the concentrated solution. This substance was very soluble in water. On standing several days *in vacuo* over sulfuric acid it slowly crystallized. On ignition it burned with a smoky flame leaving a residue of sodium sulfite and sulfate. It was not obtained sufficiently pure for analysis. The aqueous solution, slightly acidified with acetic acid, gives no precipitate with phenylhydrazine. What was apparently the free sulfonic acid was prepared, in a very small yield only, by digesting a few grams of the salt with glacial acetic acid. This mixture was extracted with chloroform yielding an oily, acid substance totally different from the original material.

The ketone reacts with one molecule only of phenylhydrazine. The resulting phenylhydrazone, melting sharply at 161°, gave the following analysis; 0.2057 gram substance gave 14.2 cc. of nitrogen measured at 30° and 760 mm. Calculated for $C_{16}H_{20}O_4 : N.NH.C_6H_5$, 7.33 per cent. nitrogen; found, 7.48 per cent. nitrogen.

Only one double bond is reactive to Hanus' iodine solution, although more than one is undoubtedly present. 0.2035 gram of the ketone absorbed 0.171 gram iodine; calculated for one double bond. 0.176 gram iodine. The double bond in the group —HC=CH—CO—, indicated by the reaction with bisulfite, is very reactive and is probably the one which reacts in this instance.

A small sample of the ketone was dissolved in acetic anhydride and heated for 1 hour on the steam bath, but the original substance was recovered unchanged. Higher temperature or acetyl chloride quickly destroys the compound.

On treating the ketone with caustic potash in a strong alcoholic solution, crystals of a potassium salt soon begin to separate out in the form of masses of minute needles. The salt was filtered with suction and recrystallized from absolute alcohol with the addition of potassium ethylate. The lead salt, made by adding lead nitrate to an aqueous solution of the salt, is amorphous when first precipitated, changing in the course of a few hours to crystals. Under the microscope these crystals proved to be rhombic plates, the acute angles of which measured approximately 72°. The lead salt decomposed with almost explosive violence when combustion analyses were attempted. Two lead determinations gave 65.2 and 65.4 per cent. of lead. Fully neutralized lead succinate should contain 64.0 per cent. of lead but according to Beilstein[1] it is slightly basic in composition when precipitated from a neutral solution. The salt is therefore lead succinate.

The odor evolved when 0.5 gram of the original material is treated with a little alcohol, fused zinc chloride and a few drops of hydrochloric acid is apparently identical with the odor of diethyl succinate.

Saponification of 10 grams of the ketone and distillation of a portion of the mixture yielded ethyl alcohol. The iodoform reaction gave iodoform, slowly at 30° and very quickly at 60°.

Summary.

The differences between the essential oils of *Michelia champaca* L. and *Michelia longifolia* L. are clearly shown. The value of champaca oil is largely due to the presence of phenylethyl alcohol and its esters. The most characteristic compound in the oil from the flowers of *Michelia longifolia* L. is the methyl or ethyl ester of methylethyl acetic acid. An unstable ketone separates from champaca oil, which has been shown to be the succinic acid ester of a ketone alcohol and ethyl alcohol. The ketone alcohol probably has the formula $C_{10}H_{12}O_2$ and contains the group —HC=CH—CO—. The flowers of both species studied contain an oxidizing enzyme. It is believed that such oxidizing enzymes play an important role in the formation of aldehydes and ketones in essential oils. The study of the crystallin ketone will be continued.

I desire to express my thanks to Dr. Carlos Jährling, of Manila, for many

---

[1] Beilstein, *Org. Chemie*, 1, 655.

helpful suggestions and much encouragement during the course of the investigation.

GÖTTINGEN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE OXIDATION OF METANITROBENZOYLFORMALDEHYDE.

BY WILLIAM LLOYD EVANS AND EDGAR JOHN WITZEMANN.

Received September 9, 1911.

In a previous report on the preparation and the oxidation of *m*-nitrobenzoylcarbinol[1] it was indicated that a study would be made of some of the substituted benzoyl carbinols for the following purposes: (1) to ascertain whether the same general course of reaction is followed as has been previously developed for this series of compounds[2] and (2) to discover what possible effect, if any, the introduction of substituents into the ring might have on these compounds towards oxidizing agents previously considered. This paper, which constitutes the second report on this work, deals solely with the preparation and the oxidation of *m*-nitrobenzoylformaldehyde. Briefly, the results of our experiments are as follows: (1) *m*-nitrobenzoylformaldehyde can be isolated as an actual oxidation product from *m*-nitrobenzoyl carbinol by means of copper acetate; (2) *m*-nitrobenzoylformaldehyde with potassium permanganate, potassium permanganate and sodium hydroxide, potassium ferricyanide and sodium hydroxide, freshly precipitated silver oxide and sodium hydroxide, freshly precipitated mercuric oxide and sodium hydroxide, yields *m*-nitrobenzoic acid exclusively; (3) both freshly precipitated silver oxide and mercuric oxide in the absence of an alkali were not reduced at room temperature by *m*-nitrobenzoylformaldehyde; (4) at 100° both of the reagents mentioned in (3) reacted in the same manner as the reagents in (2), *i. e.*, to give *m*-nitrobenzoic acid; (5) *m*-nitrobenzoylformaldehyde with hot aqueous solutions of copper acetate undergoes the benzilic acid rearrangement giving *m*-nitromandelic acid; (6) with alkalies the aldedyde undergoes the same rearrangement.[3] From the experiments on *m*-nitrobenzoyl carbinol previously reported and also from those herein given, the following conclusions may be drawn: (1) *m*-nitrobenzoyl carbinol and *m*-nitrobenzoylformaldehyde follow the same general course of reaction as the corresponding non-substituted compounds; (2) the two nitro-substituted compounds are more sensitive to reagents in the presence of alkalies; (3) there is a more general tendency for the oxidation reactions to progress to the benzoic acid (*i. e.*, *m*-nitrobenzoic acid) stage in the case of the two nitro-substituted compounds rather

---

[1] Evans and Brooks, THIS JOURNAL, 30, 404.

[2] Evans, *Am. Chem. J.*, 35, 115.

[3] Nef, *Ann.*, **335**, 271, 272; **357**, 215, 231, 299, 302, 305, 308, 309.