

be brought into a glass tube, and hermetically sealed, it appears to be capable of preservation for an indefinite period.

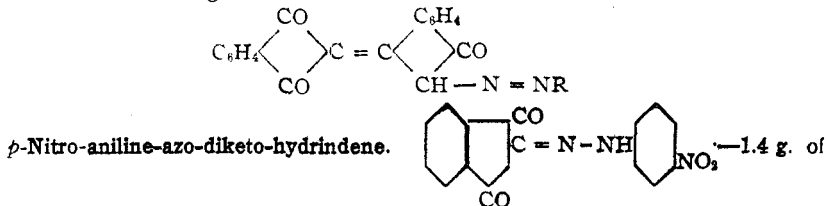
Although a product based upon the results of this investigation may be made synthetically which represents to a considerable degree the fragrance of the peach, the exact reproduction of the natural aroma of the fruit presents an apparently insurmountable difficulty. This is largely due to the fact that in the preparation of its esters linalool undergoes intramolecular changes with the formation of the isomeric compounds geraniol and terpineol or their respective esters, and as these esters have similar boiling points no means are available for their separation. It is also well known that in the esterification of linalool dehydration of the alcohol occurs to some extent, with the formation of terpenes, which are difficult to eliminate completely from the product. This is particularly the case in the preparation of linalyl formate, even when the usual precautions are observed and the ester is distilled in a vacuum. Furthermore, the linalyl esters, when obtained in the purest possible state, are subject to somewhat rapid decomposition on exposure to the air.

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### NOTES.

**Azo Compounds from Diketo-hydrindene.**<sup>1</sup>—It is generally known that substances containing a hydrogen atom replaceable by a metal when treated with diazo chlorides give the corresponding azo compounds. This fact suggested to us that 1,3-diketo-hydrindene which has a  $>CH_2$  group situated between two "CO" groups would react with diazo chlorides in a similar way, giving azo compounds. We prepared a few azo compounds with *p*-nitro-aniline, benzidine, *p*-toluidine and  $\beta$ -naphthylamine, and diketo-hydrindene, in the hope that they might be found to be useful as dye stuffs. They all give very insoluble sodium salts and the colors are very fast. We dyed several pieces of linen with them indirectly; but whether they will be of any commercial interest remains to be seen.

Diketo-hydrindene changes very readily to anhydro-*bis*-diketo-hydrindene. In the case of benzidine we have actually isolated a condensation product of *bis*-diketo-hydrindene and the corresponding diazo compound by bringing about the coupling of the constituents at ordinary temperature instead of in a freezing mixture.



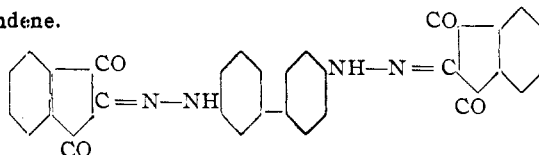
<sup>1</sup> Read before the All-India Science Congress, 1920.

*p*-nitro-aniline was diazotized with suitable precautions and 1.5 g. of diketo-hydrindene dissolved in excess of sodium hydroxide solution was gradually added to it. The temperature was not allowed to rise above 5°. A solid of yellow color separated. This was allowed to stand for 2 hours, was acidified with dil. sulfuric acid, filtered and then thoroughly washed free from acid. This was dried and recrystallized from pyridine. The compound does not melt even at 280°. It dissolves in conc. sulfuric acid with a red color. In potassium hydroxide it dissolves to form a magenta colored solution.

*Analyses.* Subs., 0.1347: CO<sub>2</sub>, 0.3010; H<sub>2</sub>O, 0.0401. Subs., 0.1718: N<sub>2</sub>, 21.6 cc. (24°, 754 mm.).

Calc. for C<sub>15</sub>H<sub>9</sub>O<sub>4</sub>N<sub>3</sub>: C, 61.0; H, 3.0; N, 14.2. Found: C, 60.9; H, 3.2; N, 13.9.

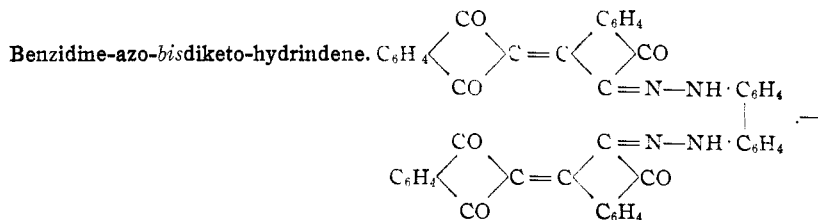
**Benzidine-azo-diketo-hydrindene.**



1.84 g. of benzidine was tetrazotized and to this 3 g. of diketo-hydrindene, dissolved in excess of sodium hydroxide solution was gradually added, the temperature being kept below 5°. This was allowed to stand for some time and then acidified. The dark red precipitate that separated was filtered and washed repeatedly. The compound was insoluble in almost all the solvents, such as alcohols, ether, chloroform acetone, xylene and pyridine. With conc. sulfuric acid it gives a violet colored solution.

*Analysis.* Subs., 0.1649: N<sub>2</sub>, 17.5 cc. (32°, 756 mm.).

Calc. for C<sub>30</sub>H<sub>18</sub>O<sub>4</sub>N<sub>4</sub>: N, 11.3. Found: 11.3.

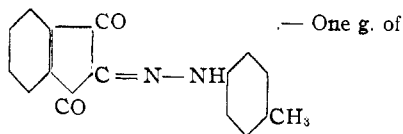


1.84 g. of benzidine was tetrazotized as usual and to this an equivalent quantity of alkaline solution of diketo-hydrindene was added. The solution was kept overnight at ordinary temperature (about 26°), then acidified, filtered and washed.

*Analysis.* Subs., 0.2294: N<sub>2</sub>, 14.9 cc. (28°, 766 mm.)

Calc. for C<sub>45</sub>H<sub>26</sub>O<sub>8</sub>N<sub>4</sub>: N, 7.6. Found: 7.5.

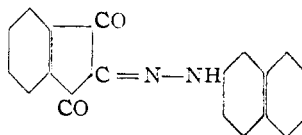
***p*-Toluidine-azo-diketo-hydrindene.**



*p*-toluidine was diazotized in the usual way and coupled with 1.5 g. of diketo-hydrindene in sodium hydroxide solution at 5°. This was acidified, filtered, washed and dried. It was recrystallized from acetic acid. It separated in fine yellow silky flakes, melting at 211°. It dissolves in conc. sulfuric acid to form a chocolate colored solution.

*Analysis.* Subs., 0.1743; N<sub>2</sub>, 16 cc. (23°, 756 mm.).

Calc. for C<sub>16</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>: N, 10.6. Found: 10.3.

**$\beta$ -naphthylamine-azo-diketo-hydrindine.**

1.43 g. of  $\beta$ -naphthylamine was diazotized and coupled with 1.5 g. of diketo-hydrindene in alkali solution at 5°. This was acidified, filtered, washed and dried. It was recrystallized from acetic acid. It melts at 205°. It forms a deep brown colored solution.

*Analysis.* Subs., 0.1439. N<sub>2</sub>, 12 cc. (26°, 754 mm.).

Calc. for C<sub>19</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>: N, 9.3. Found: 9.17.

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**The Odorous Constituents of Apples.**—It has come to our notice that a paper has been published by Shintarô Kodama<sup>1</sup> which, as abstracted in *J. Chem. Soc.*, **120**, i, 220 (1921) bears the following title: "Odorous Constituents of Apples. Esters Derived from Leucic Acid." In the original publication the title of the paper is: "On the Odor of Apples. Ethereal Oils Obtained from Leucic Acid." After stating, "Power and Chesnut have proved that amyl esters of formic, acetic, and hexoic acids are the principal odorous constituents of apples,"<sup>2</sup> Kodama proceeds to describe certain esters prepared from by-products of the decomposition of proteins, such as ethyl  $\alpha$ -acetoxy-*iso*-hexoate, and the corresponding methyl ester; ethyl- $\alpha$ -benzoyloxy-*iso*-hexoate; ethyl  $\alpha$ -*isovaleryl-iso*-hexoate, etc. Inasmuch as these compounds or "esters derived from leucic acid" do not occur in apples, and therefore do not represent their odorous constituents, the title given by Kodama to his communication is not only misleading but entirely unwarranted. It has consequently seemed desirable to call attention to these facts in order to avoid any possible confusion in the literature on the subject.

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**The Occurrence of Methyl Anthranilate in Grape Juice.**—The use of fruit juices as beverages has become more extended and greatly increased in recent years, and considerable attention is now being given to the control of their quality and purity. One of the substances that has been suspected of being added to natural grape juice for the purpose of improving its flavor is methyl anthranilate, and it is well known that this compound,

<sup>1</sup> Kodama, *J. Tokyo Chem. Soc.*, **41**, 965-975 (1920).

<sup>2</sup> THIS JOURNAL, **42**, 1509-26 (1920).

in a dilute state, possesses a decided grape-like odor. Inasmuch as the examination of some samples of commercial grape juice, according to the method recently published by one of us,<sup>1</sup> has clearly indicated the presence of methyl anthranilate, some of those interested in these products appear to have been led to the conclusion that in such instances an artificial flavoring agent had been employed. In consequence of these deductions it has naturally become of much importance to determine whether a pure and entirely unsophisticated grape juice may not contain small amounts of methyl anthranilate. An opportunity for conducting such an investigation has been made available through the kind coöperation of Dr. J. S. Caldwell, of the Bureau of Plant Industry, U. S. Department of Agriculture, who has provided us with a large number of samples of grape juice expressed by himself during the autumn of 1920 from many different and well determined varieties of the fruit. Although the examination of all these samples has not yet been completed, the observations that have thus far been made enable us to conclude that methyl anthranilate is a natural and apparently constant constituent of grape juice. The amounts that are present in the numerous varieties of the grape appear to differ very greatly, and by far the most decisive results of the test have thus far been obtained from the red juices of the Concord type. By the distillation of 500 cc. of the grape juice the amount of methyl anthranilate found has in no case exceeded 0.001 g., as determined by comparative tests with the pure substance, but even this small amount, as has previously been shown,<sup>1</sup> is sufficient to produce a deep red color or precipitate by the interaction of the diazotized compound with  $\beta$ -naphthol. In the case of the light colored juices the amount of methyl anthranilate present, as indicated by the distillation of 500 cc. of liquid, has thus far been observed to be not more than 0.0001 g., and is frequently less, but in few instances could it be regarded as entirely absent.

It has seemed to us desirable to present these preliminary observations regarding the occurrence of methyl anthranilate in grape juice in order that those engaged in the examination or control of commercial products may not be led to wrong conclusions respecting their purity. The more complete results of the investigation of this subject must necessarily be reserved for a later communication.

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<sup>1</sup> THIS JOURNAL, 43, 377 (1921).