The recovery is practically quantitative and the quality of the product satisfactory for use in making butyl bromide.

Conclusions

1. A study has been made of the factors influencing the formation of octane from butyl bromide by the Wurtz reaction.

2. Based upon this study, a method has been developed for the formation of octane in rather large amounts and with yields of 65–70% based upon butyl bromide.

3. Butene and at least two higher saturated hydrocarbons are also formed. The boiling points of the hydrocarbons suggest dodecane and hexadecane.

MOUNT VERNON, IOWA

[CONTRIBUTION FROM THE LABORATORY OF FOODS AND SANITATION, UNIVERSITY OF WISCONSIN]

CAROTIN: A PIGMENT OF HONEY[1]

BY H. A. SCHUETTE AND PHYLLIS A. BOTT

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Color and quality in honey have from time immemorial borne an inverse relationship to each other in the minds of the average consumer, the more deeply pigmented honeys, as a rule, commanding a lesser price. As a result of this, the practice of designating its color has become universal in the grading of honey to the end that certain loosely defined names for these colors have come into use. It is only within recent years, however, that these colors have been defined with the aid of a spectrophotometer.[2]

Since these color designations are but an attempt to describe the pigmentation of a particular honey, and since this pigmentation is due wholly if not in part to red, orange or yellow coloring matters, it seemed but reasonable to assume that the latter are of the carotinoid type. To harmonize this assumption with factual evidence was the purpose of the study herein recorded.

Experimental

A highly pigmented buckwheat honey, described in trade parlance as amber colored, was selected for study since it seemed to offer the greater promise for the recovery of the necessary quantity of pigment for identification.

Attempts at removal of the coloring matter by precipitation with those clarifying agents which are commonly used in "purifying" a sugar con-

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[1] Constructed from a thesis submitted by Miss Bott to the Faculty of the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Master of Science, June, 1924.

[2] E. L. Sechrist, U. S. Dept. Agr., *Dept. Circ. 364*, **1925**, p. 3.

taining solution preliminary to analysis, followed by drying and extraction of the resulting precipitate, were abandoned after repeated trials during the course of which numerous variables centering around the dilution of the honey, the nature of the precipitant and the character of the solvent were introduced. Clarification was never complete because of the colloidal nature of the non-sugars; the extraction of the coloring matter from the dried precipitate was not quantitative because of what appeared to be a physico-chemical combination between pigment and sugars or albuminous matter of the honey; and finally the pigment in part was invariably lost by oxidation because the whole operation is time consuming.

An adaptation, with slight modifications to suit the material in question, of the method developed by Palmer and Eckles[3] for the extraction of carotin from blood serum proved to be successful in this case. The procedure is as follows.

One kg. of honey was intimately mixed with an equal weight of plaster of Paris in an ordinary one-gallon ice-cream freezer. To the resulting plastic mass 150 cc. of 95% ethyl alcohol was added and, when this had been thoroughly incorporated in the mass, 500 cc. of petroleum ether (b. p. 60–70°). The contents of the freezer were then stirred for about twenty minutes, the solvent was removed and the extraction continued with successive, but smaller, quantities of the ether until fresh portions were no longer colored. Approximately 800 cc. of solvent was used per kilo of honey.

The residue from 15 kg. of honey represented a yield of 0.01% of a crude pigment which in petroleum ether solution was of a yellowish-orange color and in carbon disulfide an intense orange-red. The colors of these solutions were similar to those prepared from the carotin which had been extracted from carrots by the procedure of Euler and Nordenson.[4]

Purification of the crude carotin was effected by fractional precipitation with absolute ethyl alcohol from carbon disulfide solution. The pigment so obtained was subsequently qualitatively identified[5] as carotin by its resistance to the action of alkalies, by the fact that it was not adsorbed from carbon disulfide solution by finely divided calcium carbonate, and that with ferric chloride it produced a green coloration but none that was characteristic with concentrated sulfuric acid.

Final proof of identity was established by a determination of its adsorption spectrum in carbon disulfide solution. By means of a Hilger constant deviation prism spectroscope illuminated by an iron arc, spectrophotographs were made of solutions of the carotin when placed in 1-inch cells provided with quartz ends. Carotin solutions[4] prepared from the pigments of carrots served as controls. It was observed that absorption of light occurred in the region of 4700–5250 Å. and that a portion of the visible violet rays and all of the rays in the region of the ultraviolet were absorbed. This is a characteristic function of carotin.

Summary

It has been shown that at least one of the pigments of buckwheat honey can be isolated with petroleum ether in the presence of ethyl alcohol

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[3] Palmer and Eckles, *J. Biol. Chem.*, **17**, 224 (1914).

[4] Euler and Nordenson, *Z. physiol. Chem.*, **56**, 223 (1908).

[5] Ref. 3, p. 225.

and calcium sulfate (plaster of Paris), a method applied by Palmer in the removal of pigments from blood serum, and that this pigment is carotin.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

PARA-CYMENE STUDIES.
X. PARA-CYMYLENE-2,5-DIAMINE AND CERTAIN NEW DYES

BY ALVIN S. WHEELER AND R. W. BOST[1]

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Of the four possible *p*-cymylenediamines two are known, the 2,6-diamine described by Alfthan[2] and the 2,5-diamine, the latter only in the form of its hydrochloride as described by Liebermann and Ilinski.[3] The free base was apparently isolated by Kehrmann and Messinger[4] for they state that it was so easily oxidized in the air that it could only be kept as the hydrochloride. Wallach and Schrader[5] prepared the diacetate, melting at 260°. Wheeler and Brooks[6] obtained the same diacetate on reducing 2-acetoamido-5-nitrocymene, followed by acetylation. A method superior to all others was found in the reduction of an azo derivative of 2-aminocymene, a method first used by Martius and Griess.[7] The aminocymene was coupled with diazotized sulfanilic acid, the resulting dye being reduced with stannous chloride. A poor yield is obtained if aniline is substituted for sulfanilic acid.

We locate the second amino group in position 5 for several reasons. This position is para to the amino group already present and is the point where coupling should take place according to analogous reactions. Secondly, the melting point of the diacetate is 260°, which is the same as that of the diacetate obtained from the reduction product of thymoquinonedioxime. Further proof was obtained by converting the diamine into thymoquinone, melting at 45° and described by Carstanjen,[8] and its monoxime, melting at 154–6°, and finally into hydrothymoquinone, melting at 139.5°.

p-Cymylene-2,5-diamine is so unstable in the air that no description of it has appeared in the literature. We isolated it in an atmosphere of nitrogen and at reduced pressure in a specially constructed apparatus.

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[1] An abstract of a thesis submitted in June, 1928, to the Faculty of the University of North Carolina by R. W. Bost in candidacy for the degree of Doctor of Philosophy.

[2] Alfthan, *Ber.*, **53**, 86 (1920).

[3] Liebermann and Ilinski, *Ber.*, **18**, 3200 (1885).

[4] Kehrmann and Messinger, *Ber.*, **23**, 3562 (1890).

[5] Wallach and Schrader, *Ann.*, **279**, 375 (1894).

[6] Wheeler and Brooks, THIS JOURNAL, **49**, 2834 (1927).

[7] Martius and Griess, *Chem. Zentr.*, **1866**, 136.

[8] Carstanjen, *J. prakt. Chem.*, [2] **3**, 53 (1871).