When first made, no difference in color could be detected between beet or cane sugar syrups of the same concentrations. Upon the development of moulds, some of the syrups became discolored; this, however, was noted in both cane and beet sugar syrups.

Shaw[3] has compared the merits of beet and cane sugar for preserving fruits and making jellies and has found the two sugars to have almost the identical sucrose content, which would be expected. He also found no difference between jellies made with beet and cane sugar, and of 2000 cans of preserved fruit he found but 6 from the beet sugar lot and 7 from the cane sugar lot to spoil during two years of storage. This loss, it is stated, was due to imperfect sealing.

From the evidence at hand it appears that beet and cane sugar may be used with equally good results for all purposes. The process of refining sugar has been so perfected that a uniform product can be supplied. The greatest source of danger, it seems, is contamination by moulds and bacteria, but with modern processes of refining both beet and cane sugar may be produced equally free from contamination by organisms.

SUMMARY.

Chemical and polariscopic examination failed to establish any difference between the beet and cane sugars examined, though of the almost negligible amounts of ash, nitrogen and invert sugar found in both the beet and cane sugar samples, the cane sugar, on the average, contained the most.

Fermentation with yeast showed the process to proceed the same for both sugars.

Of the eight samples examined, more organisms were found in beet than in cane sugar. Any difference between given samples of the two sugars must be concluded to be due to the degree of refinement or to contamination by moulds and bacteria, the latter being the more probable.

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CHEMICAL RESEARCH DEPT.,
PARKE, DAVIS & COMPANY.

A METHOD FOR MANUFACTURING ETHYL OENANTHYLATE.*

BY CHARLES H. ROGERS.

Nearly all fruits possess very distinctive flavors and these flavors may be imparted to such substances as confections, jellies, ice cream, etc., by simply mixing in sufficient quantities the fruit, either in preserved or fresh form or the juice therefrom, with the material. In many instances, however, it is not practical to prepare an extract from the respective fruits which is sufficiently concentrated to give the desired fruit flavor when used in moderate quantities. These conditions have led to the use of artificial fruit essences which are made up of esters, alcohols, aldehydes, lactones, etc., mixed in various combinations and proportions to imitate more or less the various fruit flavors. In concentrated form these artificial flavors are usually more pungent and crude smelling than the sapid and odorous principles

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[3] G. W. Shaw, *Univ. of Cal. College of Agr., Cir.* No. 33, 1907.

* Northwestern Branch A. Ph. A., February meeting, 1923.

of fruits which they are supposed to imitate. Food products flavored with artificial essences are unquestionably lacking in delicacy and refinement; nevertheless, they do have a semblance of the flavor of the true fruit. These essences are of value because the original fruit flavor may be had in a highly concentrated form.

Many esters alone possess very distinctive flavors and are often sold as artificial oils of the respective fruits which they represent. Examples: pineapple oil is ethyl butyrate; banana oil, amyl acetate; apple oil, amyl valerianate, etc.

In reviewing the work that has been done on artificial essences it is found that one ester in particular is used more than any other in making complex mixtures used to imitate various fruit flavors. It was observed that oenanthylic ethyl ester plays an important part in the manufacture of raspberry, gooseberry, grape, cherry, apricot, currant, bourbon, and other artificial essences. Ethyl oenanthylate may be purchased in the open market but this product is made by esterifying cocoanut oil and is a mixture of the ethyl esters of lauric, myristic, palmitic, and other higher fatty acids. A review of the literature dealing with the manufacture of ethyl oenanthylate has led us to a study of the methods suggested for its preparations. It is the purpose of this paper to discuss the one method of preparing pure ethyl oenanthylate that was used successfully in our laboratory.

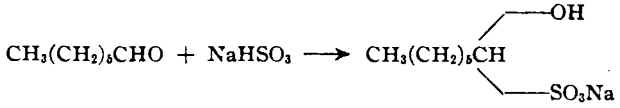
PREPARATION OF OENANTHOL (NORMAL HEPTALDEHYDE).

Three hundred grams of No. AAA castor oil were placed in a round-bottomed, long-necked, one-liter distilling flask which was connected by a cork stopper and glass tube to a water condenser. The jacket of the condenser contained cold water, but not running water. Experiments have shown that if the delivery end of the condenser be fitted into a suction flask and a partial vacuum produced, the distillation will proceed more rapidly, although extra precaution must be taken to prevent foaming. The flask was then heated on a sand-bath with a triple Bunsen burner. A few small pieces of clay were introduced into the flask to prevent bumping. The distillation was continued until the odor of acrolein became very noticeable and only small amounts of the substance distilled. This required about four hours. The decomposition of the castor oil sometimes takes place very rapidly. In fact, this reaction often occurs with sufficient explosive violence to blow the cork out of the distilling flask and discharge the contents. This is to be guarded against because the material that is expelled closely resembles an asphaltic paint and is most difficult to clean from anything with which it comes in contact. The residue in the flask should be poured out while still hot or else the flask is very hard to clean. The following reaction takes place:

$$\underbrace{CH_3(CH_2)_5.CH(OH).CH = CH.(CH_2)_8COOH}_{\text{Ricinoleic acid}} \longrightarrow \underbrace{CH_3(CH_2)_5CHO}_{\text{Oenanthol}} + \underbrace{C_{10}H_{19}COOH}_{\text{Undecylenic acid}}$$

FORMATION OF THE BISULPHITE ADDITION PRODUCT.

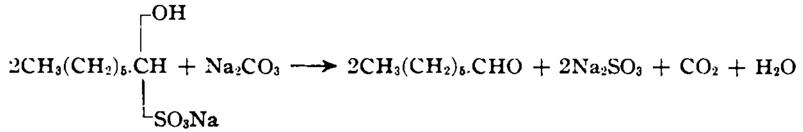
The distillate, which consisted of oenanthol and water, was placed in a separating funnel and the water drawn off. The aldehyde was then run into a 500-mil Erlenmeyer flask and shaken with a cold, saturated aqueous solution of sodium bisulphite for about ten minutes and then allowed to stand for an hour. The sodium bisulphite solution was prepared by saturating a solution of fifty grams of sodium hydroxide in 200 mils of water with sulphur dioxide; oenanthol bisulphite separates and may be filtered off on a Hirsch funnel and washed with a little cold water.



$$CH_3(CH_2)_5CHO + NaHSO_3 \longrightarrow CH_3(CH_2)_5CH\begin{cases} OH \\ SO_3Na \end{cases}$$

REGENERATION OF OENANTHOL.

A two-liter flask was filled one-third full of a saturated solution of sodium carbonate. To this was then added from 100 to 150 grams of the sodium bisulphite addition product of oenanthol. A condenser was connected to the flask and also a tube introduced that reached to the bottom of the same and through which steam could be introduced. The flask was gradually warmed until the temperature reached about 100° C., then steam was introduced very slowly at first to prevent foaming, and finally more rapidly until no more oenanthol distilled over. The normal heptaldehyde was separated from the water in a separatory funnel and shaken for five or ten minutes with fused calcium chloride. The oenanthol was separated and distilled, the distillate collected between 150 and 155° C.



$$2CH_3(CH_2)_5.\overset{\overset{OH}{|}}{\underset{\underset{SO_3Na}{|}}{CH}} + Na_2CO_3 \longrightarrow 2CH_3(CH_2)_5.CHO + 2Na_2SO_3 + CO_2 + H_2O$$

OXIDATION OF OENANTHOL TO OENANTHYLIC ACID..

The oenanthol was dissolved in about an equal quantity of acetone. To this solution was added about twice the theoretical amount of powdered potassium permanganate. The flask was kept cool with cold water in order not to allow the reaction to become too violent. When the manganese dioxide settled out, a pink color indicated that sufficient amount of potassium permanganate had been added. When the oxidation was complete the solution was rendered distinctly acid with dilute sulphuric acid and a saturated solution of sodium acid sulphite was added until the manganese dioxide and any excess potassium permanganate were dissolved. The solution was then practically colorless or a pale amber color.

$$2CH_3(CH_2)_5.CHO + O_2 \longrightarrow 2CH_3.(CH_2)_5COOH$$

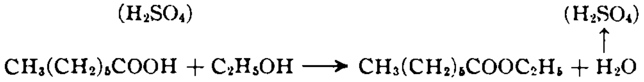
PURIFICATION OF THE OENANTHYLIC ACID.

The solution resulting after the oxidation separated into two distinct layers; the upper layer containing the acetone solution of oenanthylic acid and the lower aqueous liquid containing potassium sulphate, manganese sulphate, and sodium bisulphate, etc. The liquid was then placed in a separatory funnel and the aqueous liquid drained off and discarded. Because of the miscibility of acetone with water in all proportions the oenanthylic acid was washed free from the ketone by shaking repeatedly with water and separating the lower layer. When the aqueous extract of the oenanthylic acid no longer smelled of acetone the oenanthylic acid was dissolved in about twice its volume of ether and shaken with a saturated aqueous solution of sodium carbonate until no more carbon dioxide was expelled. (Great care must be exercised if this is done in a separatory funnel.) The aqueous solution of the sodium salt of oenanthylic acid was extracted once with a 25-mil portion of ether. In this way any of the oenanthol which had not been oxidized will go in solution in the ether, while the acid being present as its sodium salt remains in solution in the water. To the extracted aqueous solution was then added hydrochloric acid to a distinct acid reaction. The purified oenanthylic acid formed a distinct layer on the surface of the aqueous liquid.

$$2CH_3(CH_2)_5COOH + Na_2CO_3 \longrightarrow 2CH_3(CH_2)_5COONa + CO_2 + H_2O$$
$$2CH_3(CH_2)_5COONa + 2HCl \longrightarrow 2CH_3(CH_2)_5COOH + 2NaCl$$

ESTERIFICATION OF OENANTHYLIC ACID.

The esterification of the oenanthylic acid may be accomplished in one of several ways. The silver salt of oenanthylic acid may be made and this treated with ethyl iodide, under which condition ethyl oenanthylate results while silver iodide is precipitated. The method that was used in our laboratory was to dissolve the oenanthylic acid in about twice the theoretical quantity of absolute alcohol to which five mils of concentrated sulphuric acid were added and the mixture refluxed for about twelve hours.



$$CH_3(CH_2)_5COOH + C_2H_5OH \xrightarrow{(H_2SO_4)} CH_3(CH_2)_5COOC_2H_5 + \overset{\overset{(H_2SO_4)}{\uparrow}}{H_2O}$$

RECOVERY OF ETHYL OENANTHYLATE.

The alcoholic solution of ethyl oenanthylate was then poured into a quantity of water in order to separate the ethyl oenanthylate from the excess of alcohol present. This mixture was extracted with ether in which the ester is soluble, and the ether layer separated. The ether solution of ethyl oenanthylate was then washed with a very weak aqueous solution of sodium carbonate (not over two per cent.) in order to convert any unesterified oenanthylic acid to the water-soluble sodium salt. This was then separated and the ether layer washed with water. The ethyl oenanthylate was then treated with anhydrous sodium sulphate or fused potassium carbonate. (Fused calcium chloride should not be used.) The ether was then allowed to evaporate and the oenanthylic ethyl ester distilled.

The author acknowledges the assistance of Dr. Smith and Mr. Netz in this work.

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ANALYSES OF ONE HUNDRED PRESENT-DAY ALCOHOLIC BEVERAGES.*

BY HENRY KRAEMER.

In presenting a paper on this subject it is necessary to define one's attitude so that there be no misconstruction placed on the data which are given. Any article, letter, or questionnaire at this time on the subject of alcoholic beverages is to be viewed with suspicion as to its purposes and the influence which prompted it.

The Constitution of the United States as expressed in the 18th Amendment prohibits the manufacture and sale of intoxicating liquors. Respect for the law

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* Read at the Scientific Section of the American Pharmaceutical Association, August 18, 1922, Cleveland, Ohio.