It will be noted in Table II that the results obtained from No. 2 are very irregular. This irregularity is due to the fact that the material is practically insoluble in water, making uniform suspensions difficult. A wide range of concentrations of No. 2 was added to the optimum concentration of each of the other fractions, but in no case did No. 2 improve the yields.

The optimum concentrations of Fractions 1, 3 and 4 were tested in various combinations, typical results being given in Table III.

TABLE III

OPTIMUM CONCENTRATION

Opt. concn. of	1	2	3	4	1–3	1–4	3–4
Series 1	372	192	345	440	737	452	350
Series 2	355	180	320	422	640	497	377

It is apparent that the combination of Nos. 1–3 gives much greater stimulation than the optimum of either fraction alone. Nos. 1 and 3 cannot be identical materials since the increase in concentration of either alone above the optimum would decrease the yeast crop.

Conclusion

These results indicate that extracts containing bios contain at least two different yeast growth stimulants.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

BAUER OIL, THE HIGH-BOILING RESIDUE FROM MOLASSES FUSEL OIL.[1] A SOURCE OF CAPRIC ACID

BY C. S. MARVEL AND F. D. HAGER

RECEIVED NOVEMBER 19, 1923

Many investigations have been carried out on the composition of fusel oil from various sources but most of the work has been done on the lower-boiling fractions. A few articles have appeared in which the composition of the higher-boiling portions is discussed.

Rowney[2] has reported *iso*amyl caprate in corn fusel oil. Fischer[3] and later Grimm[4] have reported this ester in wine fusel oil and Johnson, in potato fusel oil.[5] More recently, Hilger[6] has found capric, lauric and palmitic acids in corn fusel oil. Luce[7] has reported pelargonic, capric and lauric acids in fusel oil. The fusel oil from sweet

---

[1] The material used in this investigation was furnished by the U. S. Industrial Alcohol Company, New Orleans division.

[2] Rowney, *Ann.*, **79**, 236 (1851).

[3] Fischer, *Ann.*, **118**, 312 (1861).

[4] Grimm, *Ann.*, **157**, 267 (1871).

[5] Johnson, *J. prakt. Chem.*, **62**, 262 (1854).

[6] Hilger, *Chem. Zentr.*, **1894**, I, 981.

[7] Luce, *J. pharm. chim.*, **22**, 136 (1920).

potato brandy[8] has been said to contain *iso*amyl palmitate and also capric, pelargonic and lauric acids. One investigation[9] on beet molasses fusel oil has shown that traces of fatty acids and their esters are present, but none of these is identified.

In all of the investigations only small quantities of the higher-boiling portions seem to have been available for study. As a result there may be some question as to the accuracy of the identification of some of the compounds that have been reported in the literature as occurring in this fraction. Recently a source for comparatively large quantities of the higher-boiling portion of molasses fusel oil has been found and this investigation of its composition has been made.

At the New Orleans plants of the U. S. Industrial Alcohol Company, alcohol is made from blackstrap molasses, chiefly Cuban. The molasses is diluted with water to which the necessary inorganic chemicals are added and fermented with a desirable yeast. The fermented material is then run through a continuous "beer still" heated with live steam, which delivers the "high wines" at the top and dealcoholized slop at the bottom. The high wines, containing the acetaldehyde, alcohol, and other volatile products of fermentation, are usually run about 65% alcohol by volume. The high wines are redistilled from a kettle still, fitted with a fractionating column of the plate type. The fractions obtained are the fumes (mainly acetaldehyde), 95% alcohol, alcohol of lower proof, fusel oil and water.

In finishing a charge, the fusel oil had been run up to the fifteenth plate of the column. The operators found on the lowest plate in the column another oil which naturally was much higher-boiling than fusel oil. It was found later that this oil was always left on the lower plate of the column and on the surface of the water remaining in the kettle after the alcohol and fusel oil had been taken off. This new oil was given the name of Bauer oil.[10]

Bauer oil can be isolated in only small quantities in the distillation process. This is shown by the fact that only about one quart of oil can be obtained from 25,000 gallons of high-wines. This quart of oil must be separated from about 10,000 gallons of water that remain in the kettle. Since the oil is very high-boiling and distils slowly with steam it is quite probable that some of it is lost in the beer still and runs out in the slop.

Bauer oil is a dark, brownish-red, oily liquid with a very disagreeable odor resembling that of pyridine, although no nitrogen is present. It is lighter than water, in which it is insoluble. It is readily soluble in organic solvents. A few preliminary tests indicated that the oil is mainly a mixture of esters of naturally occurring fatty acids together with a very

---

[8] Yoshitomi, Soejima and Imoto, *J. Pharm. Soc.* (*Japan*), **486**, 661 (1922); *C. A.*, **16**, 4295 (1922).

[9] Boswell and Gooderham, *J. Ind. Eng. Chem.*, **4**, 667 (1912).

[10] Henry Bauer, foreman of fermenting and distilling departments at the New Orleans plants, first noticed this oil.

small amount of non-saponifiable material which is responsible for the color and odor.

The oil was therefore distilled under reduced pressure using a modified Claisen flask[11] to give good fractionation. By repeating this process a few times the oil was separated into four definite fractions boiling over a few degrees range. The fractions were then identified as being mainly the ethyl esters of capric, lauric, myristic and palmitic acids. Each fraction contained a very small amount of a yellow, non-saponifiable liquid that could be separated from the ester only by saponification of the latter followed by steam distillation. The presence of this material gave the ester fractions a yellow color and the disagreeable odor of the crude oil. No indication of the presence of any appreciable quantities of esters of other acids was found. Only ethyl esters were present.

Bauer oil is especially interesting since it furnishes a very convenient raw material for the preparation of capric acid. The common fats do not contain a sufficient quantity of capric acid to make them useful as a source for this material. For this reason capric acid has always been one of the most expensive of the naturally occurring fatty acids. One gallon of Bauer oil after fractionation yields 650 cc. of the ethyl caprate fraction. From the ester by saponification and distillation of the free acid, a 70% yield of capric acid melting at 29–30° can be obtained. The oil also furnishes good yields of lauric and palmitic acids but they are more conveniently obtained from other raw materials.

The non-saponifiable material already mentioned has not been identified, as only a small quantity has been obtained and this boils over quite a wide range. From 535 g. of the ethyl caprate fraction by saponification and steam distillation about 30 g. of yellow oil was obtained. This oil is somewhat unsaturated, as it decolorizes potassium permanganate solution and decolorizes a carbon tetrachloride solution of bromine without the formation of hydrogen bromide. It gives a very deep red solution with cold concd. sulfuric acid. When shaken with concd. hydrochloric acid the oil does not dissolve but turns dark brown and the acid layer shows a marked fluorescence resembling that of a fluorescein solution. The oil contains a very small amount of sulfur but no nitrogen.

Experimental Part

Preliminary Tests.—The Bauer oil had an amber color and a very penetrating pyridine-like odor. Qualitative tests showed the absence of nitrogen or sulfur in appreciable quantities. The oil decolorized a very small amount of bromine in carbon tetrachloride and no hydrogen bromide was formed. There was some oxidation with potassium permanganate. When boiled for some time with aqueous alkalies almost all of

---

[11] Noyes and Skinner, This Journal, 39, 2718 (1917).

the oil dissolved, giving a reddish-brown solution. The oil dissolved in cold concd. sulfuric acid to give a deep red solution. A 200cc. sample distilled under 35mm. pressure boiled at 130° to 235°, leaving only about 5 cc. of residue in the distilling flask.

Fractional Distillation of Bauer Oil.—A 750cc. portion of crude Bauer oil was distilled from a 1-liter modified Claisen flask[11] and cut into 10° fractions. These fractions were redistilled thrice from a 250cc. flask. The final fractions collected under 6mm. pressure were —100°, 21 cc.; 100–105°, 131 cc.; 105–118°, 27 cc.; 118–127°, 25 cc.; 129–134°, 191 cc.; 134–149°, 33 cc.; 149–154°, 82 cc.; 154–174°, 43 cc.; 174–180°, 80 cc.; 180–195°, 15 cc. After each distillation some residual tarry material was left in the distilling flask.

The main fractions, therefore, boiled at 100–105°, 129–134°, 149–154° and 174–180° at 6 mm. These boiling points agree well with the boiling points of the ethyl esters of capric, lauric, myristic and palmitic acids under the same pressure. The intermediate fractions are undoubtedly mixtures of these esters. The fractionation of more than a gallon of Bauer oil gave results very similar to those obtained with the smaller quantity.

Identification of the Four Main Fractions.—A portion of each of the main fractions was boiled with 10% aqueous sodium hydroxide until saponification of the ester was complete. The aqueous solution was distilled and the first 10 to 15 cc. of distillate collected separately to be examined for the alcohol part of the ester. The distillation was continued until pure water distilled. A yellow oil floated on the surface of the distillate and was shown to be the non-saponifiable part of the original oil. When this was collected in the distillate the alkaline solution in the distilling flask was made acid and the fatty acid isolated by extraction with ether and purified by vacuum distillation or recrystallization.

The alcohol formed by the saponification was salted out of the first 10 to 15 cc. of the distillate by saturating it with potassium carbonate. No attempt was made to isolate the alcohol and distil it. It was identified by conversion into the 3,5-dinitrobenzoic acid ester by treatment with the corresponding acid chloride. The ester melted at 90–91° while ethyl 3,5-dinitrobenzoate melts at 92°. A mixed melting point of the ester from the unknown alcohol with ethyl 3,5-dinitrobenzoate completed the identification of the alcohol in the Bauer oil esters as ethyl alcohol. The same alcohol was isolated from each of the ester fractions.

The fatty acid obtained from the ester fraction boiling at 100–105° at 6 mm. was purified by distillation under reduced pressure. It boiled at 165–170° at 25 mm. and melted at 29–30°. A sample weighing 0.3768 g. required 22.55 cc. of 0.0956 *N* sodium hydroxide for neutralization, which gives a neutralization equivalent of 174.7. The amide, prepared by conversion to the acid chloride with phosphorus pentachloride followed by treatment with ammonium hydroxide solution, melted at 96° after one recrystallization from petroleum ether. These constants agree closely with those of capric acid which boils at 170° at 25 mm.,[12] melts [13] at 31.3° and has a neutralization equivalent of 172.2. Capramide melts at 98°.[14]

---

[12] Bagard, *Bull. soc. chim.*, [4] **1**, 348 (1907).

[13] Houben, *Ber.*, **35**, 3592 (1902).

[14] Hofmann, *Ber.*, **15**, 984 (1882).

The fatty acid obtained from the ester fraction boiling at 129–134° at 6 mm. was purified by both vacuum distillation and recrystallization from dilute alcohol. This acid melted at 42–43°. A sample weighing 0.4119 g. required 21.05 cc. of 0.0956 *N* sodium hydroxide for neutralization, which gives a neutralization equivalent of 204.6. The amide prepared from the acid chloride and ammonium hydroxide melted at 97°. The constants identify the acid as lauric acid which melts[15] at 43.6° and has a neutralization equivalent of 200.2. Lauramide melts[16] at 99°. A mixed melting point of the acid isolated from the ester with known lauric acid completed the identification.

The fatty acid obtained from the ester fraction boiling at 149–154° (6 mm.) was purified by vacuum distillation and recrystallization from glacial acetic acid; m. p., 49–51°. A sample weighing 0.3150 g. required 13.3 cc. of 0.1010 *N* sodium hydroxide for neutralization, which gives a neutralization equivalent of 231. Myristic acid melts[15] at 53° and has a neutralization equivalent of 228.2. A mixture of the acid prepared from Bauer oil with pure myristic acid melted at 49–51°.

The fatty acid obtained from the ester fraction boiling at 174–180° (6 mm.) was purified by recrystallization from glacial acetic acid; m. p., 62–63°. A sample weighing 0.300 g. required 12.1 cc. of 0.0956 *N* sodium hydroxide for neutralization, which gives a neutralization equivalent of 258.5. Palmitic acid melts[17] at 62.6° and has a neutralization equivalent of 256.3. A mixed melting point of the acid with pure palmitic acid melted at 62–63°.

Preparation of Capric Acid.—A mixture of 200 g. of the ethyl caprate fraction and 750 cc. of 10% sodium hydroxide solution was refluxed for a few hours until saponification was complete. The condenser was then arranged for distillation and the solution was boiled until only water distilled. The distillate contained the non-saponifiable material that has been mentioned before. The alkaline solution remaining in the flasks was reddish-brown. This color was not removed by treatment with boneblack but was removed by treatment with a little potassium permanganate solution. The color need not be removed to obtain good capric acid. The capric acid was precipitated with acid, collected in ether and distilled under reduced pressure. The lowest-boiling fraction was yellowish and was discarded. The capric acid collected at 160–170° (25 mm.) was light yellow and melted at 28–29°; yield, 130 to 145 g. One redistillation gave 115 to 130 g. of nearly white acid boiling at 165–170° (25 mm.) and melting at 29–30°.

Non-saponifiable Material from Ethyl Caprate Fraction.—The non-saponifiable material was obtained by the steam distillation of the alkaline saponification mixture as described in the preceding paragraph. This oil was not soluble in water and was collected in ether and distilled under reduced pressure. It boiled at 112–142° (20 mm.). There was no indication of a definite boiling point. From 535 g. of ethyl caprate only 30 g. of this non-saponifiable material was obtained. Even less was obtained from the higher-boiling ester fractions. The oil decolorized potassium permanganate solution and also a carbon tetrachloride solution of bromine. It dissolved in cold concd. sulfuric acid to give a deep reddish-brown solution. When treated with concd. hydrochloric acid the oil became brownish-red and the hydrochloric acid solution showed a marked fluorescence resembling that of fluorescein. When heated with metallic sodium there seems to be a reaction with some evolution of gas. The sodium became coated with a reddish layer. Qualitative analysis showed that no nitrogen was present but traces of sulfur were found. The oil did not react with phenylhydrazine.

---

[15] Krafft, *Ber.*, **15**, 1724 (1882).

[16] Caspari, *Am. Chem. J.*, **27**, 306 (1902).

[17] Scheij, *Rec. trav. chim.*, **18**, 188 (1899).

Summary

The high-boiling residue from cane molasses fusel oil has been found to consist mainly of the ethyl esters of capric, lauric, myristic and palmitic acids together with a little non-saponifiable material.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY AT THE UNIVERSITY OF WISCONSIN]

DEAMINIZATION.[1] III. EVIDENCE OF THE EXISTENCE OF ALIPHATIC DIAZONIUM SALTS FROM THE FORMATION OF CHLORO-OXIMINO COMPOUNDS

BY GLENN S. SKINNER

RECEIVED NOVEMBER 19, 1923

The nitrites of aromatic primary amines lose one molecule of water to give diazohydrates which according to Hantzsch[2] give diazonium salts with acids through tautomeric change. The nitrites of aliphatic primary amines give by the loss of two molecules of water the diazo compound as the first isolable decomposition product which still contains the nitrogen of the amine. These nitrites of aliphatic bases are regarded as very unstable compounds, but it has been shown by Wallach[3] that some are so stable as to be crystallizable from water in the absence of the last trace of acid. With respect to the diazo compounds themselves it has been shown by Staudinger and others[4] that the substitution of so-called negative groups on the carbon atom bearing the amino group greatly increases the stability. Aliphatic diazonium salts have not been isolated.

It seemed reasonable that typical aliphatic diazonium salts must exist from a review of their well-known reactions although they do not undergo certain reactions of aromatic diazonium compounds. For example, the coupling reaction does not take place, but with water, alcohol and acids they react to give products which are exactly analogous. However, it may be argued that the true diazo compound, $RCHN_2$, is first formed and that this reacts to give compounds which are similar to those in the aromatic series. In the production of the aliphatic diazo compound from the amine the reaction may well pass through either the diazohydrate or the diazonium salt, but as long as they have not been isolated it is still open to question. The isolation of certain heterocyclic diazonium salts and derivatives which are obtained by the coupling reaction from antipyrine, triazole and pyrazole shows that the existence of such compounds is not

---

[1] Previous papers: Skinner, THIS JOURNAL, **45**, 1498 (1923). Barker and Skinner, *ibid.*, **46**, 403 (1924).

[2] Engler and Hantzsch, *Ber.*, **33**, 2150 (1900).

[3] Wallach, *Ann.*, **353**, 318 (1907).

[4] Staudinger and Gaule, *Ber.*, **49**, 1897 (1916).