

DOUBLER STILL WITH BEER STILL IN THE BACKGROUND

IN THE manufacture of whisky from the fermentation mass or beer, the mixture is distilled through a beer still into a tank called the "singling tank." The crude, so-called low wines contain about 50 per cent alcohol and are further fractionated by distilling through the doubler. The first and middle fractions are run directly into the whisky well; the last fraction or tails, containing about 10 to 35 per cent alcohol, is run back into the singling tank to be mixed with the next run from the beer still.

As the concentration of alcohol falls in the doubler a white, insoluble, fatlike material appears in the trial box. Although most of this goes back into the singling tank, some collects in the condenser and is partially dissolved and washed out by the higher alcoholic content of the next distillation. This appears in the heads or foreshots of the next distillation and is colored a distinct green. This part of the insoluble material goes directly into the whisky well and dissolves in the strong alcohol present. Thus a part of the original volatile fatty material collects in the singling tank, and part finds its way into the whisky. The trade calls this material "verdigris" which is an unfortunate name since it has no connection with the verdigris of commerce. For lack of a better name, it will be called "whisky verdigris" in this article.

The amount of this material is small in comparison to the volume of alcohol produced. Probably 250 grams per 30,000 liters of high wines would be a fair approximation, although no exact figures are available and would be very difficult to obtain. Of this amount only a part is washed into the whisky well and dissolved. In addition, some is probably in solution in the distillate when the alcoholic content is high.

The exact nature of the so-called congeners of whisky is not known since they occur in such small amounts; nevertheless they are the deciding factor in the flavor or taste that a whisky

WHISKY VERDIGRIS ANALYSIS

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will have. An analysis of this fatty material would at least indicate the nature of some of the congeners, although no exact figures could be given.

Only one reference to this material has been found in the literature. Allen (2) states that the foreshots of a distillation when diluted with water produce turbidity, and finally oily globules appear. A cursory examination of this oil showed that part of it could be distilled. Although the nonvolatile material consisted chiefly of fatty acids, the volatile portion contained acids, esters, and unsaponifiable material, and had a most intolerable odor. It is remarkable that no complete analysis has ever been made because it is present at all distilleries and offers a method of determining qualitatively some of the congeners in whisky.

Through the courtesy of W. T. Black, a former graduate student at the University of Kentucky, approximately 350 grams of the whisky verdigris were obtained. About half of the sample came from the singling tank and the other half from the trial box of the doubler. This sample would not be a true picture of the material dissolving in the whisky, but it seems reasonable to expect that the variation in composition would be small.

Experimental Procedure

Three hundred thirty-seven grams of the wet, pasty, whisky verdigris were extracted by centrifuging with 2.5 liters of ether in twenty-one portions. Eighty-two grams of dry, ether-insoluble material remained as a green fluffy solid.

The green ether solution was extracted with 2 *N* potassium hydroxide, and from this soap solution 25.5 grams of dry acids were obtained which were solid at room temperature.

The ether phase, upon drying and evaporating, yielded a brown oil containing about 0.1 gram of suspended cupric oxide which was removed by centrifuging. The oil, after drying over sulfuric acid, weighed 90.1 grams. From the quantity of cupric

TABLE I. ANALYTICAL DATA ON REDISTILLED FRACTIONS

Fraction No.	Temp. at 2 Mm. ° C.	Weight Grams	Mean Mol. Wt.	Iodine No. (Hanus)	Unsatd. Esters ^a	Ethyl Oleate	Ethyl Linolate	Ethyl			Unsataponifiable Matter
								Caprate	Laurate	Palmitate	
1	75-90	5.1	221	9.2	0.44	0.32	0.12	2.83	1.83
2	115-133	3.9	259	11.5	0.43	0.31	0.12	..	1.92
3	138-146	20.1	296	24.3	4.65	3.34	1.31	15.45	..
4	148-150	9.4	298	37.6	3.36	2.42	0.94	6.04	..
5	150-152	4.1	308	43.3	1.69	1.22	0.47	2.41	..
6	152-156	16.5	309	92.5	14.50	10.44	4.06	2.00	..
7	156-158	9.6	314	117.5	9.3	6.70	2.60	0.30	..
8	158-162	3.9	320	105.8	3.9	2.81	1.09
9	Residue	1.1	349	93.1	1.1	0.79	0.31
10	Residue (preliminary distn.)	9.2	7.5	5.40	2.10	0.10	1.66
Total		82.9	33.75	13.12	2.83	3.75	27.85	1.6
Per cent		40.79	15.82	3.42	4.53	33.59	1.94

^a The iodine number 105 was used in these calculations.

^b Expressed as from this fraction rather than as distributed throughout the samples.

oxide obtained, it was evident that the ether-soluble cupric salts were negligible.

The total weight of the dried fractions was 197.6 grams, a weight loss of 41.3 per cent due chiefly to water. The composition given in Table II was calculated from this quantity.

Neutral Ether-Soluble Fraction

Preliminary experiments indicated the presence of a large amount of ethyl esters and the complete absence of glyceryl esters. Constants were determined as follows: iodine number, 61.5 (Hanus); saponification number, 187.9; unsaponifiable matter, 1.94 per cent.

Preliminary distillation of 85 grams of this fraction at 2 mm. yielded 74.3 grams of oil which were cut into six fractions distilling over a range of 98° to 180° C., and 9.2 grams of an oily residue. Redistillation of these fractions into eight volatile and one nonvolatile fraction at 2 mm. is summarized with the analytical data in Table I.

The various fractions were saponified with aqueous potassium hydroxide, and the soap solutions were distilled until the iodoform reaction was negative. These alcohol distillates were combined for the determination of higher alcohols. The soaps were then extracted with ether, and these extracts were combined for the investigation of the unsaponifiable matter.

FRACTION 1 yielded acids melting at 20° to 21° C., and with a neutral equivalent of 187. A 2-gram fraction was hydrogenated with the Adams catalyst to render the unsaturated acids nonvolatile (5), and was steam-distilled. Barium salts were prepared from the steam distillate, and they were crystallized from water according to Allen (1). Beginning with the most insoluble crystals, the percentages of barium were as follows: 25.42, 25.77, 27.65, 28.15, 28.69. Barium laurate and caprate require, respectively, 25.64

and 28.65 per cent. Inasmuch as the two extremes check closely, the saturated esters are expressed as laurate and caprate.

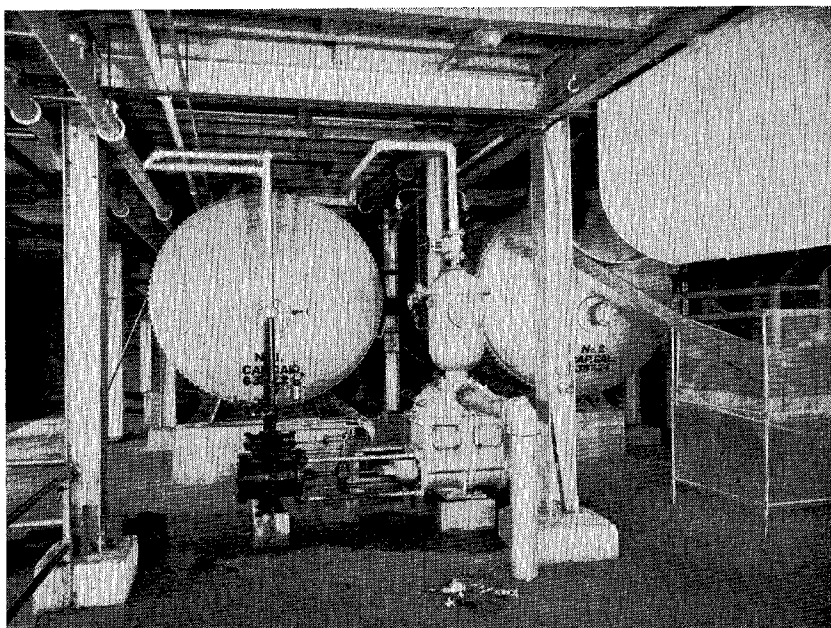
FRACTION 2 was not analyzed since it was small, and attempts to isolate acids lower than palmitic in fraction 3 proved impossible.

FRACTIONS 3, 4, 5, 6, and 10 invariably yielded palmitic as the only saturated acid by crystallization from alcohol (4). Throughout the investigation palmitic acid was characterized by its melting point of 62.5 ± 0.2° C. and its neutral equivalent of 256.3 ± 1.0.

FRACTIONS 7 and 8 were combined and their acids subjected to the lead salt-ether separation according to Jamieson (8), except that the ether-insoluble salts were removed and washed by centrifuging. This yielded 0.15 gram of palmitic acid and 6.23 grams of liquid acids, neutral equivalent 283 and iodine No. 115. The unsaturated acids were brominated according to Baughman and Jamieson (3). No hexabromide was obtained, but crystals from petroleum ether proved to be linolic acid tetrabromide, melting at 113° to 114° C., and analysis of the noncrystalline residue from the mother liquor gave 39.40 per cent bromine. Tetrabromide and dibromide require, respectively, 53.33 and 36.18 per cent bromine; hence a more saturated acid than linolic is present and is regarded as oleic. The iodine number of the liquid acids, 115, calculated to ethyl esters, 105, was used in calculating the distribution of oleate and linolate in the fractions of Table I.

ALCOHOLS. Although the alcohol distillates from all fractions gave positive iodoform tests, it was desirable to identify ethyl alcohol positively; hence it was salted out of the saponification distillate from 7 grams of fraction 6 and formed a 3,5-dinitrobenzoate which melted at 91.5° C.

Fusel oil was determined in the combined distillates by the method of Penman, Smith, and



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CONVERTERS FOR SACCHARIFICATION OF GRAIN STARCHES

Lawshe (12). Using the synthetic standard and vanillin, the concentration calculated to the neutral ether-soluble fraction was 0.154 per cent.

UNSAAPONIFIABLE MATTER. The ether extracts of the soap solutions upon evaporation yielded 1.4 grams of a viscous oil having somewhat the odor of corn. It contained no nitrogen or sulfur and gave negative tests for sterols, alcohols, aldehydes, ketones, and unsaturated compounds, although a slight coloration was produced when it was treated with strong sulfuric acid. Repeated crystallization from alcohol yielded 0.2 gram of an odorless, white, waxy solid, melting at 42.5° C. and insoluble in and giving no coloration with cold concentrated sulfuric acid. Since the quantity was small and the purity questionable, it was not analyzed, but was considered to be a hydrocarbon.

Free Acids

Constants were determined as follows: weight, 25.5 grams; iodine number, 51.68; neutral equivalent, 268.2.

Separation by the lead salt-ether method as previously described yielded 8.88 grams of liquid acids (iodine number, 114) and 13.86 grams of solid acids (neutral equivalent, 258.3; iodine number, 5.09). The liquid acids were assumed to be of the same character as those obtained from the ester fractions. The solid acids after one crystallization from alcohol proved to be palmitic, melting point 62° to 62.5° C., and neutral equivalent 256.4. The calculated distribution of the free acids in per cent is palmitic 54.74, oleic 32.60, linolic 12.66.

Ether-Insoluble Material

This fraction had an ash content of 30.3 per cent, which was analyzed as follows: cupric oxide, 26.25; ferric oxide, 23.87; silica, 31.90 per cent.

Seventy-nine grams of the green solid were digested on the steam bath with 6 *N* sulfuric acid, cooled, and filtered. The clear blue filtrate was distilled and required less than 1 cc. of 0.1 *N* alkali for neutralization; hence only traces of water-soluble volatile acids were present. The filter cake upon extraction with ether yielded 29 grams of solid acids (iodine number, 3.90), which were considered to be saturated. Crystallization from alcohol yielded pure palmitic acid, melting point, 62.3° to 62.8° C., and neutral equivalent, 256.1.

The green solid when leached with hot alcohol was dissolved, leaving a brown solid. Upon filtering and cooling, the alcohol solution deposited green crystals; hence the palmitic acid is considered to be held as a cupric salt.

Discussion of Results

The higher fatty acids and their derivatives found in whisky verdigris without doubt originate mainly in the corn (3) which makes up from 60 to 89 per cent of the total grain used in making Bourbon whisky from which the sample was obtained. The corn oil alone does not offer an explanation of the presence of laurate and caprate esters, although Hilger (6) reported the free acids to be present in fusel oil. The occurrence of the various fatty acids and their derivatives in the beer is easily understood, but their presence in the distillate is more difficult to explain. Although it is known that the higher fatty acids are volatile in steam, or at least volatile in steam containing the vapors of more volatile acids, it must be remembered that this is not purely a steam distillation. In support of the evidence of Arnold, cited by Lewkowitsch (9), the writers were able to isolate 0.2 gram of pure palmitic acid from 3000 cc. of steam distillate from the acids of fraction 3 of the ether-soluble material.

It is possible that the acids distill and cling to the copper condenser, and that partial salt formation (11) and esterification take place there. The majority of the esters are probably formed in the beer, and many other possibilities are obvious although none appears to explain satisfactorily the

absence of stearic acid or its derivatives. Although this acid has been reported in fusel oil (6), the writers were unable to find any indication of its presence in whisky verdigris.

The absence of the cupric salts of the unsaturated acids is easily correlated with the generally higher solubilities of the salts of liquid acids in organic solvents.

The presence of silica and iron oxide in the ash was not understood until it was learned that the singling tank from which part of the sample was removed had been regularly charged with spring water while the sample was being collected. Neither of these substances could reasonably be expected to pass through the doubler.

Whisky verdigris has a strong odor of green whisky and may be said to be yeasty; although none of the substances mentioned by Hochwalt and others (?) were found, their hydrogenation process may owe part of its effectiveness to the reduction of the unsaturated derivatives which otherwise become rancid.

A cursory survey of the literature revealed no definite information as to the copper content of whisky; however, Lythgoe, Berry, and Hall (10) state that copper was present in 10 per cent of the distilled beverages intended for sale in Massachusetts, and Wood (14), quoting Hayes, states that new spirits from copper stills are likely to be contaminated with that metal. Hayes believes that this copper is deposited upon aging.

TABLE II. ANALYSIS OF WHISKY VERDIGRIS SAMPLE ON A DRY BASIS

Ethyl caprate	1.56%	Copper	2.70%
Ethyl laurate	2.07	Silica	4.03
Ethyl palmitate	15.32	Iron oxide	3.03
Ethyl oleate	18.60	Palmitic acid held as green ether-insol. salt	28.80
Ethyl linolate	7.11	Ether-sol. unsaponifiable matter, chiefly hydrocarbons	0.88
Palmitic acid	7.06	Fusel oil	0.07
Oleic acid	4.20	Total	97.12
Linolic acid	1.69		

The highest value found by Valaer and Frazier (13) for the nonvolatile acids in new whisky was 2.4 grams per 100 liters. In 197.6 grams of dry whisky verdigris 25.5 grams of free acids have been found; hence if the sample is homogeneous, it may be calculated that about 1000 liters will be required to contain the sample, or that new whisky contains 0.02 per cent of this material. Since the congeners are usually represented at 0.25 to 0.50 per cent, it is evident that all of the congeners have not been accounted for.

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