

## THE POISON IN ILLICIT LIQUOR.

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Since the passage of the Volstead Law attention has been repeatedly directed to the condition of profound stupor and even death after imbibing "bootleg" liquor. Thus Gerty (1) of the Cook County Psychopathic Hospital, Chicago, in contrasting the prevalent alcoholic poisoning with alcoholism of the pre-prohibition variety states that significant differences can be detected. He asserts that the type of poisoning now seen differs from ordinary alcoholic poisoning in the following ways: 1. The poison takes effect more rapidly, and the patient is brought to the hospital sooner because of the gravity of his symptoms. 2. A smaller amount of the prevalent beverage is required to incapacitate and the effect is more profound and more often fatal. 3. Mental deterioration is a common sequel, even after a few sprints.

Doran and Beyer (2) point out that evidence in the shape of reports by the press; heads of hospital staffs; public officials, federal, State and city; show that while alcoholism is less prevalent, its attendant and after effects are more serious. These authors discuss the effects of drinking mixtures containing methyl alcohol and mixtures made from denatured alcohol, and point out that the popular knowledge of these facts has led many people to resort to liquor of seemingly known and recent origin under the impression that being locally made it is at least safe and pure. Doran and Beyer (2) also say that for generations the moonshiner of the mountains knew that the "heads" or first runnings of the distillation and the "tails" should be thrown away. He also knew that the middle run must be redistilled several times in order to make what was to him a passable "mountain dew." He was also extremely careful of his yeast. He did not know that the heads were high in aldehydes or that the tails were high in fusel oil, yet he knew by experience that unless he did do these things even the strong man of the hills could not stand up under the load. From this old practice there developed the large controlled grain distillery. Even the distillery product is not considered potable when first made but is aged in wooden barrels for years before being considered fit for sale as beverage liquor.

Crompton and Tolman (3) in a very extensive series of whisky analyses covering all ages of legitimately made whiskys, showed conclusively that the fusel oil content of whisky was not eliminated on aging as long as eight years but is even increased. The harmful effect of new whisky is therefore not due to its fusel oil content. In the aging of whisky in wood there is a slow reaction between small quantities of organic acids and higher alcohols with the formation of highly flavoring and odorous esters. These changes are slight, however, and do not seem sufficient to Doran and Beyer to account for the marked difference in the physiological effects noted when new or raw whisky is compared with old.

Doran and Beyer (2) as a result of many thousands of analyses, found that whisky which was brought into the laboratory in connection with raids on moonshine distilleries usually showed a high content of aldehyde. The "ranker" the liquor, the higher the aldehyde content. They explain this by pointing out that

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the moonshiner does not control the fermentation of his mixture and there results a considerable oxidation of the ethyl alcohol into acetaldehyde and even acetic acid. The simple pot still and their eagerness for more profits in not discarding heads and tails does the rest and the resulting liquor presented to the trusting purchaser has everything needed to produce a knockout.

Doran and Beyer (2) find an average aldehyde content of 30 parts per one hundred thousand for their samples of moonshine as compared with an average aldehyde content of 3.9 parts per one hundred thousand, as found by Crompton and Tolman, (3) for new whisky made under better conditions in pre-Volstead days. The fusel oil and the other constituents in the two series are essentially the same. Doran and Beyer also found traces of copper and zinc salts in their samples. Since aldehydes are so markedly increased these authors advance the hypothesis that this is the toxic substance present in moonshine liquor, but performed no animal experiments. They point out that these aldehydes can be removed by more careful fractionating and by polymerization on aging in wood.

Statistics collected by McNally (4) of the Cook County Coroner's Office also show that deaths from alcoholism are on the increase. His chemical analyses of illicit liquors failed to show a definite toxic substance responsible for the increase in deaths. He gave moonshine liquor in daily doses of 1 cc. to rats and found that they died in a few months. A second series of rats was given for many months 2 cc. per day of a solution containing 200 parts of acetaldehyde per one hundred thousand in 50 per cent alcohol without causing death. A third series used as controls were given 1 cc. per day for many months of pure grain alcohol of the same strength without harm. Hence, these results of McNally indicate that the toxic substance present in moonshine is not acetaldehyde since the quantity of similar substances administered was much higher than found by Doran and Beyer (2) in moonshine.

Hunt (5) also hesitates to believe that this compound is responsible for the harmful effect of illicit liquors; for, as he points out, acetaldehyde is only seven or eight times as poisonous as ethyl alcohol itself and in the samples analyzed by Doran and Beyer there was on an average about fifteen hundred times as much alcohol as acetaldehyde. A person would have to consume almost his own weight of the liquor in order to get a fatal dose of acetaldehyde; of course he would die of alcoholic poisoning long before he could get a dangerous dose of acetaldehyde (Hunt).

Hunt's own investigations of samples of illicit liquors alleged to have caused death in man have demonstrated their toxicity for animals to be fully accounted for by the ethyl alcohol they contained; he is inclined to think that, unless the victims of such poisoning had taken something besides the liquor analyzed, the results were due to the quantity of alcohol drunk or the manner in which it was taken, rather than to its quality. The depth of intoxication and the danger to life depend, as Hunt points out further, on the concentration of alcohol in the blood, and this is determined not only by the amount of alcohol taken but also by its concentration. There is a rather small margin between the amount of alcohol in the blood necessary to cause deep intoxication and that sufficient to cause death; hence, if a person takes a large amount of strong alcohol within a short time, he may get enough to cause not only intoxication but even death.

In this connection Mellanby (6) found 0.446 per cent alcohol in the blood of dogs produced only slight intoxication; 0.468 per cent resulted in profound collapse. Other reports indicate a greater margin of safety.

The condition of profound stupor and even death sometimes ascribed to a bad grade of moonshine may be thus due to its ethyl alcohol content alone. It may be explained by the tendency of some individuals to exceed their normal capacity when unwillingly deprived of their accustomed liquor for a prolonged period on account of the difficulty of obtaining it.

Studies of MacNider (7) indicate that ethyl alcohol administered to animals (dogs) over a period of six to twelve weeks in daily doses of 10 cc. per Kg. of a 40 per cent solution is only slightly nephrotoxic. Naturally nephropathic animals are more susceptible to the toxic effect of the same amount of alcohol than are normal individuals of the same species. However, when normal dogs are given instead of pure alcohol an equivalent dose of alcoholic distillate obtained without refining from a fermented mixture of corn meal and molasses, there develops evidence of its nephrotoxic action, which is shown functionally by a pronounced albuminuria. On nephropathic animals, the effect is even more pronounced. Associated with a reduction in urine formation occurs a decrease in the elimination of phenol-sulphonephthalein, a retention of non-protein nitrogen in the blood and a reduction of its alkali reserve. Fatty changes arise in the glomerular vessels, and the tubular epithelium also may show evidence of injury. According to MacNider, the toxicity of the unrefined "distillates" from the fermented mixtures is not primarily due to their content of ethyl alcohol but to some undetermined substance. Purified ethyl alcohol should not be held responsible for the insidious harm that even small quantities of undesired accompaniments in crude distillates may bring about.

"Traces of allyl alcohol if produced in the fermentation tend to be eliminated along with fusel oil in alcoholic distillation and when fusel oil is refined, accumulates in the normal propyl fraction, where the amount may reach 3 per cent or more. The pungent odor and the marked physiological action of some of the fusel oil products are probably due almost entirely to their allyl content." (8a) This unsaturated alcohol is discussed in greater detail later.

Attempts have also been made to explain the poisonous properties of illicit liquors as due to their content of "fusel" oil. Crompton and Tolman found that new whiskeys contained an average "fusel" oil content of 95.2 parts per one hundred thousand and that it remained practically unchanged after aging. This is practically the same as found by Doran and Beyer (2) in seized moonshine liquors. For these reasons the poisonous properties of properly distilled liquors are not due to the fusel oil content. However, the situation may be very different when the distillation is carelessly done and the "tails" are not rejected. Many car loads of fusel oil are obtained annually as a by-product of legally conducted distilleries. Some moonshiners, however, operated under very crude conditions and do not remove the fusel oil. One crude still seized consisted of a metal gasoline drum and a piece of pipe. Under the best conditions "fusel" oil is not a factor in increasing the poisonous properties of illicit liquors but under bad conditions it may well be especially in the case of chronic drinkers.

"Fusel Oil" is an impure mixture of higher alcohols, principally amyl alcohol.

It is used as a solvent for paints and in chemical industries; the inhalation of vapors may cause headache and palpitation of the heart. Animal experimenters show it to be about 40 times as toxic as ethyl alcohol and a few cases of poisoning in human beings have been reported.

The toxicity of alcohols, at least in acute intoxication, increases up to a certain point with the size of the molecule; thus, ethyl alcohol is more toxic than methyl, propyl alcohol is more toxic than ethyl alcohol, butyl more toxic than propyl and amyl more toxic than butyl, and primary alcohols more toxic than secondary alcohols.

The following table is based on the lethal dose of these alcohols for cats (Macht) (9):

	Formula.	Molecular weight.	Toxicity.
Methyl alcohol	$\text{CH}_3\text{OH}$	32	1.0
Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	46	1.2
Propyl alcohol	$\text{C}_3\text{H}_7\text{OH}$	60	2.95
Butyl alcohol	$\text{C}_4\text{H}_9\text{OH}$	74	19.7
Amyl alcohol	$\text{C}_5\text{H}_{11}\text{OH}$	88	39.0

This table holds true for the relative toxicity in acute poisoning but does not tell the entire story in reference to methyl alcohol in subacute poisoning because it does not take into account the secondary effect of methyl alcohol on the optic nerve. These figures are not exact for man but the toxicity for man is probably *greater* than shown because poisons which affect the highly differentiated nerve structures very powerfully are proportionally more dangerous the more highly developed the nervous system of the animal.

#### COPPER AND LEAD.

Mallory (10) using rabbits showed that copper acetate causes hemo-chromatosis (pigment cirrhosis of the liver). Analysis of a limited number of samples of distilled liquors showed from a trace to 185 mg. of copper per liter, evidently derived from the solvent action of organic acids on the copper worm of the condenser. Mallory also says that the Director of the Division of Foods and Drugs of the department of Public Health of Massachusetts has tested 798 samples of "hooch" and found copper present from a trace up to 32 mg. to the liter in 10.8 per cent. Samples of even "home brew" have been found on chemical examination to show the presence of 25 mg. of copper to the liter. A man drinking a quart of whisky per day containing the maximum amount of copper found, will take into his system about a gram of copper per week which is comparable to the amount required slowly (2 months) to produce pigment cirrhosis in rabbits and monkeys. Several cases having an alcoholic history and coming the post-mortem table had pigment cirrhosis of the liver but did not have an increased content of the copper in the liver. Several cases exposed to occupational hazards of copper also had pigment cirrhosis but no increased copper in the liver. Therefore, under maximum conditions copper may be the toxic element in moonshine liquor but such a possibility is remote.

Vaughan (11) reports three cases of lead poisoning apparently due to whisky which he found to contain lead probably derived from the distilling apparatus.

"Bootleg" liquors are not only raw home brew products, but are also synthetic preparations, sometimes, made from denatured alcohol. New York City authorities (12) state that more than 450 people died in New York City alone during 1924 as a result of taking moonshine or hootch. Some of it is made from wood alcohol and ethyl alcohol denatured with wood alcohol, benzene, bichloride of mercury, ether, kerosene, fusel oil, sulphuric acid, diethylphthalate, propyl alcohol, phenol, formaldehyde and many other substances.

Prohibition enforcement officials at New York City claim that about 20% of the stuff sold in New York City is smuggled into this country, the remaining being manufactured here, mostly from partially denatured alcohol intended for industrial purposes obtained under permits issued to bootleggers under three formulas, known as 39A, 39B and 40.

The first formula is for the manufacture of barbers' supplies, liniments and rubbing alcohols, and is denatured with acetone, isopropyl alcohol, quinine alkaloids and benzene; the second formula is for cleansing soaps for the kitchen and for stove and shoe polish, and is denatured with diethylphthalate and benzene; the third formula is for the manufacture of perfumes and cosmetics and is denatured with brucine, acetone and isopropyl alcohol. Instead of making it into these substances, the denatured alcohol is made into "Old Scotch" and "Gordon Gin" and "Jamaica Rum."

The Connecticut Agriculture Experiment Station (13) investigated samples of alleged whisky and found aside from one series containing wood alcohol no foreign substance which in kind or amount could be regarded as a probable cause of death. Much of the alcohol used in preparation of present-day liquors is obtained by the rectification of denatured alcohol, particularly the specially denatured type. Such alcohols generally show on analysis traces of denaturants that have carried over in the process of purification. There is no authoritative opinion that traces of such substances as diethylphthalate, isopropyl alcohol, benzene and acetone are likely to produce serious effects. However, there is always the possibility of inefficient purification with increased danger. In nearly half of the Connecticut samples tested the alcohol appeared to have been derived wholly, or in part, from denatured alcohol.

#### WOOD ALCOHOL.

Wood alcohol poisoning has repeatedly occurred from drinking bootleg liquors (14, 15). The wood alcohol has been used through ignorance and has been used as the only alcohol present or has been derived from grain alcohol denatured with methyl alcohol. Wood alcohol poisoning was known before the passage of the Volstead Act. Even in 1910 (15) wood alcohol was a fairly constant ingredient of the cheaper wines, brandies and whiskies sold in the low resorts of the East Side, in proportions ranging from 24 to 43 per cent and has been repeatedly found in soft drinks and toilet preparations.

Methyl alcohol is usually obtained from the destructive distillation of wood, although it is also made synthetically. Crude samples of wood alcohol have an extremely disagreeable odor and taste due to the impurities present. These impurities are acetone, methyl acetate, allyl alcohol, furfural, etc.

"Methyl alcohol is produced in the United States in grades varying from the denaturing wood spirit, containing 18 to 30 per cent acetone, with considerable

amounts of allyl alcohol and other impurities up to the best grade of acetone, free methyl alcohol, which is also practically water free. It finds use as a denaturant of ethyl alcohol—the lower grades as a complete denaturant and the so-called ‘commercially pure’ methyl alcohol (99%) in some of the special formulas (8b).”

It has been claimed that the impurities are responsible for the peculiar toxicity of wood alcohol and it has been even claimed that pure methyl alcohol is no more toxic than ethyl alcohol. However, several investigators (16, 17) have found very little difference between pure methyl alcohol and ordinary commercial samples.

It has also been claimed that the impurities present do not produce the characteristic effects. The impurities to which attention has principally been directed are furfural and acetone. The toxicity of furfural in acute poisoning, based on the lethal dose for rabbits, is about ten times as great as methyl alcohol (18). Acetone is more fatal than methyl alcohol in acute intoxication but not very much so (16). The presence of allyl alcohol has been ignored as it was thought to be present in too small amounts to be significant.

“The allyl alcohol content of crude wood spirit is 0.3 to 0.5 per cent. The wood spirit used for denaturing has a somewhat higher allyl alcohol content, the latter have been increased by the addition of those fractions from the refining which are high in allyl alcohol (8c).” The above quotation from Burghart was probably intended to apply to practices in England since the specifications of the Internal Revenue Department of this country give an upper limit for unsaturated compounds such as allyl alcohol permitted in wood alcohol used for denaturing purposes.

This alcohol  $\text{CH}_2:\text{CH}.\text{CH}_2\text{OH}$  is a pungent liquid with a burning taste and mixes readily with alcohol, water and ether. Boiling point  $96.6^\circ\text{C}$ . Specific gravity, 0.8573 at  $15/15^\circ\text{C}$ . It is oxidized to acrolein and formic acid by dilute oxidizing agents. In dogs it was found that when given by mouth 0.05 cc. per Gm. of allyl alcohol in one per cent solution causes death in about seven hours. The toxicity based upon the lethal dose, is therefore about 150 times that of methyl alcohol. Allyl alcohol was found to be present to the extent of 0.5 per cent in one sample of wood alcohol obtained from the drug store and labeled chemically pure methyl alcohol.

The symptoms of allyl alcohol poisoning are similar to those commonly ascribed to wood alcohol especially the marked hyperemia of the gastric mucosa, intense vomiting, convulsive movements and coma. One animal receiving a sublethal dose developed in two days an opacity, apparently of the cornea, with blindness in one eye. This cleared up in two days more. Hunt describes similar optic symptoms in dogs given methyl alcohol. Upon subsequent histological examination he found the retinal cells degenerated.

The practical bearing of this is that some cases of so-called wood alcohol poisoning due to the use of this alcohol in illicit liquors as a substitute for ethyl or grain alcohol, may be due, in part at least, to the presence of allyl alcohol as an impurity in sufficient quantities to be significant.

Nine samples of seized liquors were examined for allyl alcohol and it was not found. This series is too small to be particularly significant especially since these samples complied with all of the official U. S. P. tests for whisky and may be considered as well-made preparations. Since it has been shown to be present in fermented liquors and also in wood alcohol, illicit liquors should be examined for

its presence. It has been shown to be highly toxic and even small quantities would materially increase the poisonous properties of liquors containing it. It is the only highly toxic substance definitely found present and should be investigated further.

COMMENT.

There are at least three classes of illicit liquors:

I. Properly made whisky and brandy.

II. Synthetic liquors.

III. Moonshine or home-brew liquors.

*I.*—The first class of liquors is in all respects the same as carefully made liquor of pre-prohibition days and has never been seriously suspected of containing toxic substance other than ethyl alcohol. Some of this is smuggled into the country and some obtained from domestic supplies in storage. Serious effects following the ingestion of this class of preparations is in all probability due as Hunt has suggested, to an over-dose of ethyl alcohol. Acute poisoning as a result of drinking bouts has long been known and is not surprising since the concentration of alcohol in the blood depends on the concentration of the alcohol in the liquor used and the rapidity of its ingestion. The margin between the concentration of alcohol in the blood required to produce intoxication and that causing collapse is not great.

*II.*—Synthetic preparations are made from alcohol and artificial flavors. The alcohol may be grain alcohol of good quality or it may be alcohol either from rectified denatured alcohol or from denatured alcohol which has not been made safer by rectification. Poisoning from synthetic liquors may therefore be due to any one of a large number of substances used as denaturing agents. Methyl alcohol is the substance which has been reported most frequently. Poisoning has also been reported from other denaturing agents such as nitrobenzene. These miscellaneous types of poisoning from denaturing agents are either rare or have escaped detection in many instances.

*III.*—The third class of liquors are those fermented and distilled surreptitiously and are known as "moonshine." Some of these are made under conditions comparable to legally made liquors and do not differ materially in composition from them. Others are fermented carelessly and are high in aldehydes as shown by Doran and Beyer. Although actual analyses are not available, there is reason to believe that the eagerness for profits result in incomplete fractional distillation with the inclusion of so-called "heads" and "tails." The former high in aldehydes, the latter high in "fusel oil." The evidence already reviewed would indicate that the poisonous property of moonshine liquors is not due to acetaldehyde which would be in the heads and that the quantity of fusel oil present is usually not great enough to increase the toxicity appreciably. The experiments of McNally and of MacNider show that the samples of moonshine used in their experiments were more toxic than an equivalent quantity of grain alcohol. The moonshine used by MacNider was distilled from fermented corn meal and molasses but not refined. His carefully controlled experiments under conditions which correspond to chronic poisoning, indicate that there is some undetermined substance present in his samples other than ethyl alcohol. It should be pointed out, however, that

these conclusions apply only to unrefined distillates prepared under his particular conditions which correspond to a poorly made moonshine.

A few cases of poisoning from lead derived from the still have occurred, but are probably rare. Poisoning from copper derived from the distilling apparatus is a remote possibility.

#### SUMMARY.

An examination of the evidence which from the nature of the problem is far from exact seems to prove that most cases of poisoning as a result of drinking bootleg liquor are due to the ingestion of an overdose of ethyl alcohol. The next most important constituent responsible for poisoning is methyl alcohol. A few cases of poisoning have been shown to be due to lead derived from the solder use in making the joints in the distilling apparatus. Poisoning from any one of the large number of denaturing agents is possible. Poisoning is also possible from poorly made liquors containing excessive amounts of "heads" and "tails." The results of MacNider show that the continual use of poorly made moonshine damages the kidneys of animals whose kidneys are not quite normal and also the kidneys of normal animals. This injury occurs even in the absence of acute symptoms. The particular chemical compound responsible for the damage has not been determined but the unsaturated alcohol related to acrolein and known as allyl alcohol is suspected.

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