THE CHEMICAL EXAMINATION OF THE OIL OF

MENTHA VIRIDIS.

BY

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INTRODUCTION.

According to the Pharmacographia (J 481) Mentha viridis was first examined by Kane(Philosophical Magazine XIII (1838) p. 444.) He recorded the sp. gr. of the oil as being 0.914 and the boiling point as 160°. The oil yielded him a considerable amount of st

Gladstone (J.C.S. ii (1864) P.11) found the oil to contain a hydrocarbon "almost identical (Pharmacographia P.481) with oil of turpentine in odour and physical properties, mixed with an oxidized oil, to which is due the peculiar smell of the plant." The latter boiled at 225 had a sp. gr. of 0.951 and the formula $C_{10} H_{14} O$.

Flueckiger (Pharm. Jour. (1876) P.75) prepared from it the crystalline hydrosulphide $(Ca H_{14} O)_2 SH_2$. From this the original compound was regenerated. Its chemical identity with carvone from caraway oil was thus established. It was also pointed out that the carvone from spearmint oil was laevogyrate to the extent to which the caraway carvone was dextrogyrate.

In 1885 Trimble (Proc. G.P.G. V.33 P.500.) in answer to the query, "what is the chemical relation, if any, between spearmint and peppermint oils," makes the following statement:

"Sufficient investigation has already been made of spearmint oil to prove that it is different from oil of peppermint; consequently attention has been directed to determine whether there is any chemical relation between them, and at the same time corroborating the work already done by others."

Trimble further states with reference to Gladstone's works, "that, with the exception of the odor, this carvole appears to be identical with that of caraway, dill and nutmeg."

Flueckeger had already called attention to the fact that the carvone from spearmint was a physical isomer to that of caraway.

Dill is known to contain dextrogyrate carvone, while nutmeg does not contain any.

Fraction 160-165 of the oil examined by Trimble contained over three per cent. of oxygen and is stated

to have had a peculiar terebinthinous odor, whereas, the odor of spearmint had disappeared; no hydrocarbon, however, was identified.

In Summary, Trimble states "Oils of spearmint and peppermint probably contain hydrocarbons, which are identical." That such a statement is practically meaningless today was shown by Power and Kleber in their examination of peppermint oil.

With regard to odor, that there is no difference between carvone of caraway and spearmint, was pointed out by Flueckiger, who states, "Es ist bemerkenswert wie sogar der Geruch der beiden Modifikationen der Carvole mit zunehmender Reinheit mehr und mehr uberinstimmt."

The truth of this statement was demonstrated during the past year in this laboratory by Mr. E.R. Ladwig. (unpublished results.)

Carvone regenerated from carvoxime still retained a trace of the minty odor of the original oil. If this regenerated carvone is converted into the hydrosulphide,

the hydrosulphide purified by crystallization and the carvon regenerated a second time by means of alcoholic potash and distilled with water vapor, not a trace of the minty odor remains; whereas. the laevogyrate carvone regenerated from the carvoxime differs in congealing and melting points from caraway carvone.

The laevogyrate carvone regenerated a second time from the hydrosulphide does not differ in congealing and melting points from caraway carvone prepared in a similar manner. The absolute chemical and physical identity, with the exception of the rotatory power, is thereby conclusively furnished.

The only chemical constituents, however, that have been isolated up to 1893 were laevogyrate carvone and laevogyrate limonene.

Gladstone, Trimble and others had called attention to the presence of hydrocarbons and Trimble mentioned the terebinthinous odor of a low boiling fraction of the oil, besides this no chemical clew, as to what constituent of the oil furnished the peculiar minty odor has ever been hinted at. W. F. Gilman, in 1893, identified laevogyrate

~~limonene~~ pinene in one of the low boiling fractions by means of the nitrosochloride and nitrol-benzylamine base. He also called attention to the fact that ~~limonene~~ pinene is only one of the constituents of the low boiling fraction of the oil without, however, being able to identify any of the others.

EXPERIMENTAL PART.

In their attempt to ascertain something about the chemical composition of spearmint oil, all investigators, as far as recorded, restored the fractional distillation of the original oil under ordinary pressure. Any person who has fractionated even a comparatively small amount of spearmint oil must know how unsatisfactory this process is, as decomposition takes place constantly. To resort to fractional distillation under diminished pressure though possessing advantages over the distillation under ordinary pressure, is likewise unsatisfactory.

Goldschmidt has shown that carvone condenses with hydroxylamine to form the comparative stable carvoxime. This suggested a process that ought to prove an advantage over fractional distillation, no matter under what pressure.

Spearmint oil was therefore treated in the following manner:

SEPARATION OF CARVONE.

To a solution of 100 grns. of spearmint oil in 250 c.c. of alcohol, 40 grms. of hydroxylamine hydrochlorate and 60 grns. of sodium bicarbonate were added. This mixture was heated in a flask connected with an upright condenser for half an hour. The product was then distilled with water vapor. The non-ketone constituents of the oil unaffected by the hydroxylamine pass over with the water vapor practically unchanged. The carvone from the oil remains behind as carvoxime, which crystallizes upon cooling. In this manner a separation of the ketone and non-ketone constituents of the oil can be affected without serious detriment to such substances of the oil as are decomposed by the application of higher temperatures. This process has been used in this laboratory, not only for the separation of these two classes of constituents for further investigation of the oil, but also as a means of ascertaining the per centage of carvoxime in volatile oils.

ISOLATION OF AN ALCOHOL $C_{10}H_{17}OH$.

The works of A. Von BAEYER, on the reduction products of carvone, namely, on di- and tetra hydra carveol¢, the readiness with which the latter in particular splits off water, together with the experience collected in the distilling of spearmint oil, whereby water is split off from some constituent of the oil, suggests the advisability of testing for like substances in the oil.

Jacobson demonstrated that calcium chloride could be used for the purpose of isolating at least one alcohol, namely, geraniol from oil of geranium. He heated oil of geranium with excess of calcium chloride on a water bath for several hours, filtered the hot oily solution and upon cooling collected a crystalline addition product of geraniol and calcium chloride. From this geraniol was easily regenerated with water.

This same experiment was tried on spearmint oil. The non-ketone constituents, which were obtained by distillation with water vapor after the carvoxime reaction was complete, were separated from the aqueous distillate

and dried with anhydrous copper sulphate. The dried oil had a sp. gr. of 0.9 at 20° and a rotatory power of 39.446. To a quantity of this oil powdered calcium chloride was added, the mixture heated for half an hour on a water bath at about 50°; after cooling the crystals were separated with the aid of a force filter washed with dried ether and then dissolved in water. This experiment was several times repeated. Upon solution of these crystals in water an oil separated out. The traces of oil dissolved in the water were shaken out with ether and the ether allowed to evaporate spontaneously. Only a small amount of the oily substance was thus obtained.

	I.	II.	
C.	77.4	78.1	Calculated for $C_{10}H_{18}O$.
H.	13.12	11.16	

The remaining oil 0.8863 grns. was dissolved in ether to this solution and 20 c.c. of absolute ether were gradually added, the oil being kept cold. About 3 c.c. of this solution were added when permanent coloration set in.

From the bromine addition product ether was allowed to evaporate spomtaneously, the oil was added to an alcoholic solution of potash, heated to boiling for some time, then distilled with water vapor. From the aqueous distillate a very small quantity of oil separated, too small to accomplish anything with.

If any conclusions are permissable from this experiment, it may be supposed that spearmint oil contains an unsaturated alcohol $C_{10}H_{18}O$.

Further attempts to isolate this alcohol have thus fas not met with any success.

OXIDATION OF THE NON-KETONE CONSTITUENTS OF THE OIL WITH BECKMAN'S MIXTURE.

While trying to prepare pure laevogyrate carvone, Mr. E.R. Ladwig (unpublished results) observed that the carvone regenerated from carvoxime still possessed the minty odor and differed from caraway carvone regenerated from the hydrosulphide, no only in odor, but also in congealing and melting points.

On the other hand, laevogyrate carvone regenerated from the hydrosulphide was free from the minty odor

and agreed with caraway carvone, prepared in a similar manner, in congealing and melting points. This seemed to indicate the possible existence of a ketone, which, unlike the carvone, does not combine with a hydrosulphide, but, like most ketones, condenses with hydroxylamine.

In as much as Beckman's mixture does not effect pinenene, limonene, cymene, menthone, and other substances but oxides menthone to menthole, linalole to citral, etc., it was thought that this reagent could possibly be employed in the further study of the non-ketone constituents of the oil.

It must not be forgotten that some ketoxime might be hydralized by continued distillation with water vapor and also that regenereated ketone might be found in the so-called non-ketone constituents of the oil.

Six grms of spearmint oil were shaken with a solution of 15 grms. potassium bichromate in 70 grms. of water and 10 grms. of sulphuric acid. Comparatively small quantities of the oil were used in each experiment in order to avoid heating. As a rule the unoxidized oil

after separation had to be shaken with a fresh quantity of the mixture. After the oil was no further reduced by Beckman's mixture, it was distilled with water vapor, the oily distillate was almost colorless and possessed a decided minty odor of spearmint.

It is in this product evidently that the substance bearing the minty odor of spearmint oil must be looked for. It was impossible, however, on account of the lack of time to isolate this substance at present.

Approved
Edward Kremers.