

SCIENTIFIC SECTION

PHILIPPINE GINGER.

BY PATROCINIO VALENZUELA.

(Continued from p. 661, August 1926.)

EXTRACTION WITH ALCOHOL.

The peculiar condition in which the drug (Lot II) had arrived on account of the long time of transportation precluded drying, grinding, and extraction with selective solvents in the usual manner. Hence, the rhizomes, weighing 26 kilos, were sliced as rapidly as possible and the thin slices exposed to the extracting influence of alcohol. The process of fractional percolation was resorted to and the alcohol of the most concentrated extract recovered and used over again. The process was repeated until the extract obtained upon evaporation of the last tincture was practically colorless. Thus there were obtained as final products:

- A. An alcoholic distillate, and
- B. A liquid extract containing sufficient alcohol to insure its preservation while the time-consuming process of extraction was going on. This extract was shaken out repeatedly with petroleum ether. Upon evaporation of the hydrocarbon there was obtained an extract.
- C. Which weighed about 925 grams, corresponding to a yield of 3.55 per cent with reference to the original drug. This was steam distilled and yielded.
 - I. A volatile oil, 46.4 grams, or about 0.172 per cent computed with reference to the original drug, and
 - II. A residue, chiefly fatty oil weighing 88.5 grams or 0.363 per cent.

The alcoholic distillate (A) which remained at the end of the extraction and which naturally contained other volatile constituents besides ethyl hydroxide and which amounted to about 10 gallons was redistilled in a 60-liter copper still so that the last portion was collected in five separate liter fractions. Upon refractionation of each of these fractions the bulk of the alcohol was removed between 78° and 80° Fractions 80° to 85° were relatively small and consisted practically of ethyl alcohol. The fractions above 85° showed a slight turbidity and had an aromatic odor. In several instances even a few drops of oil had separated. However, the amount of volatile oil thus obtained was too small for separate study, hence was combined with the volatile oil obtained by steam distillation of the petroleum ether extract.

The volatile oil (C-I) obtained upon distillation of the petroleum ether extract of the concentrated alcoholic extract with water vapor was soluble in about 16 volumes of 80 per cent alcohol.

The only volatile oil obtained from Philippine ginger is that reported by Bacon (1) which had been obtained by the usual process of distillation. For the sake of comparison the constants are herewith tabulated:

	Valenzuela.	Bacon.
d_{25}°	0.8374	0.8850
n_{D25}°	1.4620	1.4830 (30° C.)
α_D	-7.43° (50 mm.)	-5.9° (30° C.)
S. V.	..	14

The aqueous distillate from which the volatile oil described above had been separated was cohobated twice. The first cohobation yielded 1.6 cc. or 2.88 per cent of the original oil, the second 0.4 cc. or 0.72 per cent, hence a total of 2 cc. or 3.61 per cent. The density of this oil was 0.8369. This was combined with the original oil to which was also added the small amount obtained from several fractionations of the alcoholic distillate.

The combined oil was examined with the following results:

Schiff's reagent gave a positive result indicating the presence of aldehyde.

Ferric chloride gave a negative test for phenol.

The following chemical constants were determined:

	I.	II.
Acid value.....	2.22	...
Ester value.....	32.33	33.28
Ester value (after acetylation).....	88.65	87.97

Comparison of the above values with those recorded in the literature shows that the acid value is practically within those reported.¹ The ester values both before and after acetylation were almost twice as high as those reported in the literature. Bacon (*loc. cit.*) reported a saponification value of 14.

Fractionation.—Thirty-nine cc. of the combined oil were submitted to fractional distillation under diminished pressure, using a 100-cc. Claisen flask heated over a bath consisting of an alloy of bismuth (40), lead (40) and tin (20). (M. p. 111° C.). The results were as follows:

Fraction.	Volume in cc.	B. p.	Pressure.	d_{25}° .	$n_{D_{25}^{\circ}}$.	α_D (50 mm.).
I	6.2	below 43° C.	6 mm.	0.7718	1.4250	..
II	4.2	43–100° C.	5 mm.	0.8188	1.4430	..
III	7.0	100–115° C.	5 mm.	0.8855	1.4800	–0.62°
IV	5.6	115–118° C.	5 mm.	0.8910	1.4900	..
Residue					1.5090	

The distillation was not carried farther because of decomposition.

Fraction I was practically colorless and very aromatic. It was almost insoluble in alcohol and an attempt to obtain a clear solution failed, thereby rendering the determination of the optical rotation of the alcoholic solution impossible.

Fraction II was almost colorless and possessed an odor somewhat characteristic of ginger.

Fraction III was slightly greenish in color and had a slight resinous odor.

Fraction IV was yellowish in color and also had a slight resinous odor.

The residue was thick, reddish brown and had a resinous odor.

The Aldehyde.—The volatile oil was shaken with an equal volume of 30 per cent sodium bisulfite solution. This was allowed to remain in contact with the oil over night. The oil was then separated and dried with anhydrous sodium sulphate. The aqueous solution containing the aldehyde addition product was neutralized with sodium carbonate and steam distilled. The aqueous distillate was collected in fractions as follows:

Fraction.	Volume.	Appearance.	Odor.	Aldehyde reaction.
I	105 cc.	Slightly turbid	Aromatic	Positive to Schiff's test Positive to ammoniacal silver nitrate test.

¹ G.-H.-K. "The Vol. Oils," 2, 282 (1916).

Fraction.	Volume.	Appearance.	Odor.	Aldehyde reaction.
II	155 cc.	Very slightly turbid	Practically odorless	Faint reaction with Schiff's reagent. Negative to ammoniacal AgNO ₃ test.
III	70 cc.	Clear	Odorless	Negative to Schiff's reagent. Negative to ammoniacal AgNO ₃ test.
IV	80 cc.	Clear	Odorless	Negative to Schiff's reagent. Negative to ammoniacal AgNO ₃ test.

The combined Fractions II, III and IV were tested with metanitrobenzhydrazide with negative results.

Semicarbazone.—Fraction I was shaken out several times with ether. Upon evaporation of the solvent, very few and small droplets of yellowish oil with a pleasant odor were obtained. These were dissolved in 5 cc. of alcohol and the semicarbazone prepared. The yield was very small but sufficed for a melting-point determination. It melted at 144–145° C. This does not agree with that of the semicarbazones of the aldehydes previously found in ginger.

Fatty Oil. (C-II).—This reddish brown, pungent, thick, fatty extract was obtained by repeated extraction of the non-volatile portions of the residue from steam distillation with petroleum ether and subsequent evaporation of the hydrocarbon. It had a specific gravity of 1.0694 and gave the following saponification values: 41.78 and 41.04.

The whole amount of the fatty extract was saponified with an excess of alcoholic potash for an hour. After recovery of the ethyl hydroxide, a brownish black semi-solid soap was obtained. This was melted on a water-bath and dissolved in about five times its volume of hot water. Upon cooling, the unsaponifiable matter was extracted several times with ether. The fatty acids were then liberated by addition of sufficient amount of hydrochloric acid (equal volumes of concentrated hydrochloric acid and water). The fatty acids which separated on the top were removed from the aqueous layer and filtered hot. These fatty acids were in form of a brownish black oily liquid, left a permanent transparent spot on paper, possessed a persistent odor of ginger, were slightly pungent to the taste and weighed about 45.5 grams, corresponding to a yield of about 0.175 per cent of the original drug.

The ether from the unsaponifiable matter was allowed to evaporate and the residue set aside for examination. See unsaponifiable matter.

Fatty Acids.—Assuming that these consisted of a mixture of solid and liquid fatty acids, an attempt was made to isolate the individual constituents by the method of Muter and de Koningh's¹ modified by Lane² and Lewkowitsch.³

The method which was slightly modified was as follows:

The fatty acids were saponified with sufficient amount of alcoholic potash using phenolphthalein as indicator. Considerable difficulty was encountered in deciding upon the end-point because of the reddish brown color of the solution.

¹ *Analyst*, p. 61 (1889).

² *Jour. Amer. Chem. Soc.*, 15, 110 (1893).

³ "Chem. Techn. and Ana. Oils, Fats and Waxes," 6th ed., vol. 1, p. 556 (1921).

This was accomplished by dropping from time to time a small drop of the indicator along the side of the Erlenmeyer flask. Thus, by careful observation, the end-point was determined when the red color was permanently produced after shaking by the contact of the liquid with the phenolphthalein on the side of the flask. Upon evaporation and on cooling, a reddish brown soap was obtained. This soap was melted and added to about 100 cc. of boiling 20 per cent lead acetate solution. On cooling, the brownish lead soap acquired a sticky consistency while the supernatant liquid was turbid and yellowish. The lead soap was washed several times with boiling distilled water. After five washings, the latter became practically colorless although slightly turbid. The lead soap thus obtained was melted and sufficient amount of petroleum ether added. Twitchell and Lane² were among those who suggested the use of petroleum ether in separating the lead soap of the liquid fatty acids from the solid. The soap and petroleum ether were heated to boiling on a water-bath and set aside over night. The petroleum ether layer was then decanted and treated with about 20 cc. of equal volumes of water and hydrochloric acid. Upon standing in a separatory funnel the fatty substance in the petroleum ether was separated mechanically.

The lead soap left after treatment with petroleum ether was then extracted with ether. A brownish ethereal fatty extract was obtained. This was set aside for further examination (see fatty substance extracted by ether).

The residue which was supposed to contain the lead soap of the solid fatty acids was treated as described under solid fatty acids.

Fatty Substances Extracted by Petroleum Ether.—Upon evaporation of the solvent, 18 grams of a dark brown fatty liquid were obtained. This was divided into two portions which were examined separately.

First Portion.—The determination of the acid value was first made. The weighed substance was dissolved in previously neutralized alcohol and then titrated with an alkali. The following results were obtained:

Fraction.	Weight of substance.	Acid value.
I	0.8676	23.93
II	0.9150	25.00

The above values were exceedingly low. Since not all of the fatty substance went into solution, the contents of the flasks wherein titrations were made were allowed to stand over night. Then the supernatant liquid was poured into another flask. The undissolved portions were dried over calcium chloride and weighed. By subtracting the weights of the undissolved portions from the original weights, the following acid values were obtained:

Fraction.	Weight of substance.	Acid value.
I	0.4120	50.41
II	0.4900	49.47

Another duplicate determination of the acid value was further made by using an excess of the alkali and titrating back the excess with acid. The substance was

¹ E. Twitchell, *Jour. Amer. Chem. Soc.*, 17, 289-295 (1895). Also *Jour. Soc. Chem. Ind.*, 14, 515 (1895).

² N. J. Lane, *Jour. Soc. Chem. Ind.*, 26, 597 (1907).

first dissolved in previously neutralized alcohol and then heated to boiling. Then titrations were made while hot. The results were as follows:

Fraction.	Weight of substance.	Acid value.
I	1.1540	51.19
II	1.2630	53.43

Such close figures obtained in the titrations were noteworthy. Comparison, however, of these figures with the known neutralization values of the liquid fatty acids do not reveal definitely the fatty acids present obtained from the lead soap soluble in petroleum ether. Presumably, such low neutralization values may be accounted for by the presence of other substance extracted by petroleum ether other than the lead soap of the liquid fatty acids.

Second Portion.—The isolated liquid fatty acids from the lead soap of the petroleum ether were converted into their bromo derivatives according to the method of Lewkowitsch¹ in order to effect their separation if possible. The acids were dissolved in 40 cc. of ether containing 2 cc. of glacial acetic acid. The solution was kept at a temperature of 5° C. and bromine was gradually added to a slight excess, keeping the ethereal solution at the same temperature. Then it was allowed to stand for four hours to permit the separation of the hexabromides. No separation took place hence indicating the absence of linolenic acid.

The solvent was then evaporated and the residue dissolved in petroleum ether. The solution was allowed to stand over night at a temperature below 5° C. No separation of tetrabromides took place.

Upon evaporation of the solvent a brownish black semi-solid fatty substance was obtained. This had a fatty odor and congealed on cooling. In order to decide whether this was oleic acid dibromide, the bromine content was estimated according to Stepanow's method.² The process was slightly modified by using a slight excess of 10 per cent silver nitrate solution, filtering the AgBr and washing the latter with 95 per cent alcohol and drying to constant weight over calcium chloride. The results were as follows:

Weight of substance.....	0.6586
Weight of AgBr.....	0.6194
Calculated percentage of Br in $C_{18}H_{34}O_2Br_2$	36.13 per cent
Found.....	40.82 per cent

The difference in the bromine content may be due to the presence of small quantities of other bromides which did not separate but dissolved with the oleic dibromide. The slightly high iodine value (see iodine value of the acid extracted by ether) seems to corroborate this view.

Fatty Substance Extracted by Ether.—Upon evaporation of the ether, a brownish black, semi-solid fatty extract was obtained. This was treated with 20 cc. of equal volumes of hydrochloric acid and water. The fatty substance remained as a brownish sticky paste even after stirring for some time. However, a reaction had certainly taken place as indicated by the increase in volume of the aqueous solution. The supernatant liquid (aqueous solution) was separated and the undissolved portion was set aside over night in a desiccator over calcium chloride. The acid

¹ "Chem. Tech. and Ana. Oils, Fats and Waxes," 6th ed., vol. 1, p. 579 (1921).

² *Ber.*, 9, 4056 (1906); "Kamm's Qual. Org. Ana." p. 168 (1923).

value of this fatty substance was determined. The weighed substance was dissolved in previously neutralized alcohol and then titrated directly with alkali. The following results were obtained:

Fraction.	Weight of substance.	Acid value.
I	1.0670	51.96
II	1.9680	54.46
		Average 53.21

These values are, indeed, too low. However, it is again interesting to note here that the figures found are almost the same as those found in connection with the acids extracted by petroleum ether. In the titration it was observed that quite an amount of lead chloride was mixed with the acids. Hence, the separation of the acids was made by repeated extraction with ether. Quite an amount of white precipitate was obtained which proved to be lead chloride.

The acid values of the ether extract freed from lead chloride were as follows:

Fraction.	Weight of substance.	Acid value.
I	0.9682	93.89
II	0.7780	95.00

The neutralization values given above seem to indicate the presence of substance or substances other than fatty acids.

The iodine value of the ether extract was determined. The weighed substance was dissolved in 10 cc. of chloroform and placed in a 500 cc.-wide-mouth glass-stoppered bottle. Twenty-five cc. of iodine solution were added and then the bottles were placed in a cool and dark place and allowed to stand for 30 minutes with occasional shaking. At the same time a blank test was made. The results were as follows:

Fraction.	Weight of substance.	Iodine value.
I	0.2028	104.51
II	0.2316	104.12

The iodine value of oleic acid is 90.07. The results may be accounted for by the presence of small quantities of more unsaturated fatty acids.

Oxidation of the Liquid Fatty Acids.—In view of the indications of the presence of other unsaturated fatty acids which were not obtained in the preparation of the bromo derivations with exception of oleic acid, the oxidation of the liquid fatty acids by means of a dilute alkaline solution of potassium permanganate was carried out according to the process of Lewkowitsch.¹

The process was carried out as follows: 1 gram of the liquid acid obtained from the ether extraction was neutralized with 1.2 cc. of caustic potash of 1.27 sp. gr. (17 per cent solution). The resulting soap which was a brownish semi-solid mass was dissolved in 66.6 cc. of water and heated on a water-bath until a solution of the soap was obtained. Then an equal volume of a 1½ per cent KMnO_4 solution was added in a very fine stream with the aid of a burette with constant stirring of the solution. After all the KMnO_4 solution had been added, the mixture was allowed to stand for 10 minutes. Sulphurous acid solution was then slowly added with constant agitation until all the precipitated manganese peroxide was dissolved and an acid reaction was imparted to the solution.

¹ "Chem. Tech. and Ana. Oils, Fats and Waxes," 6th ed., vol. 1, p. 575 (1921).

The brownish white precipitate was separated by means of a filter and washed with a very small amount of ether. Then it was dissolved in about 70 cc. of ether. The ethereal solution was evaporated to about 10 cc. On cooling, a slightly brownish substance was obtained which melted at about 130° C. When once crystallized from alcohol, it melted at 135° C. Dihydroxystearic acid melts at 137° C.¹

On dissolving the precipitate with ether, a small quantity of yellowish white precipitate separated. This melted at 175° C. The small amount of precipitate was twice recrystallized from alcohol from which perfectly white crystals melting at 171–172° C. were obtained. Saticic acid melts at 173° C. The quantity of the acid was too small to admit of further characterization. This indicates the presence of linolic acid. The slightly higher iodine value of the acid extracted by ether and bromine content of the dibromide may be due to the presence of linolic acid.

On neutralization of the acid filtrate (from sulphurous acid treatment) with caustic potash and evaporation to a small volume, no precipitate was formed. This seemed to indicate the absence of other hydroxy acids.

Solid Fatty Acids.—The residue left after extraction of the lead salts with ether was treated with about 20 cc. of equal volumes of hydrochloric acid and water. A large amount of PbCl₂ separated which was removed. The ether was evaporated, leaving a brownish solid cake. This mass when dried between filter papers weighed about 5 grams.

The acid value of this mass was determined:

Fraction.	Weight of substance.	Acid value.
I	0.5360	89.11
II	0.5450	92.00

These values did not reveal very much of the nature of the solid acids present in the mass.

Fractional crystallization was then effected. The mass obtained was dissolved in warm alcohol. Traces of lead chloride which separated were eliminated by filtration. The alcoholic solution was then concentrated and set aside for crystallization. After 3 hours, no crystallization took place. The solution was further concentrated to a slight extent and cooled in ice water. After cooling for about an hour, an exceedingly small amount of brownish solids separated out. These were collected on a force filter and dried on filter paper. Weight 2.6 milligrams, m. p. 60–65° C.

The mother liquid was concentrated further and then placed in a freezing mixture whereby a greater amount of slightly brownish solids were obtained. Weight 0.3200 gram, m. p. 55–56° C. Purification was effected by dissolving in about 75 cc. of alcohol and decolorizing the solution with charcoal. After two recrystallizations from alcohol, a very small amount of perfectly white crystals were obtained, melting at 70° C. Stearic acid melts at 69.3° C.

Other solid acids may possibly be present also but the small quantity of the material did not permit of their separation. The first crop of crystals weighing

¹ Lewkowitsch, "Chem. Techn. Ana. Oils, Fats, and Waxes," 6th ed., 1, 577 (1921). Cp. Lewkowitsch, *Ibid.*, 233.

2.6 milligrams melted at 60–65° C. and could not be purified further, hence it could not be established whether other solid acids are present besides stearic.

UNSAPONIFIABLE MATTER.

Attempts were made to isolate phytosterol either as such or as acetate. In the case of the former, the unsaponifiable matter was twice extracted with absolute alcohol, and then set aside for crystallization. No crystals, however, separated even after standing over three months. The unsaponifiable matter left after extraction with absolute alcohol was then acetylated by Lewkowitsch's process.¹

The 4.8572 grams of the substance thus treated was completely dissolved in acetic anhydride and no separation took place. According to Lewkowitsch, this is indicative of the presence of aliphatic alcohols.

The determination of the saponification value of the acetylated unsaponifiable matter gave the following results:

Fraction.	Weight of substance.	Saponification value.
I	1.1640 Gm.	117.14
II	1.1416 Gm.	119.44

The acetate of melissyl (myricyl) alcohol¹⁷ (C₃₀H₆₂O) has a saponification value of 116.7. Although the unsaponifiable matter of ginger may contain other higher alcohols, the indications seem to suggest the presence of melissyl alcohol as its main constituent.

ALCOHOLIC EXTRACT:

The alcoholic extract which had been shaken out with petroleum ether was then treated with a saturated solution of basic lead acetate added drop by drop while the reacting mixture was being continuously stirred. A slightly yellowish white precipitate was obtained. The precipitate was separated on a force filter and allowed to dry. The dried precipitate was then reduced to No. 20 powder and suspended in distilled water. Then the lead was separated by passing hydrogen sulphide until the washings did not precipitate further upon the addition of diluted sulphuric acid. The black precipitate (PbS + adhering substances) mixed with sufficient quantity of charcoal was then extracted with alcohol by refluxing for about one hour. Upon evaporation of the solvent, white needle-like crystals with a slight brownish tint were obtained. These crystals melted at 119° C. When the precipitate was afterwards extracted with ether in the cold, another crop of



Fig. 12.—Crystals of vanillyl alcohol.

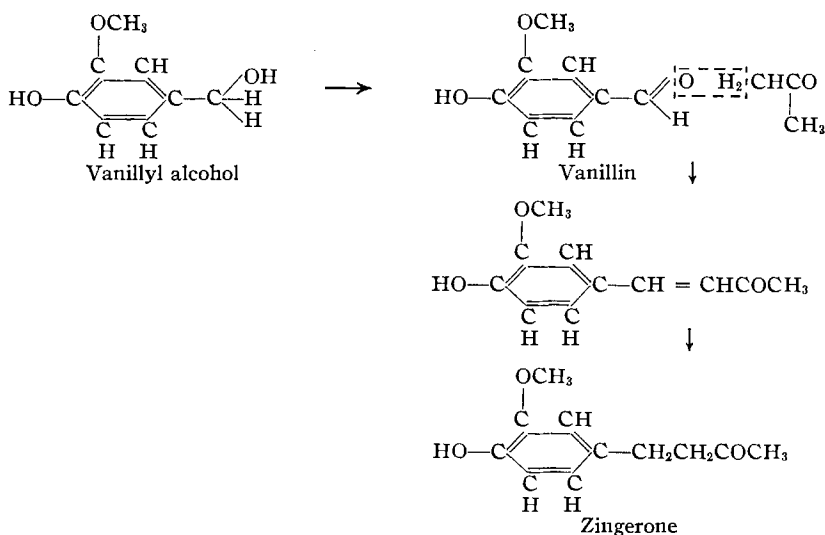
¹Lewkowitsch, "Chem. Tech. and Ana. Oils, Fats, and Waxes," 6th ed., 1, 613 (1921).

²Lewkowitsch, "Chem. Tech. and Ana. Oils, Fats, and Waxes," 6th ed., 1, 617 (1921).

perfectly white crystalline needles were left upon evaporation of the solvent. A third and even a fourth crop of crystals were obtained. These crystals melted at 115° to 116° C. The total amount, however, was small. Their appearance is revealed by the accompanying photomicrograph (Fig. 12). With a drop of concentrated H_2SO_4 a faint brownish violet color was produced. The crystals dissolved in alcohol as well as in ether. Their odor recalled that of vanilla. Vanillyl alcohol, $(HO\text{---}\langle\text{C}_6\text{H}_4\rangle\text{---}CH_2OH)$ and acetovanillon, $(HO\text{---}\langle\text{C}_6\text{H}_4\rangle\text{---}COCH_3)$ both melt at 115° C.

Attempts to prepare the semicarbazone and the oxime gave negative results for acetovanillon. Although the amount obtained was not sufficient to permit of further characterization, the tests so far made seem to indicate that the substance is vanillyl alcohol.

The presence of vanillyl alcohol indeed plays an important rôle in the biogenesis of some of the pungent principles of the ginger rhizome. As pointed out elsewhere zingerone, one of the pungent principles of ginger has been synthesized by the condensation of vanillin and acetone and the subsequent reduction of the unsaturated ketone. With the presence of vanillyl alcohol in ginger rhizome, it may be assumed that a similar synthesis can be effected by the plant. The formation of zingerone from vanillyl alcohol may be indicated by the following reactions:



The Pungent Principles.—After the isolation of vanillyl alcohol with ether, the residue (PbS, etc.) was refluxed with alcohol for several hours. Upon evaporation of the solvent a light, yellowish brown, very thick syrupy residue was obtained. By subsequent extraction of the alcoholic residue with ether in the cold and evaporation of the solvent a similar product was obtained. This had an extreme pungent taste. Presumably, this is similar to the “gingerol” of Thresh. No crystals have so far separated after standing over two months. Assuming that it may contain zingerone, shogaol and probably other bodies of definite chemical composition which have so far not been identified in Philippine ginger, attempts were made to

prepare the derivatives. The amount was not large enough to admit of fractionation by distillation.

The preparation of a semicarbazone yielded unsatisfactory results. Besides a resinous substance melting between 138 and 140°, crystals were obtained upon evaporation of the mother liquid. These, however, may have been but a mixture of the reagents used. According to Nomura (2) both the phenylhydrazone and the semicarbazone of zingerone could not be obtained in a pure state because of the instability of these compounds. Lapworth (3) also states that whereas zingerone "readily yields a crystalline phenyl hydrazone and semicarbazone" these compounds are "difficult to purify as they quickly decompose in solution." Attempts to prepare an oxime likewise yielded a resinous product.

Isolation of Sugar from Alcoholic Extract.—The yellowish filtrate obtained upon separation of the basic lead acetate precipitate was freed of excess of lead by means of hydrogen sulphide. It gave a positive reaction with Fehling's solution.

Part of the filtrate was dried in an electric oven at about 45° C. another part in a vacuum oven at 60° C. In both cases a brownish residue was obtained which had an odor of acetic acid.

Preparation of Phenylglucosazone.—The osazone was prepared according to Fisher's method. (4) Masses of fine yellow crystals separated after about five minutes. They melted at 198°, after recrystallization from diluted alcohol at 204°. Phenylglucosazone melts between 204° and 205°.

Oxidation of the Sugar to Saccharic Acid.—Since phenylglucosazone may be obtained from either glucose or fructose, the saccharine residue was oxidized with nitric acid according to Gans and Tollen's process (5). Potassium acid saccharate was thus obtained identifying the sugar present in the original filtrate as glucose. Further evidence of the identity of this sugar was supplied by the reduction of picric acid to picramic acid. Two grams of the product were dissolved in about 5 cc. of water. Then about 3 cc. of saturated solution of picric acid and 1 cc. of 10 per cent KOH solution were added. On warming on a water-bath a blood-red coloration was developed.

Yield of Sugar.—The amount of glucose contained in the saccharine extract obtained after drying in the oven was determined by means of Munson and Walker's method. (6) Four grams of material yielded 0.828 gram of CuO, the equivalent of 3.916 grams of glucose = 97.9 per cent. This corresponds to 0.137 per cent of glucose in the rhizomes.

REFERENCES.

- (1) S. P. Mulliken, "Identif. Pure Org. Compounds," Vol. I, p. 95 (1904).
- (2) *Jour. Chem. Soc.*, 111, 771 (1917).
- (3) *Ibid.*, p. 785.
- (4) H. L. Fisher, "Lab. Manual Org. Chem.," 2nd ed., p. 127 (1924).
- (5) *Ann.*, 249, 215 (1888).
- (6) *Jour. Am. Chem. Soc.*, 28, 163 (1906); *Ibid.*, 29, 541 (1907); *U. S. Dept. Agric. Bur. of Chem. Bull.*, 107 (rev.), p. 241; *Circ.*, 82.

SUMMARY AND CONCLUSIONS.

1. The histological study shows that there is practically no difference between the anatomical structures of Philippine ginger and that of commercial varieties.

2. An attempt to raise plants from rhizomes (Lot III) in the Pharmaceutical Garden gave unsatisfactory results. Transferred to the green house, three of the rhizomes developed plants of full size.

3. Fresh rhizomes contain about 80 per cent of moisture, whereas partially air dried rhizomes yield about 70 per cent. The high moisture content of the first two lots shipped from Manila is indicative of partial decomposition undergone by the rhizomes.

4. Ash determinations reveal an ash content within the standard requirements for ginger.

5. The presence of oxidase in the fresh rhizome is indicated.

6. The limit of pungency of 1, peridermal; 2, cortical; 3, parenchymal, and the 4, entire rhizome was determined. The cortical portion was found to be most pungent. The peridermal portion gave a limit of pungency greater than the parenchymal which indirectly shows that the periderm may affect the yield of the pungent and possibly other constituents.

7. A yield of 0.172 per cent of volatile oil was obtained. This oil has the following properties: d_{25° , 0.8374; n_{D25° 1.4620; α_D -7.43 (50 mm.); A. V., 2.22; E. V., 32.80 (average); E. V. (after acetylation) 88.31 (average).

8. The presence of aldehyde having been indicated a small amount was isolated yielding a semicarbazone melting at 144–145°.

9. Oleic, linolic and stearic acids were isolated and identified.

10. The presence of melissyl alcohol and possibly other higher alcohols in the unsaponifiable matter was suggested.

11. An exceedingly small quantity of vanillyl alcohol was isolated.

12. A pungent material was isolated but the amount was too small to admit of the identification of a definite chemical compound.

13. About 0.137 per cent of *d*-glucose was isolated. The isolation of this sugar and that of vanillyl alcohol suggests the possible presence of vanillyl glucoside.

14. A hypothesis of the biogenesis of zingerone in ginger rhizome is recorded.

15. Philippine ginger does not differ materially from the other commercial varieties. Considering the current price in the Philippines, *viz.*, \$0.05 to 0.20 per kilo of the partially air dried and \$0.35, 0.50 and 0.60 per pound of the dried African and Jamaica varieties, respectively, the commercial possibilities are promising.

THE ACTION OF CAFFEINE ON THE POISONED HEART.*¹

BY CHARLES C. HASKELL.

From a consideration of the action of caffeine on the normal animal, this drug would seem to be nearly an ideal circulatory stimulant. By an effect on the medullary center, caffeine tends to cause vasoconstriction; as a rule, however, the peripheral action, manifested on the vessel wall predominates, so that vascular relaxation of a moderate degree is produced. Along with this action on the vessels,

* Scientific Section, A. Ph. A., Des Moines meeting, 1925.

¹ The expense incident to this investigation was met by a grant from the Research Fund of the AMERICAN PHARMACEUTICAL ASSOCIATION.