

Reports of A. Ph. A. Committees

Abstracts from the Report on the Progress of Pharmacy for the year 1912, by C. Lewis Diehl, Reporter.

(Second Installment.)

Fehling's Solution: Evolution of the Original (Empirical) to the Present-day (Exact) Composition.—O. Lünig contributes the results of an inquiry into the gradual evolution of the originally simple, though empirical formula given by Fehling (1848), to that modernly insisted on, which requires great exactitude in the quantities of copper sulphate (34.639 gm.) and of sodium hydroxide (51.6 gm.) to the liter. By his original formula, Fehling simply endeavored to produce a stable solution, without reflecting upon the possible use of the reagent for the quantitative determination of glucose; he directed that 40 gm. pure crystallized cupric sulphate be dissolved in approximately 160 gm. water, and to the cold solution the addition of 160 gm. potassium tartrate in 500 gm. caustic soda solution, sp. gr. 1.12 and sufficient water to make 1 liter at 15° C. But subsequently (1849), believing that 1 Mol. of sugar corresponds to 10 Mols. of cupric sulphate, he recommended the further addition of water so as to produce 1154.4 cc. of the reagent, which possessed this relation to the sugar, and this soon led to the reduction of the cupric sulphate to 34.639 gm. in the formula producing the original volume of 1 liter. The author then interestingly describes the further evolution until the present formula, used almost universally, was adopted, this consisting, as is well known, of two solutions, to be mixed in equal volumes as required, viz.: No. 1, 34.639 gm. Cupric Sulphate dissolved in water to make 500 cc.; No. 2, 51.6 NaOH (in 100 cc. Water) and 173.0 gm. Rochelle Salt in sufficient water to make 500 cc. The author proves from the literature that the insistence on the fractions of copper sulphate and NaOH is not necessary. The quantities may be rounded off to 34 and 51 gm. respectively, and this should be done in the published formulas for this solution.—Apoth. Ztg., XXVII (1912), No. 10, 91-92.

Fern Rhizomes: Anthelmintic Value of Various Sorts.—In view of the statement that the ethereal extract of *Dryopteris dilatata* is at least four times as active as the corresponding extract of the official *Aspidium filix-mas rhizome*, and has therefore been suggested to replace male fern in the various pharmacopœias, H. Rosendahl has examined a number of anthelmintic fern rhizomes, his results confirming the inferiority of *Dryopteris dilatata*. The yield of ethereal extract is about the same (10%); but while it takes from 8-10 gm. of oleo-resin of *Aspidium* to drive off the *Bothricephalus latus*, it requires only 2 gm. of the oleo-resin prepared from the rhizome of *Dryopteris dilatata*, or 4 gm. of that from *D. dilatata* var. *spinulosa*—the latter yielding however as much as 17% of oleo-resin. The rhizomes of other ferns yielded very small percentage of oleo-resin: *Filicis aquilini*, 20%; *Filicis feminae*, 0.9%; *Filicis alpestris*, 0.7%. Under the microscope these extracts exhibit various crystalline structures which serve well for their identification.—Apoth. Ztg., XXVI (1911), No. 27, 217; from Svensk. Farmaceutist Tidskrift, 1911, No. 5, 85-89.

Ferrous Salts: Dimethylglyoxim a Sensitive Reagent for Ferrous Salts.—If to a drop of the solution of a ferrous salt a little tartaric acid is added, followed by about 1 cc. of alcoholic solution of dimethylglyoxim and the mixture is then supersaturated with ammonia, an immediate intense red coloration results, resembling that produced by rosolic acid with alkalis. The reaction is more sensitive than any of the known ferrous reactions, but is not so stable on exposure to air, because the ferrous compound is slowly converted into the ferric state and the color disappears when this conversion is complete. It reappears, however, on the addition of a reducing agent, such for example as stannous chloride, metallic zinc, etc. The reagent is not suitable for the determination of small traces of ferrous salts, either by themselves or in admixture with ferric salts, since by the supersaturation of the acid fluid with ammonia considerable heat is developed, resulting in the

rapid conversion of the ferrous to ferric oxide, which does not give the reaction.—Pharm. Ztg., LVII (1912), No. 13, 126; from Chem. Ztg., 1912, No. 6.

Fixed Oils and Fats: Improved Method of Determining the Iodine Number.—G. O. Gaebel has used with advantage the potassium bromide-bromate solution, directed in the G. P. V. for phenol determinations, for the determination of the iodine number in fats and oils. The bromate solution is prepared by dissolving 1/60 Mol. of potassium bromate and 5/60 Mol. of potassium bromide in sufficient water to make 1 liter, and the determination of the iodine number is carried out with this as follows:

The usual quantity of fat or oil is weighed into a glass-stoppered flask of about 400 cc. and dissolved in 10 cc. of carbon tetrachloride; 50 cc. of the bromide-bromate solution are added, mixed by rotating in the flask, and the mixture is strongly acidulated with 30 cc. of diluted sulphuric acid (1:5). The flask is then securely closed with the slightly paraffined glass stopper, vigorously shaken once or twice, and then set aside at the room temperature protected from light. After permitting time for the complete reaction, the absorbed bromine is determined by carefully raising the stopper, adding about 1 gm. potassium iodide dissolved in a little water, then shaking vigorously and, after a few minutes, adding about 50 cc. of water, using this for rinsing the stopper and upper part of the neck of the flask. Finally the iodine liberated by the excess of bromate used is titrated in the usual manner with 1/10 N-thiosulphate, using starch paste as indicator. A blank experiment is made with 50 cc. of the bromide-bromate solution, and from the data so obtained the iodine number is readily ascertained by calculation (1 cc. 1/10 N, $\text{Na}_2\text{S}_2\text{O}_3=1$ cc. 1/10 N—Br. =1 cc. 1/10 N—I=0.012692 gm. iodine). The results correspond quite accurately with the Hübl numbers given in the G. P. V.—Arch. d. Pharm., 250 (1912), No. 1.

Fluidextracts: Methods of Valuation.—Dr. E. Amort and Dr. W. Rothe, staff-apothecaries of the German War-Department, commendably discuss the progress that has been made in the methods of valuation of medicaments in general, but find that the proposed methods for the valuation of galenic preparations, such as fluidextracts and tinctures, are as yet deficient and lacking in exactness, being in many instances confined to determinations of specific gravity and resi-

due of evaporation. The authors have subjected a number of fluidextracts to examination and make a detailed report of their observations and results. In a series of six purchased samples of fluidextracts of condurango they obtained in four of them figures which varied materially from those obtained with a fluid extract of their own preparation. They conclude from their results that the determination of specific gravity and dry residue of evaporation alone gives no criterion of quality, but that the shaking out process with suitable solvents, in conjunction with the determination of dry residue, affords a valuable criterion of quality and conscientious adherence to the prescribed process of preparation. To this should be added the determination of the tannin precipitate and of the nitrogen content of the fluidextract.—Pharm. Ztg., LVII (1912), No. 18, 175-176.

Formosa Opium: Characters.—K. Dieterich reports the results of a chemical examination of three authentic specimens of Formosa opium, received from Dr. Ishizu, the Japanese Commissioner having charge of the Japan Division of the International Hygienic Exhibiton. These opiums were, unlike the ordinary opiums, apparently obtained by a method of extraction, and therefore essentially extracts of opium, but inferior not alone to extracts obtained from the drug but to the opium itself. The three samples were identical in appearance, of a brown-black color, thick-liquid, extract-like, and in odor resembled the ordinary extract. Under the lens they were shown to be free from the plant-elements that characterize ordinary opium. Subjected to analysis by two of his chemists (Weinhausen and Mix) the results were as follows:

	No. 1	No. 2	No. 3
Moisture	24.37	20.68	25.96
Ash	3.58	3.74	2.55
Water Soluble substance			
dried at 100°.....	64.14	61.26	63.56
Morphine Content.....	5.27	7.55	5.71

The presence of meconic acid was determined in each of the samples.—Pharm. Zentralh., LIII (1912), No. 5, 114.

Lactic Acid: Reactions.—C. Reichard has made comprehensive investigations of certain lactic acid reactions, and describes a number that are particularly characteristic, such, for example as those obtained with potassium dichromate, ammonium heptamolybdate, and potassium ferricyanide. The addition of a little pulverized potassium di-

chromate to a drop of lactic acid, produces gradually, over blue-green, a nickel-green coloration, while ammoniumheptamolybdate produces under the same conditions at first a sky-blue color, also gradually changing to nickel-green. A solution of potassium ferricyanide yields with lactic acid a characteristic yellow coloration.—Pharm. Zentralh., LIII (1912), No. 3, 51-56.

Lecithin: Question of Solubility in Water.

—In view of the interest that has in recent years been manifested in medicine and pharmacy concerning lecithin and its preparations, resulting in the endeavor to present it for internal exhibition in form of solutions, wines, and syrups, Dr. P. Salzmann has made a comprehensive inquiry to ascertain from the literature whether the assumption that lecithin from egg-yellow is soluble in water to form clear solutions is justified by the facts. According to the most recent researches, lecithin is a monaminophosphatid, containing for one atom of phosphorus one atom of nitrogen, and is composed of glycerophosphoric acid, cholin, and two fatty acids—probably stearic and palmitic or oleic. It is characterized by the latest writers (for example by Thierfelder) as presenting a plastic, wax-like mass, soluble in alcohol, ether, chloroform, carbon disulphate, benzol, and fixed oils, but simply swells up in water, forming a pasty mass which, when greatly diluted, forms a colloidal solution. It is therefore regarded by the author mentioned, and by others who have made comprehensive studies of the subject, as being an "organic colloid," capable of suspension in water so as to produce an apparent solution, but readily precipitated from such suspension by many substances, such as acids, metallic salts, etc., and even by alcohol, which by itself dissolves lecithin readily and completely. To meet a demand for water-soluble lecithin, such a preparation has recently been introduced under the name of "water-soluble egg-phosphatid." Examined by R. Cohn, this product was found to contain sodium chloride, glycerin, nitrogenous matter, glycerophosphoric acid and water, but not a trace of lecithin. This product is therefore in no sense a lecithin preparation, nor are the solutions, syrups and wines that are made from it.—Pharm. Ztg., LVII (1912), No. 14, 134.

Milk Sugar: Contamination with Bacteriae.—Experiments made by Dr. H. Kühn to determine the queries whether commercial milk sugar is contaminated with *bacteriae*,

and if so, what is their nature, convince him that commercial milk sugar frequently does not respond to hygienic requirements, and that besides inorganic and nitrogenous impurities, as has already been pointed out by others, it also contains bacterial impurities which, in some cases, are of an exceedingly dangerous nature.—Pharm. Ztg., LVII (1912), No. 11, 105; from Südd. Apoth. Ztg., 1912, No. 1.

Paraldehyde: Estimation of Acidity and Acetaldehyde.—While the G. P. V. defines Paraldehyde to be a "clear, colorless liquid, containing about 4% of acetaldehyde," it gives tests which do not correspond with a paraldehyde containing 4% of acetaldehyde. Moreover, the pharmacopœia is silent regarding the acidity, although all paraldehydes have an acid reaction, which increases by age and has the effect of vitiating the test by consuming a portion of the liberated alkali before its titration with HCl. After a comprehensive study, E. Riebter finds that paraldehyde should not contain more than 0.5% of acetaldehyde, since it is quite possible to obtain such paraldehyde on the market, as shown by the analytical results obtained with commercial samples. If, however, the G. P. persists in admitting paraldehyde containing as much as 4% of acetaldehyde, the tests should be carried out as follows:

Ten gm. of paraldehyde are dissolved in 100 cc. of water by agitation; 2 drops of phenolphthalin solution are added, followed by KOH solution, drop by drop, until the last drop produces a red color. For this purpose not more than 0.5 cc. of normal KOH solution should be required, indicating a maximum content of 0.3% of acetic acid (1 cc. N-KOH solution=0.06003 gm. Acetic Acid). Now, 20 cc. of sodium sulphite solution (25 gm. of crystallized salt in 100 cc. of water) are added, and the mixture of 20 cc. of the same sodium sulphite solution is then ascertained, and deducted from the amount first obtained. The remainder should not exceed 9.1 cc. Normal HCl, indicating a maximum content of 4% of acetaldehyde; or not more than 1.15 cc. if the sample contains only 0.5% of acetaldehyde (1 cc. Normal HCl=0.044 gm. acetaldehyde). As the result of his experiments, the author feels justified in recommending the following pharmacopœial definition for a good paraldehyde: Sp. Gr., 0.998—1000; acidity, 0.3%; acetaldehyde, 0.5%; metaldehyde (not heretofore

considered), 0.1 to 0.2%.—Pharm. Ztg., LVII (1912), No. 13, 125.

Solomon's Seal: Proximate Examination of the Fruits.—Ernest A. Rayner reports the results of a proximate examination of the berries of Solomon's Seal (*Polygonatum biflorum*), picked at Saginaw, N. C., in the summer of 1910. These berries, when dried, resembled huckleberries in size and appearance. The outer husk is relatively small, the main part of the berry consisting of a cluster of about ten small, round, hard, and very tough seeds. The analysis showed them to contain: Sugars (glucose and a trace of fructose), 12.48%; Oil (mainly ricinolate), 2.00%; nitrogen, 1.88%; Ash (SiO_2 , Fe_2O_3 , Al_2O_3 , CaO , MgO , K_2O , Na_2O , P_2O_5 , SO_3), 2.27%; other substances, cellular tissue, water, 81.37%.—Chem. News, June 21, 1912, 289-290.

Thorium: Separation and Estimation with Sebacic Acid.—While working upon the separation of thorium from the rare earths, T. O. Smith and C. James observed that sebacic acid gave a precipitate in a neutral solution which appeared to be quantitative. The thorium sebacate settles readily as a voluminous granular precipitate and is easily separated on the filter, while solutions of cerium, lanthanum, yttrium, etc., give no precipitate with sebacic acid even upon boiling. In order to test the availability of sebacic acid for the estimation of thorium, 50 cc. of a standardized solution (0.005572 gm. ThO_2 in 1 cc.) were heated in a 250 cc. flask to the boiling point, a slight excess of a hot solution of sebacic acid was slowly added, with continuous stirring, and the precipitate, which was formed at once, was immediately collected and washed on a filter with boiling water, then rapidly dried, ignited, and weighed as thorium dioxide. A series of experiments demonstrated the accuracy of the method, and, furthermore, that the presence of other rare earths—cerium, lanthanum, praseodymium, neodymium, samarium, gadolinium, etc., did not vitiate the result. The thorium sebacate washes readily, and the operation may be performed with ease in a very short time.—Chem. News, March 8, 1912, 109.

Tincture of Iodine: Liability to Change and Expedients for Its Prevention.—Th. Budde, staff-apothecary in the German War Department, finds that under ordinary conditions there is a loss of iodine as such in the tincture of iodine of the G. P. amounting to as much as 20%, in the course of 9 months, resulting in the formation of hydrogen iodide,

acetic ether and aldehyde. This change is particularly rapid during the first 8 days, but is materially retarded by the addition of 3.5 gm. of KI or NaI for 10 gm. of iodine. Nevertheless, the changes during 6 months are so great that a tincture should not be dispensed after it has been prepared that long. Moreover, it should be preserved in glass-stoppered bottles, contained in a tin can lined with asbestos on the inner side, the asbestos containing an iodine-combining substance. It has been a problem of the military sanitary authorities to devise means for supplying this tincture in a practically unchanged condition. This has been solved by supplying sealed vials, each containing 10 gm. of iodine and 3.5 gm. of potassium, 10 of such vials being enclosed in a card box. When the tincture is needed, the contents of a vial are dissolved in 90 gm. of alcohol, with instruction not to use the tincture so prepared after it is 6 months old.—Pharm. Ztg., LVII (1912), No. 18, 176.

Tungsten: New Assay Method.—B. M. Divani observes that when tungsten is in the condition of tungstate it is possible to precipitate and estimate the tungsten in the form of the trioxide— WO_3 —all that is needed being to acidify the solution with HCl, HNO_3 , or even H_2SO_4 . But tungstic acid being slightly soluble in mineral acids, it is usually advised to render it insoluble by repeatedly evaporating (and resolution of) the acidulated solution and finally warming the dry residue for some time at 120°C . To avoid this tedious and time-consuming operation, the author now suggests for study a method based upon the precipitation of tungstic acid by an excess of a solution of freshly-prepared stannous chloride (50 gm. crystals per 200 cc.) which precipitates the tungsten in the form of the tungsten oxide— W_2O_5 —the reaction being quite sensitive. In the experiment described by the author, 2 gm. of absolutely pure tungstic acid was dissolved in just enough concentrated ammonia water, and the solution diluted to 1 liter. To 50 cc. of this solution 20 cc. of the solution of stannous chloride is added, the mixture is boiled for a few minutes and the precipitate washed with warm water; then calcined and weighed. The flocculent precipitate settles rapidly in the water, so that the washing is quickly effected without loss. The results are quite accurate, as proven by a number of experiments described.—Chem. News, Feb. 2, 1912, 56; from Chem. Engineer, XIV, No. 24.

Turpentine Oils: Products of Oxidation

by *Atmospheric Air*.—American oil of turpentine, pinene from the same, Russian oil of turpentine, and sylvestrene prepared from the same, were subjected by C. T. Kingzett and R. C. Woodcock to the oxidizing effect of exposure to atmospheric air, in two series of experiments:

(1) By exposing the oils with an equal volume of water to a current of air at 65° C. for 24 hours, and then examining the aqueous solution.

(2) By exposing the oils previously dried over ignited calcium chloride, to a current of dry air at 65° to 69° C. during several weeks (when they showed the following specific gravities: Amer. turpentine oil, 0.931; pinene, 0.962; Russ. turpentine oil, 0.940; sylvestrene, 0.958), then shaking with half the volume of water, and examining the solution. The results were as follows:

First Experiment.

Yield of Oxidation products:		
	Formic Acid	Acetic Acid
Amer. Oil.....	0.017%	0.038%
Pinene	0.14%	0.057%
Russ. Oil.....	0.026%	0.108%
Sylvestrene	0.16%	0.086%
	Formaldehyde	Acetaldehyde
Amer. Oil.....	Indications	None
Pinene	Indications	None
Russ. Oil.....	Indications	None
Sylvestrene	Indications	None

Second Experiment.

Yield of Oxidation products:		
	Formic Acid	Acetic Acid
Amer. Oil.....	0.055%	0.024%
Pinene	0.054%	0.186%
Russ. Oil.....	0.13%	0.08%
Sylvestrene	0.059%	0.264%
	Formaldehyde	H ₂ O ₂
Amer. Oil.....	None	0.71 vol.
Pinene	Indications	0.348 vol.
Russ. Oil.....	None	1.06 vol.
Sylvestrene	Indications	0.532 vol.

—Chem. News, Jan. 19, 1912, 26-27.

Water: Decomposition by Magnesium at Ordinary Temperature.—Arthur W. Knapp observes that when magnesium is mixed with water no reaction is observed at ordinary temperatures, although the formation of magnesium hydroxide and the liberation of hydrogen is an exothermic reaction. This is commonly explained by saying that the film of hydroxide first formed covers the metal and retards further action. The author finds, however, if magnesium powder be added to ten times its weight of water, and then to this mixture such an amount of palladium

chloride as contains about one-hundredth part of the weight of magnesium used, a brisk evolution of hydrogen occurs. The temperature rises rapidly until the water boils and considerable white hydroxide is formed. The reaction is explained by the initial reduction of palladious chloride to metallic palladium, which acts as a catalytic agent. The small amount of magnesium chloride formed possibly also accelerates the reaction at first by dissolving the hydroxide; but the palladium, which has accelerated the *decomposition* of the water, soon accelerates its *formation*, for it is warm, and some of it rising on the bubble-films, which separate the hydrogen from the air, causes the hydrogen to ignite spontaneously.—Chem. News, May 31, 1912, 253.

Urine: Source of Error with Nylander's Test for Sugar.—Dr. E. Strauss has observed that certain substances interfere with the characteristic reaction for sugar by Nylander's test in the urine of diabetics (the production of a black color or precipitate by the reduction of the alkaline bismuth solution to metallic bismuth). Among these he finds iodthion, which when administered passes into the urine and is liable to form a complex compound with the bismuth salt, which protects the bismuth from the reducing action of the sugar. The author, furthermore, finds that iodthion does not interfere with the reaction produced by glucose upon Fehling's solution.—Pharm. Ztg., LVII (1912), No. 15, 148; from Munch. Med. Wschr., 1912, No. 2.

Urine: Source of Error in Trommer's Sugar-Test.—In accordance with the directions for carrying out Trommer's test for sugar in urine, a fairly concentrated solution of sodium hydroxide is added, followed by the careful addition of cupric sulphate, so long as the cupric hydroxide is redissolved, whereupon the liquid is heated until it begins to boil. Professor N. Schulz finds, however, that if the addition of the reagent is reversed, two periods arise which are liable to lead to deception: the first, due to great solvent power of urine on cupric hydroxide, and the second, due to the liability of reduction by normal urine after comparatively short boiling. The author, therefore, warns against a deviation from the order of the original directions, for those who still prefer to operate by Trommer's method, but recommends as preferable the method depending on the use of Fehling's solution, or better yet, Heine's modified solution.—Pharm. Ztg., LVII (1912), No. 15, 148; from Munch. Med. Wschr., 1912, No. 5.