ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS

Food and Drugs

Determination of Phosphorus in Fruits and Fruit Products. H. W. Gerritz. (*J. Assoc. Off. Agric. Chem.*, 1939, **22**, 131–137.)—Zinzadze's method has been adapted to the use of the neutral wedge photometer (*J. Assoc. Off. Agric. Chem.*, 1936, **19**, 130) and to the analysis of samples prepared by wet ashing. (1) *Zinzadze's reagent.*—The directions and precautions given by Zinzadze (*cf.* ANALYST, 1932, **57**, 411; 1936, **61**, 198) are followed exactly, a ten-fold dilution being used in the actual determination. (2) *Preparation of sample.*—A portion of the sample containing 1 to 3 mg. of phosphorus pentoxide is transferred to a 500-ml. Kjeldahl flask. For the determination of phosphorus in the water-soluble portion of fruits and fruit juices 25 ml. (equivalent to 3·75 g.) of the sample solution prepared according to the official methods (*Methods of Analysis, A.O.A.C.*, 1935, XXVI, [*b*] or [*c*] are used, and for jams and jellies 50 ml. of the prepared solution. Fifteen ml. of conc. nitric acid, 5 ml. of conc. sulphuric acid, 5 or 6 small glass beads, and a few pieces of broken porcelain are added, and the liquid is boiled over a moderate flame until copious fumes of sulphuric acid are evolved. If there is

pronounced charring, the liquid is cooled slightly and a little more nitric acid is cautiously added (with jams 3 additions of the acid may be necessary). The liquid is boiled again until fumes are evolved, 0·5 ml. of 60 per cent. (reagent quality) perchloric acid is added, and the "fuming" is continued for a few minutes. The digest should now be colourless or slightly greenish-yellow. If necessary, a further 0·5 ml. of the perchloric acid is added and the "fuming" is continued for 3 or 4 minutes. The liquid is cooled somewhat, 50 ml. of water are added, and the solution is boiled until fumes appear, to remove traces of nitric acid, after which it is cooled, treated with 25 ml. of water, made up to 100 ml. and thoroughly mixed. (3) *Determination of phosphorus.*—Twenty ml. are transferred to a 100-ml. flask (a Kohlrausch sugar flask has been found convenient) with a mark at 60 ml. Three drops of sodium alizarin sulphonate solution (0·20 g. of sodium alizarin monosulphonate dissolved in 100 ml. of water and filtered) are added, and the liquid is neutralised with conc. potassium hydroxide solution (prepared from phosphate- and arsenate-free potassium hydroxide and stored in a paraffin-lined container); the colour of the liquid is adjusted to yellow by means of *N* potassium hydroxide solution and *N* sulphuric acid, each being added dropwise with constant mixing until a single drop of the sulphuric acid just changes the colour to yellow. The liquid is diluted to the 60-ml. mark and mixed. The flask is placed in a boiling water-bath and brought to that temperature, a drop or two of the *N* sulphuric acid being added if the colour becomes pink. Exactly 10 ml. of Zinzadze's reagent (10-fold dilution) are added, the liquid is mixed, and the heating in the bath is continued for exactly 20 minutes. (It is important that the standards and unknown solutions be heated at the same temperature.) The solution is cooled, diluted and mixed, and the colour intensity is measured by means of the neutral wedge photometer, with a 1-inch cell and No. 66 filter (4·5 MM Corning dark pyrometer red No. 241; with B & L "Smoke C" glass, wedge filter 65, *i.e.* the same as 66 plus a half MM of Jena BG18, is used) and Jena 0–2 neutral wedge. The method covers a range up to 0·6 mg. of phosphorus pentoxide in the final 100 ml. of solution. Standards covering this range are prepared by placing 0, 2, 4, 6, 8, 10 and 12 ml. of standard phosphate solution containing 0·05 mg. per ml. (prepared by dissolving 0·1917 g. of pure dry potassium dihydrogen phosphate in about 200 ml. of water, adding 10 ml. of *N* sulphuric acid and 6 drops of 0·1 *N* potassium permanganate solution, and diluting to 2 litres) in 100-ml. flasks with marks at 60 ml. Two ml. of dilute (1 : 1) sulphuric acid and 3 drops of the indicator are introduced into each flask, with water to make about 20 ml. These standards are then treated in the same way as the sample, beginning with the neutralisation, developing the colour, cooling, making up to volume, and determining the colour intensity in the neutral wedge photometer. If alkali of suitable purity has been used, the 0 standard should give a reading not more than 10 to 15 mm. greater than the reading with pure water. A large-scale graph of the standards is made, mg. of phosphorus pentoxide being plotted against photometer readings. The sample photometer readings are converted into mg. of phosphorus present in the final 100-ml. portion by means of this graph. The photometer need be calibrated only once for each batch of reagents if the adjustment is not altered. In the analysis of heterogeneous samples, *e.g.* fresh fruit, for total phosphorus, it may be necessary to digest a larger

portion in order to eliminate sampling and weighing errors. It is then convenient to take double the sample (7·5 g.) and add double the volume of sulphuric acid (10 ml.). The digest is made up to 200 ml. and a 20-ml. aliquot part is transferred to a 100-ml. flask for colour development. The weight of sample digested may be varied to suit the nature of the sample, provided that the final 20-ml. portion contains about 1 ml. of sulphuric acid and 0·2 to 0·6 mg. of phosphorus pentoxide. The method has been found to be applicable to the analysis of materials of higher phosphorus-content, such as semolina macaroni. Zinzadze mentions that iron, nitrate and arsenic interfere with the development of the colour with his reagent. Nitrates are not present in solutions prepared as described, and neither iron nor arsenic is ordinarily present in sufficient quantity in fruit or fruit products to cause interference. If fruit were contaminated with spray residue to the extent of, say, 0·1 grain of arsenic trioxide per lb., it would make a positive error in the phosphate determined of only 1·4 mg. per 100 g. If the presence of excessive quantities of iron or arsenic is suspected the procedure is modified as follows:—The above directions are followed to the point "until a single drop of the sulphuric acid just changes the colour to yellow." Ten ml. of exactly *N* sulphuric acid and 10 ml. of 8 per cent. sodium bisulphite solution are added, and the solution is diluted to 60 ml. The flask is heated in a boiling water-bath for 1 hour and the directions given above are then followed, beginning "Exactly 10 ml. of Zinzadze's reagent (10-fold dilution) are added." The standards must, of course, then be treated in the same manner (see also Abstract, p. 455). E. M. P.

Contamination of Parsley with Arsenic. J. M. Rowson and C. E. Waterhouse. (*Pharm. J.*, 1939, **142**, 329.)—The arsenic-content of a sample of dried parsley (leaf and a little stalk) was 6 p.p.m. That of the herb before drying was: leaf and stalk, 1; root (with a little adhering earth), 1·5 p.p.m. (washing the fresh herb very thoroughly before analysis did not alter this result), and for a similar sample from a different locality it was 3 p.p.m. As fresh parsley normally loses from 60 to 80 per cent. of its weight on drying, the arsenic must have been present in the original sample. Cultivation experiments are in progress to investigate the possibility of the assimilation of arsenic by parsley. E. B. D.

Unusual Adulterant of Olive Oil (Quinoline Yellow). J. Pritzker and R. Jungkunz. (*Z. Unters. Lebensm.*, 1939, **77**, 254–256.)—A specimen of olive oil described as "guaranteed pure and genuine extra vierge" gave constants differing little from the normal values for genuine olive oil, but when examined in ultra-violet light the sample showed an intense grass-green fluorescence. Parallel determinations were therefore made with two samples of olive oil of French origin and a sample of tea-seed oil of Chinese origin. The "guaranteed pure" oil showed great similarity to pure olive oil and to tea-seed oil and, since it did not answer to tests for arachis, sesame, cotton-seed or kapok oil, suspicion was aroused that it was a mixture of olive and tea-seed oils. The possibility of its consisting entirely of tea-seed oil was excluded by the m.p. of the phytosteryl acetate prepared from it, *viz.* 120° C., the m.p. of phytosteryl acetate prepared from tea-seed oil being 156 to 157° C. In the fractional precipitation of its fatty acids (Kreis and Roth, *Z. Unters. Nahr. Genussm.*, 1913, **25**, 84) the sample yielded

only 0·68 g. of solid fatty acids from 20 g. of oil, whereas pure olive oil should yield at least 2·2 g. Another suspicious feature was the fact that the lead salts began to separate in 4 hours, as with tea-seed oil, whereas with pure olive oil the separation begins within an hour. These results pointed to the presence of a considerable amount of another oil, possibly tea-seed oil. In addition, the oil contained an artificial dye which was not detected by the usual methods (*Schweiz. Lebensmittelbuch*, 4th Ed., Bern, Zimmermann & Co., 1937), but was detectable by the method of Lecoq and Prince (*Guide pratique d'Analyses alimentaires*, Paris: Vicot Frères, 1921). The oil (5 g.) was dissolved in 5 ml. of petroleum spirit, the solution was shaken with 5 ml. of glacial acetic acid, and the acid layer was separated and evaporated to dryness. A deep yellow residue was obtained. It was not possible to identify the dye by dyeing tests, but when the fluorescence of the oil in ultra-violet light was compared with that of a series of dyes dissolved in almost colourless arachis oil, the conclusion was reached that the dye was quinoline-yellow. A. O. J.

Water Melon Seed Oil. A. J. Nolte and H. W. von Loesecke. (*J. Amer. Chem. Soc.*, 1939, **61**, 889–891.)—Air-dried seeds of melons (culls) grown in south central Florida, of the variety Cuban Queen (*Citrullus vulgaris*), a round or slightly oval melon with brownish black seeds, had the following composition:—moisture, 8·84; fat (ether extract), 26·52; protein, 17·31; ash, 2·36 (water-soluble, 0·05; insoluble, 2·31); undetermined, 44·97 per cent. The yellowish-brown oil was extracted with petroleum spirit and filtered; it contained 0·06 per cent. of volatile constituents and had the following characteristics:—sp.gr. at 25/25° C., 0·9197; n_D^{20}, 1·4669; saponification value, 197·4; iodine value (Hanus), 133·8; Reichert–Meissl value, 0·29; Polenske value, 0·72; acetyl value, 7·5; Hehner value, 89·2; acid value, 0·42; unsaponifiable matter, 1·19 per cent.; unsaturated acids (corr.), 78·96 per cent., with iodine value, 166·6; saturated acids (corr.), 14·56 per cent. The fatty acids consisted of palmitic, 8·84; stearic, 5·61; arachidic, 0·72; oleic, 13·03; linolic, 68·38 per cent. D. G. H.

Seed Fat of *Hodgsonia capniocarpa*. T. P. Hilditch, M. L. Meara and W. H. Pedelty. (*J. Soc. Chem. Ind.*, 1939, **58**, 26–29.)—The seed kernels of this plant, which is a Malayan climber of the Natural Order *Cucurbitaceae*, yielded to petroleum spirit 62 per cent. of a pale yellow oil with saponification equivalent 284·3, iodine value 65·5, acid value 0·8, and unsaponifiable matter 0·3 per cent. The component acids were found to consist of myristic, 0·7; palmitic, 39·5; stearic, 8·3; arachidic, 0·7; hexadecenoic, 1·0; oleic, 26·0; linolic, 23·8 per cent. mol. The chief constituents of the fat were found to be: "oleo"dipalmitins, 33; "oleo"-palmitostearins, 27; palmito-di"oleins," 24; tri-unsaturated glycerides (oleo-linolins), 13 per cent. mol., with possibly very small quantities of stearo-di"oleins." A small proportion (2·5 per cent.) of fully-saturated components was present. The occurrence of 13 per cent. of tri-unsaturated glycerides is distinctive, owing to the fact that oleic and linolic acids are both present in about the same high proportion. A comparison of the fatty acids with the component acids of shea butter, in which the ratio of unsaturated to saturated acids is very similar, but in which linolic acid forms only a very minor proportion of the unsaturated group,

gave:—fully saturated (*a*) shea butter, 4·5; (*b*) *H. capniocarpa*, 2·5; mono-unsaturated, (*a*) 34·5, (*b*) 60; di-unsaturated mono-saturated, (*a*) 56·5; (*b*), 24; and tri-unsaturated, (*a*) 4·5; (*b*), 13 per cent. The specific nature of the glycerides in this fat is evidently the result of combinations of four major component acids (palmitic, stearic, oleic, and linolic) to form triglycerides, whereas in fats previously studied it has been necessary to consider only the three acids, palmitic, stearic and oleic. D. G. H.

Chemical Examination of *Bragantia wallichii* (Lour). B. L. Manjunath and M. S. Shankara Rao. (*J. India Chem. Soc.*, 1938, **15**, 646–648.)—The root of *Bragantia wallichii*, Lour. (Sanskrit Chakrani, N. O. *Aristolochiaceae*, growing in the Western Ghats) has been used in the proportion of 4 g. of root made into a paste with 14 ml. of lemon juice, with beneficial results, in cases of cholera and diarrhoea. Fifty g. of powdered root were successively extracted with solvents and yielded extracts as follows: petroleum spirit, 0·48; ether, 0·78; chloroform, 0·49; ethyl acetate, 0·48; absolute alcohol, 3·70 per cent. Constituents volatile in steam amounted to 0·05 per cent., and 0·03 per cent. of alkaloid was present. About 50 kg. of root were extracted, and the extracts were examined in detail. The fatty acids of the dark brown oil from the petroleum spirit extract were palmitic, a small amount of crude lignoceric, oleic and linolic. A yellow substance separated from the ethereal extract, and the ethereal solution was successively extracted with 5 per cent. hydrochloric acid, potassium bicarbonate, potassium carbonate and potassium hydroxide solutions. The hydrochloric acid extract was combined with the hydrochloric acid extract of the chloroform extract, and these gave positive tests with reagents for alkaloids. The yellow substance, which was also obtained on acidifying the alkali extracts from ether and chloroform, and from the ethyl acetate extract, was identified as *iso*aristolochic acid after crystallisation from glacial acetic acid and alcohol. Unlike the acid itself, the methyl derivative was tasteless. D. G. H.

Action of Strychnine and Quinine on Bordeaux B. D. B. Dott. (*Pharm. J.*, 1939, **142**, 328–329.)—As previously stated (*Pharm. J.*, 1938, **141**, 261; Abst., ANALYST, 1938, **63**, 827) the strychnine separated from compound syrup of glycerophosphates is yellow even after re-precipitation with ferrocyanide, owing to the formation of a compound of strychnine with the acid of Bordeaux B. Also, the strychnine cannot be correctly determined by titration. It may be crystallised from the impure precipitate by extraction of a benzene solution with water and acid followed by addition of alkali and extraction with chloroform and evaporation, this process being repeated if necessary. When solutions containing equivalent quantities of strychnine hydrochloride and the dyestuff (termed sodium azorubrate) are mixed, part of the strychnine is precipitated as an azorubrate and part remains in the filtrate, which is coloured red. Analysis by two methods (*a*) and (*b*), showed that the precipitate contained (*a*) 52·06 and (*b*) 52·31 per cent. of strychnine. Theoretically, the di- and mono-strychnine salts contain 59·43 and 42·22 per cent. respectively of alkaloid. With quinine hydrochloride solution the dye gave a precipitate containing 57·0 per cent. of quinine (theoretical for di-quinine salt, 58·69 per cent.). It is considered therefore that Bordeaux B

should not be used for colouring liquids containing strychnine or other precipitatable alkaloids. Solubilities in water at room temperature:—strychnine azorubrate, 1 : 1000; quinine azorubrate 1 : 2270. E. B. D.

Valerian: A New Alkaloid. J. J. Blackie and D. Ritchie. (*Pharm. J.*, 1939, **142**, 299–300.)—A water-soluble base possessing physiological activity is present in appreciable quantity in dried valerian root. The base is soluble in cold or hot water and in alcohol, very sparingly soluble in ethyl acetate, and insoluble in acetone, chloroform or ether. It is precipitated by ether in flocculent particles from its solution in amyl alcohol. It has not yet been found possible to crystallise the base or to prepare crystalline derivatives. When distilled in a high vacuum (0·01 mm.) it decomposes at 200° C. Apparently it is not a pyrrole derivative, the presence of which in the root was reported by Cionga (*Comptes rend.*, 1935, **200**, 780), as the vapours evolved on heating the base with zinc dust did not give the characteristic red colour on pine wood. Intravenous injection of the base into a cat under urethane anaesthesia caused a fall in blood pressure, with a secondary effect upon the heart; it also had an inhibitory effect on peristalsis. These physiological effects require confirmation when the base has been obtained in a pure condition. Methods of separating the base from the root by extraction with amyl alcohol after removal of oil, resins, etc., are described in detail. E. M. P.

Methyl Alcohol Content of Tobacco Leaf and Ribs. W. Preiss. (*Z. Unters. Lebensm.*, 1939, **77**, 272–281.)—It has been shown by numerous workers that tobacco smoke contains methyl alcohol derived mainly from methyl pectic esters, and it is generally agreed that the methyl alcohol yield from unfermented tobaccos may reach 0·9 per cent., and that during fermentation that of cigar tobacco is reduced to 0·04—0·2 per cent. and that of cigarette tobacco to about 0·5 per cent., so that, as a rule, the pale tobaccos yield more methyl alcohol than the dark tobaccos. When the coarser parts of the leaf (midrib and large veins) are used, Neumann-Wender (*Münch. Med. Woch.*, 1933, **80**, 737) observed an increased yield of methyl alcohol, constituting a potential source of danger to the smoker. Since the pectic esters are largely responsible for the methyl alcohol occurring in the smoke, it appears necessary to determine the amounts of pectin and lignin and the methyl alcohol derived from them. Also, a determination of methyl alcohol derived from lignin would indicate the proportion of woody tissue in the tobacco. Methods based upon those of von Fellenberg (*Biochem. Z.*, 1918, **85**, 45, 118) were used to distinguish between the methyl alcohol derived from these two sources. To determine the methyl alcohol derived from pectin, 1 g. of finely powdered tobacco was treated with 20 ml. of water and allowed to stand for 2 hours. The mixture was treated with 5 ml. of 10 per cent. sodium hydroxide solution, allowed to stand overnight, and after the addition of 2·5 ml. of 20 per cent. sulphuric acid, it was distilled until 18 to 19 ml. had been collected. This distillate, after the addition of 1 ml. of 20 per cent. sulphuric acid, was redistilled until 14 to 15 ml. of distillate had been collected. To this distillate 5 drops of 10 per cent. sodium hydroxide solution and 5 drops of 10 per cent. silver nitrate solution were added, and 12 ml. of distillate were collected. Finally, this distillate was redistilled from animal charcoal until exactly 10 ml. had been collected. An

aliquot portion (3 ml.) was taken for the determination of methyl alcohol. For the determination of the total methyl alcohol from pectin and lignin, 0·5 g. of powdered tobacco was mixed with 15 ml. of 72 per cent. sulphuric acid and boiled gently in a distillation apparatus at such a rate that not more than 1 or 2 ml. of distillate were collected in 10 minutes. When the liquid had cooled, 25 ml. of water were added, and 27 to 28 ml. were distilled. The distillate was neutralised to litmus paper with 10 per cent. sodium hydroxide solution and, after the addition of 5 drops in excess and 5 drops of 10 per cent. silver nitrate solution, the mixture was distilled, and 20 to 21 ml. of distillate were collected. The treatment with sodium hydroxide and silver nitrate was repeated, and the distillate of 12 ml. was redistilled from animal charcoal until exactly 10 ml. of distillate were obtained; an aliquot portion (3 ml.) of this was used for the determination of methyl alcohol. The methyl alcohol concentrates (3 ml.) obtained by these methods were treated in 100-ml. flasks with 1 ml. of alcoholic sulphuric acid (20 ml. of absolute alcohol and 40 ml. of conc. sulphuric acid diluted with water to 200 ml.) and 1 ml. of 5 per cent. potassium permanganate solution, shaken well, allowed to stand for exactly 2 minutes, and treated with 1 ml. of 8 per cent. oxalic acid solution and 1 ml. of conc. sulphuric acid. As soon as the solution became colourless, 5 ml. of fuchsin-sulphurous acid solution (5 g. of fuchsin, 12 g. of crys. sodium sulphite and 100 ml. of N sulphuric acid diluted to 1 litre) were added. The solution was allowed to stand for exactly one hour, water was added (25 ml. for amounts up to 1 mg. of methyl alcohol in 10 ml. of distillate, 50 ml. for larger amounts), and the solution was compared in a colorimeter with standard solutions prepared from pure methyl alcohol treated in the same manner. The amount of methyl alcohol present was determined by means of a calibration curve constructed for the instrument. The Lange photo-electric colorimeter is recommended. The methyl alcohol derived from pectin bodies is very small in the large-leaved tobaccos of the alkaline group; in European pipe-tobacco it may reach about 0·4 per cent. Tobacco ribs yield less pectin methyl alcohol than the whole or stripped leaf. In oriental cigarette tobaccos of the acid group the pectin-methyl alcohol content is higher than in the alkaline group and amounts to about 0·5 per cent. Methyl alcohol derived from lignin amounts to about 0·2 per cent. in the large-leaved tobaccos, 0·4 per cent. and more in the ribs, and 0·12 per cent. in the stripped leaves. Oriental tobaccos yield about 0·1 per cent. of methyl alcohol from lignin. The amount of lignin methyl alcohol obtained is a measure of the lignified tissue in the tobacco product and may be used to determine approximately the amount of rib and vein present. The methods described provide a useful means of following the effects of the processes of tobacco manufacture upon its pectin and lignin contents.

A. O. J.