green precipitate was dried and powdered and boiled with several liters of ether for days. The part insoluble in the ether was dissolved in boiling absolute alcohol and 5.5 g. remaining insoluble. Concentration of the alcoholic filtrate yielded about 6 g. further. After crystallization from dilute pyridine several times a light green semi-crystalline product was obtained which was an impure phytosterolin. With much difficulty 3.7 g. of phytosterolin melting at about 285–295°, was obtained.

Calc. for $C_{33}H_{56}O_6$: C, 72.3; H, 10.2. Found: C, 71.9; H, 10.2.

The acetate melted at 167–168°.

0.4919 g. acetate made up to a volume of 20 cc. with chloroform showed a rotation of 1.114° in a 20 cm. tube at 23° whence $[\alpha]_D^{23} = -22.6$.

The ether extract from which the crude phytosterolin had been filtered off was extracted with solutions of ammonium carbonate, sodium carbonate and potassium hydroxide, and then the ether upon evaporation contained but a slight quantity of dissolved substance. The alkaline extracts which contained quantities of chlorophyll yielded nothing of interest upon acidification.

The chloroform extract of the resin amounted to 85 g.

A further quantity of phytosterolin (2.75 g.) was obtained here. Nothing was isolated by alkaline extractions. The fraction was not glucosidic.

The ethyl acetate extract of the resin (14 g.). A small quantity (3.9 g.) of adonitol separated as the extraction proceeded. It melted at 102–3°.

Calc. for $C_5H_{12}O_5$: C = 39.5; H = 7.9. Found: C = 39.3; H = 7.8.

The alcoholic extract of the resin (90 g.). A very small amount of the toxicity was in this fraction. However, the material itself was quite toxic (0.0411 g. per 1 g. frog). An acid and an alkaline hydrolysis failed to yield anything of interest. The solution reduced Fehling's solution directly, but this reduction was increased after heating with aqueous acid.

KALAMAZOO, MICH.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, HERCULES POWDER COMPANY.]

A QUANTITATIVE ESTIMATION OF ACETIC, PROPIONIC AND BUTYRIC ACIDS.

BY R. D. CROWELL.

Received November 19, 1917.

The separation of the lower acids of the acetic series from each other has been accomplished more or less satisfactorily by methods based upon the following principles:[1]

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[1] Allen's "Commercial Org. Analysis," 1, 515–519 (1914). Owing to the inadequacy of library facilities it was impossible to consult the original literature on this subject.

(1) Butyric acid and the higher homologs may be partially separated from the lower members of the series by saturating their aqueous solutions with calcium chloride, the butyric and higher acids rising to the surface as oils.

(2) On partial neutralization and distillation mixtures of valeric and butyric acids may be partially separated.

(3) Mixtures of any two can be estimated by distillation, neutralization with barium hydroxide of known strength and weighing the dried barium salts.

(4) Duclaux claims to be able to estimate quantitatively mixtures of these acids by means of the difference in the rate of distillation of the various homologs.

(5) It has been stated that butyric and valeric acids are extracted from a water solution by shaking with benzene while formic and acetic acids remain in the water. As far as we could ascertain, none of these methods have been found suitable for a routine laboratory analysis for acetic, propionic and butyric acids.

Phelps and Palmer state[1] that the solubilities of quinine acetate, propionate and butyrate in carbon tetrachloride are different enough to be of possible use in the separation of the three acids but give no results of actual experiments.

Experimental.

Thinking it possible that quinine sulfate might be used in a method of analysis the following experimental work was done:

About 0.3 g. of solid barium acetate was dissolved in 25 cc. warm water. 0.6 g. quinine sulfate was added and the resulting mass, containing solid barium sulfate, quinine acetate, and unchanged quinine sulfate was evaporated to dryness at 50° at a pressure of about 15 cm., 75 cc. of carbon tetrachloride were then added to the flask and boiled on a steam bath for 10–15 minutes. The solution was then cooled to 25° and filtered. The residue was thoroughly washed with carbon tetrachloride, bringing the filtrate to a volume of 100 cc. and the filtrate distilled over 20 cc. phosphoric acid. The distillate was titrated with 0.25 *N* barium hydroxide and the equivalent amount of acid compared with that originally present. This was repeated with barium propionate and butyrate with the following results:

TABLE I.

	Amount present.	Amount recovered.	% recovered.
	Butyric Acid.		
1	0.1693 g.	0.1076 g.	63.6
2	0.1692 g.	0.1076 g.	63.6

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[1] I. K. Phelps and H. E. Palmer, *J. Biol. Chem.*, **29**, 199 (1917).

TABLE I (*continued*).

	Amount present.	Amount recovered.	% recovered.
	Propionic Acid.		
1	0.1612 g.	0.0975 g.	60.5
2	0.1259 g.	0.0717 g.	60.0
	Acetic Acid.		
1	0.0860 g.	0.0067 g.	7.9
2	0.1720 g.	0.0138 g.	8.0

The butyric acid recovery was too low. After trying (1) excess quinine sulfate, and (2) a mixture of absolute alcohol and carbon tetrachloride, with no better results, this work was abandoned.

The solubilities of barium acetate, propionate and butyrate in alcohol, were then considered, but proved to be too close to one another to permit of a separation of the three acids in this way. The following table gives the results obtained in this experiment:

TABLE II.

Solubilities in 97% C_2H_5OH.

Salt.	Solubilities per 100 cc. 1.	2.	3.	Average.
Barium acetate	0.0730 g.	0.0742 g.	0.0704 g.	0.0723 g.
Barium propionate	0.1616 g.	0.1610 g.	0.1638 g.	0.1631 g.
Barium butyrate	0.1728 g.	0.1662 g.	0.1710 g.	0.1700 g.

A combination of the first and fifth principles cited above was then considered. This consists in the extraction of butyric acid from an aqueous solution, to which a salting agent has been added, by means of an immiscible organic solvent. For this extraction a solvent must be chosen in which acetic acid is relatively insoluble. Obviously the solubility of propionic acid in this solvent does not matter as a mixture of any two of these acids can be readily analyzed as stated under (3).

After trying benzene, toluene, carbon tetrachloride, distillate (high boiling gasoline), gasoline and kerosene, the latter was selected as the organic solvent, first because it extracts a large percentage of the butyric acid, with but little acetic acid, and second because it is relatively safe to handle. (The efficiency of the extraction is increased by the presence of a salting agent in the water layer, calcium chloride being usually used.) After trying a large number of different highly soluble salts a saturated solution of calcium chloride to which has been added a little potassium chloride (20 g. to a liter) was found to be most satisfactory.

Experimental data showing relative solubility of acetic and butyric acids in organic solvent and aqueous layer.

Organic solvent: kerosene 15 cc.

Aqueous solution: 15 cc. saturated calcium chloride—potassium chloride, 1 cc. **butyric acid.**

TABLE III.

(1).

	Titration in cc. 0.25 *N* Barium Hydroxide.		Percentage Acid in Layers.	
	Water layer.	Kerosene layer.	Water layer.	Kerosene layer.
1	3.2 cc.	40.5 cc.	7.3%	92.7%
2	3.0 cc.	40.8 cc.	6.2%	93.8%
3	3.0 cc.	37.9 cc.	7.5%	92.5%
4	3.0 cc.	38.6 cc.	7.2%	92.8%
5	3.3 cc.	39.7 cc.	8.7%	92.3%
		Average,	7.2%	92.8%

5 cc. 10% Acetic Acid.

(2).

	Water layer.	Kerosene layer.	Water layer.	Kerosene layer.
1	35.1 cc.	0.90 cc.	97.5%	2.5%
2	31.0 cc.	0.75 cc.	97.7%	2.3%
3	37.6 cc.	0.92 cc.	97.6%	2.4%
4	37.4 cc.	0.70 cc.	98.2%	1.8%
5	36.1 cc.	0.80 cc.	97.8%	2.2%
		Average,	97.7%	2.3%

With the total acidity of a sample and the total weight of CH_2 groups present known, the accuracy of the determination of all three acids depends on the accuracy with which the butyric acid present can be determined. By assuming that the kerosene layer contains only propionic and butyric acid, after being shaken with all three acids in the salting solution, and by analyzing this solvent layer for the butyric and propionic acids by means of the total acidity and a salt weight there is obtained a value for the butyric acid which will vary a more or less definite amount from the true butyric acid content. This factor depends upon the manipulation of the method and solubility in water layer, etc., and will be considered after the outline of the method finally adopted, which follows.

The accuracy of the method depends to a great extent upon the desiccation of the salts. The barium salts, if much propionate is present, are not satisfactory, even if desiccated for 40 hours or more in a high vacuum at 100°. The sodium or potassium salts if weighed in tared squat weighing bottles (60 by 30 mm.), after heating 12 hours at 200°, proved to be the most satisfactory.

Method.

An amount of sample equivalent to about 7.5 g. of acid is diluted or concentrated to 250 cc. (in a volumetric flask). This is the standard sample.

(1) A 50 cc. sample of this is pipetted into a 200 cc. precipitating jar and 2.5 cc. of 50% sulfuric acid is added (to prevent the precipitation of

silver acetate, etc.). Then, sufficient solid silver sulfate is added to precipitate all the chlorides present. This is then stirred with an electric stirrer (one such as used at soda fountains is very satisfactory) until when filtered it shows an excess of silver when tested with hydrochloric acid. It is filtered and 25 cc. of the filtrate are pipetted into a 250 cc. florence flask. 20 cc. 33% phosphoric acid and a few bits of brick are added to the flask, which is then connected to a 30 cm. Liebig condenser and a dropping funnel. It is then distilled until the residue amounts to about 20 cc., then 20 cc. carbon dioxide-free water is added by means of the dropping funnel and the distillation continued as before. This is repeated three times to insure complete distillation of volatile acids.

The distillate is caught in a 250 cc. flask and titrated with 0.25 *N* sodium hydroxide using phenolphthalein as indicator. The titrated distillate is boiled down to about 8 cc. and transferred to a tared squat weighing bottle, in which it is evaporated to dryness on a steam bath. The weighing bottle and contents is then desiccated at 220° for 12 hours and weighed.

The total acidity expressed as sodium acetate subtracted from the salt weight gives the weight of CH_2 groups. This figure, multiplied by 4.2, to correct for dilution and size of sample, gives the total weight of CH_2 groups per 100 cc. sample.

(2) A 150 cc. portion of the standard sample is pipetted into a precipitating jar and freed from chlorine, as the 50 cc. portion was in (1). 100 cc. of the chlorine-free filtrate are pipetted into a Kjeldahl flask fitted with condenser and dropping funnel. 20 cc. of 33% phosphoric acid are added and the distillation carried on until 20–22 cc. residue remain in the flask. 20 cc. carbon dioxide-free water are added, drop by drop, and the distillation continued until 20–22 cc. remain again. This is repeated three times. The distillate is caught in a 500 cc. Pyrex flask and titrated with 0.25 *N* barium hydroxide and phenolphthalein. This neutralized distillate is then concentrated to a volume of from 5 to 8 cc. To this concentrated neutralized distillate is added from a buret the equivalent of the 0.25 *N* barium hydroxide titration in 4 *N* hydrochloric acid. Since hydrochloric acid is a much stronger acid than acetic, butyric or propionic, the volatile organic acids are now liberated in a 10 cc. volume.

This concentrated acid solution is carefully poured into a 300 cc. separatory funnel. The flask is then washed with 25 cc. of saturated calcium chloride, saturated with potassium chloride, which is then poured into the funnel. This is repeated with another 25 cc. portion of salting solution and two 25 cc. portions of filtered kerosene. The separatory funnel is well shaken, the butyric acid passing into the kerosene together with some of the propionic. On settling, the salting solution layer is run off and discarded. A 10 cc. portion of salting solution is added to the kerosene in the funnel, which is then shaken and allowed to separate into two layers again. This salting solution layer is then run off and discarded, carrying with it practically all of the remaining acetic acid.

To the kerosene in the funnel is now added 150 cc. of carbon dioxide-free water, and the whole titrated with 0.25 *N* barium hydroxide and phenolphthalein with frequent shaking. Barium propionate and barium butyrate being insoluble in kerosene, pass into the water layer as fast as formed by the neutralization of the free acids in the kerosene. Thus, when the end point is reached the water layer may be drawn off into a 250 cc. graduated flask which is filled to the graduation with repeated 30 cc. water washings of the kerosene, and the kerosene discarded.

The whole of this 250 cc. solution is then treated with 12.5 cc. 50% sulfuric acid and 3 g. of silver sulfate as before to free it from chlorine. 200 cc. of the chlorine-free filtrate are pipetted into a Kjeldahl flask and distilled over 40 cc. 33% phosphoric acid, and washed three times with 20 cc. portions of carbon dioxide-free water as with the other distillations. The distillate is caught in a 500 cc. Pyrex flask, titrated with 0.25 *N* sodium hydroxide and evaporated to a 5 to 8 cc. volume, and transferred to tared weighing bottles. It is then evaporated to dryness on a steam bath and dried to constant weight in an electric oven at 200°. This gives the salt weight of sodium propionate and sodium butyrate.

The sodium propionate equivalent of the 0.25 *N* sodium hydroxide titration subtracted from this salt weight gives the weight of CH_2 groups present as butyric acid in the distillate. This value for the butyric acid obtained by multiplying this CH_2 weight by C_3H_7COOH/CH_2 corrected for dilution will not quite equal the true butyric acid content of the sample, since there is a definite proportional loss during extraction. To correct for this a factor F is inserted. This CH_2 group weight must therefore be multiplied by the following factors to give the butyric acid weight in 100 cc. of the standard sample:

F; 1.05, to correct for sulfuric acid addition; 1.25, to correct for aliquot portion taken for distillation; $6.286 = C_3H_7COOH/CH_2$.

This butyric acid weight multiplied by $(CH_2)_2/C_3H_7COOH = 0.3142$ gives the weight of CH_2 groups present as butyric acid in 100 cc. of the standard sample. Now, in (1) the total CH_2 groups present as butyric and propionic acid was determined, hence subtracting from the total weight of CH_2 groups present as butyric acid, gives the weight of CH_2 groups present as propionic acid in 100 cc. of standard sample. This weight of CH_2 groups multiplied by $C_2H_5COOH/CH_2 = 5.29$, therefore, gives the propionic acid per 100 cc. sample.

The acetic acid per 100 cc. is determined as follows:

4.2 times the 0.25 *N* sodium hydroxide titration of the distillate from the 25 cc. sample in (1) gives the cc. of 0.25 *N* NaOH equivalent to the total volatile acid in 100 cc. of the original sample. Now, if the propionic and butyric acid weights per 100 cc. are converted into the equivalent number of cc. of 0.25 *N* NaOH and subtracted from the total volatile acid titration computed above, the difference will be the cc. of 0.25 *N* NaOH equivalent to the acetic acid per 100 cc. of sample.

Determination of F.

Applying the above method, the mean factor F, by which the butyric acid found in the kersene layer is to be multiplied to correct for incomplete salting was next determined.

TABLE IV.

Sample No.	Butyric acid present, g.	Butyric acid found, g.	Factor.	Acid ratio HAc–HPr–HBu.
1	0.9338 g.	0.7685 g.	1.215	0:0:1
2	0.9379 g.	0.8333 g.	1.125	0:1:1
3	0.9890 g.	0.9209 g.	1.074	1:1:1
4	0.9749 g.	0.8507 g.	1.146	1:1:1
5	1.9630 g.	1.7669 g.	1.111	1:1:1
6	0.1953 g.	0.1713 g.	1.140	3:3:1
7	0.1953 g.	0.1898 g.	1.029	3:3:1
8	0.1953 g.	0.1735 g.	1.125	3:3:1
		Average,	1.120	

Applying the average factor to the analysis, the following data on the accuracy of the butyric acid determination was obtained:

TABLE V.

Sample No.	Butyric acid present.	Butyric acid reported.	Per cent. Error.
1	0.9338	0.8607	7.8%
2	0.9379	0.9333	0.5%
3	0.9890	1.0314	4.2%
4	0.9749	0.9528	2.2%
5	1.9630	1.9789	0.7%
6	0.1953	0.1919	1.7%
7	0.1953	0.2126	8.1%
8	0.1953	0.1943	0.5%
		Average error,	3.2%

To determine the effect of this error upon the estimation of all three acids, samples were run containing various ratios and analyzed for all three acids with the following results:

TABLE VI.

Complete Analysis.

	Present.				Reported.				
No.	Hac. %	HPr. %	HBu. %	Total acid. %	Hac. %	HPr. %	HBu. %	Total acid. %	Mean error. %
1	0.720	0.350	0.195	1.255	0.700	0.380	0.190	1.270	4.7
2	0.720	0.340	0.195	1.255	0.760	0.280	0.210	1.250	7.8
3	0.720	0.340	0.195	1.255	0.720	0.340	0.190	1.250	0.7
4	0.720	0.340	0.195	1.255	0.720	0.330	0.200	1.250	1.5
5	0.631	0.590	0.560	1.782	0.623	0.598	0.566	1.787	1.0
6	0.631	0.590	0.560	1.782	0.679	0.546	0.559	1.784	3.8
								Average,	3.25

NOTE.—Acids used in making up standard samples: (1st) glacial acetic acid, (2nd) propionic acid, prepared by saponifying the ethyl ester, fraction used boiling between 139–142°, (3rd) butyric acid, prepared from the ester, boiling at 161–163°.

SAN DIEGO, CALIF.

NOTE.

Rapid Organic Combustion.—We wish to report here on a method of rapid combustion as it is practiced in our laboratory. There is nothing essentially new in the principle of the method as employed by us. To Dennstedt,[1] to Beck[2] and to Miss Marie Reimer[3] belong the credit of building up the theory and practice of the rapid combustion. However, in our laboratory where the demand made on every furnace is very great and where combustions are made continually, there were many occasions when none of the three methods worked satisfactorily, even when carried out exactly under the original conditions given by their respective authors. In the course of years some of the imperfections of the three methods were corrected, and the advantageous parts of all were combined in one, so that finally we have a combustion tube which served for more than three hundred combustions without change of the catalyst.

Cerium dioxide was employed as the catalyst, as suggested by Beck. It was soon found that when the dioxide was prepared in the manner described by the original authors, samples were obtained that differed considerably in their efficiency. Often the catalyst was exhausted after a very few combustions. On other occasions the dioxide was inactive from the start, and at times an inactive dioxide improved after several combustions, but became exhausted after a few additional combustions. As the same source of cerium nitrate gave samples of dioxide of variable

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[1] Dennstedt, M., "Anleitung zur vereinfachten Elementaranalyse," III. Aufl. Hamburg, 1910, p. 66.

[2] Beck, J., *Ber.*, 46, 2574 (1913).

[3] Reimer, M., THIS JOURNAL, 37, 1636–38 (1915).