If a similar reaction had taken place in the treatment of α-β-oxy-brom-dihydro-brom-isoapiol with ethyl alcoholic potash, a compound having the following composition would have resulted:

$$C_6Br\begin{cases} O \\ O>CH_2 \\ OCH_3 \\ OCH_3 \\ CH(OH)-CH(OC_2H_5)-CH_3 \end{cases}$$

This substance contains 46.28 per cent. of carbon and 5.23 per cent. of hydrogen, which are quite different from the figures obtained by analysis. For the present, therefore, we prefer to retain the ketone formula above-mentioned. This line of investigation will be continued and extended to some other substances of a similar constitution.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE NO. 47.—SENT BY H. W. WILEY.]

THE COMPOSITION OF FRESH AND CANNED PINEAPPLES.

BY L. S. MUNSON AND L. M. TOLMAN.

Received January 2, 1903.

THE work undertaken in connection with the investigation of the composition of fresh and canned pineapples consists of the analysis of (1) fresh pineapples from various sources, (2) canned pineapples that were put up under supervision of the Consuls General of the United States at Singapore and Nassau, and (3) commercial samples of canned pineapples.

DESCRIPTION OF SAMPLES.

Of the thirty-eight samples of fresh pineapples examined, twenty-one were from Florida, ten from Cuba, four from Porto Rico, two from the Bahamas and one from Jamaica. The Florida pineapples were largely obtained from representative growers; the Cuban pineapples were nearly all purchased on the market at Havana; the Porto Rican pineapples were obtained from F. D. Gardner, Director of Porto Rican Experiment Station; the Bahama samples were obtained on the market in New York; and the sample from Jamaica was obtained in the Washington market. So far as possible, the samples obtained were the well-ripened fruit, but in some cases they were shipped so far that it was not

practicable to use the thoroughly ripened fruit but such as would stand shipment. Samples 804 to 808 and 818 were secured early in the season and were very green. Their composition shows them to be of inferior quality and therefore they have been excluded from the averages for total solids and for sugars. The first sample of fresh pineapples was received March 4, 1902, and the last sample September 26, 1902, and samples were secured at varying intervals between these dates.

Sixteen samples of canned pineapples were obtained from the Consul-General at Singapore. Of this number, ten were put up in the normal pressed juice of the pineapple without addition of cane-sugar and six were put up in the pressed juice to which cane-sugar had been added. Two samples were obtained from the Consul-General at Nassau, preserved without addition of cane-sugar.

The forty-two samples of commercial canned pineapples came from Singapore, the Straits Settlements and from the Bahamas.

METHODS OF ANALYSIS.

The methods of analysis employed in this work were essentially those given under "Fruits and Fruit Products, Provisional Methods for the Analysis of Foods," Bulletin 65, Bureau of Chemistry. The total solids were determined by drying in a water-oven with asbestos for twenty hours. Solids in the syrup were calculated from the specific gravity, using the table of H. Ellion. Reducing sugars were determined by Meissl's method for invert sugar, and cane-sugar was determined both by the increase in reduction after inversion with hydrochloric acid, and by double polarization. The polarimetric method used was that of the German Official Chemists, and cane-sugar was calculated by the Herzfelt formula,

$$S = \frac{100(A - B)}{141.89 + 0.05B - \frac{T}{2}}.$$

Results by the two methods agreed very closely, especially where the amount of cane-sugar was small. With samples of high content of cane-sugar, the results by the reduction method were less reliable, owing to the influence of the cane-sugar upon the reduction.

While the acids of pineapples are largely citric they are ex-

pressed in this paper as H_2SO_4 for the reason set forth in a previous contribution from this laboratory.[1]

ANALYTICAL DATA.

Table I contains the results of analyses of the fresh pineapples. As will be seen by reference to this table, there is no material difference in composition due to the source of the pineapples; neither does the variety seem to have any influence on the composition. Insoluble solids, ash, acids, and protein do not show a wide variation, while on the other hand the samples show a wide difference in the content of sugars. As is well known, the sugars develop very rapidly with the ripening of the fruit. On the other hand the other constituents appear to be present in equally large amounts in the green fruit. Of particular interest is the relative amounts of reducing- and cane-sugars in the fresh fruit. In nearly all cases the cane-sugar is largely in excess of the reducing sugar. The average amount of reducing sugar in all the samples of fresh fruit is 3.91 per cent. while the average amount of cane-sugar is 7.59 per cent.—nearly double the amount of reducing sugar.

Table II contains the results of the analyses of the pineapples canned under direction of the Consuls General at Singapore and Nassau. The samples put up without addition of cane-sugar were preserved in expressed pineapple juice, the amount of juice added being about 30 per cent. of the entire contents of the can. So far as content of total sugars are concerned, therefore, the composition of these canned pineapples should not be materially different from the composition of the normal fresh fruits. Other constituents, especially insoluble solids, will be lowered by the addition of the juice as comparison of Tables I and II shows. While the amount of total sugar is practically the same as in the fresh fruit, the relative proportions of reducing- and cane-sugars are entirely different, due to the inverting action of the organic acids during the processes of canning. In many cases the amount of the cane-sugar remaining is quite small, the average for all the samples being 3.41 per cent. of cane-sugar and 7.99 per cent. of reducing sugars—just the reverse of the condition in the fresh fruit. This condition also holds in the samples put up with addition of cane-sugar, and with the commercial samples.

[1] This Journal, **23**, 347 (1901).

TABLE I.—COMPOSITION OF FRESH PINEAPPLES.

Serial Number.	Variety.	Solids.		Ash.		Acids as H_2SO_4.	Protein (N × 6.25).	Sugars.			Polarizations.		
		Total. Per cent.	Insoluble. Per cent.	Total. Per cent.	Alkalinity as K_2CO_3. Per cent.	Per cent.	Per cent.	Reducing. Per cent.	Cane. Per cent.	Total as Invert. Per cent.	Direct. °V.	Invert. °V.	Temperature. °C.
	FLORIDA:												
571	Spanish red.....	11.93	1.60	0.438	0.321	0.847	0.406	1.94	5.98	8.24	4.75	— 3.08	22.0
807		8.06[1]	1.55	0.326	0.390	0.366	0.494	1.74[1]	2.96[1]	4.86[1]	1.85	— 2.20	23.4
808		10.19[1]	1.59	0.434	0.497	0.825	0.419	1.44[1]	5.37[1]	7.09[1]	4.35	— 2.30	28.4
1054	Spanish red.....	16.53	1.48	0.505	0.377	0.509	0.418	5.89	8.71	15.06	6.70	— 4.45	28.0
1055	Porto Rico.....	12.27	1.48	0.408	0.345	0.307	0.262	4.06	6.49	10.89	5.00	— 3.30	28.0
1056	Egyptian queen..	18.86	1.47	0.548	0.377	0.483	0.381	5.20	8.48	14.13	6.85	— 4.01	28.0
1059	Sugar loaf.....	15.06	1.51	0.356	0.337	....	0.275	3.64	9.12	13.24	8.00	— 3.85	30.0
1060	Spanish red.....	13.30	1.55	0.361	0.243	....	0.474	4.40	6.48	11.22	5.00	— 3.30	30.0
1061	Abakka.....	10.78	1.45	0.385	0.292	....	0.331	3.95	4.68	8.88	3.90	— 2.20	30.0
1062	Blood.....	11.82	1.29	0.446	0.317	....	0.406	3.02	6.13	9.48	5.15	— 2.75	30.0
1063	Spanish red.....	17.52	1.68	0.428	0.374	....	0.418	4.54	10.20	15.28	8.55	— 4.62	30.0
1064	Smooth cayenne.	12.93	1.27	0.378	0.355	0.444	0.400	3.17	7.51	11.08	6.20	— 3.30	27.8
1066	Smooth cayenne.	14.85	1.03	0.373	0.322	0.445	0.393	9.75	2.98	12.89	0.20	— 3.63	27.8
1067	Abakka.....	13.70	1.31	0.349	0.278	0.465	0.419	5.28	6.35	11.97	4.70	— 3.52	27.8
1068	Porto Rico.....	12.20	1.84	0.526	0.478	0.545	0.569	3.98	6.03	10.33	4.60	— 3.08	27.8
1069	Abakka.....	12.73	1.27	0.466	0.418	0.620	0.306	4.38	6.22	10.93	4.80	— 3.30	27.8
1070	Spanish red.....	13.10	1.49	0.464	0.596	0.300	0.475	4.52	6.53	11.40	5.20	— 3.19	27.8
1071	Pernambuco	15.60	1.68	0.487	0.403	0.560	0.406	4.33	8.27	13.03	6.50	— 4.23	27.8
1092	Egyptian queen..	13.62	...	0.479	0.459	0.565	0.469	3.62	7.44	11.45	6.40	— 3.08	30.0
1093	Abakka.....	11.02	1.02	0.395	0.276	0.400	0.338	4.08	4.91	9.45	3.40	— 3.02	25.8
1125	Spanish red.....	15.25	...	0.401	0.316	0.560	0.494	4.53	8.22	13.19	6.70	— 4.20	21.0
	Average.....	13.85	1.45	0.421	0.370	0.515	0.407	4.44	6.88	11.69			
	CUBAN:												
572	Spanish red.....	12.63	1.35	0.272	0.272	0.561	0.406	2.19	6.81	9.36	6.70	— 2.36	21.0
646	Sugar loaf.....	11.45	1.70	0.324	0.355	0.646	0.206	1.76	6.12	8.20	4.80	— 3.19	23.0

[1] Not included in averages.

TABLE I (continued).—COMPOSITION OF FRESH PINEAPPLES.

Serial Number.	Variety.	Solids.		Ash.		Acids as H_2SO_4.	Protein (N × 6.25).	Sugars.			Polarizations.		
		Total. Per cent.	Insoluble. Per cent.	Total. Per cent.	Alkalinity as K_2CO_3. Per cent.	Per cent.	Per cent.	Reducing. Per cent.	Cane. Per cent.	Total as invert. Per cent.	Direct. °V.	Invert. °V.	Temperature. °C.
CUBAN:													
647	Spanish red	14.12	1.64	0.319	0.328	0.602	0.381	3.00	8.76	12.23	7.10	-4.33	23.0
802	Spanish red	13.45	1.63	0.457	0.461	0.670	0.475	2.31	8.23	10.97	7.20	-3.57	27.6
803	Sugar loaf	12.67	1.80	0.277	0.223	0.502	0.513	2.76	6.77	9.89	5.90	-3.09	27.6
804		9.13[1]	1.49	0.313	0.353	0.673	0.512	1.34[1]	4.60[1]	6.18[1]	3.50	-2.53	23.4
823	Spanish red	17.53	1.54	0.425	0.401	0.511	0.387	3.76	10.48	14.79	9.20	-4.18	28.6
855	Sugar loaf	16.53	1.33	0.342	0.360	0.457	0.363	4.55	9.43	14.48	8.10	-4.29	22.6
860	Spanish red	15.38	1.81	0.444	0.476	0.624	0.375	2.84	9.65	12.00	8.35	-4.07	25.8
1053	Sugar loaf	16.99	1.64	0.296	0.327	0.359	0.357	4.65	9.73	14.89	8.50	-3.90	26.0
	Average	14.52	1.59	0.347	0.356	0.561	0.397	3.09	8.44	11.87			
BAHAMA:													
809		14.97	1.52	0.387	0.410	0.798	0.500	2.56	9.18	12.23	8.10	-4.07	28.4
868	Spanish red	14.65	1.59	0.408	0.409	0.747	0.462	2.75	8.98	12.21	7.85	-3.74	25.8
	Average	14.81	1.56	0.398	0.410	0.772	0.481	2.65	9.08	12.22			
PORTO RICAN:													
805		8.69[1]	1.64	0.416	0.399	0.697	0.431	1.35[1]	3.67[1]	5.22[1]	2.30	-2.36	23.4
818	Cabezona	8.48[1]	1.63	0.332	0.304	0.807	0.519	2.74[1]	3.30[1]	6.22[1]	2.30	-1.92	28.6
819	Pan de Azucar	14.14	1.69	0.404	0.437	0.524	0.444	2.97	8.22	11.62	7.15	-3.41	28.6
820	Caraquena	17.69	1.83	0.333	0.370	0.838	0.531	4.59	9.97	15.09	8.20	-4.62	28.6
	Average	15.91	1.70	0.371	0.378	0.716	0.481	3.78	9.09	13.36			
JAMAICA:													
806		9.23[1]	1.48	0.410	0.410	0.646	0.475	1.28[1]	4.67[1]	6.19[1]	3.55	2.58	23.4
	Av'ge of all samples	14.17	1.52	0.396	0.370	0.603	0.420	3.91	7.59	11.90			
	Maximum	18.86	1.83	0.548	0.596	0.847	0.569	9.75	10.48	15.28			
	Minimum	10.78	1.02	0.272	0.223	0.300	0.206	1.76	2.98	8.20			

[1] Not included in averages.

TABLE II.—COMPOSITION OF CANNED PINEAPPLES PUT UP UNDER DIRECTION OF CONSULS GENERAL AT SINGAPORE AND NASSAU.

Serial Number.	Solids.		Ash.		Acids as H_2SO_4.	Protein ($N \times 6.25$).	Sugars.			Polarizations.		
	Total. Per cent.	Insoluble. Per cent.	Total. Per cent.	Alkalinity as K_2CO_3. Per cent.	Per cent.	Per cent.	Reducing. Per cent.	Cane. Per cent.	Total as invert. Per cent.	Direct. °V.	Invert. °V.	Temperature. °C.
Preserved in natural juice without addition of cane-sugar.												
SINGAPORE:												
1103	14.34	1.18	0.447	0.312	0.450	0.566	8.92	3.28	12.38	0.90	—3.30	23.0
1104	14.26	1.31	0.357	0.295	0.466	0.562	9.54	3.34	13.06	0.90	—3.52	23.0
1105	14.41	1.20	0.474	0.338	0.472	0.438	10.96	1.85	12.91	—1.10	—3.52	23.0
1106	13.48	1.15	0.476	0.329	0.490	0.481	9.56	2.44	12.13	0.00	—3.20	23.0
1107	17.44	1.44	0.434	0.352	0.436	0.488	10.56	4.11	14.89	1.60	—3.80	24.4
1108	13.10	1.34	0.309	0.257	0.450	0.506	7.44	4.20	11.86	2.30	—3.20	24.4
1109	10.96	1.16	0.242	0.214	0.250	0.500	5.84	3.85	9.90	2.30	—2.65	24.4
1111	11.70	1.62	0.333	0.301	0.333	0.412	7.53	2.08	9.72	0.30	—2.50	24.4
1112	11.28	0.87	0.330	0.253	0.294	0.444	6.59	3.00	9.83	1.40	—2.60	24.4
1113	12.95	1.83	0.391	0.308	0.299	0.356	7.30	3.17	10.64	1.60	—2.70	24.4
Average..	13.39	1.31	0.379	0.300	0.389	0.475	8.42	3.13	11.73			
NASSAU:												
1013	10.00	1.07	0.257	0.300	0.443	0.250	5.44	2.96	8.55	1.65	—2.09	26.0
1014	16.35	2.18	0.563	0.663	0.711	0.456	6.20	6.61	13.16	4.65	—3.68	26.0
Average..	13.18	1.63	0.410	0.482	0.577	0.403	5.82	4.79	10.86			
Preserved in natural juice with addition of cane-sugar.												
SINGAPORE:												
1114	18.07	1.02	0.370	0.286	0.378	0.412	11.93	4.63	16.70	1.50	—4.50	24.4
1115	18.48	1.38	0.267	0.164	0.202	0.350	12.68	4.88	17.82	1.55	—4.75	24.4
1116	18.15	1.60	0.460	0.329	0.260	0.400	7.51	8.82	16.80	7.00	—4.30	24.4
1117	18.61	2.06	0.505	0.336	0.284	0.456	9.02	7.83	17.26	6.50	—4.60	24.4
1118	19.11	1.25	0.450	0.328	0.417	0.450	15.39	2.41	17.93	1.65	—4.80	24.4
1119	16.61	1.33	0.334	0.234	0.378	0.375	13.28	2.28	17.93	0.20	—4.25	24.4
Average..	18.17	1.44	0.398	0.280	0.320	0.407	11.63	5.14	17.41			

TABLE III.—COMPOSITION OF CANNED PINEAPPLES—COMMERCIAL SAMPLES.

	Specific gravity of syrup.	Solids in syrup. Per cent.	Solids. Total. Per cent.	Solids. Insoluble. Per cent.	Ash. Total. Per cent.	Ash. Alkalinity as K_2CO_3. Per cent.	Acids as H_2SO_4. Per cent.	Protein (N × 6.25) Per cent.	Sugars. Reducing. Per cent.	Sugars. Cane. Per cent.	Sugars. Total as invert. Per cent.	Polarizations. Direct. °V.	Polarizations. Invert. °V.
SINGAPORE—(Twenty-one samples):													
Average...	1.0869	20.15	21.03	1.17	0.284	0.225	0.269	0.461	9.61	7.88	17.86	5.01	-5.22
Maximum.	1.1112	25.30	26.84	1.67	0.363	0.282	0.433	0.569	13.73	16.48	25.10	15.00	-6.60
Minimum.	1.0744	18.18	18.45	0.92	0.208	0.164	0.156	0.388	7.05	4.34	14.87	0.00	-4.40
STRAITS SETTLEMENTS—(Ten samples):													
Average...	1.0868	20.08	21.04	1.08	0.259	0.225	0.259	0.466	10.51	7.54	18.45	4.53	5.37
Maximum.	1.0998	22.86	24.28	1.27	0.322	0.324	0.323	0.569	15.18	10.65	21.94	7.70	6.27
Minimum.	1.0717	16.79	17.32	0.91	0.224	0.138	0.171	0.394	7.70	4.70	14.55	0.00	4.20
BAHAMAS—(Eleven samples):													
Average...	....	....	14.13	1.39	0.381	0.304	0.558	0.335	7.96	2.78	9.98	0.56	3.31
Maximum.	....	....	26.78	2.51	0.497	0.388	1.176	0.456	12.84	9.05	22.37	4.70	7.15
Minimum.	....	....	8.54	0.88	0.222	0.199	0.220	0.200	5.55	0.53	6.33	2.40	1.32

Table III contains the results of analyses of forty-two samples of canned pineapples from Singapore, the Straits Settlements and the Bahamas. It is apparent from the high content of sugars that practically all of the canned pineapples from Singapore and the Straits Settlements are preserved with addition of cane-sugar. On the other hand, the analyses indicate that but few of the samples from the Bahamas have had any addition of cane-sugar.

A study of the data contained in the foregoing tables fails to bear out the common supposition that the pineapples grown upon or near the equator contain more sugar than those grown at some distance farther north, and in fact, the normal content of sugar in pineapples grown in Florida differs so little from that of pineapples grown at Singapore that the difference is practically negligible.

It may not be out of place to state at this point, that these investigations were undertaken in the Bureau of Chemistry at the request of the Secretary of the Treasury for the purpose of establishing a basis of classification for imported pineapples for the guidance of the appraisers. Since the classification of these bodies for dutiable purposes depends upon the answer to the question of whether or not sugar has been added during the process of preserving, it was necessary, first to establish the normal content of sugar in the pineapples. It is evident, from inspection of the analyses, that since the normal pineapples contain a large quantity of cane-sugar, the mere presence of this substance would be no evidence whatever of its artificial addition. It is further evident, that if a syrup containing practically the same quantity of sugar as the natural syrup of the pineapple were added, it would be quite impossible, by a mere determination of the sugar present, to detect the addition. The only guide in this case would be to determine the relation of the sugar present to the total insoluble matters of the pineapple.

If, on the other hand, a syrup rich in sugar were added in preserving, it would be easily detected by the increase in the percentage of sugar in the contents of the can.

In looking over the literature accessible to us relating to the analysis of pineapples, at the commencement of these investigations, we were surprised to find that no paper has been published on this subject except one by Buignet in "Les Sucres," published by Maquenne (Paris, 1900).

The average content of sugar found by Buignet, *viz.*, 13.9 per cent. as invert sugar is not materially different from the amount found in these investigations.

THE EFFECT OF MOISTURE ON THE AVAILABILITY OF DEHYDRATED PHOSPHATE OF ALUMINA.

BY FRED. W. MORSE.

Received January 3, 1903.

THE author has from time to time encountered samples of phosphatic material, which have borne the name of concentrated phosphate, and which really are dehydrated phosphate of alumina and iron.

Such materials usually contain approximately 45 per cent of phosphoric anhydride, of which more than 0.5, and sometimes as much as 0.8, will dissolve in a neutral solution of ammonium citrate.

The phosphatic mineral from which this fertilizer is made, is obtained principally from the islands of Redonda and Grand Connetable in the West Indies, and is a hydrated phosphate of alumina and iron.

The author has made several analyses of the mineral from the former island, and a number of analyses have been published by Shepard,[1] Tate,[2] and Hitchcock,[3] while only one analysis made by Andouard,[4] is yet known to him of the latter phosphate. The composition of the two phosphates is very similar. The phosphoric anhydride ranges from 35 per cent. to 39 per cent. in cargoes and as high as 43 per cent. in the richest specimens.

The water contained in the mineral is nearly proportional to the phosphoric anhydride, the ratio averaging $2P_2O_5$ to $9H_2O$. Two analyses including Andouard's give $10H_2O$, while two analyses have been as low as $8H_2O$. The proportion of Al_2O_3 to Fe_2O_3 is irregular; usually the former exceeds the latter, especially in the richer specimens.

The process of preparing the mineral for use as a fertilizer, was patented by the late Stephen L. Goodale,[5] who described the prin-

[1] *Am. J. Sci.*, **47**, 428.
[2] *J. Soc. Chem. Ind.*, **5**, 570.
[3] *Bull. Geol. Soc. Am.*, **2**, 6-9.
[4] *Ann. Agronom.*, **21**, 171.
[5] "Conversion of Hydrous Phosphates of Alumina and Iron." Monograph, 1893.