REPORT OF PROGRESS ON THE ORGANIC ACIDS PRODUCED BY THE BACTERIAL DECOMPOSITION OF PLANT MATERIAL

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This investigation was started at the University of Illinois by W. V. Howard and A. N. Murray under the direction of the National Research Council and the American Petroleum Institute. The original problem was "Limestones and Dolomites as Reservoir Rocks." It was found by these investigators that the porosity in limestones and dolomites occurs below unconformities. This condition suggests that the porosity was developed by chemical reactions between the limestones and carbonic acid and other acids, while these rocks were at or near the surface of the earth.

The action of carbon dioxide on limestones and the amounts of carbon dioxide which are available to produce porosity by solution of these rocks are very well known, but the other acids, largely those connected with plant life and the decomposition of plant material, have never been investigated. To obtain some idea of the amounts of acids produced by the bacterial decomposition of plant material, Howard and Murray ran the following experiment:

Two four-liter flasks were filled with dry leaves, each flask was inoculated with 25 cc. of solution obtained by washing 25 gms. of surface soil with 100 cc. of distilled water and allowing the solution to settle for 10 minutes. The remaining space in the flask was filled with distilled water and a small hole left for gas to escape. These flasks were kept at room temperature and pressure and at different time intervals the acidity of the liquid in one of these flasks was determined. The following table gives the results:

Time in days	*Normality*
41	0.10934
99	0.5009
110	0.02336
120	0.02127

A liter of this 0.1 normal acid will react with 5 gms. or 1.853 cc. of calcite. If the acids generated in one year at the above rate acts on 100 sq. cm. of limestone surface, it will render a layer 1.094 cm. thick 15 per cent porous and in 10,000 years it will render a layer 10,940 cm. or 358 ft. thick 15 per cent porous or remove a layer 53.8 ft. thick from the surface. Granting that because of unfavorable conditions of formation, oxidation, loss by rain wash, and neutralization only 1 per cent of the organic acids produced by bacterial decomposition of plant material are effective, they will render a stratum 3.58 ft. in thickness 15 per cent porous in 10,000 years. This is slightly less than the amount of solution accomplished by carbonic acid in the Kentucky River basin on the assumption that all the calcium in the water of this river has been taken into solution by the fomation of the acid carbonate. These findings seem to suggest that the organic acids play a more important part in the development of porosity in limestone below unconformities than has been originally credited to them.

The kinds of acids which may be produced by such decomposition process have been little studied. The experiments of bacteriologists and chemists in connection with the retting of flax, a similar process, have shown that members of the fatty acid group such as acetic, butyric, valeric, and formic are present in the waste products of bacterial decomposition. It is for the purpose of determining the acids and other compounds associated with such a process that the present investigation has been started. The preparation of these acids was begun in the fall of 1928 by charging two separatory flasks with 350 gms. of leaves and 3000 cc. of distilled water and inoculated with soil bacteria washed from 100 gms. of surface soil. The charges stood at room temperature and pressure for 384 days, at the end of which time the liquid was drained off and more water added to the leaves. The liquid obtained from each flask was distilled separately and the distillate collected in flasks through temperatures ranging from 97 C. to 135 C. The portions which were distilled at the lower temperatures were clear pale yellow liquids which possessed a sour rancid odor similar to that of butyric acid, while those which were distilled at the higher temperatures were liquids of dark yellow color containing some oily substance which was only slightly soluble in water. The latter fractions had a peculiar bunt odor in addition to that of butyric acid. They are believed to be, in part at least, decomposition products produced by the heat applied during distillation. Each fraction of the distillate was tested by the Duclaux method. The results obtained, according to the Duclaux table of constants in "Kamm's Qualitative Organic Analysis," indicate the presence of butyric and propionic acids. In this test .15 normal solution of sodium hydroxide was used as a base in titrating the acid with phenolpthalein as an indicator. The following table gives the results of the titrations:

Flask No. 1					Flask No. 2				
No. of Frac. tion	No. of Titration	Name of Acid Indicated	Values of Duclaux Constants	Values of Constants Obtained	No. of Frac. tion	No. of Titration	Kind of Acid Indicated	Values of Duclaux Constants	Constants Obtained by Titration
1	1	Butyric	17.9	18.48	1	1	Butyric	17.9	15.14
1	2	Butyric	15.9	16.31	1	2	Butyric	15.9	14.28
1	3	Butyric	14.6	13.93	1	3	Propionic	11.3	12.57
2	1	Butyric	17.9	16.28	2	1	Propionic	11.9	13.82
2	2	Butyric	15.9	15.05	2	2	Propionic	11.7	13.23
2	3	Butyric	14.6	13.05	2	3	Propionic	11.3	11.76
3	1	Butyric	17.9	16.95	3	1	Propionic	11.9	13.57
3	2	Butyric	15.9	14.98	3	2	Propionic	11.7	13.33
3	3	Propionic	11.3	12.64	3	3	Propionic	11.3	12.38
4	1	Butyric	17.9	15.16	4	1	Propionic	11.9	13.68
4	2	Propionic	11.7	13.42	4	2	Propionic	11.7	12.80
4	3	Propionic	11.3	12.01	4	3	Propionic	11.3	11.93
5	1	Butyric	17.9	15.53	5	1	Propionic	11.9	14.51
5	2	Butyric	15.9	13.88	5	2	Propionic	11.7	12.25
5	3	Butyric	14.6	13.03	5	3	Propionic	11.3	12.25
					6	1	Propionic	11.9	12.91
					6	2	Propionic	11.7	12.22
					6	3	Propionic	11.3	11.25