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GEOCHEMICAL FEATURES OF HYDROXY ACIDS IN SOIL SAMPLES FROM THE McMURDO DRY VALLEYS, ANTARCTICA

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Abstract: Hydroxy acids in 12 soil samples from the Wright and Taylor Valleys of the McMurdo Dry Valleys (Ross Desert) in southern Victoria Land, Antarctica have been studied to clarify their features and to elucidate the source materials. A suite of 3-hydroxy (C_8-C_{30}) and (ω-1)-hydroxy (C_{22}-C_{30}) acids presenting the predominance of even-carbon numbers were found in the soil samples, while 2-hydroxy (C_8-C_{30}) and ω-hydroxy (C_8-C_{30}) acids showed no even-carbon predominance. These hydroxy acids are probably attributed to the degradation products of wind-transported cyanobacterial mats in and around streams, lakes and ponds, as well as to the past biological activity, involving bacteria, cyanobacteria and fungi, rather than originating from the Beacon Supergroup of Gondwanaland sediments and living organisms.

1. Introduction

Hydroxy acids including 2-, 3-, ω- and (ω-1)-hydroxy, and dihydroxy acids are commonly distributed in various lacustrine and marine sediments (EGLINTON *et al.*, 1968; BOON *et al.*, 1977; VOLKMAN *et al.*, 1980; CRANWELL, 1981; CARDOSO and EGLINTON, 1983; GOOSSENS *et al.*, 1986). In Antarctica vascular plants are absent, except in the northern part of the Antarctic Peninsula. So, organic components including hydroxy acids in Antarctica can be expected to be considerably different from those in the mid and lower latitudes. Little is known on the occurrence of hydroxy acids in Antarctica. Only MATSUMOTO *et al.* (1988, 1989) reported 2-, 3-, (ω-1)-, and 9-, 10-dihydroxy acids in lake waters and/or sediments of the McMurdo Dry Valleys (Ross Desert) of southern Victoria Land, Antarctica.

The features of hydroxy acids in soil samples of the McMurdo Dry Valleys are interesting from the viewpoint of geochemistry, because long-chain *n*-alkanes and *n*-alkenes with the predominance of odd-carbon numbers, and long-chain *n*-alkanoic acids with the predominance of even-carbon numbers are major components (MATSUMOTO *et al.*, 1981, 1990a, b). Here we report 2-, 3-, ω- and (ω-1)-hydroxy acids in soil samples from the McMurdo Dry Valleys in Antarctica to elucidate their features and discuss them in relation to their source materials.

2. Materials and Methods

The features of sampling sites and samples have been reported before (MATSUMOTO *et al.*, 1990a). Briefly, the valley depression is covered with moraine and fluvioglacial deposits of Pleistocene to Recent ages (MCKELVEY and WEBB, 1962). Only soil-like materials are distributed in some valley depressions. In December 1983, soil samples were collected from the east side of Don Juan Pond in the Wright Valley, and from the surroundings of Lake Bonney in the Taylor Valley of the McMurdo Dry Valleys (Fig. 1), and were kept frozen at $-20°C$ until analyzed in 1987–88.

The analytical methods of hydroxy acids are given elsewhere (MATSUMOTO and NAGASHIMA, 1984; MATSUMOTO *et al.*, 1988). Shortly, soil samples (40–80 g) were refluxed with 0.5 M potassium hydroxide in methanol (80°C, 2 h) and extracted with ethyl acetate after acidification. Hydroxy acid fraction was obtained through a silica gel column chromatography (160×5 mm i.d., 100 mesh, 5% water). Trimethylsilyl ether methyl ester derivatives of hydroxy acids were analyzed using a Shimadzu QP1000 gas chromatograph-mass spectrometer (GC-MS). The GC-MS was operated using a fused silica capillary column (DB-5, $30\ m \times 0.32$ mm i.d., film thickness 0.25 μm) connected to an on-column injector. The column temperature was programmed from 70 to 120°C at 25°C/min, then 120 to 310°C at 6°C/min. The temperatures of molecular separator and ion source were maintained at 320 and 250°C, respectively. The flow rate of helium carrier gas was 4.3 m*l*/min. Mass spectra (m/z 50–600) were obtained continuously with a scan speed of 1.3 s at 70 eV.

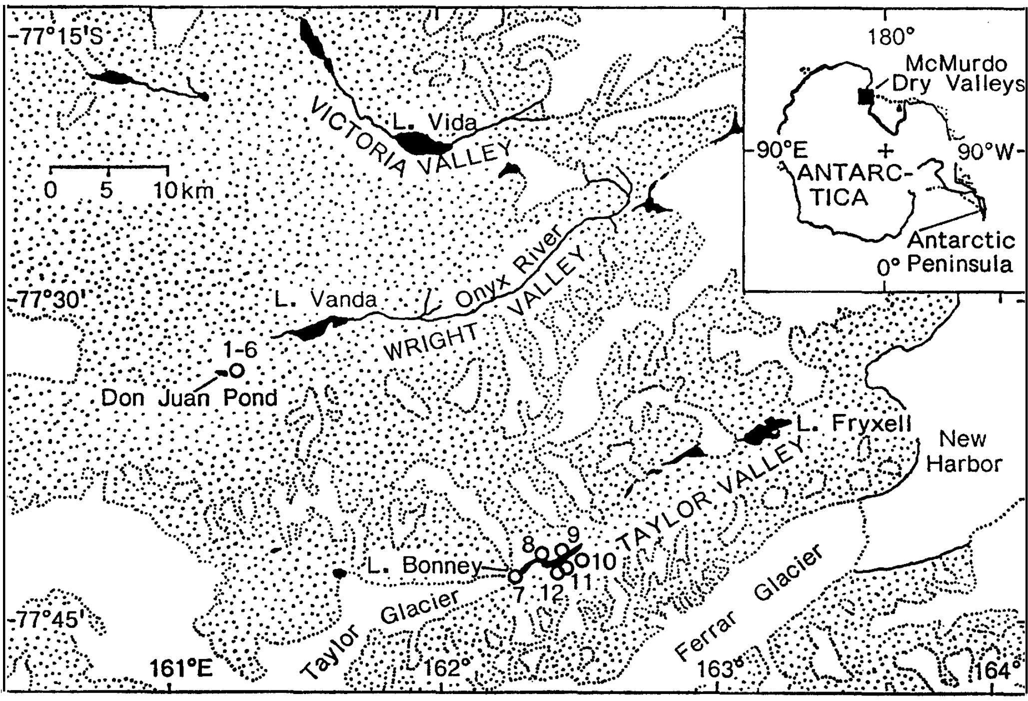

Fig. 1. Sampling locations of soil samples in the McMurdo Dry Valleys of southern Victoria Land, Antarctica. ▒: Ice-free area. 1–6: Don Juan-1–Don Juan-6. 7: Bonney-W1. 8: Bonney-C1. 9: Bonney-E2. 10: Bonney-E8. 11: Bonney-E9. 12: Bonney-E12.

3. Results and Discussion

3.1. Features of hydroxy acids

A series of normal 2-hydroxy (C_8-C_{30}), 3-hydroxy (C_8-C_{30}), ω-hydroxy (C_8-C_{30}) and (ω-1)-hydroxy (C_{22}-C_{30}) acids were found in soil samples, together with *iso-* and *anteiso-* 2- and 3-hydroxy acids (Figs. 2–5). 9, 10-Dihydroxyhexadecanoic acid was tentatively identified only in the Bonney-Wl sample. Also, short-chain (ω-1)-hydroxy acids were suggested to be present in some soil samples, but these were not included in this discussion. The total concentrations of 2-, 3-, ω- and (ω-1)-hydroxy acids were lower than 150, 49, 140 and 28 ng/g of dry soil, respectively (Table 1), which are much lower than

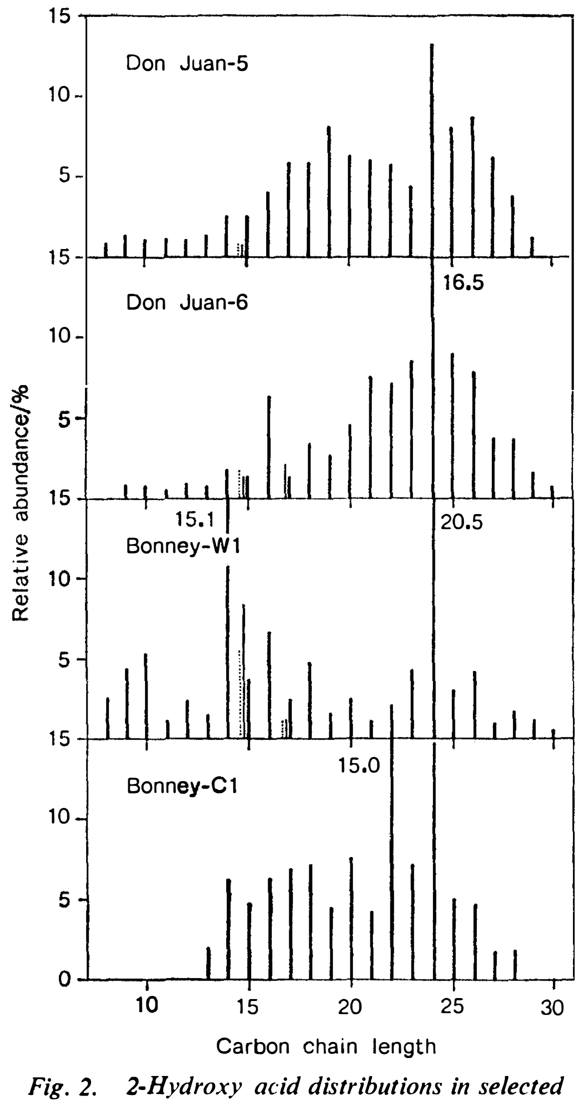

Fig. 2. 2-Hydroxy acid distributions in selected soil samples from the McMurdo Dry Valleys (total=100%). Bold solid line: Normal 2-hydroxy acids. Dotted line: Iso-2-hydroxy acids. Solid line: Anteiso-2-hydroxy acids.

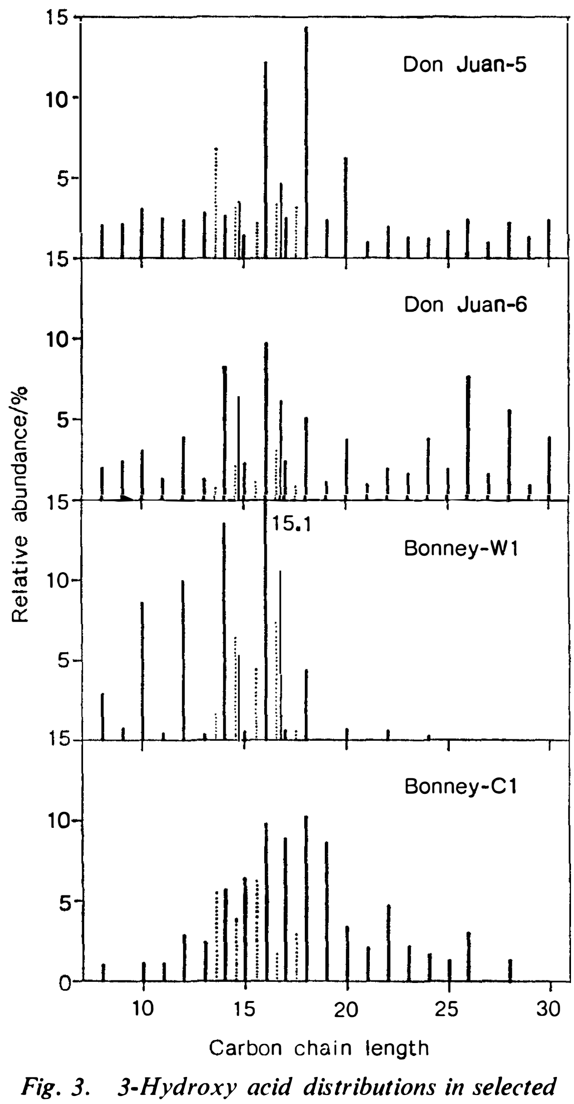

Fig. 3. 3-Hydroxy acid distributions in selected soil samples from the McMurdo Dry Valleys (total=100%). Bold solid line: Normal 3-hydroxy acids. Dotted line: Iso-3-hydroxy acids. Solid line: Anteiso-3-hydroxy acids.

those in sediment samples of the McMurdo Dry Valleys (MATSUMOTO *et al.*, 1988). Although the compositions of these hydroxy acids varied considerably among the soil samples, the most predominant 2-, 3-, ω- and (ω-1)-hydroxy acids were chiefly 2-C_{24} or 2-C_{26}; 3-C_{16}, 3-C_{14} or 3-C_{18}; ω-C_{14} or ω-C_{13}; and (ω-1)-C_{28} or (ω-1)-C_{26} with decreasing abundances, respectively (*e.g.*, Figs. 2–5).

In general, the long (C_{20}-C_{30})/short (C_{12}-C_{19})-chain acid ratios for 3- and ω-hydroxy acids were smaller than unity, whereas those for 2- and (ω-1)-hydroxy acids were opposite (Table 1). Carbon preference indices (even/odd ratios) calculated for short (CPI_s, C_{12}-C_{18})- and long (CPI_l, C_{20}-C_{30})-chain components showed that 2- and ω-hydroxy acids are near unity, but 3- and (ω-1)-hydroxy acids are considerably greater than unity except for some cases (Table 1). Generally, these CPI_s and CPI_l values are considerably smaller than those in Recent lake and pond sediments in the world, including those in

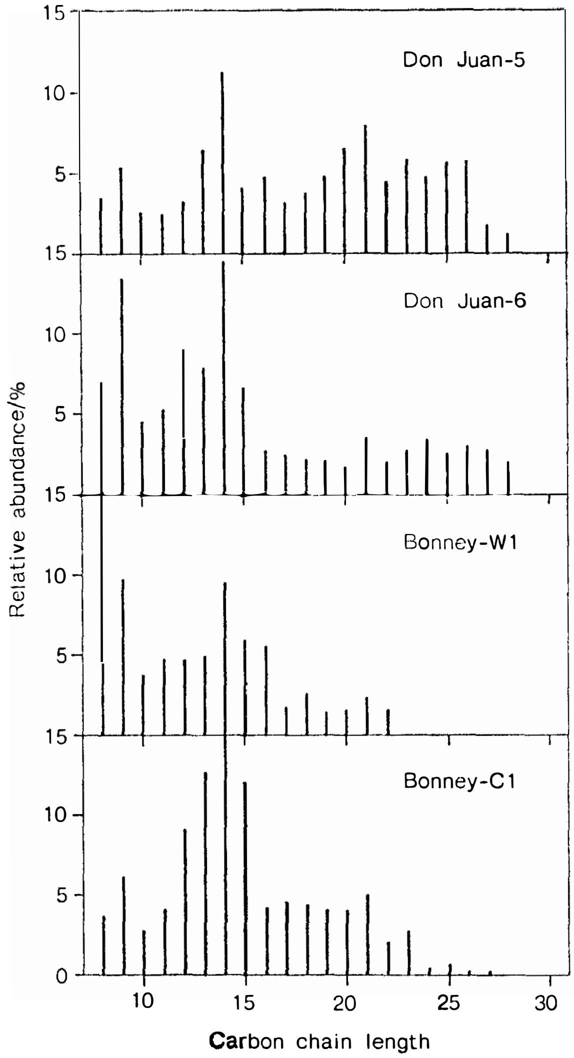

Fig. 4. ω-Hydroxy acid distributions in selected soil samples from the McMurdo Dry Valleys (total = 100%).

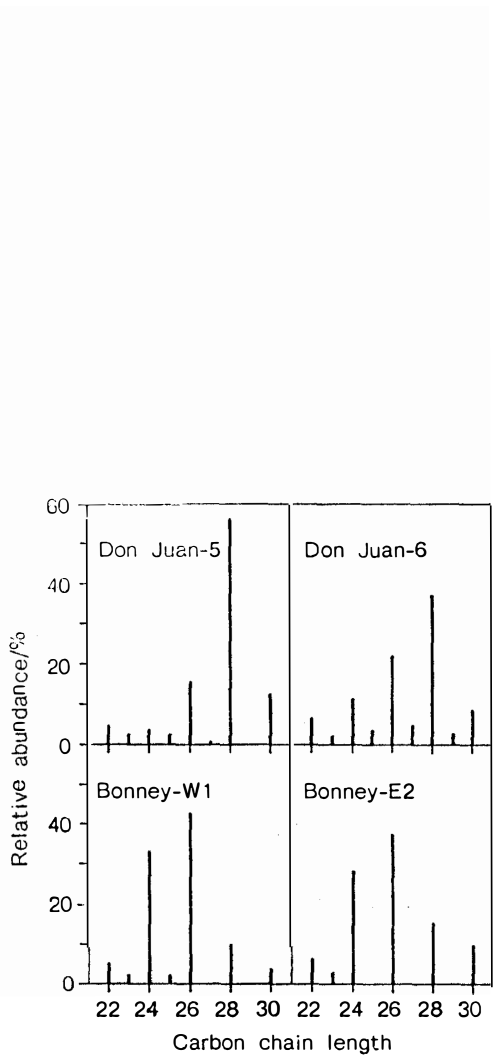

Fig. 5. (ω-1)-Hydroxy acid distributions in selected soil samples from the McMurdo Dry Valleys (total = 100%).

Table 1. Concentrations (ng/g of dry soil), long (C_{20}–C_{30}, L)/short (C_{12}–C_{19}, S)-chain ratios and carbon preference indices for short (CPI_s, C_{12}–C_{18})- and long (CPI_l, C_{20}–C_{30})-chains of n-hydroxy acids in soil samples from the McMurdo Dry Valleys, Antarctica.

Sample	2-Hydroxy acid				3-Hydroxy acid*				ω-Hydroxy acid				(ω-1)-Hydroxy acid#		
	Conc.	L/S	CPI_s	CPI_l	Conc.	L/S	CPI_s	CPI_l	Conc.	L/S	CPI_s	CPI_l	Conc.	L/S	CPI_l
Wright Valley															
Don Juan-1	LD	ND	ND	ND	LD	ND	ND	ND	LD	ND	ND	ND	LD	ND	ND
Don Juan-2	130	3.5	0.83	0.77	47	1.3	4.8	2.2	30	0.45	0.91	1.1	20	>1	8.0
Don Juan-3	78	0.92	0.94	0.82	18	0.61	3.4	2.0	20	0.25	1.0	1.0	5.6	>1	15
Don Juan-4	150	1.9	1.1	1.4	45	0.63	7.0	4.7	55	1.7	1.3	1.3	28	>1	74
Don Juan-5	68	1.9	0.91	1.3	24	0.53	3.5	2.0	43	0.94	1.3	0.97	15	>1	16
Don Juan-6	59	3.6	2.5	1.3	18	0.88	3.7	3.1	34	0.45	1.2	0.98	10	>1	6.2
Taylor Valley															
Bonney-W1	46	0.93	2.9	2.9	49	0.03	21	ND	18	0.13	1.4	1.1	12	>1	23
Bonney-C1	29	1.6	1.1	2.2	48	0.35	1.3	1.8	140	0.22	0.99	0.67	2.9	>1	3.9
Bonney-E2	11	2.3	1.5	1.5	9.2	0.27	4.5	ND	7.6	0.20	1.0	1.1	3.9	>1	32
Bonney-E8	11	1.8	1.5	1.8	LD	ND	ND	1.1	32	0.14	1.1	0.82	3.9	>1	4.4
Bonney-E9	3.7	1.9	1.7	0.90	3.8	0.07	5.8	ND	8.1	0.12	0.89	1.1	3.0	>1	6.5
Bonney-E12	27	0.86	1.3	1.5	31	0.23	6.7	2.3	29	0.16	0.87	1.2	9.0	>1	11

LD: Less than detection limits.
ND: No data.
* Data from MATSUMOTO *et al.* (1990b).
# Short-chain (ω-1)-hydroxy acids were suggested to be present, but were not included in the table.

the McMurdo Dry Valleys as well as living organisms (VOLKMAN *et al.*, 1980; MATSUMOTO and NAGASHIMA, 1984; MATSUMOTO *et al.*, 1984, 1988; KAWAMURA *et al.*, 1987).

3. 2. Sources of hydroxy acids

Various types of hydroxy acids occurring in organisms suggest that most organisms are capable of producing hydroxy acids either as biochemical intermediates, cell constituents or as extracellular lipids (BOON *et al.*, 1977; DREWS and WECKESSER, 1982; CARDOSO and EGLINTON, 1983; MATSUMOTO and NAGASHIMA, 1984; MATSUMOTO *et al.*, 1984; MATSUMOTO and KANDA, 1985; GOOSSENS *et al.*, 1986).

As discussed above, the CPI_8 and CPI_1 values of our hydroxy acids are considerably smaller than those in living organisms and Recent sediments. Thus it is unlikely that the hydroxy acids directly originate from either living organisms or Recent organic matter, although it is suggested that these were derived from ancient source materials. Indeed, living cells of cyanobacteria and microalgae were not found in the soil samples, but small amounts of cyanobacterial envelopes were detected in some soil samples (MATSUMOTO *et al.*, 1990a). Also, the occurrence of hydroxy acids in sedimentary rocks is not common, because hydroxy acids are not well preserved over geological time (CARDOSO and EGLINTON, 1983). Thus, living organisms and the erosion of the Beacon Supergroup sedimentary rocks can be excluded from the major sources of our hydroxy acids.

A large number of lakes and ponds are distributed in the Wright and Taylor Valleys. Caynobacterial mats containing various microorganisms are commonly distributed in and around streams, lakes and ponds, including Lake Bonney. The valley floors are very windy, and thus the dried cyanobacterial mats are probably wind-transported and their detritus are accumulated at soil sampling sites during a long period of time. These organic matter may have contributed as a source of hydroxy acids. The occurrence of *iso*- and *anteiso*-2- and 3-hydroxy acids can be explained by the contribution of bacteria (MATSUMOTO *et al.*, 1988, 1989).

Also, the soil sampling sites are composed of moraine of Pleistocene to Recent ages. This moraine is reported to contain glacially eroded various organic matter formed by biological activity in the pre- and inter-glaciation of Antarctica, in addition to the Beacon Supergroup sedimentary rocks (MATSUMOTO *et al.*, 1990a, b). Furthermore, it is probable that *in situ* biological activity between Pleistocene and Recent ages produces organic matter, which are probable sources of hydroxy acids in soil samples.

Consequently, various hydroxy acids in soil samples of the McMurdo Dry Valleys were probably derived from the degradation products of wind-transported cyanobacterial mats containing various microorganisms in and around streams, lakes and ponds as well as from the past biological activity, rather than originating from the Beacon Supergroup of Gondwanaland sediments and *in situ* living organisms. Further study on biological activity, including vascular plants in the pre- and inter-glaciation periods of Antarctica should be fruitful.

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