

# Hydrocarbons, Sterols and Hydroxy Acids in Antarctic Mosses

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南極の蘚類中の炭化水素, ステロールおよびヒドロキシ酸

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**要旨:** 南極南ビクトリアランドのマイヤーズ谷, ロス島およびベストフォールドヒルズから得られた蘚類, *Pottia heimii*, *Sarconeureum glaciale*, *Bryum pseudotriquetrum* 中の炭化水素, ステロールおよびヒドロキシ酸を測定した. n-アルカン ( $n\text{-C}_{18}\text{-n-C}_{33}$ ), アルケンならびにトリテルペン炭化水素 ( $\text{C}_{30}\text{H}_{50}$ ) が検出された. ステロールは 7 種類が同定され, 24-メチルおよび 24-エチルコレスト-5-エン-3 $\beta$ -オールが主成分 (>85%) であった. 2-, 3-,  $\omega$ -1-,  $\omega$ -ヒドロキシそれに 9, 16-, 10, 16-ジヒドロキシ酸が検出された. 9, 16- または 10, 16-ジヒドロキシヘキサデカン酸がもっとも卓越していた. ステロール組成は蘚の種類による差異は小さいが, 炭化水素とヒドロキシ酸組成は試料間で大きく異なり, 生育環境や共存微生物の影響が示唆された. 一方, これらのステロールおよびジヒドロキシ酸は, 南極における蘚類の生物地球化学的指標化合物として重要と考えられる.

**Abstract:** Hydrocarbons, sterols and hydroxy acids were studied in Antarctic mosses, *Pottia heimii*, *Sarconeureum glaciale* and *Bryum pseudotriquetrum*, to characterize their composition and to find their biogeochemical markers, collected from the Miers Valley of southern Victoria Land, Hut Point Peninsula of Ross Island and Vestfold Hills of Queen Elizabeth Land. Hydrocarbons ranging from  $\text{C}_{18}$  to  $\text{C}_{33}$ , including n-alkanes, alkenes and a triterpene ( $\text{C}_{30}\text{H}_{50}$ ) were found in the mosses. Four stenols and 3 stanols were identified. The major sterols were 24-methyl- and 24-ethylcholest-5-en-3 $\beta$ -ols, constituting more than 85% of the total sterols in all the mosses. 2-, 3-,  $\omega$ -1-,  $\omega$ -hydroxy and 9, 16- and 10, 16-dihydroxy acids were identified or suggested to be present. The most prominent hydroxy acid was 9, 16- or 10, 16-dihydroxyhexadecanoic acid. The sterol composition of *P. heimii* was similar to those of *S. glaciale* and *B. pseudotriquetrum*. However, those of hydrocarbons and hydroxy acids differ considerably in the moss samples, suggesting the influences of environmental conditions and microorganisms contained as impurities. On the other hand, high abundances of 24-methyl- and 24-ethylcholest-5-en-3 $\beta$ -ols, along with the dominance of 9, 16- or 10, 16-dihydroxyhexadecanoic acid, may be useful indicators of mosses in soil, water and sedimentary environments of Antarctica.

## 1. Introduction

From the geobotanical viewpoint, Antarctica is characterized by the absence of vascular plants except in the Antarctic Peninsula and its adjacent regions. Mosses, lichens and other cryptogamic organisms, such as algae, cyanobacteria, bacteria and

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fungi are known to be widely distributed in the ice-free regions of Antarctica. Mosses are the largest plants growing there, so that they are considered to be important sources of organic matter in the ice-free regions of Antarctica. Thus the characterization of organic constituents in mosses and relation of their markers should be important to elucidate the biogeochemical cycles of organic constituents in the ice-free regions of Antarctica. For instance, stenols found in the sediment samples from Lake Hunazoko in the Syowa Oasis and Deep Lake in the Vestfold Oasis have been suggested to be originated from mosses around the lakes (MATSUMOTO *et al.*, 1983). Although many scientists have studied organic constituents in bryophytes, mosses and liverworts, in the world, as reviewed by HUNECK (1983), very little is known on the organic constituents in Antarctic mosses. MATSUMOTO *et al.* (1982) have reported sterols of a moss collected from the lower Taylor Valley of the Dry Valleys. Here we characterize organic constituents, *i.e.*, hydrocarbons, sterols and hydroxy acids, for Antarctic mosses, *Pottia heimii*, *Sarconeurum glaciale* and *Bryum pseudotriquetrum*, and discuss their features in relation to the biogeochemical markers.

## 2. Materials and Methods

### 2.1. Sampling sites and samples

The McMurdo Sound region, including the Dry Valleys of southern Victoria Land, is the widest ice-free area of approximately 4000 km<sup>2</sup>. In the Miers Valley of the McMurdo Sound region, mosses are distributed chiefly on the sides of streams, margins of the Miers and Adams Glaciers and in the surroundings of Lake Miers. Sparsely scattered moss vegetation is formed at the Crater Hills near the McMurdo Station, the Hut Point Peninsula of Ross Island. The Vestfold Hills in the Queen Elizabeth Land are also ice-free areas of 413 km<sup>2</sup>, where mosses occur commonly around margins of some freshwater and saline lakes near the continental ice sheet (PICKARD, 1982).

During the 1981–82 austral summer, moss samples were collected from the Miers Valley of southern Victoria Land, Crater Hills of Ross Island and Mossel Hut of Vestfold Hills (Table 1). The moss samples were taken into polyethylene bags and kept frozen (−20°C) until analyses except for *S. glaciale*-2 which was dried and stored at room temperature. The moss samples contain sandy materials and microorganisms as impurities. The three species used for this study are described briefly as follows:

*Pottia heimii* prefers calcareous soil beside saline lakes or crystalized salts and also found on moraines at the terminus of the continental ice. This species coincides

Table 1. Sampling locations of Antarctic mosses.

Moss*	Locality
<i>Pottia heimii</i> -1	Miers Valley, South Victoria Land (78°06'S, 164°00'E)
<i>Pottia heimii</i> -2	Miers Valley, South Victoria Land (78°06'S, 164°00'E)
<i>Sarconeurum glaciale</i> -1	Crater Hill, Ross Island (77°50'30"S, 166°44'E)
<i>Sarconeurum glaciale</i> -2	Mossel Hut, Vestfold Hills (68°34'S, 78°11'E)
<i>Bryum pseudotriquetrum</i>	Miers Valley, South Victoria Land (78°06'S, 164°00'E)

\* Containing sandy materials and microorganisms as impurities.

with the mosses being hitherto published as *Bryum antarcticum*, which is reduced to the synonym of *Pottia heimii* (KANDA, 1981). This moss is known to occur in the polar regions, the subantarctic, Antarctic Peninsula, Victoria Land, Enderby Land, boreal, subarctic and arctic regions.

*Sarconeurum glaciale* forms small cushion or hummock on sandy soil or rocks in drier areas and it is often accompanied with crustaceous lichens on the surface. This species belongs taxonomically to the family Pottiaceae same as *Pottia heimii*. In Antarctica, it is distributed in the Antarctic Peninsula, Victoria Land and Prince Elizabeth Land.

*Bryum pseudotriquetrum* forms large turfs at the wet sites near freshwater streams and/or lakes, or in the area inundated by meltwater from snow drift during the summer. In Antarctica, this specific name should be used for most plants hitherto published as *Bryum algens* and *B. inconnexum* (OCHI, 1979). This species is wide-spreading in the Antarctic ice-free areas, and is commonly found in mountainous areas of the world.

## 2.2. Analytical methods

The extraction methods of organic constituents were reported in detail elsewhere except for the separation of saturated and unsaturated hydrocarbons, and are noted here briefly (MATSUMOTO *et al.*, 1979, 1982). Moss samples were first homogenized by stirring with an Ace Homogenizer AM7 (Nihon Seiki Ltd.), saponified with 0.5 M potassium hydroxide methanol under reflux (80°C, 2 h). The hydrolyzates were extracted with ethyl acetate after acidification with concentrated hydrochloric acid. The ethyl acetate extracts were evaporated to dryness, dissolved in 50  $\mu$ l benzene/ethyl acetate (1/1) and chromatographed through a silica gel column (180 $\times$ 5 mm i.d., 100 mesh, 5% water). Hydrocarbons, fatty acids-sterols and hydroxy acids were eluted with 2 column volumes of hexane, 3 column volumes of benzene/ethyl acetate (95/5) and 4 column volumes of benzene/ethyl acetate (1/1). The hydrocarbon fractions were further separated into saturated and unsaturated hydrocarbon fractions using a silica gel column impregnated with 10% silver nitrate (60 $\times$ 6 mm i.d., 100 mesh). Saturated and unsaturated hydrocarbons were eluted with 3 column volumes of hexane and 3 column volumes of benzene/ethyl acetate (1/1), respectively. The fatty acids-sterols fractions were further subjected to an alkaline silica gel column impregnated with 10% potassium hydroxide (180 $\times$ 5 mm i.d., 100 mesh). Sterol fractions were eluted with 3 column volumes of benzene/ethyl ether (1/1), evaporated to dryness and trimethylsilylated with 25% *N,O*-bis(trimethylsilyl)acetamide acetonitrile solution (room temp., 2 h). Hydroxy acid fractions were methylated with 14% boron trifluoride methanol (80°C, 2 h) and then trimethylsilylated with the silylation reagent (room temp., 2 h) to obtain hydroxy acid trimethylsilyloxy ether methyl esters.

Hydrocarbons and the derivatives of sterols and hydroxy acids were analysed by the use of a combined Shimadzu LKB 9000 gas chromatograph-mass spectrometer equipped with a coiled glass column (2.0 m $\times$ 3 mm i.d.) packed with 1% silicone OV-1 on 80–100 mesh Chromosorb W AW DMCS. The column temperature was programmed from 100 to 290°C at 8°C/min. The flow rate of helium carrier gas was 30 ml/min. The temperatures of injection block, molecular separator and ion source were maintained at 290, 310 and 330°C, respectively. Mass fragmentograms and mass

spectra were obtained at an ionization energy of 20 and 70 eV. respectively, with an accelerating voltage of 3.5 kV.

The identification of hydrocarbons, sterols and hydroxy acids was carried out by the comparison of retention times and mass spectra with those of authentic standards and published literature (EGLINTON *et al.*, 1968a, b; BOON *et al.*, 1977; CARDOSO *et al.*, 1977; MATSUMOTO *et al.*, 1979, 1982; MATSUMOTO and HANYA, 1981). The quantitation of the organic constituents was performed by the comparison of peak heights or areas on the gas chromatograms or mass fragmentograms with those of authentic standards. The analytical uncertainty was within  $\pm 12\%$ .

### 3. Results and Discussion

#### 3.1. Hydrocarbons

Hydrocarbons ranging in carbon chain lengths from  $C_{15}$  to  $C_{38}$ , including normal alkanes, alkenes and/or a triterpene having empirical formula of  $C_{30}H_{50}$  were found in the Antarctic mosses (Table 2). The major hydrocarbons (greater than 10% of the total hydrocarbons) for *P. heimii*-1 and -2, *S. glaciale*-1 and -2, and *B. pseudotriquetrum* were  $C_{19:1}$  (carbon chain length: numbers of unsaturation),  $C_{30}H_{50}$ ,  $C_{17:1}$  and  $n-C_{21:0}$ ; unidentified-X,  $C_{17:1}$  and  $C_{20:1}$ ;  $n-C_{18:0}$ ,  $C_{30}H_{50}$ ,  $n-C_{17:0}$  and  $n-C_{19:0}$ ;  $C_{20:1}$  and  $C_{19:1}$ ; and  $C_{30}H_{50}$  and  $C_{21:4}$  (tentatively identified) in decreasing abundances, respectively. The hydrocarbon compositions were considerably different among the samples studied even in the same species, although it is possible that the hydrocarbon composition of *S. glaciale*-2 sample changed during storage because this sample was stored at room temperature in the dried condition. In our case, the influences of storage conditions on the hydrocarbon compositions may, however, be small, because labile unsaturated hydrocarbons in this sample were rather greater than those of *S. glaciale*-1 which was kept frozen. In addition, the sterol composition of *S. glaciale*-1 was similar to that of *S. glaciale*-2 as discussed below (Table 3). *B. pseudotriquetrum* can be characterized by the high abundances of  $C_{30}H_{50}$  and  $C_{21:4}$ , along with an extremely small amount of n-alkanes. Normal alkanes ranging from  $n-C_{15}$  to  $n-C_{35}$ , together with the dominance of odd-carbon numbers, were found in many kinds of mosses and liverworts (MATSUO *et al.*, 1972; CORRIGAN *et al.*, 1973; HUNECK, 1983). Polyunsaturated hydrocarbons ( $n-C_{21:4}$ ,  $n-C_{21:5}$ ) were also identified in *Polytrichum commune* spores (KARUNEN, 1974).

Of special interest is the occurrence of the triterpene hydrocarbon ( $C_{30}H_{50}$ ) in *P. heimii*-1, *S. glaciale*-1 and -2, and *B. pseudotriquetrum* (Table 2). As we know, no one has reported the presence of  $C_{30}H_{50}$  in mosses, although it has been detected in some cyanobacteria as a major hydrocarbon component (GELPI *et al.*, 1970; MATSUMOTO and NAGASHIMA, unpublished results) and a green alga, *Chlamydomonas reinhardtii* (MATSUMOTO and NAGASHIMA, unpublished results). In the mosses, *P. heimii*-1, *S. glaciale*-1 and *B. pseudotriquetrum*,  $C_{30}H_{50}$  also was the major constituent of hydrocarbons (15.6–51.4%).

The Odd/even ratios of n-alkanes for *P. heimii*-1 and -2 indicated the dominance of odd-carbon numbers, which are similar to those of mosses and liverworts reported previously (MATSUO *et al.*, 1972; CORRIGAN *et al.*, 1973; HUNECK, 1983), but seem to be somewhat greater than those of *S. glaciale*-1 and -2.

Table 2. *Hydrocarbons found in Antarctic mosses.*

	<i>Pottia heimii</i> -1	<i>Pottia heimii</i> -2	<i>Sarconeurum glaciale</i> -1	<i>Sarconeurum glaciale</i> -2	<i>Bryum pseudotriquetrum</i>
Composition (%)					
n-Alkane					
15:0	—	—	3.2	0.2	—
16:0	—	—	6.7	0.2	—
17:0	5.7	3.6	15.3	2.7	0.8
18:0	2.9	2.1	19.3	2.5	—
19:0	4.1	1.6	13.7	2.5	—
20:0	4.3	1.8	9.8	2.5	—
21:0	10.3	3.2	3.5	2.6	—
22:0	3.1	1.2	1.7	1.9	—
23:0	6.6	2.4	0.9	3.1	—
24:0	1.0	0.5	0.4	1.2	—
25:0	2.4	1.1	0.5	1.8	—
26:0	0.5	0.3	—	1.1	—
27:0	2.2	1.7	—	3.3	—
28:0	0.4	0.3	—	0.6	—
29:0	3.5	4.9	—	2.2	—
30:0	0.5	0.5	—	0.2	—
31:0	5.4	8.7	—	1.2	—
32:0	—	—	—	—	—
33:0	—	0.4	—	—	—
Alkene					
17:1	13.7	22.4	—	2.8	8.1
18:1	—	—	—	1.7	—
19:1	16.7	—	—	19.0	—
20:1	—	14.5	9.4	45.6	—
21:4*	—	—	—	—	39.7
X	—	28.8	—	—	—
Triterpene (C <sub>30</sub> H <sub>60</sub> )	16.7	—	15.6	1.1	51.4
Odd/even**	3.2	4.1	0.98	1.9	Large
Concentration (μg/g)	0.84	1.5	1.8	10	7.5

\* Tentatively identified.

\*\* Ratios of odd- to even-carbon numbers for n-alkanes.

—: Not detected.

The hydrocarbon compositions and contents of mosses may change due to increasing ages and to environmental conditions. In addition, the contribution of microorganisms such as bacteria and fungi contained as impurities is possible. Our analytical results of hydrocarbons may, therefore, reflect these influences. The concentrations of total hydrocarbons varied considerably among the samples, ranging from 0.84 to 10 μg/g of dry sample (Table 2), presumably accounting for the above influences. Their low hydrocarbon content may be partly responsible for the existence of sandy materials contained as impurities in the samples.

Table 3. Sterols found in Antarctic mosses.

	<i>Pottia heimii</i> -1	<i>Pottia heimii</i> -2	<i>Sarconeurum glaciale</i> -1	<i>Sarconeurum glaciale</i> -2	<i>Bryum pseudotriquetrum</i>
Composition (%)					
Cholest-5-en-3 $\beta$ -ol	0.8	0.8	3.5	1.1	0.8
24-methylcholesta-5, 22-dien-3 $\beta$ -ol	1.9	3.7	0.8	0.4	8.0
24-methylcholest-5-en-3 $\beta$ -ol	60.8	59.7	45.7	61.0	47.4
24-ethylcholest-5-en-3 $\beta$ -ol	36.5	35.8	39.6	37.2	43.8
5 $\alpha$ -cholestan-3 $\beta$ -ol	—	—	—	0.3	—
24-methyl-5 $\alpha$ -cholestan-3 $\beta$ -ol	—	—	5.3	—	—
24-ethyl-5 $\alpha$ -cholestan-3 $\beta$ -ol	—	—	5.1	—	—
Concentration ( $\mu$ g/g)	200	300	130	240	160

—: Not detected.

### 3.2. Sterols

Stenols; cholest-5-en-3 $\beta$ -ol, 24-methylcholesta-5,22-dien-3 $\beta$ -ol, 24-methylcholest-5-en-3 $\beta$ -ol, 24-ethylcholest-5-en-3 $\beta$ -ol and stanols; 5 $\alpha$ -cholestan-3 $\beta$ -ol, 24-methyl-5 $\alpha$ -cholestan-3 $\beta$ -ol and/or 24-ethyl-5 $\alpha$ -cholestan-3 $\beta$ -ol were identified in the mosses (Table 3). Stanols were found only in *S. glaciale*-1 and -2, though in small amounts. These stenols have been found in many kinds of mosses and liverworts, as reviewed by HUNECK (1983). However, the occurrence of stanols in mosses is rare. 24-Ethyl-5 $\alpha$ -cholestan-3 $\beta$ -ol have been detected in peat mosses (*Sphagnum*, IVES and O'NEIL, 1958). MATSUMOTO *et al.* (1982) also reported 5 $\alpha$ -cholestan-3 $\beta$ -ol and 24-ethyl-5 $\alpha$ -cholestan-3 $\beta$ -ol in *S. glaciale* from the lower Taylor Valley. The most dominant sterol is 24-methylcholest-5-en-3 $\beta$ -ol in all the mosses studied. And the sums of 24-methylcholest-5-en-3 $\beta$ -ol and 24-ethylcholest-5-en-3 $\beta$ -ol constituted more than 85% of the total sterols in the mosses. The sterol compositions of *P. heimii*-1 and -2 are similar to those of *S. glaciale*-1 and -2, and *B. pseudotriquetrum*. These results are also consistent with those for *S. glaciale* from the lower Taylor Valley (MATSUMOTO *et al.*, 1982). The analytical results of sterols showed again that the influences of storage conditions of *S. glaciale* on the sterol composition are small. Our sterol compositions are much different from those of algae, cyanobacteria and fungi (MATSUMOTO *et al.*, 1982). Namely, the dominance of 24-methyl- and 24-ethylcholest-5-en-3 $\beta$ -ols may be useful biogeochemical markers of mosses in soil, water and sedimentary environments of Antarctica.

The concentrations of total sterols ranged from 130 to 300  $\mu$ g/g of dry sample which are much greater than those of hydrocarbons. They are believed to be one of the features of these mosses.

### 3.3. Hydroxy acids

2-, 3-,  $\omega$ - and  $\omega$ -1-hydroxy and 10, 16-dihydroxyhexadecanoic and/or 9,16-dihydroxyhexadecanoic acids were identified or suggested to be present in the Antarctic mosses (Table 4). The most dominant hydroxy acid was 10,16-dihydroxyhexadecanoic or 9,16-dihydroxyhexadecanoic acid. CALDICOTT and EGLINTON (1976) have found 8,16-, 9,16- and 10,16-dihydroxyhexadecanoic acids in *Sphagnum* mosses and indicated

Table 4. 2-,  $\omega$ - and  $\omega$ -1-hydroxy and 10, 16- and 9, 16-dihydroxy acids found in Antarctic mosses.

Hydroxy acid	<i>Pottia heimii</i> -1	<i>Pottia heimii</i> -2	<i>Sarconeurum glaciale</i> -1	<i>Sarconeurum glaciale</i> -2	<i>Bryum pseudotriquetrum</i>
Composition (%)					
2-Hydroxy					
15:0	—	2	2	3	—
16:0	9	—	3	3	—
17:0	—	—	1	—	—
18:0	Trace	—	—	2	—
18:1*	2	—	—	—	—
20:0	6	—	—	—	—
22:0	11	7	1	—	—
23:0	2	—	—	—	—
24:0	11	6	8	7	2
24:1*	16	12	12	13	5
25:0	2	1	—	1	—
25:1*	4	3	—	4	—
26:0	—	—	4	—	—
$\omega$ -Hydroxy					
16:0	—	—	23	—	—
$\omega$ -1-Hydroxy					
24:0	Trace	Trace	Trace	Trace	Trace
26:0	Trace	Trace	Trace	1	Trace
28:0	Trace	Trace	Trace	Trace	Trace
10, 16-Dihydroxy-hexadecanoic	38	69	—	66	93
9, 16-Dihydroxy-hexadecanoic	—	—	46	—	—
Concentration ( $\mu$ g/g)	84	160	110	160	44

\* Tentatively identified.

Trace: Less than 1%.

—: Not detected.

that the relative abundances may be of value in the chemotaxonomy of *Sphagnum* mosses. In our case, these dominant dihydroxy acids may be important biogeochemical markers of mosses in soil, water and sedimentary environments of Antarctica.  $\omega$ -Hydroxyhexadecanoic acid was found only in *S. glaciale*-1, although it was detected in *Sphagnum palustre* as the most prominent component (CALDICOTT and EGLINTON, 1976).

2-Hydroxy acids ranging from  $C_{15:0}$  to  $C_{26:0}$ , including unsaturated were found in the mosses of *P. heimii*, *S. glaciale* and *B. pseudotriquetrum*. The compositions of 2-hydroxy acids differ considerably among the samples, as in the case of the hydrocarbons, suggesting again the influences of the environmental conditions and contaminated microorganisms.

$\omega$ -1-Hydroxy acids with carbon chain lengths  $C_{24:0}$ ,  $C_{26:0}$  and  $C_{28:0}$  were found in the mass fragmentograms of the hydroxy acid fractions carried at  $m/z$  117, which is the base peak of  $\omega$ -1-hydroxy acid trimethylsilyloxy ether methyl esters (CALDICOTT and EGLINTON, 1976; BOON *et al.*, 1977). The most dominant  $\omega$ -1-hydroxy acid was

$\omega$ -1-C<sub>26:0</sub> in all the moss samples studied. Any marked changes in the compositions of  $\omega$ -1-hydroxy acids for the mosses were not found.

3-Hydroxy acids ranging from C<sub>10</sub> to C<sub>26</sub>, including unsaturated and branched were identified tentatively by mass fragmentography carried at  $m/z$  175, which is the characteristic peak of 3-hydroxy acid trimethylsilyloxy ether methyl esters, in the hydroxy acid fractions (EGLINTON *et al.*, 1968a, b; BOON *et al.*, 1977; CARDOSO *et al.*, 1977; MATSUMOTO and NAGASHIMA, 1984), though their concentrations were much smaller than those of 2-hydroxy acids. Further analytical study in detail should be required.

The concentrations of the total hydroxy acids ranged from 44 to 160  $\mu\text{g/g}$  of dry sample, which are much greater than those of hydrocarbons, but considerably smaller than those of sterols (Table 4).

#### 4. Conclusions

Hydrocarbons ranging in carbon chain lengths from C<sub>15</sub> to C<sub>33</sub>, including n-alkanes, alkenes and a triterpene (C<sub>30</sub>H<sub>50</sub>) were found in the Antarctic mosses, *P. heimii*, *S. glaciale* and *B. pseudotriquetrum*. The abundant sterols were 24-methyl- and 24-ethylcholest-5-en-3 $\beta$ -ols in all the mosses studied. 2-, 3-,  $\omega$ -1- and  $\omega$ -hydroxy and 10,16- and 9,16-dihydroxy acids were found. The most abundant hydroxy acid was 10,16- or 9,16-dihydroxyhexadecanoic acid. The high abundances of 24-methyl- and 24-ethylcholest-5-en-3 $\beta$ -ols as well as the dominance of 9,16- or 10,16-dihydroxyhexadecanoic acid are characteristic of the mosses and thus they are believed to be useful biogeochemical markers of mosses in soil, water and sedimentary environments of Antarctica.

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