

STRIATANE- AND PINGUISANE-TYPE SESQUITERPENOIDS AND PHYTANE-TYPE DITERPENOID FROM THE LIVERWORT *PORELLA* *NAVICULARIS*

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Key Word Index—*Porella navicularis*; Hepaticae; naviculol, striatenone; naviculide; striatane- and pinguisane-type sesquiterpenoids; phytane-type diterpenoid; chemosystematics.

Abstract—A new pinguisane-type sesquiterpene, naviculol, a new striatane-type sesquiterpene, striatenone, and a new phytane-type diterpene lactone, naviculide have been isolated from the American liverwort, *Porella navicularis* together with the previously known norpinguisone, norpinguisone methyl ester and perrottetianal, and their structures established by NMR experiments and some chemical transformations

INTRODUCTION

Most *Porella* species belong to the Jungermanniales (Hepaticae) produce various sesquiterpenoids [2]. There are two types of *Porella* species, one of which contains the intense pungent sesquiterpene dialdehyde, polygodial [2], and the other containing non-pungent substances. The former species, for example *Porella vernicosa*, commonly contain drimane-, aromadendrane- and pinguisane-type sesquiterpenoids. On the other hand, the latter species, for example *P. platyphylla* and *P. grandiloba*, do not contain drimane- and aromadendrane-type sesquiterpenoids, but they produce large amounts of pinguisanes [2–5]. In this paper we wish to report the isolation and characterization of two new sesquiterpenoids and a new diterpenoid from the American liverwort, *Porella navicularis* and discuss its chemosystematics.

RESULTS AND DISCUSSION

A combination of column chromatographic separation on silica gel and on Sephadex LH-20 of the methanol extract of the air-dried material resulted in the isolation of three new terpenoids named naviculol (1), striatenone (4) and naviculide (6), along with the previously known two sesquiterpenoids, norpinguisone (9) and norpinguisone methyl ester (10) [3, 6] and the diterpene aldehyde, perrottetianal (11) [3].

Naviculol (1)

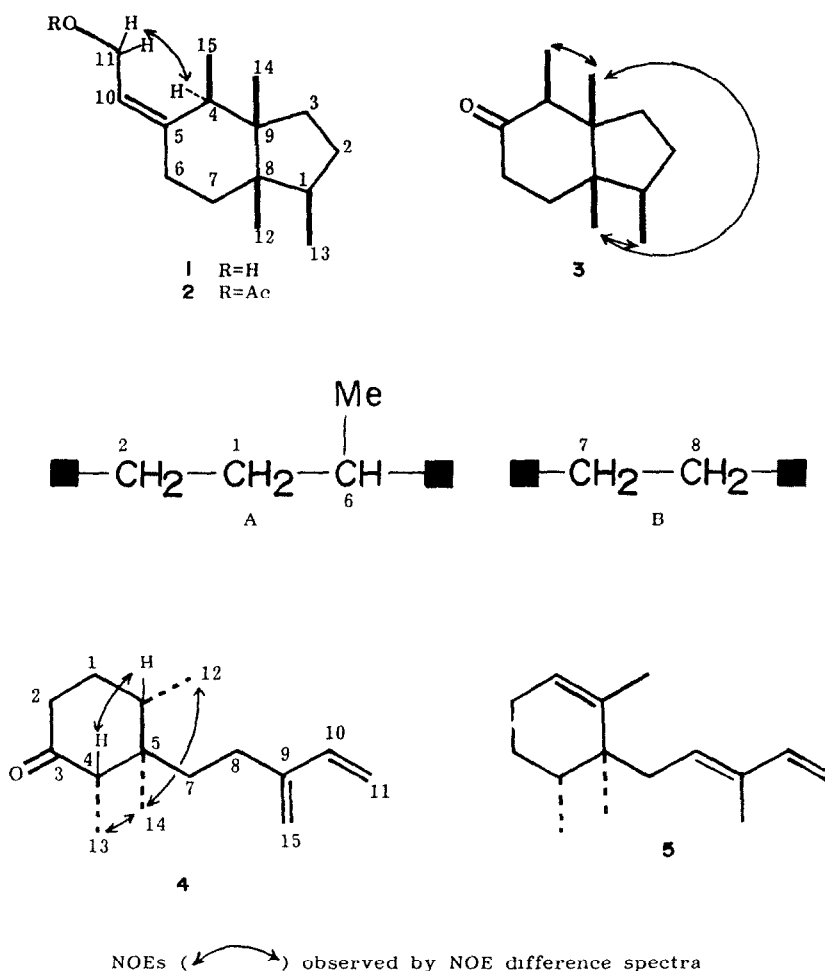
The molecular formula $C_{15}H_{26}O$ of the major component (1) was determined by high resolution mass spectrometry. The IR, 1H (Table 1) and ^{13}C NMR spectra showed the presence of a primary allylic hydroxyl group (3400 cm^{-1} ; $\delta 4.10$, 1H, *dd*, $J = 6.6, 6.4\text{ Hz}$; 4.17 , 1H, *dd*, $J = 6.6, 3.0\text{ Hz}$; $\delta 58.6$, t) which was further confirmed by the formation of a monoacetate (2) ($1720, 1230\text{ cm}^{-1}$; $\delta 2.03$, 3H). The 1H NMR spectrum of 1 contained the signals of two tertiary methyl, two secondary methyl groups and an

allylic proton at $\delta 2.46$ (q , $J = 7.3\text{ Hz}$) which was coupled with a secondary methyl group at $\delta 1.09$. The ^{13}C NMR spectrum of 1 contained the signals of four methylenes, two methines, two quaternary carbons and a methylene with a hydroxyl group. The above spectral data coupled with the molecular formula showed that 1 must be a bicyclic sesquiterpene alcohol. The 1H - 1H COSY spectrum of 1 showed that the hydroxymethyl group was correlated with a vinyl proton ($\delta 5.40$). The proton (H-1) at $\delta 2.46$ was correlated with the secondary methyl group (H-13) at $\delta 1.09$ and also with the non-equivalent methylene protons (H-2) at $\delta 1.81$ and 1.89 which were correlated with nonequivalent methylene protons (H-3) at $\delta 1.14$ and 1.26 . Furthermore, the methylene protons (H-6 α , H-6 β) at $\delta 2.34$ and 1.98 were correlated with the nonequivalent methylenes (H-7 α , H-7 β) at $\delta 1.34$ and 1.45 . Ozonolysis of 2 gave a six-membered ketone (3) (1705 cm^{-1} ; $[M]^+ 194$) with two tertiary and two secondary methyl groups. On the basis of the above spectral and chemical evidence, the structure of naviculol was determined to be a pinguisane-type sesquiterpene alcohol (1). Its stereochemistry was deduced from the following evidence. The NOE difference spectra of 1 and 3 exhibited the presence of NOEs between H-4 and H-11 in 1 and between (i) H-14 and H-12, 15 and (ii) H-12 and H-13 in 3, indicating that all methyl groups in 1 and 3 have the β -orientation, similar to those found in pinguisone whose structure has been established by X-ray analysis [7]. The absolute configuration of 1 was established by the positive Cotton effect at 290 nm in the CD spectrum of 3.

Striatenone (4)

Compound 4 had the molecular formula $C_{15}H_{24}O$ ($[M]^+ 220.1833$). The IR and ^{13}C NMR spectra displayed the presence of a ketone group (1714 cm^{-1} ; $\delta 203.0$). The 1H NMR spectrum (Table 1) had the signals of a tertiary methyl, two secondary methyl groups, an exocyclic methylene and a conjugated terminal vinyl group. The ^{13}C NMR spectrum also showed the presence of 15 carbons; three methyls, four methylenes, two methines, an exocyclic methylene, a vinyl group, a quaternary

Part 29 in the series 'Chemosystematics of Bryophytes' For Part 28, see ref. [1]

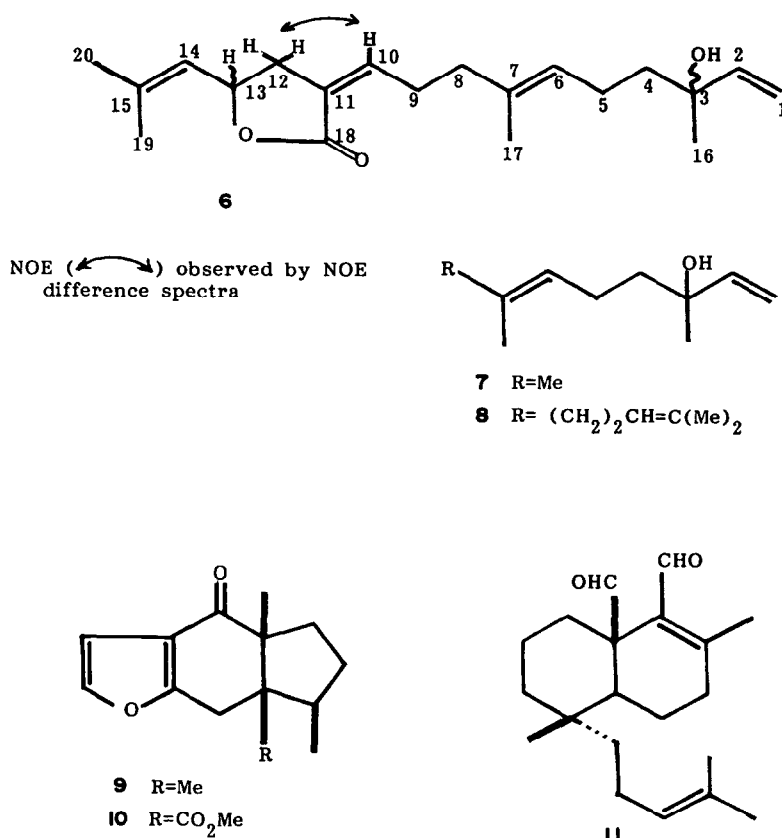


carbon and a carbonyl group, suggesting that **4** might be a monocyclic sesquiterpene ketone. Irradiation at the frequency of a quartet at δ 2.55 (H-4) led to a singlet of the secondary methyl group at δ 0.93. The ^1H - ^1H COSY spectrum of **4** showed that the proton (H-6) at δ 2.11 which was overlapped with the signal of the non-equivalent methylene protons (H-1) was correlated with the methyl proton (H-12) at δ 0.95 and with one of the non-equivalent methylene protons (H-1) at δ 1.49. The protons (H-1) were also correlated with the additional non-equivalent methylene protons (H-2) at δ 1.59 and 2.26. The protons (H-8) at δ 2.37 were correlated with the methylene protons (H-7) at δ 1.88. These results indicated that **4** had the partial structures A and B. The ^1H and ^{13}C NMR spectra of **4** were closely related to those of striatene (**5**) which was isolated from the liverwort *Ptychathus striatus* [8] except for the presence of the carbonyl and exocyclic methylene groups in place of two trisubstituted double bonds. The mass spectra of **4** and **5** also showed the same fragment ion at m/z 139 corresponding to the side chain, $[\text{C}_6\text{H}_9]^+$. Hence, striatene (**4**) has the exocyclic methylene group at C-9(15) and the ketone carbonyl at C-3 of striatene (**5**). On the basis of these data, the structure of striatene was established to be the striatane-type sesquiterpene ketone **4**. Its stereochemistry was determined by the presence of the NOEs between (i) H-4 and H-6, (ii) H-14 and H-12, 13. The

absolute configuration was also established by the presence of the positive Cotton effect at 319 nm in the CD spectrum.

Naviculide (**6**)

The mass spectrum of naviculide (**6**) showed the fragment ion at m/z 300 due to $[\text{M}-\text{H}_2\text{O}]^+$. The IR spectrum showed the absorption band due to a hydroxyl group (3600 cm^{-1}) and an α,β -unsaturated γ -lactone ($1745, 1672\text{ cm}^{-1}$, δ 169.8). The ^1H NMR spectrum (Table 1) had the signals for three vinylic methyls and one tertiary methyl group attached to a carbon bearing the hydroxyl group. The ^1H NMR spectrum also indicated the presence of three trisubstituted olefinic protons and a non-conjugated terminal vinyl group. The ^{13}C NMR spectrum (see Experimental) contained 20 carbons, an ester carbonyl, four methyl, five methylene groups, eight sp^2 carbons and two carbon atoms bearing the oxygen (δ 73.5 s; 74.1 d). In the ^1H and ^{13}C NMR spectra of **6**, the chemical shifts and signal patterns of the terminal vinyl, tertiary methyl, one of the vinylic methyls, allylic (C-5) and homoallylic methylenes (C-4) were almost identical to those of a monoterpene alcohol, linalool (**7**) and the chemical shifts of the above groups and two additional sp^3 methylene groups (C-8, 9) were also very similar to those of a sesquiterpene alcohol, nerolidol (**8**), strongly



suggesting that compound **6** had a 3-hydroxy-3,7-dimethyl-1,6-nonadiene system in the molecule. The ¹H NMR experiments confirmed the relative position of the dimethyl allyl group and the lactone oxygen in the remaining structure of **6**. Irradiation at an olefinic proton (H-4) led to the sharp signals of two vinyl methyl groups and simplification of the allylic proton (H-13) which was attached to a carbon atom bearing the lactone oxygen. Irradiation at the frequency of the allylic proton (H-13) caused the olefinic proton (H-14) signal to collapse to a singlet and the allylic methylene proton (H-12) signals led to the AB-type signals. Moreover, irradiation at the centre frequency of the olefinic proton (H-10) led to the sharp signals of the allylic protons (H-12) and a simplification of the methylene protons (H-9), which were coupled with the allylic methylene protons (H-8). The above spectral evidence suggested the structure of naviculide as **6**. The NOE difference spectrum exhibited the presence of the NOE between H-10 and H-12 indicating that the 10,11-double bond had the Z-configuration. The E-configuration of the 6,7-double bond was also suggested by the chemical shift (δ 18.4) of the methyl carbon at C-7 [9]. On the basis of the above spectral data, the structure of naviculide was established to be the phytane-type diterpene lactone (**6**). The absolute configuration at C-3 and C-13 remains to be clarified.

The present species produces neither drimane- nor aromadendrane-type sesquiterpenoids which have been found in *Porella vernicosa* complex [2-5], but it elaborates mainly pinguisane- and striatane-type sesquiterpenoids and sacculatane-type diterpenoid. These results indi-

cate that *P. navicularis* belongs to the species of the chemotype IV of Porellaceae, such as the Japanese *P. grandiloba* and European *P. platyphylla* [2, 3].

EXPERIMENTAL

The solvents used for spectral measurements were TMS-CDCl₃ [¹H NMR (400 MHz); ¹³C NMR (100 MHz)]; CHCl₃ (IR and [α]_D) and MeOH (CD). TLC, GC and GC/MS were carried out as previously reported [10].

Plant material. *Porella navicularis* (Lehn. & Lindenb.) Lindenb. was collected in Oregon State, U.S.A. in 1985 and identified by Dr S. Hattori and Prof. W. Schofield. The voucher specimen was deposited at The Institute of Pharmacognosy, Tokushima Bunri University.

Extraction and isolation. *P. navicularis* was air-dried for 3 days and mechanically ground and extracted with MeOH for 1 month. The MeOH extract was filtered and the solvent was removed to give the green oil (2.3 g) which was chromatographed on silica gel using *n*-hexane-EtOAc gradient. The fraction (160 mg) eluted by *n*-hexane-EtOAc (9:1) was rechromatographed on silica gel using the same solvent system described above to afford striatenone (**4**) (30 mg), norpinguisone (**9**) (10 mg) and norpinguisone methyl ester (**10**) (16 mg) [3, 6]. Striatenone (**4**): [α]_D²⁰ -9.1° (c 0.11); IR ν_{max} cm⁻¹: 1715, 1680, 1595, 1470, 1375, 990, 905, 890; CD Δε_{319 nm} +1.6; ¹³C NMR: δ 7.7, 15.2, 15.4 (each Me, q), 24.3, 31.1, 36.1, 41.6 (each CH₂, t), 113.1, 115.7 (each =CH₂, t), 36.2, 50.5 (each CH, d), 139.0 (=CH, d), 43.7 (C, s), 146.7 (=C, s), 203.0 (CO, s); high resolution MS. found 220.1833, C₁₅H₂₄O requires 220.1827; EIMS *m/z* (rel. int.): 220 [M]⁺ (14), 205 (15), 177 (11), 152 (45), 139 (100), 121 (24), 110 (73), 97 (90), 83

Table 1 ^1H NMR spectral data for compounds 1, 4 and 6 (ppm from internal TMS)*

H	1	4	6
1	1.68 (m)	1.49 (m, α) 2.11 (m, β)	5.06 (dd, 10.7, 1.5 \dagger) 5.21 (dd, 17.6, 1.5)
2	1.81 (m) 1.89 (m)	1.59 (m, α) 2.26 (ddd, 18.1, 13.2, 4.9, β)	5.91 (dd, 17.6, 10.7)
3	1.14 (m) 1.26 (m)		
4	2.46 (q, 7.3)	2.55 (q, 6.8)	1.57 (m)
5			2.03 (m)
6	1.98 (ddd, 13.7, 5.4, 5.4, β) 2.34 (ddd, 13.7, 12.5, 4.4, α)	2.11 (m)	5.15 (m)
7	1.34 (m, α) 1.45 (ddd, 13.7, 10.4, 5.8, β)	1.88 (m)	
8		2.37 (m)	2.10 (t, 7.8)
9			2.82 (m)
10	5.40 (dd, 7.3, 6.4)	6.40 (dd, 17.6, 11.2)	6.11 (m)
11	4.10 (dd, 6.6, 6.4) 4.17 (dd, 7.3, 6.6)	5.07 (d, 11.2) 5.25 (d, 17.6)	
12	0.94 (s)	0.95 (d, 6.8)	2.58 (br d, 12) 2.99 (br d, 12)
13	0.92 (d, 7.3)	0.60 (s)	5.14 (m)
14	0.94 (s)	0.93 (d, 6.8)	5.23 (br d, 8.8)
15	1.09 (d, 7.3)	5.01 (s) 5.03 (s)	
16			1.26 (s)
17			1.61 (br s)
19			1.73 (br s)
20			1.76 (br s)

*All signals were assigned by spin decoupling, ^1H - ^1H COSY and NOE difference experiments

\dagger Figures in parentheses are coupling constants in Hz, run at 400 MHz in CDCl_3

(18), 74 (12). The fraction (195 mg) eluted by *n*-hexane-EtOAc (4:1) was rechromatographed on a Lobar column using *n*-hexane-EtOAc (19:1) to give naviculol (1) (45 mg); $[\alpha]_D^{+48.5^\circ}$ (c 1.14); IR ν_{max} cm^{-1} 3540, 1470, 1380; ^{13}C NMR δ 16.6 (C-5), 19.2, 19.4, 21.9 (each Me, q), 30.0 (C-6), 30.4 (C-3), 38.3 (C-2), 39.5 (C-7), 40.6 (C-4), 44.0 (C-1), 44.3, 47.8 (each C, s), 58.6 (C-11), 121.7 (C-10), 147.3 (C-5), high resolution MS: found 222.1983, $\text{C}_{15}\text{H}_{26}\text{O}$ requires 222.1984. The fraction eluted by *n*-hexane-EtOAc (7:3) gave perrottetianal (11) (11 mg) [3]. The fraction (190 mg) eluted by *n*-hexane-EtOAc (1:1) was rechromatographed on Sephadex LH-20 using CHCl_3 -MeOH (1:1) to give diterpene mixtures which were further chromatographed on silica gel using C_6H_6 -EtOAc (9:1) to afford naviculide (6) (20 mg) IR ν_{max} cm^{-1} 3600, 1745, 1672, 1445, 1365, 1170, 1105, 905; ^{13}C NMR δ 15.8, 18.4, 25.7, 27.9 (each Me, q), 22.7, 25.8, 36.5, 38.8, 42.1 (each CH_2 , t), 111.7 ($=\text{CH}_2$, t), 74.1 ($-\text{O}-\text{CH}$, d), 123.6, 125.2, 142.8, 145.1 (each $=\text{CH}$, d), 73.5 ($-\text{O}-\text{C}$, s), 125.1, 134.5, 139.5 (each $=\text{C}$, s), 169.8 ($\text{C}=\text{O}$, s), EIMS m/z (rel. int.): 300 $[\text{M}-\text{H}_2\text{O}]^+$ (2), 231 (25), 163 (30), 133 (50), 119 (65), 107 (95), 105 (60), 93 (100), 91 (58), 81 (75), 79 (55), 71 (54), 69 (45).

Acetylation of 1 Compound (1) (42 mg) was dissolved in Ac_2O and pyridine (each 1 ml) and the reaction mixture was kept at room temp for 24 hr. Work-up as usual gave naviculyl acetate (2) (41 mg) IR ν_{max} cm^{-1} 1720, 1230, 1015; ^1H NMR δ 0.93 (3H, d, $J=7$ Hz), 0.97 (6H, s), 1.03 (3H, d, $J=7$ Hz), 2.03 (3H, s), 4.55 (2H, br d, $J=6.5$ Hz), 5.33 (1H, br t, $J=6.5$ Hz) EIMS m/z (rel.

int.): 205 $[\text{M}-\text{OCOMe}]^+$ (6), 204 (23), 189 (34), 133 (20), 123 (100), 109 (93), 95 (65), 81 (32), 68 (27), 56 (32), 43 (73).

Ozonolysis of 2 Compound (2) (41 mg) in MeOH (3 ml) was ozonized at -20° . The ozonide was decomposed by AcOH (0.3 ml) and Zn powder (150 mg) and the mixture was warmed at 35° for 1 hr and filtered to give an oil which was chromatographed on Sephadex LH-20, using CHCl_3 -MeOH (1:1) to afford 3 (8 mg) IR ν_{max} cm^{-1} 1705, 1470, 1380, 1140, 1010; CD $\Delta\epsilon_{290\text{nm}} +3.2$; ^1H NMR δ 0.72, 0.73 (each 3H, s, H_3 -12, H_3 -14), 0.94 (3H, d, $J=6.8$ Hz, H_3 -13), 0.96 (3H, d, $J=6.8$ Hz, H_3 -15), 1.34 (1H, dddd, $J=13.2, 12.5, 9.0, 3.7$ Hz, H-2 β), 1.44 (1H, ddd, $J=12.5, 12.5, 4.9$ Hz, H-3 β), 1.62 (1H, ddd, $J=14.2, 12.7, 4.9$ Hz, H-7 β), 1.72 (1H, ddd, $J=13.2, 8.8, 3.7$ Hz, H-3 α), 1.87 (1H, ddd, $J=14.4, 6.5, 3.9$ Hz, H-7 α), 1.93 (1H, dddd, $J=13.2, 9.0, 8.8, 4.9$ Hz, H-2 α), 2.17 (1H, ddd, $J=14.2, 4.9, 4.2$ Hz, H-6 β), 2.46 (1H, ddd, $J=12.9, 12.9, 6.1$ Hz, H-6 α), 2.56 (1H, dddd, $J=9.0, 9.0, 6.8, 6.8$ Hz, H-1), 2.61 (1H, q, $J=6.4$, H-4); ^{13}C NMR δ 8.8, 14.9, 16.5, 18.4 (each Me, q), 29.1, 32.4, 35.4, 37.5 (each CH_2 , t), 37.5, 48.4 (each CH, d), 45.6, 53.3 (each C, s), 202.1 ($\text{C}=\text{O}$, s), EIMS m/z (rel. int.): 194 $[\text{M}]^+$ (34), 179 (31), 147 (8), 137 (13), 123 (40), 109 (100), 95 (19), 82 (29), 68 (17), 56 (35), 43 (68).

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