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THREE *ENT*-SECOAROMADENDRANE-TYPE SESQUITERPENE HEMIACETALS AND A BICYCLOGERMACRENE FROM *PLAGIOCHILA OVALIFOLIA* AND *PLAGIOCHILA YOKOGURENSIS**

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Key Word Index—*Plagiochila ovalifolia*; *P. yokogurensis*; Hepaticae; plagiochilines G, H and I; methoxyplagiochilines A_1, A_2 and C; *ent*-3α-acetoxybicyclogermacrene; *ent*-secoaromadendrane-type sesquiterpene hemiacetals; *ent*-aromadendranes; *ent*-maaliol.

Abstract—A new *ent*-secoaromadendrane-type sesquiterpene hemiacetal, plagiochiline G, was isolated from *Plagiochila ovalifolia*. Four new *ent*-sesquiterpene hemiacetals, plagiochiline H and I, and two pungent methoxyplagiochilines A_1, A_2 and non-pungent methoxyplagiochiline C were also isolated from *P. yokogurensis*. The methoxylated plagiochilines A_1, A_2 and C were derived from the plagiochilines A and C during the extraction procedure. A new germacrene, *ent*-3α-acetoxybicyclogermacrene, *ent*-maaliol and the previously known *ent*-aromadendrane-type sesquiterpenes have been obtained from *P. yokogurensis*. The structures of the new compounds were elucidated by ^{1}H NMR spectral data and by chemical correlation.

INTRODUCTION

The liverworts of the *Plagiochila* species generally elaborate characteristic pungent substances. Recently, we reported the isolation and the structures of the unique *ent*-secoaromadendrane-type sesquiterpene hemiacetals, plagiochilines A (**3**), B (**4**), C (**5**), D, E, F, plagiochilide (**8**), plagiochilal A and furanoplagiochilal from *Plagiochila* species. The characteristic pungency of *Plagiochila* species was due to plagiochiline A (**3**), which also exhibited a strong insect antifeedant activity against African army worm [1–4]. More recently, we have also reported that various *ent*-secoaromadendrane-type sesquiterpenes are widely distributed in the Plagiochilaceae and that these sesquiterpenes are significant chemosystematic markers in this family [5, 6].

Further investigation of the pungent extract of *P. ovalifolia* and *P. yokogurensis* resulted in the isolation of six new *ent*-secoaromadendrane-type sesquiterpene hemiacetals and a new *ent*-bicyclogermacrene together with the previously known three *ent*-aromadendrane-type sesquiterpenes and *ent*-maaliol.

In the present paper, we wish to report the structures of three new *ent*-secoaromadendrane-type sesquiterpene hemiacetals, a new acetoxybicyclogermacrene, and three methoxylated sesquiterpene hemiacetals.

RESULTS AND DISCUSSION

An ether extract of *P. ovalifolia* was chromatographed on silica gel and then on Sephadex LH-20 to give a new *ent*-secoaromadendrane-type sesquiterpene hemiacetal, named plagiochiline G (**1**) and three unidentified *ent*-secoaromadendrane-type sesquiterpene aldehydes, together with the previously known plagiochilines A(**3**), B(**4**), C(**5**) and F [1–3]. The same treatment of the methanol extract of *P. yokogurensis* afforded five new sesquiterpene hemiacetals, plagiochilines H(**2**), I(**7**), methoxyplagiochilines A_1 (**11**), A_2 (**12**) and C (**13**), and *ent*-3α-acetoxybicyclogermacrene (**14**), together with three *ent*-aromadendrane-type sesquiterpenes (**17**–**19**) and *ent*-maaliol (**16**).

Plagiochiline G (**1**)

The first hemiacetal, $C_{21}H_{28}O_9$ (M^+ at *m/e* 424), showed the presence of three acetoxyl groups [1740, 1230 cm^{-1}; δ 2.00 (3 H), 2.16 (6 H)] and a hydroxymethyl group [3500 cm^{-1}; δ 3.26, 3.61 (each *d*, *J* = 14 Hz)]. The ^{1}H NMR spectrum (Table 1) was quite similar to that of plagiochiline D (**6**) recently isolated from *P. asplenioides* [3], except for the presence of a hydroxymethyl group in place of an acetoxyl group, indicating that plagiochiline G possessed the same secoaromadendrane-type sesquiterpene hemiacetal as **6** and a hydroxymethyl group might be located at C-13. This assumption was further supported as follows. Acetylation of **1** with Ac_2O–pyridine afforded a tetraacetate whose spectral data and chromatographic behaviour were completely identical to those of the natural plagiochiline D (**6**) [3]. The orientation of the acetoxyl and the hydroxyl groups at C-13 of **1** was confirmed by comparison of the splitting patterns of the H-14 signals of plagiochilines B (**3**) and D (**6**), whose stereochemistries were recently established [3, 4], and plagiochiline G. In plagiochilines B and D, the α-acetoxymethyl groups at C-13 appeared as AB-type doublet signals. On the other hand, the β-acetoxymethyl group at C-13 of plagiochiline D appeared as a broad singlet. In plagiochiline G, the acetoxymethyl and

* Part of this work was presented at the 23rd Symposium of the Chemistry of Terpenes, Essential Oils and Aromatics of Japan, Tottori, October 1979.

Table 1. ^{1}H NMR chemical shifts of the new *ent*-secoaromadendrane-type sesquiterpenes (ppm from internal TMS)*

	1	2	7	11	12	13	14
H-1	1.73 (*dd*, 10, 5)	2.77 (*dd*, 10, 5)	1.78†		1.67 (*dd*, 9, 4)	3.18 (*dd*, 9, 4)	4.96 (*t*, 8)
H-2	6.78 (*d*, 10)	6.45 (*d*, 10)	6.68 (*d*, 10)	6.67 (*d*, 9)	6.73 (*d*, 9)	6.41 (*d*, 9)	2.31 (*dd*, 8, 3)
H-3	6.30 (*br s*)	5.88 (*d*, 2)	6.10 (*br s*)	5.15 (*br s*)	5.20 (*br s*)	5.20 (*br s*)	5.16 (*t*, 3)
H-5							4.63 (*br d*, 10)
H-6		0.7†	0.5 (*dd*, 10)				
H-11	2.45 (*br s*)	4.72 (*s*)	2.40 (*br s*)	2.43 (*br s*)	2.43 (*s*)	4.78 (*s*)	1.46 (*d*, 2)
H-12	4.50 (*br s*)	1.55 (*d*, 2)	3.92 (*s*)	4.97 (*br s*)‡ [19]	4.90 (*br s*) 5.08 (*br s*) [19]	5.00 (*br s*) [19]	1.67 (*d*, 2)
H-14	3.26 (*d*, 12) 3.61 (*d*, 12)	1.02 (*s*)	1.07 (*s*)	1.05 (*s*)	1.07 (*s*)	1.06 (*s*)	1.03 (*s*)
H-15	4.38 (*br s*)	1.05 (*s*)	1.07 (*s*)	1.13 (*s*)	1.12 (*s*)	1.15 (*s*)	1.08 (*s*)
OAc	2.00 (s) 2.16 (s)	2.05 (s)	2.17 (s)	2.17 (s)	2.17 (s)	2.10 (s)	2.00 (s)
OMe				3.45 (*s*)	3.52 (*s*)	3.50 (*s*)	

* All assignments were confirmed by the double resonance experiments.

† Overlapped signals.

‡ The top of the signal was split with J = 3 Hz.

hydroxymethyl groups appeared as a broad singlet and AB-type doublet, respectively. These results indicated that the hydroxymethyl group at C-13 was α-oriented. Thus, the structure of plagiochiline G was established to be **1**. More recently, Nozaki *et al.* [7] reported the isolation of plagiochilines A, B, C and three secoaromadendrane-type sesquiterpene aldehydes from the same species.

Plagiochiline H (**2**)

The second new hemiacetal, $C_{17}H_{24}O_3$ (M^+ at *m/e* 276), exhibited the presence of an acetoxyl group [1755, 1240 cm^{-1}; δ 2.05 (3 H, *s*)]. The ^{1}H NMR (Table 1) and double resonance spectra also contained the signals attributable to two tertiary methyl groups, a vinyl methyl group, a vinylic proton located between an etheric oxygen and a double bond, one proton on a carbon bearing an acetoxyl group, two equivalent protons of an exocyclic methylene group and two protons on a cyclopropane ring. The ^{1}H NMR spectrum closely resembled that of plagiochiline C (**5**), except for the presence of a vinyl methyl group instead of an acetoxymethyl group, showing that plagiochiline H possessed the same secoaromadendrane-type hemiacetal as plagiochiline C and one vinyl methyl group might be attached to C-4. Reduction of **2** with $LiAlH_4$ gave a diol whose spectral data were identical to those of the alcohol (**9**) derived from plagiochilide (**8**) by the same treatment. Reduction of **8** with di-isobutylaluminium hydride gave the acetal mixture (**10**), followed by acetylation with Ac_2O–pyridine, without purification, to afford the hemiacetal whose spectral and chromatographic behaviour were completely identical to those of the natural plagiochiline H. Thus, the structure of plagiochiline H was established to be **2**.

Plagiochiline I (**7**)

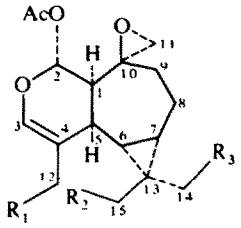
The ^{1}H NMR spectrum of the third hemiacetal, $C_{17}H_{24}O_5$ (M^+ at *m/e* 308), was very similar to that of plagiochiline A (**3**), except for the presence of a hydroxymethyl group in place of an acetoxymethyl group, indicating that plagiochiline I had the same structure as plagiochiline A and the hydroxymethyl group might be placed at C-4. Acetylation of **7** gave an intensely pungent hemiacetal whose spectral and physical constants were in accordance with those of the natural plagiochiline A (**3**). From the above spectral and chemical correlation, the structure of plagiochiline I was represented as **7**.

Methoxyplagiochilines A_1 (**11**), *A_2* (**12**) *and C* (**13**)

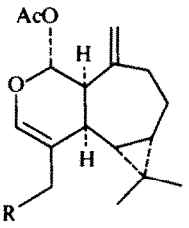
Three new *ent*-secoaromadendrane-type sesquiterpene hemiacetals, named methoxyplagiochilines A_1 (**11**), A_2 (**12**) and C (**13**) were isolated from the methanol extract of *P. yokogurensis*. It is suggested that these hemiacetals may be the artefacts of the corresponding plagiochilines A (**3**) and C (**5**). This assumption was confirmed by the following evidence. When *P. yokogurensis* and the other pungent *Plagiochila* species were extracted with ether, no methoxylated hemiacetals were obtained from either extract and high yields were obtained of plagiochilines A and C. On the other hand, the methanol extract of *P. yokogurensis* contained much lower amounts of plagiochilines and the methoxylated plagiochilines were detected by TLC. In addition, when plagiochiline A was treated with MeOH in the presence of dilute KOH, it readily gave the corresponding methoxylated hemiacetals (**11**, **12**) by the mechanism represented in Scheme 1. The stereochemistry of each of the methylated hemiacetals was established by IR, MS, and ^{1}H NMR spectra (Table 1) and by spin decoupling experiments. It is interesting to note that methoxyplagiochilines A_1 (**11**) and A_2 (**12**) had the same intense pungent taste as that of plagiochiline A (**3**) which imparts the characteristic pungency of *Plagiochila* species.

ent-3α-*Acetoxybicyclogermacrene* (**14**)

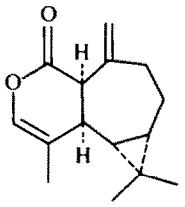
The IR spectrum of the minor component (**14**), $C_{17}H_{26}O_2$ (M^+ at *m/e* 262), isolated from *P. yokogurensis* indicated the presence of an acetoxyl group (1730, 1250 cm^{-1}). The ^{1}H NMR spectral signals (Table 1) closely resembled the corresponding signals in the spectrum of bicyclogermacrene (**15**) isolated from the same plant, with the exception of signals of an acetoxyl group and one proton on a carbon bearing the acetoxyl group, showing that compound **14** possessed the same bicyclogermacrene-type sesquiterpene skeleton as **15** but having one acetoxyl group. The location of the axial acetoxyl group was suggested to be at C-3 or C-9 in



1 $R_1 = R_2 = OAc$, $R_3 = OH$
3 $R_1 = OAc$, $R_2 = R_3 = H$
4 $R_1 = R_3 = OAc$, $R_2 = H$
6 $R_1 = R_2 = R_3 = OAc$
7 $R_1 = OH$, $R_2 = R_3 = H$



2 R = H
5 R = OAc



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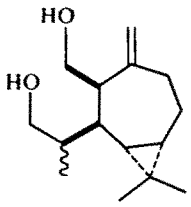

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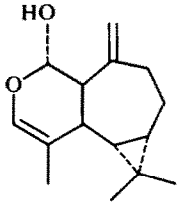

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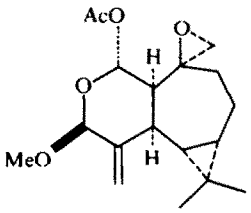

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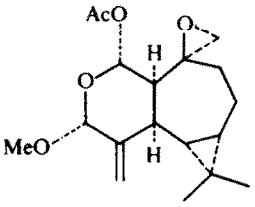

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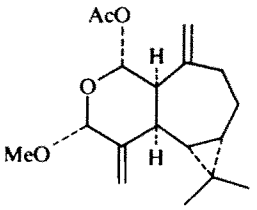

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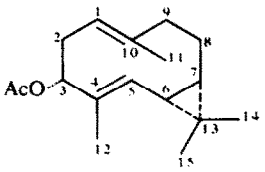

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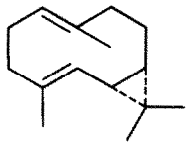

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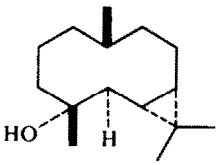

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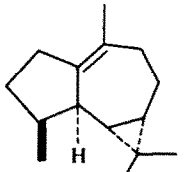

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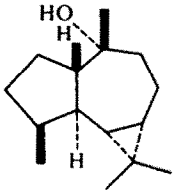

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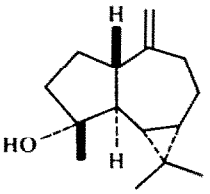

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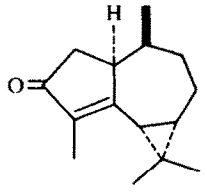

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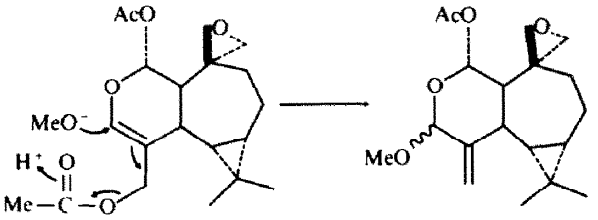

3 11, 12

Scheme 1.

bicyclogermacrene by the appearance of the triplet signal at δ 5.16 (J = 3 Hz). Several C-3 substituted germacranolides and their derivatives have been reported as natural products. The form of the triplet signal at δ 5.16 of **14** was completely superimposable on that of dihydrotamaulipin-B acetate (3α-acetoxydihydrocostunolide) [8], supporting the location of the axial acetoxyl group of **14** at C-3. This assumption was further confirmed by the spin decoupling experiments. Irradiation of the double-doublet signal at 2.31 (H-2), attributable to allylic methylene protons caused the triplet signal at 5.16 (H-3) and a broad triplet signal at 4.96 (H-2) to collapse to a sharp singlet and a broad singlet, respectively. When the triplet at 5.16 was irradiated, the allylic protons at 2.31 collapsed to a broad doublet. Thus, the structure of the new acetoxybicyclogermacrene was established to be **14**.

In addition to the above *ent*-secoaromadendrane-type sesquiterpenes and *ent*-3α-acetoxybicyclogermacrene, *ent*-maaliol (**16**) [9], *ent*-ledrene (**17**) [10], *ent*-globulol (**18**) [10, 11] and *ent*-spathulenol (**19**) [12] were isolated from *P. yokogurensis* along with *ent*-bicyclogermacrene (**15**) [3, 13–15] and *ent*-cyclocolorenone (**20**) [16, 17]. The absolute configurations of ledrene (**17**) and the three sesquiterpene alcohols (**16, 18, 19**) were opposite to those found in the higher plants. It is suggested that the precursor of the present *ent*-aromadendrane-type sesquiterpenes, *ent*-secoaromadendrane-type sesquiterpene hemiacetals and *ent*-maaliol may be *ent*-bicyclogermacrene (**15**). The details of the bioassay of the hemiacetals (**1, 2, 7, 11–13**) will be reported elsewhere.

EXPERIMENTAL

UV, IR, NMR, MS (CI and GC–MS) and $[\alpha]_D$ were measured as reported previously [3, 4].

Extraction and isolation. Plagiochila ovalifolia collected in Kochi prefecture in 1978 was air-dried for 5 days and the ground material (130 g) was extracted with Et_2O for 2 weeks. The crude extract (5.83 g) was directly chromatographed on Si gel using a *n*-hexane–EtOAc gradient to yield 11 fractions. The fraction eluted with *n*-hexane–EtOAc (2:3) was rechromatographed on Si gel using a *n*-hexane–EtOAc gradient to give the crude hemiacetals, which were purified by PLC to give plagiochiline G (**1**) (130 mg). $C_{21}H_{28}O_9$ (CI–MS, *m/e* 425); IR ν_{max} cm^{-1}: 3500 (OH), 1740, 1230 (OAc), 1670 (C=C–O–), 1190, 1170, 1145, 1130, 1090, 1065, 1005, 965, 920. The fractions eluted with *n*-hexane–EtOAc (3:2) (140 mg) and (1:1) (250 mg) were combined and the dark green oil was chromatographed on Sephadex using a $CHCl_3$–MeOH gradient to give three labile secoaromadendrane-type sesquiterpene aldehydes, named plagiochilal B (12 mg), plagiochilal C (43 mg), plagiochilal D (8 mg), and plagiochiline F (6 mg) [3].

Plagiochila yokogurensis collected in Tokushima prefecture in 1978 was dried for 5 days and the ground material (680 g) was extracted with MeOH for 1 month. The crude extract (58.80 g) was directly chromatographed on Si gel using a *n*-hexane–EtOAc gradient to yield 11 fractions as described above. The first fraction (*n*-hexane 100%) (4.30 g) was rechromatographed on Si gel impregnated with 10% $AgNO_3$ using *n*-hexane to give *ent*-bicyclogermacrene (**15**) (15 mg) [3, 13, 14] and *ent*-ledrene (**17**) (30 mg) [8, 13]. $[\alpha]_D$ −42° (*c*, 1.5); $C_{15}H_{24}$ (M^+ *m/e* 204): ^{1}H NMR: δ 0.45, 0.68 (2 H, *m*), 0.93 (3 H, *d*, J = 7 Hz), 0.98, 1.05 (each 3 H, *s*), 1.55 (3 H, *br s*). The viscous oil (5.30 g) from the fraction *n*-hexane–EtOAc (19:1) was rechromatographed on Si gel using *n*-hexane–EtOAc to give plagiochiline H (**2**) (276 mg), *ent*-3α-acetoxybicyclogermacrene (**14**) (144 mg), *ent*-maaliol (**16**) (324 mg), *ent*-globulol (**18**) (24 mg) and *ent*-spathulenol (**19**) (89 mg), respectively.

Plagiochiline H (**2**): $[\alpha]_D$ + 22° (*c*, 2.4); $C_{17}H_{24}O_3$; IR ν_{max} cm^{-1}: 1755, 1240 (OAc), 1680 (C=C–O–), 1635 (C=C), 1190, 1140, 1120, 1100, 1085, 1065, 1045, 1010, 900, 835; MS *m/e* (rel. int.): 276 (M^+, 1), 216 (M^+ − 60, 34), 173 (74), 145 (30), 121 (37), 109 (71), 105 (31), 95 (44), 91 (41), 43 (100). *ent-3α-Acetoxybicyclogermacrene* (**14**): $[\alpha]_D$ − 13.7° (*c*, 0.73), $C_{17}H_{26}O_2$; IR ν_{max} cm^{-1}: 1730, 1250 (OAc), 1210, 1150, 1040, 1020, 1000, 865, 850; MS *m/e* (rel. int.): 262 (M^+, 10), 203 (43) 202 (M^+ − 60), 159 (43), 152 (40), 137 (39), 133 (35), 132 (46), 123 (49), 121 (54), 119 (42), 109 (100), 105 (32), 95 (44), 91 (35), 43 (88). *ent-Maaliol* (**16**): mp 98–99°; $[\alpha]_D$ − 23° (*c*, 0.15) (lit. + 21.7° [10]); $C_{15}H_{26}O$ (M^+ at *m/e* 222); IR ν_{max} cm^{-1}: 3400 (OH); ^{1}H NMR: δ 0.88, 0.95, 1.06, 1.27 (each 3 H, *s*). Dehydration of **16** with $SOCl_2$–Py, followed by CC on Si gel using *n*-hexane gave a pure hydrocarbon whose spectral data were completely identical to γ-maaliene [18]. *ent-Globulol* (**18**): $[\alpha]_D$ + 60° (*c*, 1.2) (lit. −43° [9]); $C_{15}H_{26}O$ (M^+ at *m/e* 222); IR ν_{max} cm^{-1}: 3400 (OH); ^{1}H NMR: δ 0.6 (2 H, *m*), 0.93 (3 H, *d*, J = 7 Hz) 0.98, 1.02, 1.12 (each 3 H, *s*). *ent-Spathulenol* (**19**): $[\alpha]_D$ − 20° (*c*, 0.92) (lit. + 56° [19]); $C_{15}H_{24}O$ (M^+ at *m/e* 220); IR ν_{max} cm^{-1}: 3600 (OH); ^{1}H NMR: δ 0.52 (2 H, *m*), 1.08 (6 H, *s*), 1.32 (3 H, *s*), 4.73 (2 H, *br s*). The fraction eluted with *n*-hexane–EtOAc (4:1) (2.66 g) was purified by PLC to give *ent*-cyclocolorenone (**20**) (45 mg). The *n*-hexane–EtOAc (3:1) fraction (2.30 g) contained the intense pungent substances, which were rechromatographed on Si gel using a C_6H_6–EtOAc gradient to afford plagiochilines A (**3**) (250 mg) and C (**5**) (30 mg). The *n*-hexane–EtOAc (1:1) fraction (3.20 g) was rechromatographed on Sephadex using a $CHCl_3$–MeOH gradient to give methoxyplagiochilines A_1 (**11**) (300 mg), A_2 (270 mg), C (**13**) (280 mg) and plagiochiline I (120 mg). *Methoxyplagiochiline* A_1 (**11**): $C_{18}H_{26}O_5$ (CI–MS: M^+ at *m/e* 323): IR ν_{max} cm^{-1}: 1745, 1230 (OAc), 1655 (C=C). *Methoxyplagiochiline* A_2 (**12**): $C_{18}H_{26}O_5$; IR ν_{max} cm^{-1}: 1745, 1230 (OAc), 1655 (C=C); MS *m/e* (rel. int.): 262 (M^+ − 60, 2), 159 (40), 131 (42), 121 (40), 109 (40), 105 (50), 91 (75), 79 (40), 77 (39), 43 (100). *Methoxyplagiochiline C* (**13**): $C_{18}H_{26}O_4$; IR ν_{max} cm^{-1}: 1740, 1235 (OAc), 1640 (C=C); MS *m/e* (rel. int.): 306 (M^+, 0.5), 246 (M^+ − 60, 34), 203 (100), 188 (48), 175 (67), 171 (70), 147 (49), 145 (52), 143 (97), 133 (47), 131 (42), 121 (54), 119 (42), 117 (43), 109 (46), 107 (43), 67 (105), 93 (40), 91 (92), 79 (47), 77 (43), 43 (83). *Plagiochiline I* (**7**): $[\alpha]_D$ + 11.5° (*c*, 0.52); $C_{17}H_{24}O_5$; IR ν_{max} cm^{-1}: 3450 (OH), 1740, 1230 (OAc), 1670 (C=C–O–), 1180, 1160, 1140, 1120, 1100, 1080, 1060, 1005; MS *m/e* (rel. int.): 308 (M^+, 0.5), 248 (M^+ − 60, 14), 205 (53), 135 (35), 121 (30), 111 (63), 109 (34), 107 (45), 105 (36), 95 (46), 93 (33), 91 (50), 85 (36), 83 (51), 81 (38), 79 (36), 69 (36), 67 (34), 43 (100), 41 (32).

Acetylation of **1**. To a pyridine soln of **1** (70 mg) was added Ac_2O (1 ml) and the mixture allowed to stand overnight. Work-up as usual gave plagiochiline D (**6**) (65 mg) [3].

Reduction of **5** *with* $LiAlH_4$. To $LiAlH_4$ (30 mg) in dry Et_2O was added **5** (50 mg) and the mixture stirred for 1 hr at 0° Work-up as usual gave a diol (**9**) (30 mg) [1].

Reduction of **8** *with* $(diiso\text{-}Bu)_2$ AlH. To a hexane soln of $(diiso\text{-}Bu)_2$ AlH was added **8** (200 mg) with stirring at −60°. Work-up as usual gave the hemiacetal (**10**) ^{1}H NMR: δ 1.76 (H-14, *d*, J = 2 Hz), 2.80 (H-1, *dd*, J = 10,4 Hz), 5.51 (H-2, *d*, J = 10), 6.06 (H-3, *d*, J = 2 Hz). The diol also produced was acetylated with Ac_2O–pyridine, without prior purification, followed by PLC to afford plagiochiline H (**2**) (77 mg).

Methoxylation of plagiochiline A (**3**). The hemiacetal **3** (64 mg) was treated with MeOH (6 ml) in the presence of 5% KOH (0.1 ml) with stirring for 36 hr at 40–50°. The solvent was evapd and the reaction mixture was extracted with Et_2O and dried (Na_2SO_4). Evapn of the solvent gave two pungent methoxylated compounds (43 mg) whose chromatographic behaviour and GC–MS spectra were completely identical to those of plagiochilines A_1 (**11**) and A_2 (**12**).

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