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NORDITERPENES FROM *JUNIPERUS CHINENSIS*

CHING-KUO LEE, JIM-MIN FANG and YU-SHIA CHENG*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

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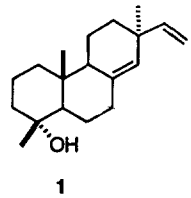
Key Word Index—*Juniperus chinensis*; Cupressaceae; norditerpenes; norabietane-type; norpimarane-type.

Abstract—One norpimarane and 11 norabietanes were isolated from the leaves of *Juniperus chinensis*. The new compounds include 19-norabieta-8,11,13-trien-4-yl formate, 18-norabieta-8,11,13-triene-4-hydroperoxide, 19-norabieta-8,11,13-triene-4-hydroperoxide, 4-hydroxy-18-norabieta-8,11,13-trien-7-one, 4-hydroxy-19-norabieta-8,11,13-trien-7-one, 4-hydroperoxy-19-norabieta-8,11,13-trien-7-one, 7α-hydroxy-19-norabieta-8,11,13-triene-4-hydroperoxide, 19-norabieta-7,13-dien-4-ol and 13β,14β-epoxy-4-hydroxy-19-norabiet-7-en-6-one.

INTRODUCTION

Juniperus chinensis is a common ornamental tree [1]. Hinokiflavone and kayaflavone have been previously reported in this plant [2, 3]. We recently isolated 13 lignans, a secoditerpene and 46 diterpenes in addition to other components from the bark and leaves [4–7]. The diterpenes include labdane-, abietane-, sempervirane-, totarane- and chinane-types. Labdane-type diterpenes are rich in the bark, whereas abietane-type diterpenes predominate in the leaves. A norditerpene, 15-oxo-16-norabieta-7,13-dien-19,6β-olide, and a bisnorditerpene, 15,16-bisnor-8,17-epoxy-13-oxolabd-11*E*-en-19-oic acid were also found, respectively, in the leaves and bark. We report here further 12 norditerpenes, including a norpimarane and 11 norabietanes, found in the leaves of *J. chinensis*.



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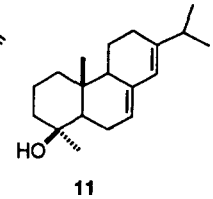

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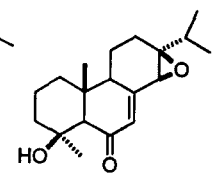

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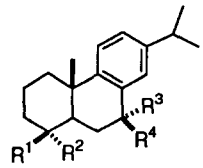

	R^1	R^2	R^3	R^4
2	CH_3	OH	H	H
3	OH	CH_3	H	H
4	OCHO	CH_3	H	H
5	CH_3	OOH	H	H
6	OOH	CH_3	H	H
7	CH_3	OH	=O	
8	OH	CH_3	=O	
9	OOH	CH_3	=O	
10	OOH	CH_3	OH	H

RESULTS AND DISCUSSION

The acetone-soluble part of the leaves of *J. chinensis* was extracted with ethyl acetate. The extract was subjected to repeated column chromatography and HPLC to give norditerpenes **1**–**12**. Compound **1** was identified as 18-norpimara-8(14),15-dien-4-ol by analysis of its physical and spectral properties (mp. [α], MS and ^{1}H NMR) [8]. The ^{13}C NMR signals were assigned by means of HMBC experiment (Table 1).

Epimers **2** and **3** were identified as 18-norabieta-8,11,13-trien-4-ol [9, 10] and 19-norabieta-8,11,13-trien-4-ol [10], respectively. These nordehydroabietanes exhibited the characteristic ABX patterns of aromatic protons in their ^{1}H NMR spectra. The Me-10 in **3** appeared at a lower field (δ1.29) than that in the epimer **2** (δ1.13) owing to the deshielding effect of the 4β-hydroxyl group. The C-4 in **2** appeared at a lower field (δ52.5) than that in **3** (δ48.7).

Compound **4** was isolated in a small amount. The exact mass at *m/z* 300.209 indicated the molecular formula $C_{20}H_{28}O_2$. By analysis of the IR and NMR spectra, **4** was determined to be 19-norabieta-8,11,13-trien-4-yl formate, the formate of **3**. The IR absorption at

*Author to whom correspondence should be addressed.

Table 1. ^{13}C NMR spectral data of compounds **1**–**12** ($CDCl_3$ solution, δ values in ppm)

C	1	2	3	4*	5	6	7	8	9	10	11	12
1	38.6	38.0	38.2	38.0	37.7	38.5	37.2	37.2	37.4	38.1	38.6	37.7
2	18.9	20.5	18.5	18.2	20.0[a]	18.5[a]	20.1	18.0	17.9	18.3	18.0	17.1
3	42.9	42.7	40.8	36.0	35.3	34.8	42.3	40.7	34.3	34.7	41.2	39.8
4	72.4	72.5	72.2	84.7	84.9	84.1	71.6	71.4	83.1	84.0	71.6	69.6
5	56.4	52.5	48.7	50.8	45.4	50.6	51.0	48.1	49.1	44.8	48.9	62.4
6	21.6	18.0	18.0	18.2	17.9[a]	18.4[a]	35.0	35.5	35.3	28.1	27.5	202.8
7	35.6	30.3	29.4	29.4	30.0	30.2	199.2	199.6	199.4	68.3	120.8	131.4
8	136.6	134.8	134.7	134.5	134.8	134.5	130.6	130.9	130.7	135.7	135.7	155.2
9	50.3	145.6	145.6	146.4	146.3	146.4	152.8	153.0	152.8	146.4	49.9	51.3
10	39.0	38.2	37.2	37.3	38.3	37.3	38.6	37.5	37.6	37.6	34.8	43.8
11	20.3	124.5	123.8[a]	124.0	124.5	124.2	123.9	123.5	123.7	127.6	22.6	15.4
12	34.5	123.9	123.9[a]	124.0	123.9	123.8	132.6	132.4	132.5	126.6	23.0	23.4
13	37.4	146.3	146.8	145.9	145.7	145.6	146.8	146.7	146.8	146.5	145.3	64.4
14	129.1	127.0	126.8	126.8	127.0	126.9	125.0	125.0	125.1	124.5	122.5	58.8
15	148.9	33.4	33.4	33.5	33.5	33.5	33.6	33.6	33.6	33.5	34.9	33.4
16	110.1	23.9	24.0	24.0	23.9	24.0	23.7	23.8	23.8	23.8	20.9	17.6
17	26.0	23.9	24.0	24.0	23.9	24.0	23.8	23.8	23.8	24.0	21.4	17.9
18			30.8	26.1[a]	24.7			30.1	23.8	24.8	30.6	31.0
19	23.5	22.9				24.4	22.7					
20	14.5	24.5	24.4	24.6[a]	18.2	25.3	22.6	23.9	24.6	24.4	13.3	13.9

*The ^{13}C signals of the formyl group in **4** appeared at δ160.5.
[a]The assignments can be interchanged.

1713 cm^{-1}, a proton signal at δ8.10 (*s*) and a carbon signal at δ160.5 (*d*) were attributable to the moiety of formic ester. The C-4 signal appearing at δ84.7 was in agreement with the structure. The Me-10 in **4** occurred at a rather low field δ1.25 owing to the strong deshielding effect of the formate group. A 7% NOE of the formate proton was observed by irradiation of Me-10, further supporting the stereochemistry.

Compound **5** showed a parent ion $[M]^+$ at *m/z* 288 corresponding to a molecular formula $C_{19}H_{28}O_2$. The ^1H NMR spectrum of **5** was similar to that of **2**, the chemical shift of C-4 in **5** (δ84.9) was, however, larger than that in **2** (δ72.5). We concluded that **5** is 18-norabieta-8,11,13-triene-4-hydroperoxide. Compound **6**, $[M]^+$ at *m/z* 288, was assigned as 19-norabieta-8,11,13-triene-4-hydroperoxide, an epimer of **5**. Owing to the deshielding effect of the 4β-hydroperoxy group [12], the Me-10 of **6** appeared at a lower field δ1.25 than the corresponding signal of **5** (at δ1.16). The axial Me-4 of **5** occurred at δ1.21, whereas the equatorial Me-4 of **6** occurred at lower field (δ1.34).

Compound **7** ($C_{19}H_{26}O_2$) showed an IR absorption at 1666 cm^{-1} attributable to a conjugated carbonyl group. Three aromatic protons of ABX pattern appeared at δ7.26 (*d*, *J* = 8.1 Hz), 7.37 (*dd*, *J* = 8.1, 1.9 Hz) and 7.85 (*d*, *J* = 1.9 Hz), an indication for a dehydroabietanone having the oxo group at C-7. The signal at δ71.6 was attributable to C-4 having a hydroxyl substituent. Compound **8** exhibited an IR absorption at 1666 cm^{-1} and three signals at δ7.27 (*d*, *J* = 8.2 Hz), 7.37 (*dd*, *J* = 8.2, 2.1 Hz) and 7.85 (*d*, *J* = 2.1 Hz) similar to the spectral properties of **7**. Epimers **7** and **8** were assigned as 4-hydroxy-18-norabieta-8,11,13-trien-7-one and 4-hydroxy-19-norabieta-8,11,13-trien-7-one, respectively. Compared with **8**, epimer **7** having a 4α-hydroxyl group displayed Me-10 at a higher field (δ1.26 vs δ1.33) and C-5 at a lower field (δ51.0 vs δ48.1) in the NMR spectra. The stereochemistry of **8** was confirmed by NOESY experiments. Thus, irradiation of Me-10 (at δ1.33) caused a NOE on H-6β (at δ2.76) and irradiation of Me-4 (at δ1.22) caused NOE effects of H-6α (at δ2.85) and H-5 (at δ1.91). Norabietanes **7** and **8** have been obtained by cobalt dehydroabietate oxidation [11], whereas this is the first report of their occurrence in nature.

Compound **9** ($C_{19}H_{26}O_3$), exhibited the exact mass $[M]^+$ ion at *m/z* 302.187 and an IR absorption at 1659 cm^{-1} attributable to a conjugated ketone. Its structure was readily determined to be 4-hydroperoxy-19-norabieta-8,11,13-trien-7-one. The H-14 resonance occurred as a doublet (*J* = 1.9 Hz) at δ7.84. Irradiation of Me-4 (at δ1.32) caused 14% NOE effect on H-5 (at δ2.08), indicating that Me-4 and H-5 are on the same face.

Compound **10** showed the exact mass ion at *m/z* 304.205 corresponding to a molecular formula $C_{19}H_{28}O_3$. Its structure was determined to be 7α-hydroxy-19-norabieta-8,11,13-triene-4-hydroperoxide by spectral analyses. The equatorial H-7β had small coupling constants (3.8 and 3.8 Hz) with two vicinal protons. The signals at δ_H1.37 and δ_C84.0 were assigned to Me-4 and C-4, respectively, by an HMBC experiment. Irradiation of Me-4 caused 11% NOE on H-5 (at δ1.94), conforming with the α-orientation of Me-4. On standing in the air, **10** (in $CDCl_3$ solution) was gradually oxidized to give a ketone **9**.

The molecular formula ($C_{19}H_{30}O$) of **11** was deduced from its exact mass $[M]^+$ ion at *m/z* 274.230. An IR absorption at 3484 cm^{-1} and a carbinol carbon signal at

δ71.6 indicated the presence of a hydroxyl group. Four carbon signals at δ120.8, 122.5, 135.7 and 145.3 as well as two vinyl protons at δ5.43 (*br s*) and 5.77 (*s*) were attributable to a conjugated diene. The structure of **11** was assigned as 19-norabieta-7,13-dien-4-ol. The Me-4 of **11** was equatorial as it had a chemical shift at δ30.6 close to the values of those signals in **3** and **8**.

Compound **12** ($C_{19}H_{28}O_3$) showed IR absorptions at 3525 and 1661 cm^{-1} attributable to the hydroxyl and conjugated carbonyl groups. The structure of **12** was determined to be 13β,14β-epoxy-4-hydroxy-19-norabiet-7-en-6-one by detailed analysis of the ^1H and ^{13}C NMR spectra. The proton geminal to epoxy group (H-14) occurred at δ3.22 as a singlet. The C-7 (at δ131.4) and C-15 (at δ33.4) signals were correlated with H-14 by an HMBC experiment. Irradiation of H-7 (at δ6.11) caused an NOE on H-14, supporting the assigned stereochemistry. Irradiation of H-5 (at δ2.30) also caused enhancements of Me-4 (at δ1.33) and H-9 (at δ2.10).

In summary, one norpimarane **1** and 11 norabietanes **2**–**12** were isolated from the leaves of *J. chinensis*. Besides the hydroperoxides **5**, **6**, **9** and **10**, isolation of the formate **4** is unique. Diterpene aldehydes having 4β-formyl groups undergo autoxidation to give norditerpene alcohols and hydroperoxides [11, 12]. A benzene solution of abieta-8,11,13-trien-19-al stirred at 18° in the air for 5 days gave 4-epidehydroabietic acid [7], 18-norabieta-8,11,13-trien-4-ol (**2**), 19-norabieta-8,11,13-trien-4-ol (**3**), 4-hydroxy-19-norabieta-8,11,13-trien-7-one (**8**) and 19-norabieta-8,11,13-trien-4-yl formate (**4**). It remains unclear whether the norditerpenes **1**–**12** are natural products or artifacts derived from autoxidation and Baeyer–Villiger oxidation of the corresponding aldehydes.

EXPERIMENTAL

Plant material. The leaves of *Juniperus chinensis* Linn. var. *kaizuka* Hort. were collected from the plant grown in the surroundings of the Department of Chemistry of the National Taiwan University. A voucher specimen is deposited in the Herbarium of our University. The leaves (1.83 kg) were soaked in Me_2CO (7 l) for a week. The Me_2CO extract was concd to give 90 g of a residue, which was diluted with H_2O and extracted ×3 with EtOAc. The combined EtOAc extracts were concd to give an oil (25.5 g), which was absorbed by 31 g of silica gel and then chromatographed on a column packed with 250 g of silica gel. By elution with gradients of hexane, EtOAc and $CHCl_3$, **12** (2.0 mg), **1** (24 mg), **11** (3.0 mg), **3** (4.8 mg), **2** (5.1 mg), **8** (15 mg), **7** (9.1 mg), **5** (8.6 mg), **4** (2.0 mg), **6** (4.0 mg), **10** (13 mg), and **9** (17 mg) were obtained in the ascending order of polarity. These compounds were further purified by HPLC using a Hibar Lichrospher Si 60 (Merck, 10 μm) column (25 cm × 1 cm).

18-*Norpimara*-8(14),15-*dien*-4-*ol* (**1**). Mp 119–120°, $[\alpha]_D^{25}$ + 86° ($CHCl_3$; *c* 0.8). Ref. [8], mp 119–121°, $[\alpha]_D^{22}$ + 92°.

18-*Norabieta*-8,11,13-*trien*-4-*ol* (**2**). An oil, $[\alpha]_D^{25}$ + 43.1° ($CHCl_3$; *c* 0.51). Ref. [10], mp 89–91°, $[\alpha]_D$ + 45°.

19-*Norabieta*-8,11,13-*trien*-4-*ol* (**3**). An oil, $[\alpha]_D^{25}$ + 46.2° ($CHCl_3$; *c* 0.48). Ref. [10], mp 65–67°, $[\alpha]_D$ + 50°.

19-*Norabieta*-8,11,13-*trien*-4-*yl formate* (**4**). An oil. $[\alpha]_D^{25}$ + 51.0° ($CHCl_3$; *c* 0.07). IR ν_{max}^{Neat} cm^{-1}: 1713 (C=O). ^1H NMR ($CDCl_3$): δ1.21 (*d*, *J* = 6.9 Hz, H-16, 17), 1.25 (*s*, H-20), 1.59 (*s*, H-18), 2.81 (*sept*, *J* = 6.9 Hz, H-15), 6.89 (*br s*, H-14), 6.98 (*br d*, *J* = 8.2 Hz, H-12), 7.16 (*d*, *J* = 8.2 Hz, H-11), 8.10 (*s*, –OCHO). EI-MS (70 eV) *m/z* (rel. int.): 300 $[M]^+$ (28), 256 (3), 239 (100), 197 (5), 159 (8). Exact mass $[M]^+$ for $C_{20}H_{28}O_2$ requires 300.2090. Found 300.2089.

18-*Norabieta*-8,11,13-*trien*-4-*hydroperoxide* (**5**). An oil, $[\alpha]_D^{25}$ + 34.3° ($CHCl_3$; *c* 0.2). IR ν_{max}^{Neat} cm^{-1}: 3377 (OOH). ^1H NMR ($CDCl_3$): δ1.16 (*s*, H-20), 1.20 (*d*, *J* = 6.9 Hz, H-16, 17), 1.21 (*s*, H-19), 2.81 (*sept*, *J* = 6.9, H-15), 6.88 (*d*, *J* = 1.7 Hz, H-14), 6.98 (*dd*, *J* = 8.2, 1.7 Hz, H-12), 7.02 (*d*, –OOH), 7.15 (*d*, *J* = 8.2 Hz, H-11). EI-MS (70 eV) *m/z* (rel. int.): 288 $[M]^+$ (23), 272 (47), 257 (52), 239 (38), 187 (100), 173 (52), 157 (28), 143 (32).

19-*Norabieta*-8,11,13-*trien*-4-*hydroperoxide* (**6**). An oil, $[\alpha]_D^{25}$ + 27.8° ($CHCl_3$; *c* 0.2). IR ν_{max}^{Neat} cm^{-1}: 3391 (–OOH). ^1H NMR ($CDCl_3$): δ1.20 (*d*, *J* = 6.9 Hz, H-16, 17), 1.25 (*s*, H-20), 1.34 (*s*, H-18), 2.80 (*sept*, *J* = 6.9 Hz, H-15), 6.87 (*d*, *J* = 1.7 Hz, H-14), 6.95 (*dd*, *J* = 8.2, 1.7 Hz, H-12), 7.06 (*s*, –OOH), 7.14 (*d*, *J* = 8.2 Hz, H-11). EI-MS (70 eV) *m/z* (rel. int.): 288 $[M]^+$ (23), 272 (30), 257 (40), 239 (24), 187 (100), 156 (23), 141 (22). Exact mass $[M]^+$ for $C_{19}H_{28}O_2$ requires 288.2090. Found 288.2079.

4-*Hydroxy*-18-*norabieta*-8,11,13-*trien*-7-*one* (**7**). An oil, $[\alpha]_D^{25}$ + 20.1° ($CHCl_3$; *c* 0.9). IR ν_{max}^{Neat} cm^{-1}: 3467 (OH), 1666 (C=O). ^1H NMR ($CHCl_3$): δ1.17 (*s*, H-19), 1.21 (*d*, *J* = 6.9 Hz, H-16, 17), 1.26 (*s*, H-20), 1.43 (*m*, H-3), 1.54 (*m*, H-1α), 1.6–1.8 (H-2), 1.88 (*m*, H-3β), 2.10 (*dd*, *J* = 14.2, 3.5 Hz, H-5), 2.27 (*br d*, *J* = 12.7 Hz, H-1β), 2.58 (*dd*, *J* = 17.9, 14.2 Hz, H-6β), 2.89 (*sept*, *J* = 6.9 Hz, H-15), 2.96 (*dd*, *J* = 17.9, 3.5 Hz, H-6α), 7.26 (*d*, *J* = 8.1 Hz, H-11), 7.37 (*dd*, *J* = 8.1, 1.9 Hz, H-12), 7.85 (*d*, *J* = 1.9 Hz, H-14). EI-MS (70 eV) *m/z* (rel. int.): 286 $[M]^+$ (72), 271 (13), 253 (29), 243 (28), 211 (29), 201 (100), 185 (18), 159 (64). Exact mass $[M]^+$ for $C_{19}H_{26}O_2$ requires 286.1934. Found 286.1936.

4-*Hydroxy*-19-*norabieta*-8,11,13-*trien*-7-*one* (**8**). An oil, $[\alpha]_D^{25}$ + 26.7° ($CHCl_3$; *c* 1.5). IR ν_{max}^{Neat} cm^{-1}: 3467 (OH), 1659 (C=O). ^1H NMR ($CHCl_3$): δ1.22 (*s*, H-18), 1.23 (*d*, *J* = 6.8 Hz, H-16, 17), 1.33 (*s*, H-20), 1.44 (*ddd*, *J* = 14.0, 14.0, 3.8 Hz, H-3α), 1.54 (*ddd*, *J* = 13.0, 13.0, 3.7 Hz, H-1α), 1.7–1.8 (H-2), 1.91 (*dd*, *J* = 13.2, 4.7 Hz, H-5), 2.01 (*m*, H-3β), 2.32 (*br d*, *J* = 13.0, H-2β), 2.76 (*dd*, *J* = 18.3, 13.2 Hz, H-6β), 2.85 (*dd*, *J* = 18.3, 4.7 Hz, H-6α), 2.90 (*sept*, *J* = 6.8 Hz, H-15), 7.27 (*d*, *J* = 8.2 Hz, H-11), 7.37 (*dd*, *J* = 8.2, 2.1 Hz, H-12), 7.85 (*d*, *J* = 2.1 Hz, H-14); EI-MS (70 eV) *m/z* (rel. int.): 286 $[M^+]$ (100), 271 (59), 253 (49), 211 (45), 201 (86), 185 (16), 159 (32).

4-*Hydroperoxy*-19-*norabieta*-8,11,13-*trien*-7-*one* (**9**). An oil, $[\alpha]_D^{25}$ + 70.6° ($CHCl_3$; *c* 0.17); IR ν_{max}^{Neat} cm^{-1}: 3353, 1659. ^1H NMR ($CDCl_3$): δ1.22 (*d*, *J* = 6.9 Hz, H-

16, 17), 1.29 (*s*, H-20), 1.32 (*s*, H-18), 2.08 (*dd*, J = 12.3, 5.7 Hz, H-5), 2.84 (*dd*, J = 18.2, 12.3 Hz, H-6), 2.87 (*dd*, J = 18.2, 5.7 Hz, H-6), 2.90 (*sept*, J = 6.9 Hz, H-15), 7.27 (*d*, J = 8.2 Hz, H-11), 7.37 (*dd*, J = 8.2, 1.9 Hz, H-12), 7.84 (*d*, J = 1.9 Hz, H-14). EI-MS (70 eV) m/z (rel. int.): 302 $[M]^+$ (8), 286 (26), 271 (49), 253 (84), 211 (63), 201 (70), 185 (42), 43 (100). Exact mass $[M]^+$ for $C_{19}H_{26}O_3$ requires 302.1883. Found 302.1872.

7α-Hydroxy-19-norabieta-8,11,13-triene-4-hydroperoxide (**10**). An oil, $[\alpha]_D^{25}$ + 16.0° ($CHCl_3$; *c*0.75). IR ν_{max}^{Neat} cm^{-1}: 3363. ^1H NMR ($CDCl_3$): δ1.20 (*s*, H-20), 1.21 (*d*, J = 6.9 Hz, H-16, 17), 1.23 (*m*, H-3α), 1.40 (*ddd*, J = 14.0, 14.0, 3.6 Hz, H-1α), 1.37 (*s*, H-18), 1.94 (*dd*, J = 12.0, 3.1 Hz, H-5), 2.10 (*ddd*, J = 13.6, 12.0, 3.8 Hz, H-6β), 2.14 (*m*, H-6α), 2.20 (*m*, H-3β), 2.23 (*m*, H-1β), 2.85 (*sept*, J = 6.9 Hz, H-15), 4.81 (*dd*, J = 3.8, 3.8 Hz, H-7), 7.10 (*dd*, J = 8.1, 2.0 Hz, H-12), 7.14 (*d*, J = 2.0 Hz, H-14), 7.19 (*d*, J = 8.1 Hz, H-11). EI-MS (70 eV) m/z (rel. int.): 304 $[M]^+$ (40), 287 (9), 271 (7), 269 (8), 254 (27), 253 (100), 211 (45), 187 (26). Exact mass $[M]^+$ for $C_{19}H_{28}O_3$ requires 304.2039. Found 304.2050.

19-Norabieta-7,13-dien-4-ol (**11**). An oil, $[\alpha]_D^{25}$ + 62.1° ($CHCl_3$; *c*0.1). IR ν_{max}^{Neat} cm^{-1}: 3484 (OH). ^1H NMR ($CDCl_3$): δ0.92 (*s*, H-20), 0.99 (*d*, J = 6.8 Hz, H-16), 1.00 (*d*, J = 6.8 Hz, H-17), 1.14 (*s*, H-18), 2.21 (*sept*, J = 6.8 Hz, H-15), 5.43 (*br s*, H-7), 5.77 (*s*, H-14). EI-MS (70 eV) m/z (rel. int.): 274 $[M]^+$ (34), 256 (83), 241 (100), 213 (36), 199 (14), 185 (86), 157 (11), 143 (17). Exact mass $[M]^+$ for $C_{19}H_{30}O$ requires 274.2298. Found 274.2297.

13β,14β-Epoxy-4-hydroxy-19-norabiet-7-en-6-one (**12**). An oil, $[\alpha]_D^{25}$ − 57.1° (MeOH; *c*0.14). IR ν_{max}^{Neat} cm^{-1}: 3525 (−OH). 1661 (conjugated C=O): UV λ_{max}^{MeOH} nm (ε): 246 (10810). ^1H NMR ($CDCl_3$): δ0.96 (*d*, J = 7.0 Hz, H-16), 0.99 (*s*, H-20), 1.01 (*d*, J = 7.0 Hz, H-17), 1.32 (*s*, H-18), 1.66 (*sept*, J = 7.0 Hz, H-15), 2.30 (*s*, H-5), 3.22 (*s*, H-14), 3.40 (*d*, J = 2.5 Hz, −OH), 6.11 (*d*, J = 3.0 Hz, H-7). EI-MS (70 eV) m/z (rel. int.): 304 $[M]^+$ (77), 290 (21), 289 (100), 286 (19), 271 (20), 243 (29), 219 (22), 147 (30). Exact mass $[M]^+$ for $C_{19}H_{28}O_3$ requires 304.2037. Found 304.2045.

Autoxidation of abieta-8,11,13-trien-19-al. The title compound (24 mg) was dissolved in benzene (15 ml) and stirred at 18° in the air for 5 days. Solvent was removed, the residue was taken up with $CHCl_3$ and the components were separated by HPLC with elution of hexane–EtOAc (5:2) to give 4-epidehydroabietic acid (12 mg), norditerpenes **2** (3 mg), **3** (3 mg), **8** (2 mg) and **4** (2 mg).

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