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# NORDITERPENES FROM *JUNIPERUS CHINENSIS*

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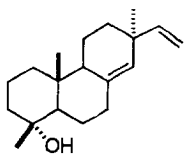
**Key Word Index**—*Juniperus chinensis*; Cupressaceae; norditerpenes; norabietane-type; norpimarane-type.

**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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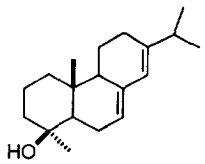


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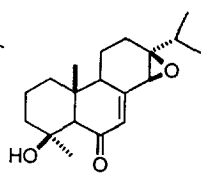


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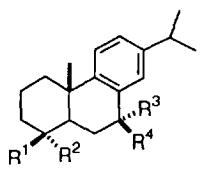


| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| **2** | $CH_3$ | OH | H | H |
| **3** | OH | $CH_3$ | H | H |
| **4** | OCHO | $CH_3$ | H | H |
| **5** | $CH_3$ | OOH | H | H |
| **6** | OOH | $CH_3$ | H | H |
| **7** | $CH_3$ | OH | =O | |
| **8** | OH | $CH_3$ | =O | |
| **9** | OOH | $CH_3$ | =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

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Table 1. $^{13}C$ NMR spectral data of compounds **1**–**12** ($CDCl_3$ solution, $\delta$ 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 $\delta$160.5.
[a]The assignments can be interchanged.

1713 $cm^{-1}$, a proton signal at $\delta$8.10 (*s*) and a carbon signal at $\delta$160.5 (*d*) were attributable to the moiety of formic ester. The C-4 signal appearing at $\delta$84.7 was in agreement with the structure. The Me-10 in **4** occurred at a rather low field $\delta$1.25 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** ($\delta$84.9) was, however, larger than that in **2** ($\delta$72.5). 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 4$\beta$-hydroperoxy group [12], the Me-10 of **6** appeared at a lower field $\delta$1.25 than the corresponding signal of **5** (at $\delta$1.16). The axial Me-4 of **5** occurred at $\delta$1.21, whereas the equatorial Me-4 of **6** occurred at lower field ($\delta$1.34).

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 $\delta$7.26 (*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 $\delta$71.6 was attributable to C-4 having a hydroxyl substituent. Compound **8** exhibited an IR absorption at 1666 $cm^{-1}$ and three signals at $\delta$7.27 (*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 4$\alpha$-hydroxyl group displayed Me-10 at a higher field ($\delta$1.26 vs $\delta$1.33) and C-5 at a lower field ($\delta$51.0 vs $\delta$48.1) in the NMR spectra. The stereochemistry of **8** was confirmed by NOESY experiments. Thus, irradiation of Me-10 (at $\delta$1.33) caused a NOE on H-6$\beta$ (at $\delta$2.76) and irradiation of Me-4 (at $\delta$1.22) caused NOE effects of H-6$\alpha$ (at $\delta$2.85) and H-5 (at $\delta$1.91). 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 $\delta$7.84. Irradiation of Me-4 (at $\delta$1.32) caused 14% NOE effect on H-5 (at $\delta$2.08), 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 7$\alpha$-hydroxy-19-norabieta-8,11,13-triene-4-hydroperoxide by spectral analyses. The equatorial H-7$\beta$ had small coupling constants (3.8 and 3.8 Hz) with two vicinal protons. The signals at $\delta_H$1.37 and $\delta_C$84.0 were assigned to Me-4 and C-4, respectively, by an HMBC experiment. Irradiation of Me-4 caused 11% NOE on H-5 (at $\delta$1.94), conforming with the $\alpha$-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

$\delta$71.6 indicated the presence of a hydroxyl group. Four carbon signals at $\delta$120.8, 122.5, 135.7 and 145.3 as well as two vinyl protons at $\delta$5.43 (*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 $\delta$30.6 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 13$\beta$,14$\beta$-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 $\delta$3.22 as a singlet. The C-7 (at $\delta$131.4) and C-15 (at $\delta$33.4) signals were correlated with H-14 by an HMBC experiment. Irradiation of H-7 (at $\delta$6.11) caused an NOE on H-14, supporting the assigned stereochemistry. Irradiation of H-5 (at $\delta$2.30) also caused enhancements of Me-4 (at $\delta$1.33) and H-9 (at $\delta$2.10).

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 4$\beta$-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 $\times$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 $\mu$m) column (25 cm $\times$ 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 $\nu_{max}^{Neat}$ $cm^{-1}$: 1713 (C=O). $^1H$ NMR ($CDCl_3$): $\delta$1.21 (*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 $\nu_{max}^{Neat}$ $cm^{-1}$: 3377 (OOH). $^1H$ NMR ($CDCl_3$): $\delta$1.16 (*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 $\nu_{max}^{Neat}$ $cm^{-1}$: 3391 (–OOH). $^1H$ NMR ($CDCl_3$): $\delta$1.20 (*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 $\nu_{max}^{Neat}$ $cm^{-1}$: 3467 (OH), 1666 (C=O). $^1H$ NMR ($CHCl_3$): $\delta$1.17 (*s*, H-19), 1.21 (*d*, *J* = 6.9 Hz, H-16, 17), 1.26 (*s*, H-20), 1.43 (*m*, H-3), 1.54 (*m*, H-1$\alpha$), 1.6–1.8 (H-2), 1.88 (*m*, H-3$\beta$), 2.10 (*dd*, *J* = 14.2, 3.5 Hz, H-5), 2.27 (*br d*, *J* = 12.7 Hz, H-1$\beta$), 2.58 (*dd*, *J* = 17.9, 14.2 Hz, H-6$\beta$), 2.89 (*sept*, *J* = 6.9 Hz, H-15), 2.96 (*dd*, *J* = 17.9, 3.5 Hz, H-6$\alpha$), 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 $\nu_{max}^{Neat}$ $cm^{-1}$: 3467 (OH), 1659 (C=O). $^1H$ NMR ($CHCl_3$): $\delta$1.22 (*s*, H-18), 1.23 (*d*, *J* = 6.8 Hz, H-16, 17), 1.33 (*s*, H-20), 1.44 (*ddd*, *J* = 14.0, 14.0, 3.8 Hz, H-3$\alpha$), 1.54 (*ddd*, *J* = 13.0, 13.0, 3.7 Hz, H-1$\alpha$), 1.7–1.8 (H-2), 1.91 (*dd*, *J* = 13.2, 4.7 Hz, H-5), 2.01 (*m*, H-3$\beta$), 2.32 (*br d*, *J* = 13.0, H-2$\beta$), 2.76 (*dd*, *J* = 18.3, 13.2 Hz, H-6$\beta$), 2.85 (*dd*, *J* = 18.3, 4.7 Hz, H-6$\alpha$), 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 $\nu_{max}^{Neat}$ $cm^{-1}$: 3353, 1659. $^1H$ NMR ($CDCl_3$): $\delta$1.22 (*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 $\nu_{max}^{Neat}$ $cm^{-1}$: 3363. $^1H$ NMR ($CDCl_3$): $\delta$1.20 (*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 $\nu_{max}^{Neat}$ $cm^{-1}$: 3484 (OH). $^1H$ NMR ($CDCl_3$): $\delta$0.92 (*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 $\nu_{max}^{Neat}$ $cm^{-1}$: 3525 (−OH). 1661 (conjugated C=O): UV $\lambda_{max}^{MeOH}$ nm (ε): 246 (10810). $^1H$ NMR ($CDCl_3$): $\delta$0.96 (*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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