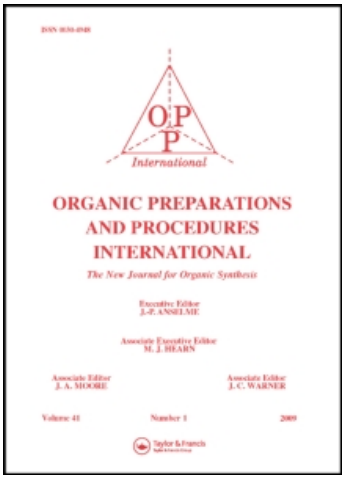

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SELENIUM OXIDE OXIDATION OF ABIETA-7,13-DIENES IN METHANOL

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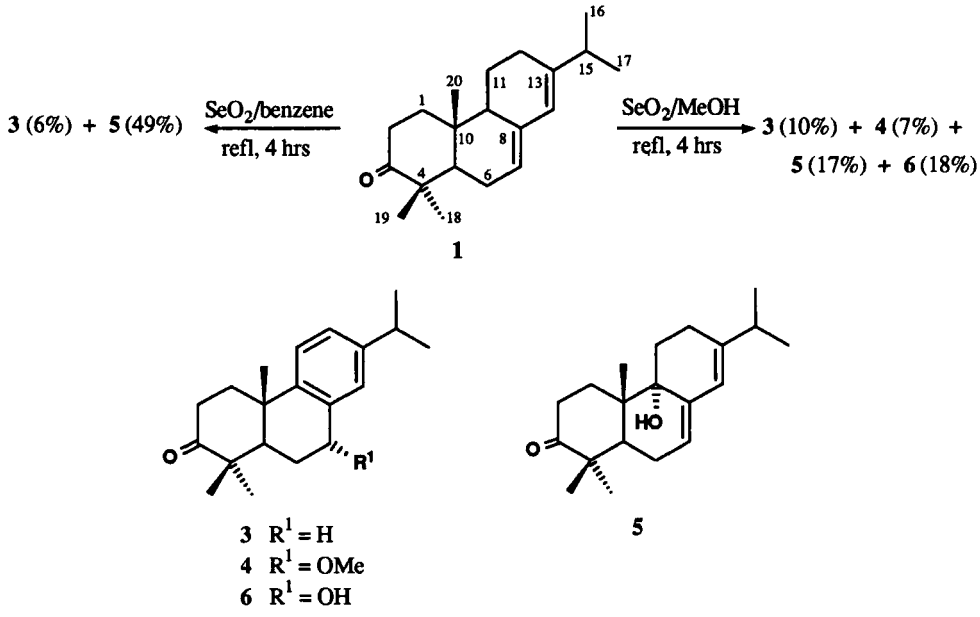
In our phytochemical studies on the composition of several species of *Juniperus* (Family Cupressaceae) and, in particular, of *J. phoenicea*, we have found that the abietane derivatives were the major components of the extracts.[1,2] The existence among these of substances containing carbonyl, carboxyl, hydroxyl and/or methoxy groups on several positions of the abietanic skeleton coupled with our interest in confirming the constitution and stereochemistry of some minor products present in the extract, prompted us to synthesize them through the oxidation of the major compounds with selenium dioxide.

Selenium dioxide generally introduces hydroxyl or carbonyl functions in allylic positions or α to carbonyl groups, but it is also able to produce dehydrogenations and to aromatize suitable substrates.[3] An example of the usefulness of this process has been published previously with a description of the oxidation of methyl abietate and abietic acid in several solvents and under different conditions.[4-6] Furthermore, with suitably functionalized isolated diene systems, SeO_2 can incorporate atoms of selenium into the molecule thereby generating different types of cyclic selenides.[7] The present work describes the oxidation of abieta-7,13-dien-3-one (**1**) and of methyl abietate (**2**) under hitherto undescribed conditions using methanol as solvent. The results obtained are compared with those achieved in benzene for both substrates.

The oxidation of abieta-7,13-dien-3-one (**1**) with an equimolar amount of SeO_2 in MeOH under reflux conditions for 4 hrs attained 89% conversion. It was possible to isolate four substances (**3-6**). Compound **3** was identified as abieta-8,11,13-trien-3-one by characterization of the aromatic ring through its IR, UV ^1H and ^{13}C NMR spectra and by comparison with an authentic natural sample isolated from *Juniperus sabina*.[8] Compounds **4** and **6** were also aromatic; they differed from abietatrienone **3** in the presence of an additional methoxyl or hydroxyl function, respectively. Thus, the ^1H NMR spectrum of compound **4** displayed signals of a methoxy group (3.48 ppm) and of the corresponding methine (4.31 ppm, *dd*, $J_1 = 3.7$, $J_2 = 1.8$ Hz). Accordingly, it was assigned the structure of 7α-methoxyabieta-8,11,13-trien-3-one (**4**) on the basis of the chemical shifts and couplings of the aforementioned signals. Compound **6** lacked a methoxy group but possessed a free hydroxyl function

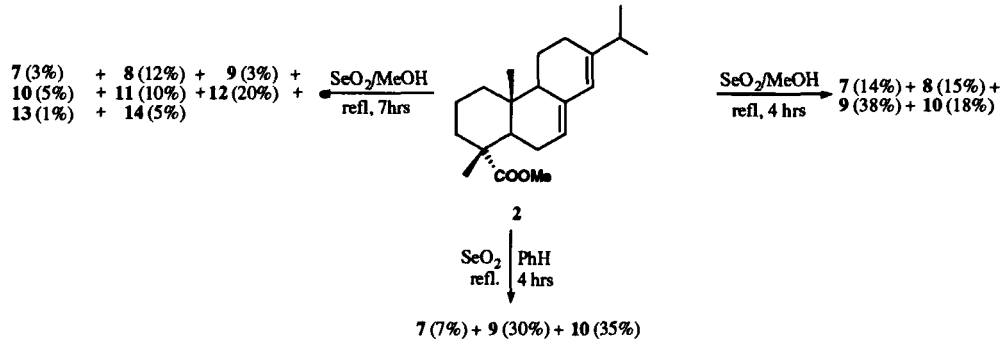
in the same position, characterized by methine signal at 4.88 ppm (*t*, J = 2.7 Hz) and 68.3 ppm in the ^1H and ^{13}C NMR spectra, respectively, and by the IR spectrum (3400 cm^{-1}). Compound **5** displayed

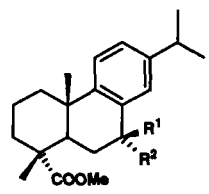


the absorptions corresponding to the starting diene system. The presence of an alcohol band in the IR spectrum (3400 cm^{-1}) and that of a signal for a non-protonated oxygenated carbon atom at 73.2 ppm, together with considerations on the shieldings of the signals assignable to C-1, C-5 and C-12 and the deshieldings on C-8, C-10 and C-11, allowed us to establish the structure of 9-hydroxyabieta-7,13-dien-3-one (**5**) for this substance. Oxidation of compound **1**, with an equimolar amount of SeO_2 in benzene for the same time under reflux led to results in consonant with those reported by Suryawanshi *et al.* for methyl abietate. We obtained abietatrienone **3** and the hydroxyketone **5**, with a conversion rate of 78.5%.

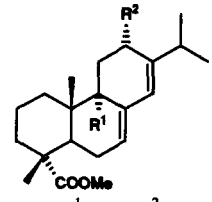
Oxidation of methyl abietate (**2**), in refluxing methanol for 4 hrs proceeded with an 81% conversion. Substances **7-10** were isolated. Compound **7** was identified as methyl dehydroabietate by comparison with an authentic sample isolated from *Juniperus phoenicea*.[9] Substances **8** and **10** were also aromatic and their structures were assigned following a similar line of reasoning to that used, respectively, for the above compounds **4** and **6**. However, whereas **8** has a methoxy group in the 7α position, as may be gathered from the methine signal, the OH group of substance **10** must have the β configuration since its geminal hydrogen atom resonates at δ 4.88 ppm (*t*, J = 8.7 Hz). Substance **9** was identified by comparison of its spectroscopic properties with those reported by Suryawanshi *et al.*[5]

The free hydroxy acid corresponding to **10** has been described previously as a natural constituent of *Cedrus deodara* [10] and other species of conifers, [11] while the 7α-hydroxy acids of abietatrienes are usually auto-oxidation products.

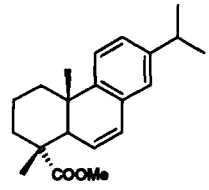




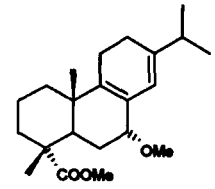
7 $R^1 = R^2 = H$
8 $R^1 = H, R^2 = OMe$
10 $R^1 = OH, R^2 = H$
12 $R^1 = OMe, R^2 = H$



9 $R^1 = OH, R^2 = H$
13 $R^1 = H, R^2 = OMe$



11



14

When the reaction time of SeO_2/MeOH on methyl abietate was lengthened to seven hours, the conversion increased to 88%. Apart from compounds **7-10**, other substances were also found such as **11-14**. The spectra of substance **11**, compared with those of **7**, disclosed the existence of an additional unsaturation on positions 6-7. Thus, its ^1H NMR spectrum showed absorptions at 5.72 (*dd*, $J_1 = 9.6$, $J_2 = 2.7$) and 6.53 ppm ($J_1 = 9.6$, $J_2 = 3.5$), respectively assignable to H_6 and H_7; its ^{13}C-NMR spectrum showed the presence of two olefinic methines at 121.7 and 129.9 ppm, confirming this proposal. Compound **12** proved to be the 7β-epimer of **8**, as was deduced from the chemical displacement and the couplings of H_7 (4.54 ppm, *t*, J = 8.5) and from comparison of its properties with those described for the free hydroxyacid isolated from conifers.[10,11] Compound **13** showed the characteristic signals of the 7,13-abietadiene system in its ^1H NMR spectrum, together with the presence of an additional methoxy group on a secondary allylic position, which must correspond to C-12, because the H_7 couplings are not affected compared with the starting products. Regarding its spatial arrangement, the methoxy group must have a 12α-axial configuration owing to the low magnitude of the couplings exhibited by its geminal proton (3.77 ppm, *t*, J = 2.8 Hz).[12,13]

TABLE 1. ^{1}H-NMR Data for Representative Abietanes (δ ppm)

H	3	4	5	6
7		4.31 *dd* (3.7; 1.8)	5.56 *sa*	
11	7.17 *d* (8.1)	7.18 *sa*		7.26 *sa*
12	7.01 *d* (8.1)	7.16 *d* (1.9)		7.20 *d* (2.0)
14	6.91 *s*	7.11 *sa*	5.76 *s*	7.18 *sa*
15	2.88 *m*	2.87 *m*	2.75 *m*	2.90 *sept* (7.0)
16	1.22 *d* (7.0)	1.24 *d* (6.8)	1.04 *d* (7,3)	1.21 *d* (7.0)
17	1.22 *d* (7.0)	1.24 *d* (6.8)	1.04 *d* (7,3)	1.21 *d* (7.0)
18	1.16 *s*	1.18 *s*	1.09 *s*	1.22 *s*
19	1.29 *s*	1.26 *s*	1.15 *s*	1.26 *s*
20	1.13 *s*	1.14 *s*	1.06 *s*	1.13 *s*
-OMe		3.48 *s*		

H	8	10	11	12
6			5.72 *dd* (9.6; 2.7)	
7	4.24 *sa*	4.84 *t* (8.7)	6.53 *dd* (9.5; 3.1)	4.54 *t* (8.5)
11	7.15 *m*	7.15 *d* (7.5)	7.08 *sa*	7.15 *d* (8.1)
12	7.15 *m*	7.10 *dd* (7.5, 1.3)	6.91 *sa*	7.07 *dd* (8.1; 1.9)
14	7.15 *m*	7.38 *d* (1.3)	7.07 *s*	7.29 *d* (1.8)
15	2.85 *sept* (6.9)	2.85 *sept* (6.9)	2.84 *sept* (6.8)	2.82 *sept* (6.9)
16	1.23 *d* (6.9)	1.23 *d* (6.9)	1.23 *d* (6.8)	1.23 *d* (7.1)
17	1.23 *d* (6.9)	1.23 *d* (6.9)	1.23 *d* (6.8)	1.23 *d* (7.1)
19	1.28 *s*	1.27 *s*	1.39 *s*	1.30 *s*
20	1.16 *s*	1.25 *s*	1.07 *s*	1.25 *s*
-COOMe	3.67 *s*	3.65 *s*	3.63 *s*	3.67 *s*
-OMe	3.39 *s*			3.42 *s*

H	13	14
7	5.49 *m*	3.48 *sa*
12	3.77 *t* (2.8)	
14	5.85 *sa*	5.59 *s*
15	2.39 *m*	2.30 *m*
16	1.03 *d* (6.8)	1.04 *d* (6.8)
17	1.08 *d* (6.8)	1.04 *d* (6.8)
19	1.24 *s*	1.21 *s*
20	0.81 *s*	1.00 *s*
-COOMe	3.62 *s*	3.67 *s*
-OMe	3.35 *s*	3.30 *s*

Finally, compound **14** was assigned the structure of methyl 7α-methoxypalustrate, because in its ^{13}C and ^{1}H spectra it displayed signals corresponding to three non-protonated olefinic carbon atoms and another methine type signal,[14] apart from the fact that the proton geminal to the methoxy group resonated as a broad singlet similar to that of compound **8.**

The oxidation of methyl abietate with SeO_2/benzene under reflux was yielded substances **7** and **9** [5] in addition to **10** as the major component.

In the light of these results, and comparing them with those found in reference[5], the use of methanol as a solvent in oxidations with SeO_2 can be said to increase the number and type of functionalized products since, apart from obtaining methoxy-derivatives, substitutions on C-12, allylic isomer-

izations that lead to 8,13-abietadiene derivatives, and dehydrogenations in general that generate Δ^6 unsaturation were all noted. All of these are transformations hitherto unobserved in a number of solvents, assayed previously[5] and permit the synthesis of certain otherwise inaccessible natural products.

TABLE 2. ^{13}C NMR Data for Representative Abietanes. (δ ppm)

C	3	5	6	8	10	11	12	14
1	37.6	30.7	37.3	37.8	38.1	35.8	38.1	36.0
2	34.7	34.5	34.6	18.6	18.5	18.5	18.5	18.4
3	217.2	216.7	216.6	36.1	36.6	35.7	36.7	34.9
4	47.4	47.2	46.9	47.5	47.4	46.5	47.5	47.5
5	50.8	47.2	44.1	40.1	43.6	46.8	43.3	41.1
6	20.3	24.2	29.3	25.1	32.9	121.7	27.6	25.6
7	30.9	120.4	68.3	77.0	70.7	129.9	78.7	76.6
8	134.6	136.3	135.9	134.1	137.8	132.7	135.3	125.7
9	146.2	73.2	147.2	146.9	147.0	146.4	147.3	142.2
10	37.1	39.6	37.3	37.5	37.7	37.3	37.4	37.9
11	125.3	27.0	127.1	126.5	125.4	125.8	125.7	22.5
12	124.3	23.2	125.5	124.0	124.1	124.8	123.7	24.8
13	144.9	145.0	145.0	146.1	146.6	145.2	146.3	143.7
14	126.6	124.4	127.8	128.6	125.8	128.4	126.0	119.1
15	33.5	34.9	33.6	33.5	33.7	33.6	33.7	34.4
16	23.9	21.5	23.8	23.8	23.9	24.0	23.9	21.2
17	23.9	22.2	23.8	24.0	24.1	24.0	24.1	21.2
18	26.9	25.7	26.7	178.6	178.7	178.5	178.7	178.7
19	21.1	21.0	21.1	16,7	16.6	18.0	16.6	16.7
20	24.6	16.4	23.9	24.3	25.5	20.9	25.3	19.1
-COOMe				51.8	52.0	52.0	51.9	51.8
-OMe				56.1			55.2	56.3

EXPERIMENTAL SECTION

Melting points are uncorrected. Optical rotations (Perkin-Elmer 241 polarimeter) and UV spectra (Hitachi 100-60 spectrophotometer), (λ_{max} nm, ε are given) were determined in $CHCl_3$ and ethanol respectively. IR spectra were obtained on films (υ cm^{-1}) on a Beckmann (Acculab VIII) spectrophotometer. Low resolution EI Mass spectra (70 ev) were obtained on a Hewlett-Packard 5971 mass selective detector associated with a Hewlett-Packard 5890 gas chromatograph. ^1H NMR (200.13 MHz) and ^{13}C NMR (50.3 MHz) was carried out with TMS as internal standard, (δ ppm), (J Hz) were recorded in $CDCl_3$, on a Bruker WP 200 SY. Flash chromatography was performed on silica gel (Merck No 9385). Column chromatography over silica gel (Merck 60, 0.0063-0.2 mm) or silica gel-20% $AgNO_3$ and elution with hexane-ethyl acetate (Hex/EtOAc) mixtures. Analysis was carried out on a Perkin-Elmer 2400 CHN, Elemental Analyzer.

Selenium Dioxide Oxidation of Abieta-7,13-dien-3-one (1). ***Method A.***- A solution of SeO_2 (134 mg, 1.2 mmol) in methanol (10 mL) was added slowly to abieta-7,13-dien-3-one (1) (345 mg, 1.2 mmol) in methanol (10 mL), with stirring at 45 °. After 4 hrs at reflux under N_2, the mixture was filtered and the solvent distilled off. The residue was dissolved in ether and washed with satured aqueous Na_2CO_3 and water, dried over anhydrous Na_2SO_4 and evaporated to yield an oily crude product which was chromatographed over 20% $AgNO_3$-SiO_2 to give the following fractions:

Abieta-8,11,13-trien-3-one **3** (32 mg): eluted with hexane/EtOAc (95:5). $[\alpha]_D^{22}$ = +24.4° (*c* 0.4); UV: 241 (1400), 249 (1200), 267 (700); IR bands ($CHCl_3$): 3040, 1700, 1610, 1500, 885; MS (*m/z*): 284 (61) $[M]^+$, 269 (100) $[M\text{-}CH_3]^+$, 227 (8) $[M\text{-}(C_2H_2O\text{+}CH_3)]^+$ 185 (3), 171 (17), 159 (11), 143 (17); ^1H NMR (see Table 1); ^{13}C NMR (see Table 2).

7α-methoxyabieta-8,11,13-trien-3-one **4** (21 mg): eluted with hexane/EtOAc (95:5). $[\alpha]_D^{22}$ = +20.3° (*c* 0.7); UV: 299 (3200), 325 (2900); IR: 1720, 1600, 1510, 1100, 900, 850; MS (*m/z*): 314 (90) $[M]^+$, 299 (3) $[M\text{-}CH_3]^+$, 283 (32) $[M\text{-}CH_3O]^+$, 271 (50) $[M\text{-}(C_3H_7)]^+$, 267 (30) $[M\text{-}(CH_3OH\text{+}CH_3)]^+$, 225 (99) $[M\text{-}(CH_3OH\text{+}CH_3\text{+}C_2H_2O)]^+$, 211 (17), 197 (100), 183 (62), 176 (63), 155 (28), 141 (45), 133 (30), 128 (27); ^1H NMR : (see Table 1).

Anal. Calcd.for $C_{21}H_{30}O_2$: C, 80.20; H, 9.61; O, 10.17. Found: C, 80.32; H, 9.53

9-hydroxyabieta-7,13-dien-3-one **5** (54 mg): eluted with hexane/EtOAc (9:1). $[\alpha]_D^{22}$ =-65.7° (c 1.0); UV: 233 (7800), 241 (8000), 256 (6400); IR: 3460, 1710, 1630, 1125, 850; MS (m/z): 302 (10) $[M]^+$, 284 (21) $[M\text{-}H_2O]^+$, 269 (18) $[M\text{-}(H_2O\text{+}CH_3)]^+$, 241 (30) $[M\text{-}(H_2O\text{+}C_3H_7)]^+$, 227 (17) $[M\text{-}(H_2O\text{+}CH_3\text{+}C_2H_2O)]^+$, 213 (6), 199 (9), 185 (11), 164 (26), 146 (100); ^1H NMR (see Table 1); ^{13}C NMR (see Table 2).

Anal. Calcd. for $C_{20}H_{30}O_2$: C, 79.42; H, 9.99. Found: C, 79.60; H, 9.75

7α-hydroxyabieta-8,11,13-trien-3-one **6** (57 mg): eluted with EtOAc. $[\alpha]_D^{22}$ = +29.7° (c 0.9); UV: 214 (3700), 241 (510), 306 (140); IR: 3400, 1700, 1630, 1500, 1110, 890, 820; MS (m/z): 300 (100) $[M]^+$, 282 (5) $[M\text{-}H_2O]^+$, 267 (34) $[M\text{-}(H_2O\text{+}CH_3)]^+$, 267 (34) $[M\text{-}(H_2O\text{+}CH_3)]^+$, 257 (28) $[M\text{-}C_3H_7]^+$, 225 (95) $[M\text{-}(H_2O\text{+}CH_3\text{+}C_2H_2O)]^+$, 211(15), 197 (35), 183 (51), 162 (64), 155 (17), 141 (34), 125 (18), 115 (5); ^1H NMR (see Table 1); ^{13}C NMR (see Table 2).

Anal. Calcd. for $C_{20}H_{28}O_2$: C, 79.95; H, 9.39. Found: C, 79.98; H, 9.30

Method B.- To a solution of abieta-7,13-dien-3-one **1** (255 mg, 0.9 mmol) in benzene (25 mL), 99 mg (0.9 mmol) of SeO_2 was added. After 4 hrs at reflux (80°), and work up as in method A afforded 256 mg of crude product, which was flash chromatographed with Hexane/EtOAc mixtures to yield in order of elution: 15 mg (6%) of compound **3** and 126 mg of compound **5**.

Selenium Dioxide Oxidation of Methyl Abietate (6). Method C.- A solution of SeO_2 (230 mg, 2.1 mmol) in MeOH (20mL) was added to methyl abietate **6** (654 mg, 2.1 mmol) in methanol (20 mL). Following the procedure described in method A and after 4 hrs. at reflux (65-75°), this afforded 801 mg of crude product. This product was repeatedly chromatographed over silica gel to yield *methyl dehydroabietate* **7** (92 mg) (eluted with hexane/EtOAc (98:2)).

Methyl 7α-methoxydehydroabietate **8** (98 mg): eluted with Hexane/EtOAc (95:5), mp. 80-82° (MeOH); $[\alpha]_D^{22}$ = +9.5° (c 2.1); UV: 206 (8000), 220 (6100), 241 (600), 250 (500), 268 (250); IR bands ($CHCl_3$): 3480, 1720, 1610, 1500, 900, 830; MS (m/z): 344 (8) $[M]^+$, 313 (11) $[M\text{-}CH_3O]^+$, 312 (18) $[M\text{-}CH_3OH]^+$, 301 (13) $[M\text{-}C_3H_7]^+$, 253 (21) $[M\text{-}(CH_3OH\text{+}COOCH_3)]^+$, 237 (100) $[M\text{-}(CH_3OH\text{+}HCOOCH_3\text{+}CH_3)]^+$, 211 (5), 197 (11), 195 (18), 176 (22), 155 (11), 141 (10), 133 (11); ^1H NMR (see Table 1); ^{13}C NMR (see Table 2).

Anal. Calcd. for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.81; H, 9.27

Elution with hexane/EtOAc (9:1) furnished **9** (252 mg) and with hexane/EtOAc (8:2) furnished *methyl 7β-hydroxydehydroabietate* **10** (120 mg): $[\alpha]_D^{22}$ = +23.4° (c 0.5); UV: 212 (7100); IR bands ($CHCl_3$): 3600, 1725, 1610, 1500, 1075, 900, 830; MS (m/z): 312 (88) $[M-H_2O]^+$, 297 (8) $[M-(H_2O+CH_3)]^+$, 253 (10) $[M-(H_2O+COOCH_3)]^+$, 237 (100) $[M-(H_2O+HCOOCH_3+CH_3)]^+$, 209 (8), 197 (46), 195 (24), 179 (11), 167 (14), 165 (15), 155 (13), 1421 (16), 128 (6); ^1H NMR (see Table 1); ^{13}C NMR (see Table 2).

Anal. Calcd. for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.50; H, 9.07

Method D.-A solution of SeO_2 (290 mg, 2.6 mmol) in MeOH (25 mL) was added to a solution of methyl abietate **6** (835 mg, 2.6 mmol) in methanol (25 mL), increasing the refluxing time until 7 hrs, the usual work up afforded 807 mg of reaction product, which was chromatographed over silica gel to yield: with mixtures of hexane/EtOAc (95:5): **7** (27 mg) and *methyl abieta-6, 8, 11, 13-tetraen-18-oate* **11** (82 mg). $[\alpha]_D^{22}$ =-31.2° (c 1.1); UV: 220 (12500); IR: 1730, 1610, 1570, 895, 830, 740, 690; MS (m/z): 312 (70) $[M]^+$, 297 (7) $[M-CH_3]^+$, 253 (8) $[M-COOCH_3]^+$, 237 (100) $[M-(CH_3+HCOOCH_3)]^+$, 209 (8), 197 (45), 169 (12), 167 (16), 165 (17), 155 (15), 153 (12), 141 (13), 128 (7); ^1H NMR (see Table 1); ^{13}C NMR (see Table 2).

Anal. Calcd. for $C_{21}H_{28}O_2$: C, 80.72; H, 9.03. Found: C, 80.81; H, 8.87

Elution with hexane/EtOAc (9:1) furnished 185 mg of mixture **12** + **13**, which was resolved by preparative thin-layer chromatography with the same eluent. *Methyl 7β-methoxydehydroabietate* **12**.(165 mg). $[\alpha]_D^{22}$ = +34.6° (c 0.8); UV: 267 (500), 276 (400); IR: 1725, 1610, 1500, 895, 850, 820; MS (m/z): 344 (25)$[M]^+$, 313 (2) $[M-CH_3O]^+$, 312 (3) $[M-CH_3OH]^+$ 301 (24) $[M-C_3H_7]^+$, 269 (8) $[M-(HCOOCH_3+CH_3)]^+$, 253 (12) $[M-(COOCH_3+CH_3OH)]+$, 237 (95) $[M-(HCOOCH_3+CH_3+CH_3OH)]^+$, 209 (5), 195 (19), 176 (100), 155 (4), 133 (32); ^1H NMR (see Table 1); ^{13}C NMR (see table 2).

Anal. Calcd. for $C_{22}H_{32}O_3$: C, 76.70; H, 9.36. Found: C, 76.79; H, 9.12

Methyl 12α-methoxyabietate **13** (5 mg). UV: 235 (12500), 241 (14700), 250 (9800); IR bands ($CHCl_3$): 1720, 1620, 790; MS (*m/z*): 346 (5) $[M]^+$ 303 (100) $[M-C_3H_7]^+$, 287 (2) $[M-COOCH_3]^+$ 255 (3) $[M-(COOCH_3+CH_3OH)]^+$, 243 (5), 211 (5), 197 (2), 173 (3), 146 (27), 131 (12), 121 (35); ^1H NMR (see Table 1).

Elution with hexane/EtOAc (95:5) furnished **8** (95 mg) and with hexane/EtOAc (9:1) furnished *methyl 7α-methoxypalustrate* **14** (43 mg). $[\alpha]_D^{22}$ = +19.9° (c 0.4); UV: 211 (4600), 260 (3100); IR bands ($CHCl_3$): 1720, 1655, 1600, 860, 840; MS (m/z): 346 (14) $[M]^+$, 331 (1) $[M-CH_3]^+$, 314 (18) $[M-CH_3OH]^+$, 299 (4), 287 (1) $[M-COOCH_3]^+$, 255 (71) $[M-(COOCH_3+CH_3OH)]^+$, 239 (100) $[M-(HCOOCH_3+CH_3+CH_3OH)]^+$, 211 (5), 197 (7), 179 (55), 155 (7), 147 (7), 143 (8), 128 (7); ^1H NMR (see Table 1); ^{13}C NMR (see Table 2).

Anal. Calcd. for $C_{22}H_{34}O_3$: C, 76.25; H, 9.89. Found: C, 76.45; H, 9.70

With hexane/EtOAc (9:1) yielded 25 mg of compound **9** and with hexane/EtOAc (8:2) 40 mg of compound **10**.

Method D.- To a solution of methyl abietate **6** (254 mg, 0.80 mmol) in benzene (25 mL), 88.7 mg (0.80 mmol) of SeO_2 was added. After 4 hrs at reflux (80°) and following the procedure described

before afforded 249 mg of crude product that was chromatographed over silica gel-20% $AgNO_3$ with mixtures of hexane/EtOAc of increasing polarity to yield: **7** (16 mg), **9** (75 mg) and **10** (86 mg).

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REFERENCES

1. A. San Feliciano, J. M. Miguel del Corral, M. Gordaliza, M. A. Salinero and B. del Rey, *Fitoterapia*, **63**, 0000 (1992).

2. A. San Feliciano, J. M. Miguel del Corral, M. Gordaliza and M. A.Salinero, *An. Quim.*, **88**, 512 (1992).

3. L. F. Fieser and M. Fieser, "*Reagents of Organic Synthesis*",Vol. 1-15. Wiley Interscience, New York, 1967-1990.

4. J. Escudero, C. Márquez, R. M. Rabanal and S. Valverde, *Tetrahedron*, **39**, 3167 (1983).

5. S. N. Suryawanshi, A. Rani, T. S. Dhami and D. S. Bhakuni, *Synth. Commun.*, **19**, 2927 (1989).

6. N. Rabjohn, "*Organic Reactions*", Selenium Dioxide Oxidation, Vol 5, p. 353, Wiley, London (1949).

7. A. San Feliciano, M. Medarde, J. L. López, J. A. P. Pereira, E. Caballero, and A. Perales, *Tetrahedron*, **45**, 5073 (1989).

8. J. de Pascual-Teresa, A. San Feliciano, J. M. Miguel del Corral and A. F. Barrero, *Phytochemistry*, **22**, 300 (1983).

9. J. de Pascual-Teresa, A. San Feliciano, M. L. Tabernero, J. M. Miguel del Corral, A. F. Barrero and M. Grande, *An. Quim.*, **74**, 459 (1978).(C.A. 89:215595).

10. T. Ohomoto, M. Saito and K. Yamaguchi, *Chem. Pharm. Bull. Japan*, **35**, 2443 (1987). (*C.A.* 107:130925).

11 A.W. Ayer and B. S. Migaj, *Can. J. Bot.*, **67**, 1426 (1989).

12. J. Jakupovic, M. Grenz, F. Bohlmann and G. M. Mungai, *Phytochemistry*, **29**, 1589 (1990).

13. A. F. Barrero, J. F. Sánchez, R. Alvarez-Manzaneda, E. J. M. Muñoz Dorado and A. Haidour, *ibid.*, **30**, 593 (1991).

14 J. de Pascual-Teresa, A. F. Barrero, M. C. Caballero and A. San Feliciano, *An. Quim.*, **74**, 1093 (1978). (*C.A.* 91:74741).

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