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Oxidative Decarboxylation by Hydrogen Peroxide and a Mercury (II) Salt: a Simple Route to *nor*-Derivatives of Acetyloleanolic, Acetylursolic and Dehydroabietic Acids.

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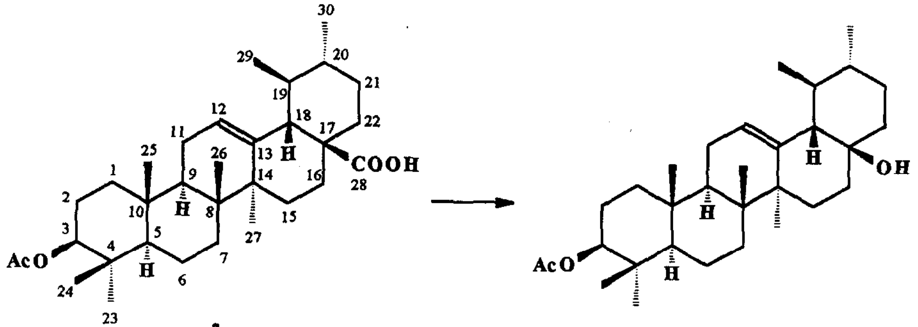
Abstract: Treatment of carboxylic acids with hydrogen peroxide in the presence of a mercury (II) salts results in oxidative decarboxylation and is an effective method for transformation of the carboxylic acids into the corresponding *nor*-derivatives, hydroperoxides and alcohols. Oxidative decarboxylation of acetyloleanolic, acetylursolic and dehydroabietic acids is described.

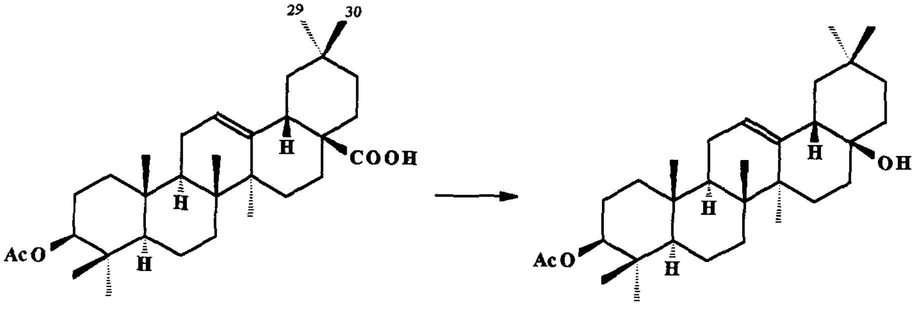
Our attempts to perform chemical modification in the ring "C" of the acetylursolic acid molecule **1** using the mercuration reaction have shown that the 12,13-double bond in this compound is inert towards mercury (II) acetate and trifluoroacetate under normal conditions[1]. However, after the tetrahydrofuran solution of the acid **1** and mercury (II) trifluoroacetate was allowed to stay for a long time, a product of oxidative decarboxylation, the *nor*-derivative **2**, was isolated from the reaction mixture in a low yield. Decarboxylation in general[2] and specifically oxidative decarboxylation[3-6] are important reactions in the chemistry of carboxylic acids. Moreover, some terpene *nor*-derivatives occur in plants, sometimes together with the starting carboxylic acids, and synthesis of such *nor*-derivatives is of interest.

It appeared that oxidative decarboxylation by a mercury salt may be performed preparatively with a good yield, by adding an aqueous solution of a base to a hot solution of carboxylic acid **1** and a mercury (II) salt in a mixture of tetrahydrofuran and 30% hydrogen peroxide. When a reducing agent (sodium borohydride) was used to transfer mercury to metallic state and facilitate isolation of organic products[7], the *nor*-compound **2** was isolated in a yield up to 80%. A similar behaviour has been shown by acetyloleanolic acid (**3**) which gave the corresponding *nor*-compound **4**. The primary product in the reaction performed was shown to be alkyl hydroperoxide, which was isolated in the oxidative decarboxylation of dehydroabietic acid (**5**): without treatment of the reaction mixture with the reducing agent after the decarboxylation, the reaction of acid **5** gave ca. 1:3 mixture of epimeric hydroperoxides **6** and **8**.

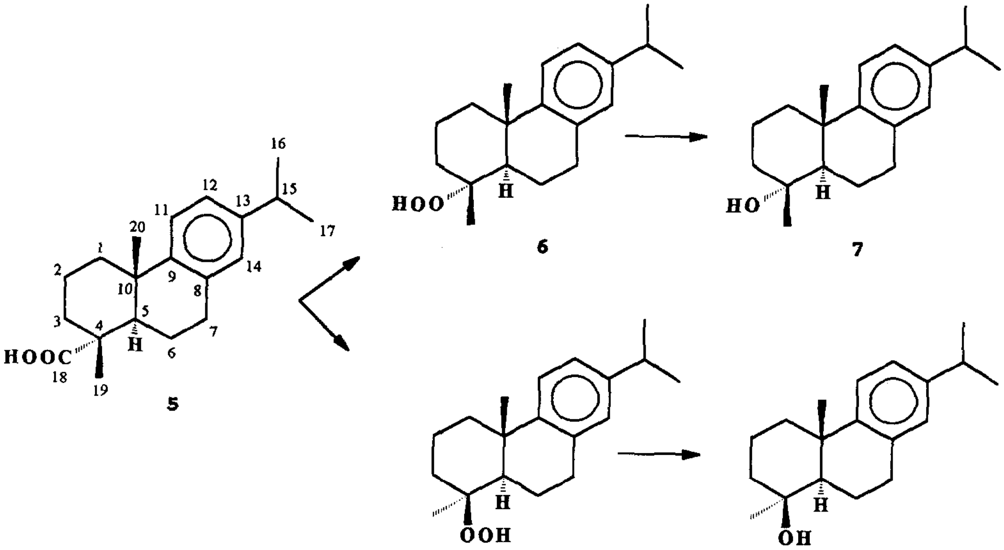
Structures of the decarboxylation products **2** and **4** were determined by NMR spectroscopy. Signal assignments (***Table 1***) were made using previously reported data[8] and 2D heteronuclear ^{13}C-^{1}H chemical shift correlation experiments. Comparison of the NMR parameters of the *nor*-derivatives **2** and **4** with those of the starting acids **1** and **3** shows the β-configuration of C-17 atom in the molecules of the reaction products.



1 **2**



3 **4**



5 **6** **7** **8** **9**

Table 1. **^{1}H and ^{13}C NMR Data for Compounds 1-4^{a,b}.**

	1^c		**2**^{d}		**3**^{e}		**4**^{f}	
i	δC^i	δH^i (*J*, Hz)	δC^i	δH^i (*J*, Hz)	δC^i	δH^i (*J*, Hz)	δC^i	δH^i (*J*, Hz)
1	38.02	[1.02, 1.58]	38.22	[1.07, 1.62]	37.91	[1.01, 1.58]	38.02	[1.03, 1.60]
2	23.31	[1.57] 2H	23.44	[1.61] 2H	23.37	[1.59] 2H	23.41	[1.60] 2H
3	80.68	4.47 *m*	80.75	4.48 *m*	80.60	4.46 *m*	80.79	4.47 *m*
4	37.43	-	37.51	-	37.54	-	37.58	-
5	55.04	[0.77]	55.19	[0.82]	55.14	[0.81]	55.18	[0.83]
6	17.92	[1.29, 1.46]	18.09	[1.39, 1.52]	18.02	[1.48] 2H	18.12	[1.39, 1.52]
7	32.58	[1.26, 1.41]	32.72	[1.38, 1.50]	32.36	[1.25, 1.41]	32.57	[1.36, 1.47]
8	39.23	-	39.51	-	39.13	-	39.51	-
9	47.21	[1.47]	47.42	[1.53]	47.41	[1.54]	47.43	[1.56]
10	36.67	-	36.75	-	36.65	-	36.82	-
11	23.04	1.85 *dd* (8.5, 3.5), 2H	23.44	1.92 *dd* (8.8, 3.7), 2H	23.24	[1.84] 2H	23.50	[1.84, 1.90]
12	125.42	5.20 *dd* (3.5, 3.5)	127.51	5.26 *dd*, J 3.7, 3.7	122.39	5.23 *dd* (3.5, 3.5)	124.13	5.28 *dd* (3.7, 3.7)
13	137.74	-	137.93	-	143.48	-	143.16	-
14	41.59	-	41.74	-	41.38	-	41.41	-
15	27.74	[1.01], 1.82 *ddd* (13.5, 13.0, 4.5)	25.87	[1.02, 2.00]	27.52	[1.03, 1.67]	25.34	[1.01, 1,97]
16	23.75	[1.59], 1.92 *ddd* (13.0, 13.0, 4.0)	28.31	[1.23, 2.00]	22.70	[1.58], 1.94 *ddd* (13.5, 13.5, 4.0)	27.22	[1.16, 2.02]
17	47.69	-	71.94	-	46.40	-	72.01	-
18	52.21	2.12 *d* (10.5), W=4	60.48	[1.55]	40.73	2.79 *dd* (13.5, 4.3), W=5	48.65	2.20 *dd* (14.0, 4.5), W=4
19	38.76	[1.26]	41.43	[1.24]	45.69	[1.12, 1.58]	48.19	[1.18, 1.60]
20	38.59	[0.94]	39.15	[0.95]	30.51	-	30.89	-
21	30.37	[1.25, 1.44]	32.21	[1.15, 1.55]	33.65	[1.17, 1.30]	36.37	[1.27]
22	36.51	[1.59, 1.65]	40.34	[1.51, 1.70]	32.31	[1.52], 1.73 *ddd* (13.5, 13.5, 4.6)	36.71	[1.48, 1.66]
23	27.84	0.81 *s*	27.97	0.85 *s*	27.89	0.83 *s*	27.95	0.85 *s*
24	16.47	0.79 *s*	16.62	0.84 *s*	16.51	0.82 *s*	16.58	0.84 *s*
25	15.30	0.90 *s*	15.42	0.95 *s*	15.23	0.91 *s*	15.25	0.93 *s*
26	16.88	0.70 *s*	17.00	0.97 *s*	17.01	0.71 *s*	16.95	0.93 *s*
27	23.28	1.01 *s*	22.88	1.04 *s*	25.74	1.09 *s*	25.32	1.11 *s*
28	184.14	-	-	-	184.32	-	-	-
29	16.81	0.80 *d* (6.5)	17.20	0.80 *d* (6.5)	32.39	0.87 *s*	32.61	0.88 *s*
30	20.98	0.89 *d* (6.0)^g	23.85	0.90 *d* (6.0)^g	23.44	0.89 *s*	23.85	0.94 *s*

[a] chemical shifts are given in ppm;

[b] ^{1}H chemical shifts put in square brackets were taken from the 2D heteronuclear ^{13}C-^{1}H chemical shift correlation spectra ($^1J_{CH}$ = 125 Hz);

[c] c = 250 mg/ml; acetate: 21.05 *q* and 170.45 *s*; 1.98 *s* 3H.

[d] c = 30 mg/ml; acetate: 21.16 *q* and 170.84 *s*; 2.02 *s* 3H.

[e] c = 50 mg/ml; acetate: 21.14 *q* and 170.92 *s*; 2.01 *s* 3H.

[f] c = 20 mg/ml; acetate: 21.18 *q* and 170.90 *s*; 2.02 *s* 3H.

[g] appreciably distorted doublet.

According to the data obtained, the resonances of C-24 and C-26 atoms have to be re-assigned relatively to the previously published data for acetylursolic (**1**)[9] and acetyloleanolic (**3**)[10] acids. Decarboxylation products **6-9** are well known[11]. NMR parameters of the dehydroabietane derivatives **5-9** are given in ***Tables 2,3***. ^{13}C NMR spectra of the nor-derivatives **6** and **7** have been already studied[12], but signal assignments given in ref.[12] for compounds **6** and **7** (C-6, C-7 and C-20 resonances) are incorrect.

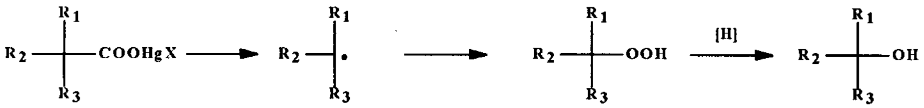
Table 2. **^{13}C NMR Data for Compounds 5-9^a.**

	5^b	6^c	7^d	8^e	9^f
1	37.80	37.55	37.83	38.35	38.02
2	18.42	19.79	20.44	18.22	18.30
3	36.64	35.10	42.51	34.61	40.61
4	47.33	84.77	72.39	83.46	72.05
5	44.46	45.20	52.21	50.42	48.52
6	21.65	17.76	17.85	18.30	17.79
7	29.87	29.80	30.20	30.04	29.24
8	134.56	134.67	134.63	134.40	134.50
9	146.63	146.17	146.23	146.32	146.58
10	36.73	38.12	38.07	37.12	36.99
11	123.98	124.34	124.41	124.06	123.80
12	123.77	123.68	123.77	123.69	123.65
13	145.59	145.48	145.44	145.51	145.39
14	126.79	126.79	126.82	126.71	126.65
15	33.34	33.28	33.30	33.04	33.30
16	23.86	23.80	23.84	23.83	23.84
17	23.86	23.80	23.86	23.85	23.86
18	185.53	-	-	24.33	30.62
19	16.07	18.07	24.41	-	-
20	24.99	24.50	22.72	25.25	24.31

^{a}chemical shifts are given in ppm; ^{b}c = 100 mg/ml; ^{c}c = 270 mg/ml; ^{d}c = 130 mg/ml; ^{e}c = 100 mg/ml; ^{f}c = 80 mg/ml.

The oxidative decarboxylation of carboxylic acids has been earlier studied extensively[3-6]. The decarboxylation of carboxyl mercurates by hydroperoxides and UV-light has been reported[13], but these reactions lead to formation of alkyl mercury compounds in a good yield.

The fact that the reaction does not form the products of skeletal rearrangements indicates a reaction route that does not involve the intermediate formation of carbocations[14]. However, the transformation of dehydroabietic acid (5) into a mixture of epimeric hydroperoxides 6 and 8 suggests formation of a free radical as an intermediate species:



The formation of an alkyl hydroperoxide due to the direct oxidation of the possible intermediate alkyl mercury compound[13] seems to be unlikely because the oxidation of the alkyl mercury compounds with molecular oxygen is usually accompanied in considerable extent by destruction of carbon skeleton[15].

The reaction found permits synthesis of *nor*-compounds (hydroperoxides and alcohols) from carboxylic acids in good yields. The most common and widely studied reagent for oxidative decarboxylation of carboxylic acids, lead tetraacetate, usually gives mixtures of unsaturated hydrocarbons with small admixtures of acetates and the corresponding alcohols[4,16]. *Nor*-hydrocarbons are also the main reaction products in the lead tetraacetate-induced oxidative decarboxylation of triterpenic acids [17-20]. Nevertheless, certain terpenic *nor*-

hydroperoxides and *nor*-alcohols may be obtained in poor yields by oxidation of the corresponding aldehydes with molecular oxygen[11,21,22].

Table 3. **^{1}H NMR Data for Compounds 5-9**[a,b]**.**

	5	6	7	8	9
H1α	[1.53]	1.45 *ddd* (13.0, 13.0, 3.5)	1.44 *ddd* (13.5, 13.5, 4.0)	1.46 *ddd* (13.0, 13.0, 4.0)	[1.45]
H1β	2.33 *m*	2.25 *ddd* (13.0, 3.0, 3.0)	2.25 *dddd* (13.5, 3.0, 3.0, 2.0)	2.34 *dddd* (13.0, 3.0, 3.0, 2.0)	2.32 *dddd* (13.0, 3.5, 3.5, 2.0)
H2α	[1.74]	[1.67]	[1.66]	[1.60]	1.62 *ddddd* (14.0, 3.0, 3.0, 3.0, 3.0)
H2β	[1.82]	[1.82]	[1.76]	[1.92]	1.99 *ddddd* (14.0, 14.0,14.0,3.5,3.5)
H3α	[1.74][c]	[1.81]	[1.40]	[1.24]	[1.44]
H3β	[1.85][c]	[1.81]	1.87 *ddd* (12.5, 4.0, 3.4)	2.26 *dm* (14.5)	1.75 *dddd* (14.0, 4.0, 3.0, 2.0)
H5	2.29 *dd* (12.5, 2.0)	2.06 *dd* (12.5, 5.0)	[1.62]	1.62 *dd* (12.5, 2.5)	1.44 *dd* (12.8, 3.0)
H6α	[1.89]	[2.04]	2.13 *ddm* (12.0, 6.5)	2.09 *dddd* (13.5, 7.8, 2.5, 2.5)	2.03 *m*
H6β	[1.58]	[1.68]	[1.70]	[1.90]	1.89 *ddd* (13.0, 10.5, 7.0)
H7α	[2.90]	[2.91]	[2.89]	2.86 *ddd* (17.5, 11.00, 7.8)	2.90 *ddd* (17.0, 10.5, 8.0)
H7β	[2.98]	[2.91]	[2.95]	2.90 *ddd* (17.5, 7.0, 2.5)	3.00 *ddd* (17.0, 8.0, 3.0)
H11	7.20 *d* (8.3)	7.19 *d* (8.0)	7.19 *d* (8.2)	7.20 *d* (8.3)	7.20 *d* (8.2)
H12	7.03 *dd* (8.3, 2.0)	7.02 *dd* (8.0, 1.7)	7.02 *dd* (8.2, 2.0)	7.01 *dd* (8.3, 2.0)	7.01 *dd* (8.2, 2.5)
H14	6.92 *br.s*	6.93 *d* (1.7)	6.92 *m*	6.91 *d* (2.0)	6.93 *d* (2.5)
H15	2.85 *qq* (7.0)	2.85 *qq* (6.9)	2.85 *qq* (7.0)	2.84 *qq* (7.0)	2.84 *qq* (7.0)
3H16	1.26 *d* (7.0)	1.26 *d* (6.9)	1.25 *d* (7.0)	1.24 *d* (7.0)	1.24 *d* (7.0)
3H17	1.26 *d* (7.0)	1.26 *d* (6.9)	1.25 *d* (7.0)	1.24 *d* (7.0)	1.24 *d* (7.0)
3H18	-		-	1.38 *s*	1.26 *s*
3H19	1.32 *br.s*	1.23 *br.s*	1.17 *br.s*	-	-
3H20	1.25 *br.s*	1.20 *br.s*	1.24 *br.s*	1.30 *br.s*	1.32 *br.s*

[a] chemical shifts are given in ppm; chemical shifts put in square brackets were taken from the 2D heteronuclear ^{13}C-^1H chemical shift correlation spectra ($^1J_{CH}$ = 125 Hz); [b] concentrations are just the same as given in *Table 2* [c] signals not assigned to α and β protons.

EXPERIMENTAL

General experimental procedures

All the solvents used were reagent quality. Petroleum ether refers to that fraction which boils in the range 40-70°C and was redistilled prior to use. Diethyl ether and tetrahydrofuran were freshly distilled. Removal of all solvents was carried out under reduced pressure and all commercial reagents were used without additional purification. Analytical TLC plates were **Silufol®** (Silpearl on aluminium foil, Czecho-Slovakia). Preparative column chromatography was performed on **SiO_2** ("KSK", Russia, 100-200 mesh, air dried and activated at 140°C for 5h). IR spectra were obtained using a **Specord M-80** infrared spectrophotometer. A **Polamat A** polarimeter was used to measure optical rotation at 578 nm. Melting points were obtained using a **Kofler** melting point apparatus and are uncorrected. Mass spectra were obtained on a **Finnigan MAT 8200** instrument using the Electron Impact Ionisation technique (40-200°C, 70eV).

^{1}**H** and ^{13}**C** NMR spectra were recorded at room temperature for **$CDCl_3$** solutions using a **Bruker AM-400** instrument (^{1}**H** 400.13 MHz, ^{13}**C** 100.61 MHz) and the solvent signal was used as internal standard: δ_H 7.24 ppm and δ_C 76.90 ppm. 2D heteronuclear ^{13}**C**-^{1}**H** chemical shift correlation spectra (XHCORRD: $^1J_{CH}$ = 125 Hz; COLOC: $^nJ_{CH}$ = 7.5 Hz) were obtained using standard Bruker NMR Software System.

Acetylursolic acid (1) {m.p. 284-287°C (**MeCN**), $[\alpha]^{20}$ +69.1° (c 3.04, **$CHCl_3$**)} was prepared by acetylation of ursolic acid with **Ac_2O-Py**. Acetyloleanolic acid (3) {m.p. 252-255°C (**EtOAc**), $[\alpha]^{19}$ +75.4° (c 1.78, **$CHCl_3$**)} was isolated from benzene extract of birch bark (*Betula sp.*). Dehydroabietic acid (5) had m.p. 169-171°C and $[\alpha]^{20}$ +59.6° (c 5.64, **$CHCl_3$**).

Preparation of nor-alcohols from carboxylic acids.

A solution of **Na_2CO_3** (0.42 g, 4 mmol) in water (2 ml) was added dropwise at stirring to a hot (50-60°C) solution of a carboxylic acid (1 mmol) and **$Hg(CF_3COO)_2$** (0.87 g, 2 mmol) in a mixture of **THF** (10 ml) and 30% aq. **H_2O_2** (1 ml). The reaction mixture was kept at the same temperature for 30 min and cooled to room temperature. A solution of **NaOH** (40 mg, 1 mmol) in water (1 ml) was cautiously added (gas evolution) followed by addition of a solution of **$NaBH_4$** (38 mg, 1 mmol) in water (2 ml). The reaction mixture was kept at vigorous stirring for 1 h, filtered, diluted with water (30 ml) and extracted with ether (20 ml). The ethereal extract was washed with water (10 ml), brine (5 ml), dried (**$MgSO_4$**). Removal of the solvent followed by column chromatography of the crude product afforded the corresponding *nor*-alcohol.

3β-(Acetyloxy)-17β-hydroxy-28-nor-urs-12-ene (2): m.p. 244-247°C (**EtOAc-MeCN**); $[\alpha]^{19}$ +75.3° (c 3.37, **$CHCl_3$**); IR (c = 1% in **$CHCl_3$**): 3590 (**O-H**); IR (**KBr**): 1715 (**C=O**, acetate), 1250 (acetate); MS (m/z): 470.3757 {**$C_{31}H_{50}O_3$** requires 470.3760} (M+, 7%), 452 (38), 437 (3), 220 (20), 202 (100), 189 (10), 132 (34), 43 (14).

3β-(Acetyloxy)-17β-hydroxy-28-nor-olean-12-ene (4): m.p. 217-220°C (**MeCN**); $[\alpha]^{20}$ +56.5° (c 1.91, **$CHCl_3$**); IR (c = 1% in **$CHCl_3$**): 3590 (**O-H**); IR (**KBr**): 1720 (**C=O**, acetate), 1250 (acetate); MS (m/z): 470.3771 {**$C_{31}H_{50}O_3$** requires 470.3760} (M+, 4%), 452 (14), 437 (3), 220 (10), 202 (100), 190 (6), 189 (7), 187 (6), 132 (11), 43 (8).

Preparation of nor-hydroperoxides from carboxylic acids

A solution of **Na_2CO_3** (0.42 g, 4 mmol) in water (2 ml) was added dropwise at stirring to a hot (50-60°C) solution of dehydroabietic acid (0.30 g, 1 mmol) and **$Hg(CF_3COO)_2$** (0.87 g, 2 mmol) in a mixture of **THF** (10 ml) and 30% aq. **H_2O_2** (1 ml). The reaction mixture was kept at the same temperature for 30 min and cooled to room temperature. The reaction mixture was diluted with water (30 ml) and extracted with ether (20 ml). The ethereal extract was washed with water (10 ml), brine (5 ml), dried (**$MgSO_4$**). Removal of the solvent gave the crude product (0.28 g) as colourless glass which was percolated through silica gel affording the mixture of hydroperoxides **6** and **8** (0.25 g, 88%, 1:3 according to ^{1}**H** NMR) which was then separated by column chromatography.

Decarboxylation of dehydroabietic acid (5) (0.50 g, 1.7 mmol) using **$Hg(NO_3)_2 \times H_2O$** (1.2 g, 3.4 mmol) instead of **$Hg(CF_3COO)_2$** gave 1:3 mixture of hydroperoxides **6** and **8** (0.39 g, 80%).

4-Hydroperoxy-18-nor-abietane (**6**): colourless glass, $[\alpha]^{20}$ +14.8° (c 9.60, $\mathbf{CHCl_3}$) {lit.[13]: $[\alpha]^{20}{}_D$ +9.7° (c 3.0, $\mathbf{CHCl_3}$)}; IR (c = 1% in $\mathbf{CCl_4}$): 3560 (**OOH**); MS (m/z): 288.2090 {$\mathbf{C_{19}H_{28}O_2}$ requires 288.2089} (M+, 30%), 272 (7), 255 (25), 239 (11), 187 (29), 185 (24), 173 (100), 143 (14), 129 (13).

4-Hydroxy-18-nor-abietane (**7**): m.p. 90-91°C (petroleum ether); $[\alpha]^{20}$ +44.3° (c 8.36, $\mathbf{CHCl_3}$) {lit.[13]: m.p. 91-92° (petroleum ether), $[\alpha]^{20}{}_D$ +47° (c 1.5, $\mathbf{CHCl_3}$)}; IR (c = 1% in **CCl4**): 3620 (**OH**); MS (m/z): 272.2135 {$\mathbf{C_{19}H_{28}O}$ requires 272.2140} (M+, 68%), 257 (100), 239 (90), 229 (11), 199 (28), 187 (81), 157 (61), 145 (20), 139 (18), 117 (16).

4-Hydroperoxy-19-nor-abietane (**8**): m.p. 103-106°C (petroleum ether); $[\alpha]^{20}$ +70.4° (c 3.75, $\mathbf{CHCl_3}$) {lit.[13]: m.p. 104-107° (petroleum ether), $[\alpha]^{20}{}_D$ +88° (c 0.34, $\mathbf{CHCl_3}$)}; IR (c = 1% in $\mathbf{CCl_4}$): 3560 (**OH**); MS (m/z): 288.2090 {$\mathbf{C_{19}H_{28}O_2}$ requires 288.2089} (M+, 64%), 256 (21), 255 (22), 239 (19), 187 (36), 185 (28), 173 (100), 143 (29), 129 (33), 43 (44).

4-Hydroxy-19-nor-abietane (**9**): m.p. 74-75.5°C (petroleum ether); $[\alpha]^{20}$ +59.8° (c 11.9, $\mathbf{CHCl_3}$) {lit.[13]: m.p. 70-72° (petroleum ether), $[\alpha]^{20}{}_D$ +56° (c 2.5, $\mathbf{CHCl_3}$)}; IR (c = 1% in $\mathbf{CCl_4}$): 3625 (**OH**); MS (m/z): 272.2135 {$\mathbf{C_{19}H_{28}O}$ requires 272.2140} (M+, 52%), 257 (100), 239 (85), 199 (28), 197 (14), 187 (54), 157 (61), 43 (19).

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REFERENCES

1. Brown, H.C.; Geoghegan, P.J. *J. Org. Chem.* **1972**, *37*, 1937-1941.
2. Spillane, W. J. Reactions of Acids and Their Derivatives. In *Org. React. Mech.;* 1987 (Publ. 1989), pp.29-89.
3. Trahanovsky, W. S.; Cramer, J.; Brixiuss, D. W. *J. Amer. Chem. Soc.* **1974**, *96*, 1077-1081.
4. Serguchev, Yu. A.; Beletskaya, I.P. *Usp. Khim.* **1980**, *49*, 2257-2285.
5. Elmore, P. R.; Reed, R. T.; Terkle-Huslig, T.; Welch, J. S.; Young, S. M.; Landolt, R.G. *J. Org. Chem.* **1989**, *54*, 970-972.
6. Sayre, L. M.; Jensen, F. R. *J. Org. Chem.* **1978**, *43*, 4700-4705.
7. Brown, H.C.; Geoghegan, P.J. *J. Amer. Chem. Soc.*, **1967**, *89*, 1522-1524.
8. Wehrli, F. W.; Nishida T. *Fortschr. Chem. Org. Naturstoffe* **1979**, *36*, 1-229.
9. Bremser, W.; Ernst, L. Fachinger, W.; Gerhards, R.; Lewis, P.; Hardt, A. *Carbon-13 NMR Spectral Data: a "Living" COM-Microfiche Collection of Reference Material;* Verlag Chemie: Weinheim, **1987**.
10. Agrawal, P. K.; Jain, D. C. *Prog. Nucl. Magn. Reson. Spectrosc.* **1992**, *24*, 1-90.
11. Avdyukova, N. V.; Shmidt, E. N.; Pentegova, V. A. *Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk* **1973**, 117-120.

12. Rezvukhin, A. I.; Solomennikova, I. V.; Bychkova, S. F.; Shmidt, E. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1979**, 2678-2685.
13. Ol'dekop, Yu. A.; Maier, N. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, 1171-1177.
14. Dessau, R. M.; Heiba, E. I. *J. Org. Chem.* **1975**, *40*, 3647-3649.
15. Razuvaev, G. A.; Zhil'tsov, S. F.; Druzhkov, O. N.; Petukhov, G. G. *Dokl. Akad. Nauk SSSR* **1963**, *152*, 633-636.
16. Bennett, C. R.; Cambie, R. C.; Franich, R. A.; Fullerton, T. J. *Austr. J. Chem.* **1969**, *22*, 1711-1720.
17. Reddy, K. D.; Raj, S. K. R.; Ramaiah, T. S.; Rao, V. V.; Nath, A. R. *Oxid. Commun.* **1987**, *10*, 305-312.
18. Sundararamaiah, T.; Rao, V. V. *J. Indian. Chem. Soc.* **1982**, *59*, 74-76.
19. Pradhan, P. B.; De, S. *Indian J. Chem.* **1982**, *21B*, 823-828.
20. Kitagawa, I.; Wang, H. K.; Saito, M.; Yoshikawa, M. *Chem. Pharm. Bull.* **1983**, *31*, 664-673.
21. Caputo, R.; Mangoni, L.; Monaco, P.; Previtera, L. *Gazz. Chim. Ital.* **1974**, *104*, 1269-1278.
22. Caputo, R.; Previtera, L.; Monaco, P.; Mangoni, L. *Tetrahedron* **1974**, *30*, 963-967.

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