SYNTHESIS OF NORHYDROPEROXIDES FROM NATURAL TRITERPENIC ACIDS

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Dedicated to the memory of Dr Václav Černý.

Treatment of triterpenoids derived from ursolic and glycyrrhetinic acids with the oxidative mixture H_2O_2–$(CF_3COO)_2Hg$–Na_2CO_3–THF results in oxidative decarboxylation. The reaction of 3*O*-acetylursolic acid (**1**) and 3*O*-acetyl-18β-glycyrrhetinic acid (**3**) affords stable norhydroperoxides, whereas decarboxylation of 3*O*-acetyl-11-oxoursolic acid (**6**) leads to unstable norhydroperoxide. The difference in properties of the norhydroperoxides is explained by the presence of a conjugated ketone, which activates the 12,13-C=C double bond for nucleophilic addition and makes possible intramolecular Michael-type addition of peroxo anion.

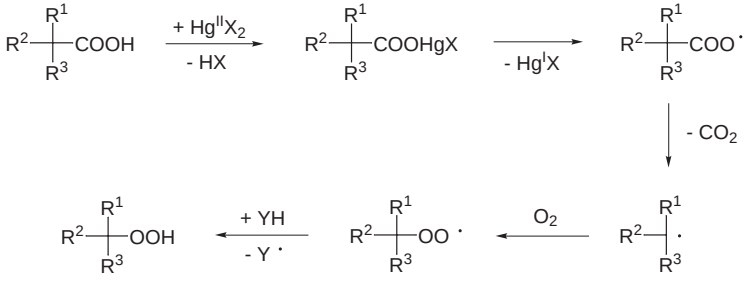
Keywords: NMR spectroscopy; Michael additions; Peroxides; Mercury; Terpenoids; Triterpenes; Oxidations; Decarboxylations.

Peroxides of natural compounds are of great interest because many of them are known to be biologically active compounds or intermediates in biosyntheses of many important metabolites[1]. Study of oxidative transformation of easily available natural pentacyclic triterpenoids are interesting from the viewpoint of development of new methods for oxidative modification of natural products and synthesis of new derivatives of natural biologically active compounds. There are several reactions leading to peroxides, some of them are general-purpose methods for the synthesis of the simplest peroxides, although most of them are not suitable for preparing peroxides of complex structure. Recently we found[2] that oxidative decarboxylation of certain terpenic acids (dehydroabietic, acetyloleanolic and acetylursolic acids) with hydrogen peroxide in the presence of a mercury(II) salts followed by reductive demercuration resulted in the formation

of nor-derivatives, hydroperoxides being the intermediates. In the present work we demonstrate the use of oxidative decarboxylation in the synthesis of triterpenic hydroperoxides and report on some peculiarities of the reaction.

RESULTS AND DISCUSSION

To test the reaction of oxidative decarboxylation for preparation of nor-hydroperoxides we had chosen the derivatives of ursolic and glycyrrhetinic acid. Because secondary hydroxy groups are oxidized in the presence of H_2O_2–$(CF_3COO)_2Hg$ we used 3*O*-acetyl derivatives of the acids. The oxidative decarboxylation was carried out as follows. A solution of sodium carbonate in water was added dropwise while stirring to a hot (50–60 °C) solution of a carboxylic acid and mercury(II) trifluoroacetate (2.0 mmol) in a mixture of tetrahydrofuran and 30% aqueous hydrogen peroxide. After the reaction was complete, the reaction mixture was filtered through alumina to remove mercury and insoluble mercury(I) compounds and subsequently extracted to isolate hydroperoxides whose formation was detected by TLC (see Experimental). The reaction seems to proceed according to the following sequence (Scheme 1). In the first step, the carboxylic acid is transformed to its mercury(II) salt which then undergoes intramolecular oxidative-reductive process to liberate a mercury(I) salt and the radical particle $(R^1R^2R^3C)COO^{\bullet}$;

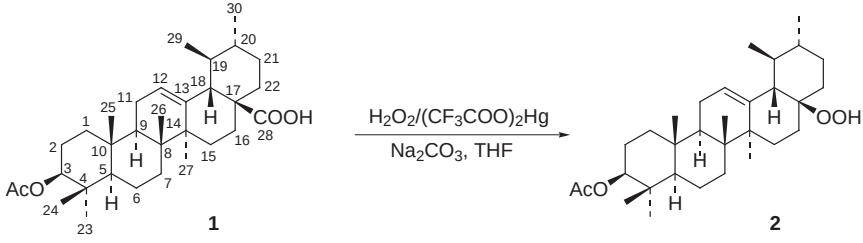


SCHEME 1

the latter then decarboxylates generating the radical $R^1R^2R^3C^{\bullet}$ which is then transformed to the hydroperoxide in the usual way. The presence of a carbonate is absolutely necessary for the reaction to take place: First, because the first step of the sequence described is reversible, the carbonate, as a base, enables the formation of the mercury(II) salt of carboxylic acid by removing trifluoroacetic acid. Second, addition of a carbonate to a hot solution of hydrogen peroxide causes liberation of a significant amount of mo-

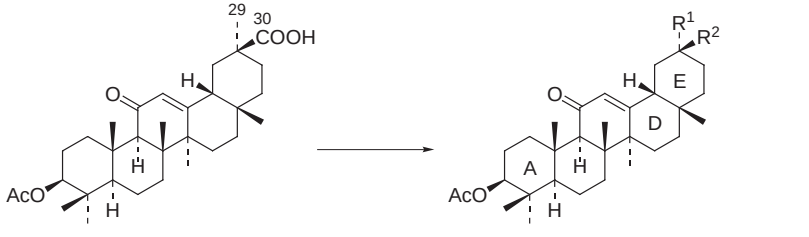
lecular oxygen, which is necessary for the reaction with the radical $R^1R^2R^3C^{\bullet}$. Decarboxylation is quite fast under the condition used, so the atmospheric oxygen cannot lead to the formation of a significant amount of hydroperoxide even when passing air (or gaseous oxygen) into the reaction mixture. At the same time, a large excess of a carbonate stops the reaction completely because of the formation of alkaline salt of the carboxylic acid, which is stable and is not subject to decarboxylation under the conditions described above.

Oxidative decarboxylation of 3*O*-acetylursolic acid (**1**) and 3*O*-acetyl-18β-glycyrrhetinic acid (**3**) proceeds smoothly to form the corresponding hydroperoxides **2**, **4** and **5** (Schemes 2 and 3). Structures of the compounds **2**, **4** and **5** were proved by IR, MS and NMR spectra. NMR spectra of compound **2** are given in Table I; the spectra of compounds **4** and **5** are given in



SCHEME 2

Table II. These hydroperoxides are quite stable compounds and were isolated by column chromatography. Peroxides **2**, **4** and **5** instantly oxidize Fe^{2+} to Fe^{3+} and I^- to I_2 on TLC plates to demonstrate the presence of a hydroperoxy group. Oxidative decarboxylation of 3*O*-acetylursolic acid (**1**) results in the sole epimer with β-oriented hydroperoxy group at C-17 carbon due to the rigid carbon frame[2], whereas in the case of 3*O*-acetyl-18β-glycyrrhetinic acid (**3**), two C-20 epimers **4** and **5** (3 : 5) are formed.



SCHEME 3

TABLE I
NMR data for compounds **2**, **6**, **7**, **8** and **9**[a]

Position	**2**[b]		**6**[c]		**7**[d]	**8**[e]		**9**[f]	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_C	δ_H	δ_C	δ_H
1	38.14	[1.07, 1.63]	38.66	[1.04]; 2.76 ddd (13.7, 3.4, 3.4)	38.66	38.38	[1.03]; 2.73 ddd (13.6, 3.6, 3.6)	38.67	[1.04]; 2.77 ddd (13.7, 3.6, 3.6)
2	23.44	[1.61] 2 H	23.42	[1.61, 1.66]	23.46	23.42	[1.61, 1.64]	23.46	[1.59, 1.65]
3	80.87	4.48 m	80.48	4.48 dd (11.7, 4.6)	80.58	80.24	4.45 dd (11.5, 5.1)	80.55	4.50 dd (11.7, 4.8)
4	37.58	–	37.89	–	37.92	37.92	–	37.91	–
5	55.25	[0.82]	54.89	0.75 dd (10.5, 1.8)	54.05	54.71	0.69 dd (10.5, 3.0)	54.99	0.77 dd (12.0, 2.0)
6	18.12	[1.41, 1.50]	17.09	[1.33, 1.49]	17.28	17.01	[1.49, 1.51]	17.28	[1.40, 1.55]
7	33.05	[1.40, 1.47]	32.75	[1.35, 1.54]	33.17	33.47	[1.31, 1.54]	33.16	[1.46, 1.59]
8	39.60	–	44.57	–	44.64	40.79	–	44.64	–
9	47.52	[1.52]	61.20	2.29 s	61.43	63.85	2.05 s	61.43	2.31 s
10	36.85	–	36.92	–	37.07	37.42	–	37.04	–
11	23.27	[1.91]	199.88	–	199.50	204.81	–	199.30	–
12	124.86	5.13 dd (3.5, 3.5)	130.64	5.56 s	130.37	59.14	2.94 s	131.09	5.53 s
13	138.79	–	162.71	–	164.04	66.76	–	164.35	–
14	41.78	–	43.52	–	43.51	40.79	–	43.53	–
15	26.02	[0.95]; 1.96 d (8.7)	28.23	[1.23]; 1.84 ddd (14.5, 14.5, 4.0)	26.71	28.94	[1.47]; 2.04 ddd (13.6, 13.6, 4.7)	26.82	[1.16]; 2.13 ddd (13.6, 13.6, 4.7)
16	24.67	[1.55, 1.97]	23.43	[1.75]; 2.05 ddd (13.6, 13.6, 3.8)	24.22	24.43	[1,21]; 2.32 ddd (13.4, 13.4, 4.7)	27.86	[1.33]; 2.09 ddd (13.6, 13.6, 4.3)

TABLE I
(*Continued*)

Position	**2**[b]		**6**[c]		**7**[d]	**8**[e]		**9**[f]	
	δ_C	δ_H	δ_C	δ_H	δ_C	δ_C	δ_H	δ_C	δ_H
17	84.07	–	47.36	–	83.47	72.79	–	72.17	–
18	54.03	1.76 dd (10.6, 1.6)	52.31	2.35 dd (11.3, 1.5)	55.01	58.82	0.75 dd (11.6, 1.8)	60.14	[1.71]
19	41.47	1.29 ddq (9.6, 11.2, 6.6)	38.34	[1.36]	41.11	40.65	[1.55]	41.22	[1.29]
20	39.05	[0.96]	38.45	[1.04]	38.92	38.76	[0.97]	38.92	[1.02]
21	31.99	[1.62, 1.57]	30.10	[1.34, 1.53]	31.70	32.39	[1.15, 1.59]	32.21	[1.21, 1.60]
22	34.87	1.73 ddd (13.4, 13.0, 4.3) 1.82 ddd (12.5, 3.5, 3.5)	36.92	[1.65] [1.77]	34.55	40.74	[1.56]; 1.78 ddd (13.8, 4.7, 3.3)	41.42	[1.54, 1.75]
23	28.01	0.85 s	27.95	0.83 s	28.04	27.99	0.84 s	28.03	0.85 s
24	16.64	0.84 s	16.56	0.82 s	16.63	16.47	0.85 s	16.63	0.87 s
25	15.34	0.95 s	16.23	1.12 s	15.99	15.88	1.09 s	16.03	1.14 s
26	17.00	0.97 s	19.08	0.86 s	19.28	23.45	1.20 s	19.37	1.14 s
27	23.00	1.04 s	20.95	1.27 s	20.51	18.51	1.30 s	20.47	1.25 s
28	–	–	182.91	–	–	–	–	–	–
29	17.15	0.82 d (6.2)	16.92	0.84 d (6.5)	17.20	17.74	0.94 d (6.5)	17.27	0.82 d (6.5)
30	20.51	0.91 d (6.1)	20.83	0.94 d (6.5)	20.30	19.90	0.90 d (6.2)	20.36	0.93 d (6.3)
CH_3COO	21.16	2.02 s	21.18	2.02 s	21.16	21.17	2.02 s	21.17	2.02 s
CH_3**C**OO	170.93	–	170.93	–	170.89	170.86	–	170.86	–

[a] Chemical shifts are given in ppm. Proton chemical shifts in square brackets were taken from the 2D heteronuclear ^{13}C-^{1}H chemical shift correlation spectra ($^{1}J_{CH}$ = 135 Hz). [b] *c* 60 mg/ml. [c] *c* 30 mg/ml. [d] Carbon chemical shifts were taken from the spectrum of a mixture (*c* 30 mg/ml) of compounds **7**, **8** and **9** (6 : 4 : 1). ^{1}H NMR: 7.5 br s (OOH); 5.48 s (H-12); 4.52 dd, *J* = 11.7 and 4.8 (H-3); 2.79 ddd, *J* = 13.7, 3.6 and 3.6 (H-1β); 2.30 s (H-9). [e] *c* 40 mg/ml. [f] *c* 20 mg/ml.

Careful analysis of carbon and proton chemical shifts allowed us to assign the major component as 20β-hydroperoxy derivative **4**. The reasons are as follows. According to the energy calculations (molecular-mechanics MM2 and semi-empirical quantum-chemical PM3) the most stable conformation of the pentacyclic carbon skeleton of 18β-glycyrrhetinic acid derivatives is the chair one for all rings except ring C which is half-chair, rings D and E being the only flexible moiety due to *cis*-fusion of the two six-membered rings. Comparison of chemical shifts for epimers **4** and **5** shows that both epimers have the same conformation of rings D and E because chemical shifts for rings A, B, C and D are very close or even the same. The shape of

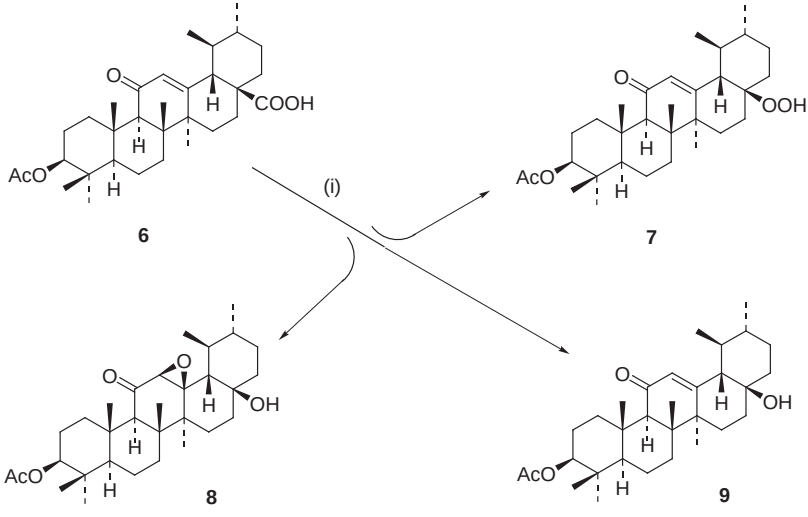
TABLE II
NMR data for compounds **4** and **5**[a]

Position	δ_C	δ_H	Position	δ_C	δ_H
1	38.60, 38.61 {5:3}	[1.0], 2.74	17	31.70, 32.56 {5:3}	–
2	23.42	[1.56, 1.65]	18	46.00, 48.44 {5:3}	2.29 ddd (13.0, 4.0, 1.5), [2.04]
3	80.53	4.3 m	19	39.87, 39.97 {3:5}	[1.43], [1.72]
4	37.91	–	20	80.08, 83.01 {5:3}	–
5	54.82, 54.86 {3:5}	[0.82]	21	29.11, 29.57 {5:3}	[1.37, 1.83], [1.46, 1.71]
6	17.21	[1.42, 1.54]	22	35.05, 37.26 {5:3}	[1.20, 1.57], [1.33, 1.53]
7	32.52	[1.38, 1.62]	23	27.90, 27.92 {5:3}	0.84 s
8	45.32, 45.36 {3:5}	–	24	16.54, 16.56 {3:2}	0.84 s
9	61.55, 61.59 {3:5}	2.33 s	25	16.27, 16.29 {3:2}	1.09 s
10	36.83	–	26	23.19, 23.31 {1:2}	1.32 s, 1.33 s
11	200.22, 200.70 {3:5}	–	27	18.56, 18.58 {5:3}	1.09 s
12	128.02, 1298.17 {5:3}	5.59 s, 5.72 s {3:5}	28	28.06	0.81 s
13	168.89, 170.26 {3:5}	–	29	20.07, 25.14 {3:5}	1.17, 1.26 {5:3}
14	43.19, 43.21 {3:5}	–	30	–	–
15	26.201	[0.97], [1.96]	**C**H_3COO	21.16	2.01 s
16	26.03, 26.30 {3:5}	[1.48], [1.79]	CH_3**C**OO	170.97	–

[a] Chemical shifts are given in ppm. Proton chemical shifts in square brackets were taken from the 2D heteronuclear ^{13}C-^{1}H chemical shift correlation spectra ($^{1}J_{CH}$ = 135 Hz); *c* 60 mg/ml; the values in braces indicate relative intensities of the signals.

the H-18 signal for the major isomer at δ 2.29 proves that the proton H-18 is equatorial with regard to ring D (J(18,16β) = 1.5 Hz) and axial relative to ring E (J(18,19β_{eq}) = 4.0 Hz and J(18,19α_{ax}) = 13.0 Hz). So, the D–E moiety has chair–chair conformation and β substituent at C-20 must be axial. Two epimers **4** and **5** demonstrate quite a big difference in carbon chemical shifts for the carbon C-29 ($\Delta\delta_C$ = 5 ppm) which can be thus easily explained in terms of different position (axial or equatorial) of the methyl. The equatorial methyl in epimer **4** must exhibit a low-field shift (δ_C 25.14 ppm) as compared to the axial methyl (δ_C 20.07 ppm) in epimer **5**. This assignment can also easily explain significant low-field shift of proton H-18 in epimer **4** ($\Delta\delta_H$ 0.25 ppm) due to the unshielding effect because of 1,3-diaxial interaction with hydroperoxy group.

In the case of oxidative decarboxylation of 3*O*-acetyl-11-oxoursolic acid (**6**) we failed to isolate and purify the corresponding hydroperoxide **7** because of its instability. NMR study of the crude reaction product showed the presence of three products in the ratio of 6 : 4 : 1, which are hydroperoxide **7**, epoxide **8** and alcohol **9** (Scheme 4).

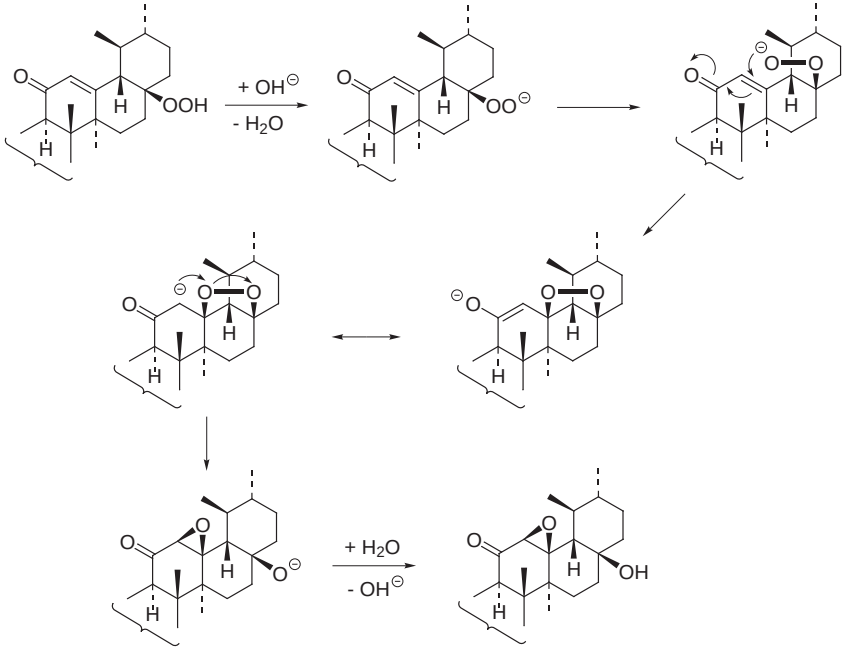


(i) $H_2O_2/(CF_3COO)_2Hg$, Na_2CO_3, THF

SCHEME 4

Our attempts to isolate hydroperoxide **7** by column or thin layer chromatography invariably resulted in decomposition of the desired product. We carefully analyzed NMR spectra of the mixture and proved that it was just hydroperoxide **7** that was initially formed as the primary reaction product.

Because NMR spectra of the mixture were very complex, we made signal assignments of hydroperoxide **7** only for carbon-13 NMR spectra (Table I). We found that simple treatment of the reaction mixture with a carbonate resulted in transformation of hydroperoxide **7** to epoxide **8**. This observation allows to rationalize the mechanism of the formation of epoxy ketone **8** as an intramolecular base-catalyzed rearrangement (Scheme 5): Michael-type addition of hydroperoxide anion to the carbon–carbon double bond of the unsaturated ketone results in endoperoxide, which then undergoes intramolecular displacement – nucleophilic substitution at the peroxide oxygen atom.



SCHEME 5

According to this scheme, the resulting product must be 12β,13β-epoxy derivative **8**. Comparison of NMR spectra of the starting compound **6** and the by-product **9** indicated, as in the above case of acetylursolic acid **1** and the corresponding hydroperoxide **2**, that configuration of the C-17 substituent remained unchanged; hence, hydroperoxide **7** must be 17β-hydroperoxy derivative. The most important feature of NMR spectra of compound **8**, which is useful for the configuration assignment, is the unusual chemical shift of the proton H-18 at δ_H 0.75 ppm. Like in the case of compounds **4**

and **5** (see the discussion above), the D–E ring moiety in **8** has chair–chair conformation, proton H-18 being equatorial in the ring D ($J(18,16\beta_{eq})$ = 1.8 Hz) and axial in the ring E ($J(18,19\alpha_{ax})$ = 11.6 Hz). The unusual up-field shift of the H-18 signal can be explained by anisotropic influence of the 12,13-epoxide: the proton H-18 lies just above the plane of the 12β,13β-epoxide and, therefore, is shielded by this small ring.

Thus, there is a big difference in the properties of norhydroperoxides **2** and **7** derived from 3*O*-acetylursolic (**1**) and 3*O*-acetyl-11-oxoursolic (**6**) acids, respectively. The unexpected instability of norhydroperoxide **7** is explained by the presence of oxo group at C-11 carbon, which activates the 12,13-C=C double bond for nucleophilic addition and makes possible intramolecular Michael-type addition of hydroperoxide anion.

EXPERIMENTAL

All solvents were freshly distilled. All the commercially available reagents were used without any purification unless otherwise stated. Thin-layer chromatography was carried out on Silufol® plates with a Silpearl silica gel layer fixed on an aluminum foil (Czech Republic). The components were visualized by spraying the plates with concentrated H_2SO_4 followed by heating at 100–150 °C. Column chromatography was performed on KSK silica gel (Russia; grain size was 0.10–0.20 mm), which was dried in air and activated by heating at 140 °C for 5 h. IR spectra (wavenumbers in cm^{-1}) were recorded on a Specord M-80 spectrophotometer in $CHCl_3$ solutions (*c* 1%). Optical rotation was measured on a Polamat A polarimeter at 578 nm in $CHCl_3$ solutions. The melting points were determined on a Kofler stage. Microanalyses were carried out on Hewlett–Packard 185 and Carlo Erba 1106 analyzers. Mass spectra were obtained on a Finnigan MAT-8200 mass spectrometer (EI, 70 eV). NMR spectra were recorded on a Bruker DRX-500 spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C) locked to the deuterium resonance of the solvent at room temperature (23–25 °C) in $CDCl_3$ solutions using a standard Bruker NMR Software System. The chemical shifts were calculated relative to the solvent signal used as internal standard: δ_C 76.900 and δ_H 7.240 ppm. The assignment of the signals was made using ^{13}C NMR spectra, which were recorded with *J* modulation (proton-noise-decoupled spectra, the opposite phases for the signals of the atoms with the odd and even numbers of the attached protons, tuning to the constant J = 135 Hz), and based on the 2D spectra: (i) homonuclear ^1H-^1H correlation (2D memory matrix size 1K × 128 for FIDs and 1K × 1K for spectrum, number of scans 8), (ii) heteronuclear ^{13}C-^1H correlation at the direct spin-spin coupling constants (2D memory matrix size 4K × 256 for FIDs and 4K × 1K for spectrum, number of scans 32, J = 135 Hz), and (iii) heteronuclear ^{13}C-^1H correlation at the long-range spin-spin coupling constants (2D memory matrix size 8K × 128 for FIDs and 4K × 1K for spectrum, number of scans 64, J = 8 Hz). NMR spectra are given in Tables I and II.

Visualization of Peroxides

A) Commercially available iron(II) sulfate heptahydrate was crystallized from ethanol to remove traces of Fe^{3+} ions. A mixture of the purified $FeSO_4 \cdot 7H_2O$ (0.834 g, 3 mmol) and am-

monium thiocyanate (0.625 g, 8 mmol) was dissolved in water (30 ml) to give a solution of iron(II) thiocyanate. The TLC plate was developed by the appropriate eluent, air-dried and treated with the freshly-prepared iron(II) thiocyanate solution to produce blood-red color of the spots of peroxides due to oxidation $Fe^{2+} \rightarrow Fe^{3+}$.

B) The TLC plate (with starch as a binding material) was developed by an appropriate eluent, air-dried and treated with aqueous solution of KI to produce dark spots of peroxides due to oxidation $I^- \rightarrow I_2$ followed by reaction of I_2 with starch.

Starting Compounds

Ursolic acid was isolated from an extract of fruits of sea buckthorn *Hippophae rhamnoides* L. (Elaeagnaceae) according to the procedure reported previously[3] and purified by crystallization from 95% aqueous ethanol to obtain the product with m.p. 276–279 °C (solvate with 1 molecule of EtOH according to ^{1}H NMR) and $[\alpha]^{22}$ +59.8 (*c* 2.24, pyridine) (ref.[4] gives m.p. 278–280 °C (MeOH) and $[\alpha]_D$ +76.8 (*c* 0.6); ref.[5] gives m.p. 279–281 °C). 3*O*-Acetylursolic acid (**1**) was prepared by treatment of ursolic acid with Ac_2O–pyridine[2]. 3*O*-Acetyl-11-oxoursolic acid (**6**) was obtained from 3*O*-acetylursolic acid (**1**) by chromic acid oxidation[6].

Preparation of Norhydroperoxides from Carboxylic Acids

A solution of sodium carbonate (0.42 g, 4.0 mmol) in water (2 ml) was added dropwise while stirring to a hot (50–60 °C) solution of a carboxylic acid (1.0 mmol) and mercury(II) trifluoroacetate (0.87 g, 2.0 mmol) in a mixture of tetrahydrofuran (10 ml) and 30% aqueous hydrogen peroxide (1 ml). The reaction mixture was kept at vigorous stirring at the same temperature for 30 min and then at room temperature for 1 h, filtered through an alumina layer, diluted with water (30 ml) and extracted with ether (20 ml). The ethereal extract was washed with water (10 ml) and brine (5 ml), and dried over anhydrous magnesium sulfate. Removal of the solvent followed by column chromatography of the crude product afforded the corresponding norhydroperoxides.

*17*β*-Hydroperoxy-28-norurs-12-en-3*β*-yl acetate* (**2**). Yield 0.2505 g (50%) from 0.5006 g (1.00 mmol) of the 3*O*-acetylursolic acid (**1**), m.p. 180–183 °C (chloroform–ethanol), $[\alpha]^{19}$ +77.6 (*c* 2.5, $CHCl_3$). IR (2% in $CHCl_3$): 3 537 (OO–H). IR (KBr): 1 713 (C=O, acetate). EI MS, *m/z* (rel.%): 486.3707 {$C_{31}H_{50}O_4$ requires 486.3705} (M^+, 4), 468 (10), 453 (17), 249 (12), 236 (31), 219 (32), 202 (100), 189 (52), 175 (28) 161 (39).

*A 5 : 3 mixture of C-20 epimers of 20-hydroperoxy-11-oxo-30-norolean-12-en-3*β*-yl acetate* (**4** + **5**). Yield 131 mg (65%) from 0.2454 g of 3*O*-acetylglycyrretic acid (**3**), m.p. 213–215 °C (chloroform–ethanol), $[\alpha]^{23}$ +118 (*c* 1.5, $CHCl_3$). IR (2% in $CHCl_3$): 3 539 (OO–H). IR (KBr): 1 732 (C=O, acetate), 1 659 (C=O, ketone). EI MS, *m/z* (rel.%): 500.3500 {$C_{31}H_{48}O_5$ requires 500.3502} (M^+, 5), 484 (5), 466 (6), 291 (35), 275 (27), 257 (15), 250 (21), 216 (24), 175 (51), 135 (57), 69 (30), 43 (100).

Oxidative Decarboxylation of 3*O*-Acetyl-11-oxoursolic Acid (**6**)

Oxidative decarboxylation of 11-oxo-3*O*-acetylursolic acid (**6**; 0.2442 g, 0.5 mmol) gave 0.2511 g of the crude product (containing **7**, **8** and **9** in the ratio 6 : 4 : 1 according to ^{1}H NMR), which was separated by column chromatography to yield oxo epoxide **8** (0.100 g, 40%) and unsaturated alcohol **9** (0.020 g, 8%).

A portion (0.1 g) of the crude product of the decarboxylation of 11-oxo-3*O*-acetylursolic acid (**6**) was treated with sodium carbonate (0.098 g, 1.0 mmol) and benzyl(triethyl)ammonium chloride (0.001 g, 0.004 mmol) in chloroform (3 ml) at room temperature at vigorous stirring for 1 h. The resulting mixture was filtered and the filtrate was concentrated at reduced pressure followed by percolation through Al_2O_3 to give colorless solid (0.082 g, 82%) whose NMR spectra demonstrated the presence of only the products **8** and **9** (10 : 1).

*17*β*-Hydroxy-11-oxo-12*β*,13*β*-epoxy-28-norursan-3*β*-yl acetate* (**8**). M.p. 270–274 °C (chloroform–ethanol), $[\alpha]^{21}$ –110 (*c* 1.3, $CHCl_3$). IR (2% in $CHCl_3$): 3 588 (O–H). IR (KBr): 1 725 (C=O, acetate), 1 699 (C=O, ketone). EI MS, *m/z* (rel.%): 500.3504 {$C_{31}H_{48}O_5$ requires 500.3502} (M^+, 7), 482 (7), 277 (29), 221 (35), 205 (100), 190 (28), 248 (59), 218 (44), 95 (31).

*17*β*-Hydroxy-11-oxo-28-norurs-12-en-3*β*-yl acetate* (**9**). M.p. 277–279 °C (chloroform–ethanol), $[\alpha]^{21}$ –81.1 (*c* 1.5, $CHCl_3$). IR (2% in $CHCl_3$): 3 588 (O–H). IR (KBr): 1 716 (C=O, acetate), 1 658 (C=O, ketone). EI MS, *m/z* (rel.%): 484.3555 {$C_{31}H_{48}O_4$ requires 484.3552} (M^+, 14), 466 (29), 409 (10), 275 (100), 257 (50), 234 (77), 217 (56), 187 (14), 161 (48).

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