

OXIDATION OF DERIVATIVES OF POLYFLUOROALKYL ESTERS OF RESIN ACIDS

L. M. Popova¹, J. L. Matveenko¹, S. V. Vershilov²

¹Saint Petersburg State University of Industrial Technologies and Design,
Ivan Chernykh str., 4, Saint Petersburg, 198095, Russia
e-mail: lorapopova@mail.ru

²Federal State Unitary Enterprise S.V. Lebedev Institute of synthetic rubber,
Hapsalskaya str. 1, Sankt-Peterburg, Russia, 198035,

Annotation: Oxidation of abietic acid and its polyfluoroalkyl esters using hydrogen peroxide over FeSO₄ results in formation of mixture of 7-oxi, 7,15-dioxi- and 7-oxoderivatives of dehydroabietic acid.

Key words: oxidation; polyfluoroalkyl ester of resin acids.

INTRODUCTION

A significant number of researches is devoted to studying the oxidation processes of abietane and pimarane type-diterpenes [1-3]. The sensitivity of resin acids to heating, influence of oxygen and light, mineral acid is due to the presence of unsaturated bonds system. The acids of abietane row are inclined to valent isomerism as well as to disproportioning (intramolecular movement of hydrogen atoms). Thus, the abietic acid is isomerized into dehydroabietic acid under the influence of catalyst and at heating. A wide range of oxidation products among which are *endo*- and hydroperoxides, epoxides, hydroxy- and keto- derivatives is another consequence of hydrogen atoms high lability in structures of tricyclic diterpenoids.

The products of oxidation of tricyclic diterpenoids derivatives are of interest due to their wide range of biological activity [3]. Using of some derivatives of tricyclic diterpenic acids (modified resin) in different fields of technics, for example, as isolation materials in electrotechnics [4], also gives grounds for studying the oxidation processes of those products. The introduction of hydrophobic fluorinated substituent can significantly improve the operational characteristics of materials.

Oxidation products of abietic acid and its esters with some polyfluoroalkanols have been studied under the influence of H₂O₂ (30%-solution) over Fe₂SO₄ as catalyst in present work. The establishing of main directions of oxidation was of our interest.

EXPERIMENTAL PART

NMR ¹H and ¹⁹F spectra were recorded on Bruker-500 at 500 MHz (470 MHz – for ¹⁹F) and Bruker Avance III-400 at 400 MHz (370 MHz – for ¹⁹F) in CDCl₃ solution, external reference – CCl₃F.

IR spectra were recorded using Shimadzu IR Prestige-2, KBr glass (thin layer, solution in CCl₄) and Shimadzu FTIR-8400S (KBr tablets, thin film).

UV-spectra were recorded using SF-2000 spectrophotometer, ethanol (96%) at $c \cdot 10^{-4}$ mole/l, thickness of absorbing layer is 1 cm.

The control over reactions passing process was carried out using TLC method at Sorbfil plates, eluent: hexane–methylenechloride – acetone (1–1–0,5).

Abietic acid (1) was isolated from SYLVAROS[®]85 Tall Oil Rosin (softening point is 63°C, Acid Number 168, produced by Arizona Chemical) using methods [5]. Esters of abietic acid were obtained using esterification reaction of abietic acid with corresponding polyfluorinated alcohols: trifluoroethanol (2), 1*H*,1*H*,3*H*-trihydrotetrafluoropropanol (3), 1*H*,1*H*,5*H*-trihydro-octafluoropenanol (4) [6].

Oxidation of abietic acid (1). 0,5 g (1.65 mmol) of abietic acid (1) was dissolved in 11 ml of toluene in flat-bottom flask equipped with a reflux condenser, 0.2 g (5.88mmol) of H₂O₂ (30%-solution) and 0.005 g (0.03 mmol) of FeSO₄ were added. The reaction mixture was kept at 30°C and intensive mixing for 5 hours. The reaction mixture was extracted using diethyl ether and washed by water till reaching neutral reaction, ether solution was dried using Na₂SO₄ (calcined), drying agent was filtered, solvent was distilled and the residuum was kept in vacuum over P₂O₅. The yield of oxidation products is 0.35 g (70%), yellow oil, R_f 0.65. IR-spectra (film), cm⁻¹: 3517 (ν_{OH}), 3005, 2959, 2930, 2870, 2653, 2535 (ν_{CH}), 1730, 1694 (ν_{CO}). UV-spectrum (EtOH), nm (lg ε): 205 (4.44), 240 (4.57), 270 (shoulder). NMR ¹H spectra, δ, ppm: 5.40 (s. 1H, C⁷H), 5.80 (s. 1H, C¹⁴H), 6.91 (s. 1H, C_{ar}¹⁴H), 7.02 (d. 1H, C_{ar}¹²H), 7.16 (d. 1H, C_{ar}¹¹H), 7.20 (d. 1H, C^{11α}H), 7.31 (d.d. 1H, C^{12α}H), 7.54 (d. 1H, C¹⁴H), 7.91 (s. 1H, C_{ar}¹⁴H), 8.02.

Oxidation of trifluoroethylabietate (2). It was done in analogous manner (1), after processing of solution of 0.57 g (1.47 mmol) of trifluoroethylabietate (2) in 6 ml of toluene 0.2 g (5.9 mmol) H₂O₂ (30%-solution), 0.0056 g (0.032 mmol) FeSO₄, 0,38 g (66%) obtained, MP is 86-87°C, R_f 0.31. IR- spectra (film), cm⁻¹: 3688, 3597, 3510 (ν_{OH}), 3027, 3014, 2934, 2873, 2654 (ν_{CH}), 1738, 1697 (ν_{CO}), 1285, 1229, 1173 (ν_{CF}). UV-spectra (EtOH), nm (lg ε): 211 (3.25). 244 (shoulder). NMR ¹H, δ, ppm. 0.86 (3H, C²⁰H₃), 1.01 and 1.02 (6H, C^{16,17}H₃), 1.26 (3H, C¹⁹H₃), 2.24 (1H, C¹⁵H), 2.35, 2.39, 2.86, 4.48 (m. 2H, CH₂O, *J*=8.5 Гц), 6.91 (s. 1H, C_{ar}¹⁴H), 7.02 (d. 1H, C_{ar}¹²H); 7.16 (d. 1H, ¹¹H), 7.32 (d.d. 1H, C^{12α}H), 7.44 (d. 1H, C¹⁴H), 7.51 (d. 1H, C¹⁴H), 7.76, 7.90 (s. 1H, C_{ar}¹⁴H), 8.10. NMR ¹⁹F, δ, ppm.: - 73.65 (d. 3F, CF₃, *J*=50 Hz).

Oxidation of 1*H*,1*H*,3*H*-trihydrotetrafluoropropylabietate (3). Oxidation of 0.38 g (0.9 mmol) of 1*H*,1*H*,3*H*-trihydrooctafluoropropylabietate in 10 ml of toluene was carried out in analogous manner (1) by processing of 0.1 g (2.9 mmol) H₂O₂ (30%-solution) over 0.0038 g (0.025 mmol) FeSO₄. Yield (3) 0.18 g (45 %), liquid amorphous substance. IR-spectra (film), cm⁻¹: 3664, 3597, 3512 (ν_{OH}), 3027, 3010,

2933, 2872, 2652, 2537 (ν_{CH}), 1696 (ν_{CO}), 1190, 1152, 1124, 1111 (ν_{CF}). UV-spectra (EtOH), nm ($\lg \epsilon$): 204 (4.36), 240 (shoulder), 252 (3.85), 270 shoulder. NMR ^1H spectra δ , ppm: 4.32 (t. 2H, OCH_2 , $J=12.8$ Hz), 5.39 (s. 1H, C^7H), 5.73 (1H, C^{14}H), 5.79 (s. 1H, C^{14}H), 5.83 (t.t. 2H, CF_2H , $J'=53.4$ Hz), 6.90 (s. 1H, $\text{C}_{\text{ar}}^{14}\text{H}$), 7.00 (d. 1H, $\text{C}_{\text{ap}}^{12}\text{H}$), 7.16 (d. 1H, $\text{C}_{\text{ar}}^{11}\text{H}$), 7.33 (d.d. 1H, $\text{C}^{12\alpha}\text{H}$), 7.38, 7.44 (d. 1H, C^{14}H), 7.54 (d. 1H, C^{14}H), 7.89 (s. 1H, $\text{C}_{\text{ar}}^{14}\text{H}$), 8.09. NMR ^{19}F spectra, ppm: -133.96 (d. 2F, $\text{C}^3\text{F}_2\text{H}$, $J=53.4$ Hz), -125.84 (t. 2F, C^2F_2).

Oxidation of 1H,1H,5H-trihydrooctafluoropentylabietate (4) Oxidation of 0.75 g (1.6 mmol) 1H,1H,5H-trihydrooctafluoropentyl-dehydroabietate (4) in 15 ml of toluene was carried out in analogous manner (1) 0.2 g (5.88 mmol) of H_2O_2 (30%-solution) over 0.0075 g (0.049 mmol) FeSO_4 . Yield 0.63 g (84%), amber oil, R_f 0.66. IR-spectra (film), cm^{-1} : 3671, 3603, 3517 (ν_{OH}), 3027, 3003, 2957, 2932, 2870, 2660 (ν_{CH}), 1738, 1695 (ν_{CO}), 1261, 1170, 1119, 1114 (ν_{CF}). UV-spectra (EtOH), nm ($\lg \epsilon$): 208 (4.11), 218 (3.72), 270 (shoulder). NMR ^1H spectra ppm.: 4.51 (t. 2H, OCH_2 $J=20$ Hz), 5.88 (t.t. 1H, CF_2H $J'=52$, $J''=4.5$ Hz), 6.92 (s. 1H, $\text{C}_{\text{ar}}^{14}\text{H}$), 7.04 (d. 1H, $\text{C}_{\text{ar}}^{12}\text{H}$), 7.19 (d. 1H, C^{11}H), 7.31 (d.d. 1H, $\text{C}^{12\alpha}\text{H}$), 7.43 (d. 1H, C^{14}H), 7.90 (s. 1H, $\text{C}_{\text{ar}}^{14}\text{H}$). NMR ^{19}F , δ , ppm.: -136 (d. 2F, CF_2H), -129 (2F, C^4F_2), -124 (2F, C^2F_2), -118 (2F, C^3F_2).

DISCUSSING THE RESULTS

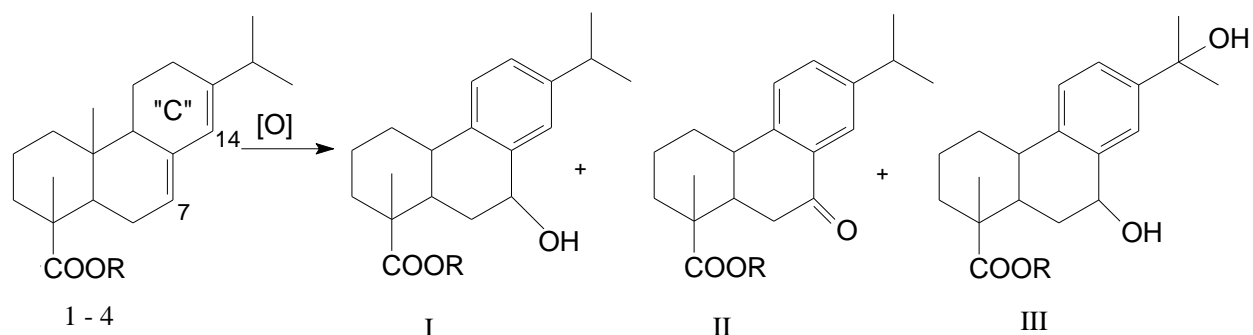
Depending on activity of oxidation system the following directions of oxidation of abietic acid (its esters) are possible: "C" ring aromatization, formation of oxy- and oxa-derivatives, opening up of "C" ring.

When KMnO_4 is acting the abietic acid and its esters form 13,14-diols and 7,8,13,14-tetrols in consistent manner [3]. The processing using such reagents as SeO_2 (C_6H_6) [7, 8] and $\text{Hg}(\text{OAc})_2$ [3] results in "C" ring aromatization as well as in appearing of OH-functions at C-7. Forming of 13,14-epoxide and 7,8,13,14-diepoxy occurs when acetic hydroperoxide is used [9, 10]. The mixture of 13-epoxy-, 13,14-dihydroxy- and 7,8,13,14-tetrahydroxy derivatives forms as a result of abietic acid methyl ester oxidation using monopero-phthalic acid [11]. The mixture of 12-keto-, 6,12-diketoabietates and 7-ketodehydroabietate was obtained when using $\text{CrO}_3 - \text{HOAc}$ (0°C) system [3]. The disclosing of "C" ring occurs when using $\text{Pb}(\text{OAc})_4$, as well as during ozonolysis [3].

The presence of dehydroabietic, 7-hydroxidehydroabietic and 7-dicarbonyldehydroabietic acid was established among main products of abietic acid H_2O_2 oxidation over catalytic complex: $[\pi\text{-C}_5\text{H}_5\text{N}(\text{CH}_2)_{15}\text{CH}_3]_3\text{PW}_{12}\text{O}_{40}$ [12].

Oxidation of abietic acid (1) as well as its esters - trifluoroethylabietate (2), 1H,1H,3H-trihydrotetrafluoropropylabietate (3), 1H,1H,5H-trihydrooctafluoropentyldehydroabietate (4) by triple excess (mole) of 30% solution of H_2O_2 over Fe_2SO_4 in toluene for 5 hours (see scheme).

Scheme



- 1 R = H;
 2 R = CH₂CF₃;
 3 R = CH₂CF₂CF₂H;
 4 R = CH₂(CF₂CF₂)₂H.

For IR-spectra of oxidation products the stripes of valent oscillations of C-H links in the field of 3027-2535 cm⁻¹ are typical as well as oscillations of carbonyl group of C=O at 1738-1730 and 1694-1696 cm⁻¹. Intensive signals in the interval of 1285-1037 cm⁻¹ correspond to ν_{C-F} valent oscillations in the spectra of oxidation products of 2-4 compounds. Besides that, in the spectra of all oxidized compounds new stripes of valent oscillations of hydroxyl groups are appearing in the field of 3688-3510 cm⁻¹.

The considering of protons signals field at C⁷ and C¹⁴, as well as at C¹¹ and C¹² (Table) provides certain information on composition of compounds 1-4 oxidation products. The presence of pair of δ 5.36 – 5.40 and 5.76 – 5.80 ppm signals corresponding to vinyl protons of –C⁷=C⁸–C¹⁴=C¹³– fragment [13] is typical for derivatives of abietic acid (1-4). In spectra of oxidation products this pair is also present in case of compounds 1 (5.40 and 5.80) and 3 (5.36 and 5.78 ppm.). The signals of protons of aromatic ring are appearing in several series (I – III) depending on disposition and quantity of hydroxyl or carbonyl functions within the interval of 6.9 – 7.9 ppm (Table) [14, 15, 13].

Table

Position in Molecule	Position of Protons Signals in Compounds Spectra (δ, ppm):			
	DHAC*	I	II	III
H-11	7.13	7.16 d (8.1)	7.30 d (8.1)	7.20 d (8.5)
H-12	7.00	7.09 dd (1.9 and 8.2)	7.41 dd (8.4 and 2.2)	7.31 dd (8.5 and 1.6)
H-14	6.88	7.38 д (1.8)	7.78 д (2.4)	7.44 д (1.6)
Sources	[13]	[15]	[15]	[14]

* dihydroabietic acid

Comparing experimental and literature data we make a conclusion, that obtained oxidation products of compounds 1-4 represent mixtures of hydroxy- and oxy- derivatives mainly of aromatic row. Series of signals of δ (ppm.) 7.16, 7.00–7.02 and 6.90–6.92 (C-11, C-12, C-14) corresponds to aromatic fragment of dehydroabietic acid and its esters. 7,15-dihydroxiderivatives (III) are among oxidation products: series of signals of 7.18–7.20 (d), 7.28–7.30 (m) and 7.43–7.44 (d). The signals of small intensity of δ 7.16 (d) ppm point out in presence of 7-hydroxiderivatives (I) in the oxidation products of compounds 1-3 and signals of δ 7.89–7.91 ppm the presence of 7-oxoderivatives (II) in oxidation products of compounds 1, 3, 4.

In ^1H NMR spectra of compounds (2-4) the signals of protons of $-\text{OCH}_2-$ group of polyfluoroalkyl fragment are present in the form of multiplets with chemical shifts of 4.48 ppm (2) and 4.32 ppm (3), 4.51 ppm (4). The signals of methane protons of $-\text{CF}_2\text{H}$ ending groups are appearing in the form of triplet of triplets with chemical shifts of 5.83 ppm (3), 5.88 ppm (4).

In UV spectra of oxidation products the absorption maximums are present in the field of 205-218 and 240-250 nm, the absorption of aromatic system is appearing in the form of shoulder in the field of 270 nm.

CONCLUSION

The oxidation of abietic acid and its esters with some polyfluoroalkanols results in aromatization of “C” ring and formation of compounds containing hydroxyl groups in positions C-7 and (or) C-15 as well as carbonyl group in position of C-7 under the influence of H_2O_2 (30%-solution) at catalysis of FeSO_4 (30°C, 5 h).

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