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THE ETHERIFICATION OF THE ALCOHOL-TELOMERS (n= 3 and 4) WITH ABIETIC ACID

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Abstract: Polyfluoroalkyl-containing esters abietic and dehydroabietic acids were synthesized by the reaction of 1H,1H,7H-perfluoroheptan-1-ole and 1H,1H,9H-perfluorononan-1-ole and abietic acid without solvent in acid catalysis. The structure of the esters was confirmed by IR, H^1 and F^{19} -NMR spectroscopy.

Keywords: Abietic acid, polyfluoroalkyl-containing esters abietic and dehydroabietic acids.

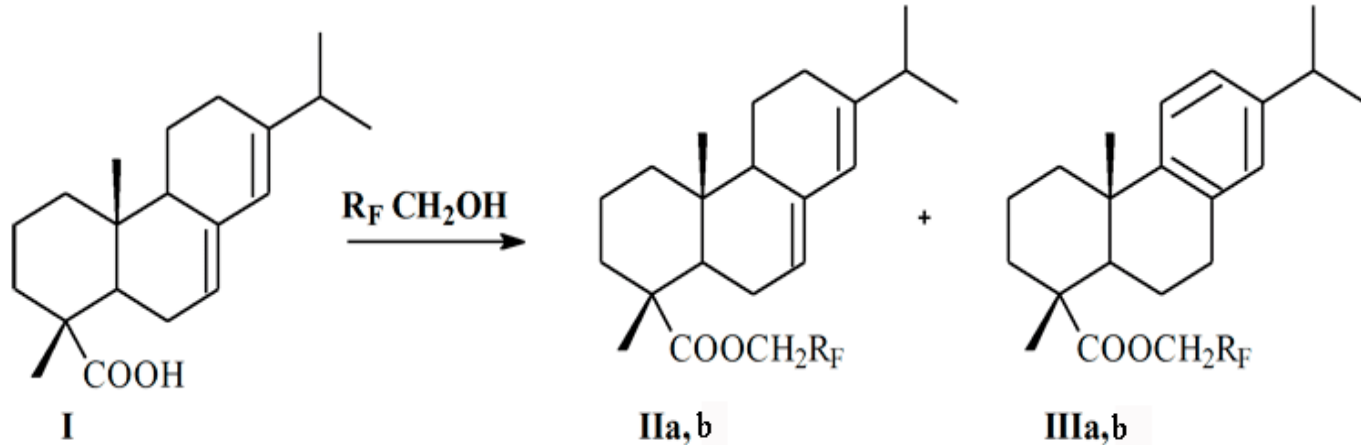
A permanent increase of hydrocarbons value gave an additional impulse to the research on complex remaking of vegetable raw materials. Crude rosin acids, being rich in tricyclic carbon acids, are a suitable source of many organic chemicals.

It is well-known, that properties of rosins (colophonys) esters depend on a kind of the rosin and a structure of the alcohols used. Different kinds of esters are used in production of synthetic resins, plasticizers, varnishers, paints etc. They are ecological products [1, 2].

Introduction of long-chain fluorinated fragments into an organic substance confer to it surface activity [3]. For this reason the fluorine contained colophony esters with such fluorinated alcohols may be oleo- and/or hydrofobizing agents, for example, of fibrous composites.

Previously [4], 1H,1H,5H-trihydrooctafluoropentyldehydroabietate was produced by esterification of 1H,1H,5H-trihydrooctafluoropentan-1-ole with dehydroabietic acid in presence of H_2SO_4 conc. More over, 2,2,2-trifluoroethyl-, 1H,1H,3H-trihydrotetrafluoropropyl-, 1H,1H,5H-trihydrooctafluoropentylabietates and – dehydroabietates and perfluorophenylabietate and dehydroabietate were synthesised by interaction of abietic acyl chloride with corresponding fluorocontained alcohols in form of sodium salts [5].

Similarly tall rosin esterification [6], polyfluoroalkyl contained esters (II and III) were synthesized by interaction of 1H,1H,7H-trihydrododecafluoroheptan-1-ole and 1H,1H,9H-trihydrohexadecafluorononan-1-ole with abietic acid (I), scheme:



The esterification of equimolecular amounts of the reagents carried out in presence of H_2SO_4 conc. as catalyzer with no solvents. After heating at $170\text{-}200^\circ\text{C}$ during 5-6 h., the reaction mass was cooled, dissolved in 50 ml of diethyl ether, washed continuously with 5% aqueous sodium hydrocarbonate solution and distilled water to neutral pH value. Then ether solution was dried with Na_2SO_4 , filtered and evaporated. The TLC method was used to control the reaction. In all cases glassy resins were formed, total issues of II and III riched 90%.

The structures of synthesised compounds were estimated by means of IR and NMR ^1H and ^{19}F methods.

The absorption peaks in the region $2997\text{-}2322\text{ cm}^{-1}$ assigned to the $\nu_{\text{C-H}}$ bonds. Skeleton vibrations of aromatic ring ($\nu_{\text{C=C}}$ and δ_{CH}) appear in the region $1488\text{-}1385\text{ cm}^{-1}$, and strong absorption found in the region $1749\text{-}1695\text{ cm}^{-1}$. Absorption associated with C-F stretching frequencies is found in the region of $1200\text{-}1134\text{ cm}^{-1}$. This a normal region for such absorption to occur (see table).

Table. Analytical and spectra data of abietic acid (I) and their esters (II and III).

Compound	Yield, %	t soft. °C	Acid. num	NMR ^1H , δ , ppm	NMR ^{19}F , δ , ppm	IR, ν , cm^{-1}
I	-	154 – 162	185	0.86 (s. 3H, C^{20}H_3), 1.01 and 1.02 (6H, $\text{C}^{16,17}\text{H}_3$), 1.26 (s. 3H, C^{19}H_3), 5.36 (s. 1H, ^7H), 5.78 (s. 1H, ^{14}H)	-	3420 2957 2932 2869 2649 2525 1698 1449 1386 1279
IIa and IIIa	90	60-66	41	0.87 (s. 3H, C^{20}H_3), 1.21 (s. 6H, $\text{C}^{16,17}\text{H}_3$), 1.23 (s. 6H, $\text{C}^{16,17}\text{H}_3$), 1.28 (s. 3H, C^{19}H_3), 2.86, 4.16 (m. 2H, CH_2O), 5.36 (s. 1H, ^7H), 5.77 (s. 1H, ^{14}H), 6.08 (t.t, $J=50.7$, $J=5.4$ Hz, 1H, CF_2H), 6.89 (s. 1H, ^{14}H), 7.01 (d. 1H, ^{12}H), 7.19 (d. 1H, ^{11}H)	-133.75 (d. $J=53.3$ Hz, 2F, $\text{C}^1\text{F}_2\text{H}$), -126.2 (2F, C^2F_2), -120.3 (2F, $\text{CH}_2\text{-C}^6\text{F}_2$), -120.2 (2F, CF_2), -119.0 (4F, 2 CF_2)	2958 2934 2871 2650 1786 1754 1695 1677 1460 1386 1279 1200 1140
IIb and IIIb	89	58-64	45	0.88 (s. 3H, C^{20}H_3), 1.21 (s. 6H, $\text{C}^{16,17}\text{H}_3$), 1.23 (s. 6H, $\text{C}^{16,17}\text{H}_3$), 1.28 (s. 3H, C^{19}H_3), 2.86, 4.16 (m. 2H, CH_2O), 5.38 (s. 1H, ^7H), 5.77 (s. 1H, ^{14}H), 6.08 (t.t, $J=50.7$, $J=5.4$ Hz, 1H, CF_2H), 6.89 (s. 1H, ^{14}H), 7.01 (d. 1H, ^{12}H), 7.19 (d. 1H, ^{11}H)	-133.7 (d. $J=52.7$ Hz, 2F, $\text{C}^1\text{F}_2\text{H}$), -126.1 (2F, C^2F_2), -120.1 (2F, $\text{CH}_2\text{-C}^8\text{F}_2$), -120.3 (2F, CF_2), -119.1 (2F, CF_2), -118.7 (6F, 3 CF_2)	2960 2932 2870 2530 1765 1693 1676 1639 1461 1374 1214 1148

The ^1H NMR spectra of the esters (II and III) showed characteristic multiplete absorption peaks at 4,16 ppm instead of usually observed triplete, that is probably connected with diastereomeric structures formation of the $-\text{OCH}_2-$ group in polyfluoroalkyl fragment. An olefin bonds conjugated protons signals appear at 5.36 (IIb) and 5.38 (IIa) (C^7H), and 5.78 (C^{14}H) (II) ppm.

One singlet absorption peak at 6.89 ppm (C^{14}H) and two doublet peaks at 7.01 (C^{12}H) and 7.19 (C^{11}H) ppm may be assigned to aromatic ring in the structure of (III).

Moreover, triplet absorption peak with chemical shift 6.08 ppm is assigned to the protons of terminal $-\text{CF}_2\text{H}$ group (see table).

Although the starting abietic acid (I) contains about 10% of dehydroabietic acid (spectral data), the main products of the esterification process were dehydroabietic acids derivatives (III) (about 90%). Analogous behavior, i.e. acid promoted didisproportionation of abietic acid under heating, was observed formerly [6, 7],

The ^{19}F NMR spectra of (II and III) shows a doublets with chemical shifts -133.75 ppm ($J_{\text{HF}} 53.3$ Hz) (IIa and IIIa), and -133.7 ($J_{\text{HF}} 52.7$ Hz) (IIb and IIIb), assigned to $-\text{CF}_2\text{H}$ groups resonance signal of fluorine atoms. The signals of fluorine atom in methylene group C^2F_2 appear as singlets at -126.2 ppm (IIa and IIIa), and -126.1 ppm (IIb and IIIb). The signals of other $-\text{CF}_2-$ groups fluorine atoms appears in the region from -120.3 – -118.7 ppm. Theirs multiplicity and integral intensity corresponds to polyfluoro alkyl telomeric fragments (see table).

Experimental part

TLC method was used to control for the reaction: Sorbfil, hexane : methilene chloride : acetone (1 : 1 : 0,5). IR spectra were registered on Shimadzu IR Prestige-2 (solutions in CCl_4). ^1H and ^{19}F NMR spectra were recorded on Bruker 500 at frequency 500 MHz (^{19}F NMR at 470 MHz), in CDCl_3 , external standart – CCl_3F . Commercial 1H,1H,7H-perfluoroheptan-1-ol (a) and 1H,1H,9H-perfluorononan-1-ol (b), so-called telomers ($n=3$ and 4, corresp.) were used as starting materials.

1H,1H,7H-Dodecafluoroheptylabietate (IIa) and -dehydroabietate (IIIa). To 5.0 g (17 mmol) of abietic acid (I) was added 6,0 (18 mmol) of 1H,1H,7H-dodecafluoroheptan-1-ole (IIa) and 2-3 drops of. H₂SO₄ conc. under argon atmosphere. After stirring for 5 h at 170°C, the reaction mass was extracted with diethyl ether (3×20 ml) at room temperature. Solution obtained was washed with aqueous 5% sodium hydrocarbonate, then with water to neutral reaction and dried under Na₂SO₄. Then the solvent was evaporated. The residue was maintained in vacuum under P₂O₅, to give 9.0 g (90% exit) of pale-yellow amorphous solid, softened at 60-66°C. Analytical and spectral data presents in table.

1H,1H,9H-Hexalecafluorononylabietate (IIb) and – dehydroabietate (IIIb). These esters were prepared in the same manner as (IIIa): from 7,8 g (18 mmol) of 1H,1H,9H-hexadecafluorononane-1-ole (II during 6 h at 200°C. Yield 10.5 g (89%), light-yellow amorphous solid softened at 58-64°C. Analytical and spectral data presents in table.

Conclusion

The interaction between fluorine contained alcohols and abietic acid in acidic media at 170-200°C led to forming of corresponding dehydroabietic esters in good yields (89-90%).

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