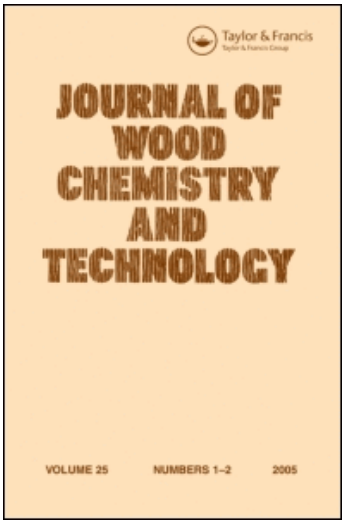

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A Variation in Acid-Catalyzed Isomerization of Abietadienoic Acids

Duane F. Zinkel[a]
[a] Forest Products Laboratory, Research Chemist USDA Forest Service, Madison, Wisconsin

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A VARIATION IN ACID-CATALYZED ISOMERIZATION OF ABIETADIENOIC ACIDS

Duane F. Zinkel, Research Chemist
USDA Forest Service
Forest Products Laboratory*
Madison, Wisconsin 53705–2398

ABSTRACT

Heating the individual common abietadienoic acid methyl esters with *p*-toluene sulfonic acid in chloroform led to the formation of methyl abietadienoates other than the equilibrium mixture of methyl abietate, palustrate, and neoabietate that is usually formed by acid-catalyzed isomerization. Of these other methyl abietadienoates, the three principal constituents comprised 10%, 4% and 2% of the monomers; these compounds were isolated and identified as methyl 13β-abieta-7,9(11)-dien-18-oate, methyl 7,9(11)-abietadien-18-oate, and methyl 8,12-abietadien-18-oate, respectively.

INTRODUCTION

The acid-catalyzed isomerization of the common abietadienoic resin acids of rosin and oleoresin (levopimaric, palustric, abietic, and neoabietic acids) has been investigated.[1] At equilibrium, the product consists primarily of abietic acid, smaller amounts of palustric and neoabietic acids, and only a trace amount of levopimaric acid. While investigating dimerization of levopimaric acid catalyzed by *p*-toluene sulfonic acid (PTSA),[2] we observed that small amounts of monomeric acids were formed in addition to the usual isomerization products. The identification of three of these unexpected isomerization products is herein described.

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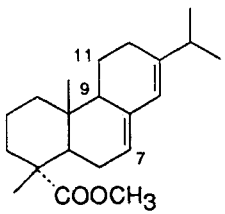
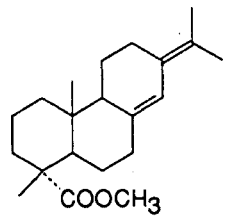


Methyl abietate



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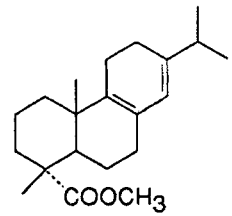

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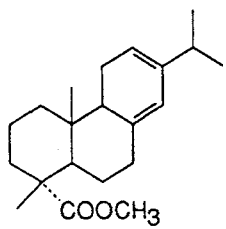

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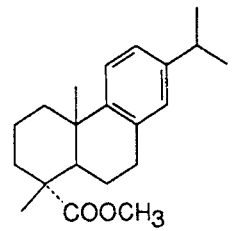
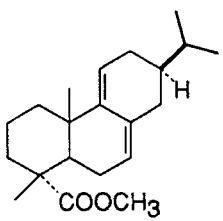


Methyl dehydroabietate



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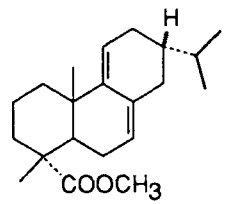

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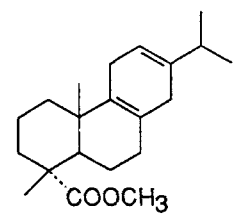

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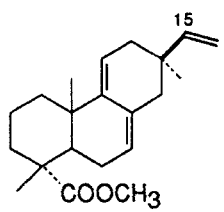
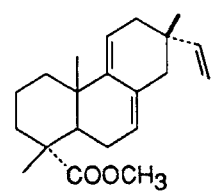


Methyl
7,9(11),15-pimaratrienoate



Methyl
7,9(11),15-isopimaratrienoate

TABLE 1

Gas Chromatographic Retention Data[a] for Products of Acid-Catalyzed Isomerization of Methyl Abietadienoates

	BDS	DB-1	
Methyl ester	190°C	190°C	170°C
Levopimarate	1.354	1.243	1.278
Palustrate	1.396	1.248	1.298
13β-7,9(11)-Abietadienoate (I)	1.655	1.364	1.429
7,9(11)-Abietadienoate (II)	1.419	1.248	1.295
8,12-Abietadienoate (III)	1.792	1.464	1.573
Abietate	2.182	1.603	1.701
Dehydroabietate	2.274	1.357	1.430
Neoabietate	2.505	1.891	2.028

[a]FSOT columns; methyl pimarate = 1.000.

RESULTS AND DISCUSSION

The course of the PTSA-catalyzed dimerization of the abietadienoic acids (as the methyl esters) in $CHCl_3$ was monitored by gas chromatography using a thin-film methyl silicone capillary column with temperature programming. This provided data for both the monomers (Table 1) and dimers. An unexpected peak appeared in the monomer portion of the chromatogram that increased during the reaction to about 10% of the total monomers. Comparison of its retention characteristic with previous data[3] suggested it to be methyl 13β-abieta-7,9,(11)-dien-18-oate. Confirmation was obtained using a polar column (butanediol succinate) but another component, not apparent in the methyl silicone column chromatogram, was observed (4% of the monomers). A number of other minor peaks were also seen, the largest of which was 2% of the total monomers.

Prior to isolation of these components, efforts were made to maximize yields of the 10%, 4%, and 2% components (compounds I, II, and III, respectively). The selection of a specific methyl abietadienoate (i.e., levopimarate, abietate, palustrate, or neoabietate) was not important because all were rapidly isomerized (about 15 min) in the PTSA solution to a monomer mixture having the same composition. This composition was similar to the equilibrium composition of 93% abietic

acid–4% palustric acid–3% neoabietic acid found for isomerization catalyzed by ethanolic hydrochloric acid.[1] An exact composition could not be obtained because of competing dimerization and some disproportionation or dehydrogenation (concerted oxidation–dehydration). Methyl levopimarate was used in a preparative scale reaction for component isolation. Typical conditions that provided near-optimal results were 1% methyl levopimarate in $CHCl_3$(w/v) containing 3% PTSA heated at 60°C for 2 h. Mole ratios greater than 2/1 PTSA to resin acid ester give the best overall yields of compounds I, II, and III. This ratio cannot be significantly increased because of the limited solubility of PTSA in chloroform (use of the chloroform-soluble and strongly acidic ethyl metaphosphate was not as effective as PTSA).

Compounds I, II, and III were isolated by a series of chromatographic separations. After removal of PTSA, the reaction product in diethyl ether was chromatographed in small portions on a silver–resin column.[4] The order of elution was dehydroabietate, I and II, abietate, and III. Repetitive recycling of selected fractions gave a mixture of I and II that was free from dehydroabietate and abietate. HPLC of this mixture using a bonded cyclodextrin column with 0.15% THF–hexane provided I and II as pure materials. Fractions enriched in III were rechromatographed on the silver–resin column followed by HPLC on the cyclodextrin column.

The GLC retention and the ^1H NMR spectrum of I were identical with our previously published data (GLC[3] and ^1H NMR[5] for methyl 13β-abieta-7,9(11)-dien-18-oate.[6] Direct GLC comparison of I and authentic 13β-abieta-7,9(11)-dienoate confirmed the identification.

The UV, IR, MS, and NMR spectral data for I and II were nearly identical, indicating similarity in structure. The ultraviolet absorption data of λ_{max} 240.5 nm (ε = 18,300) for I and λ_{max} 243.5 nm (ε = 15,800) for II were consistent with the data reported for the more constrained 7,9(11)-dienyl lanostane (λ_{max} 243 nm) and euphol (λ_{max} 240 nm) triterpene systems[7] and with our observations for 7,9(11),15-pimaratrienoate (λ_{max} 240 nm) and 7,9,(11),15-isopimaradienoate (λ_{max} 241.5 nm). The ^1H NMR spectra were consistent, therefore, only with the interpretation that II is methyl abieta-7,9(11)-18-oate.

The identification of compound III was straightforward. The GLC retention indicated this compound to be methyl 8,12-abietadien-18-oate, which was confirmed by comparison with the retention of authentic material[8] and by comparison of the ^1H NMR spectrum with that in the literature.[5]

Although the three abietadienoic acids were not found previously during laboratory acid-catalyzed or thermal isomerizations, there is precedent for the formation of these acids during the distillation of tall oil. Holmbom[9,10] postulated the presence of the three acids in distillation fractions, particularly in tall oil rosin, based on GC–MS comparison with published data.[5] However, experimental details were not presented and the identifications were not confirmed by isolation of the compounds.

EXPERIMENTAL

Gas chromatographic analysis was performed using Hewlett–Packard model 5880 gas chromatographs with butanediol succinate (BDS) and methyl silicone (DB-1) fused silica open tubular (FSOT) columns. The 14-m BDS column was operated isothermally at 190°C to determine the composition of the monomeric components.[11,12] The 15-m, thin-film (0.1-μm) DB-1 column was temperature programmed to determine the content of dimeric components.[4] All NMR spectra were obtained at 310 K with a Bruker WM 250 (250 MHz proton and 62.9 MHz carbon) FT spectrometer.** The chemical shift values (δ) for the compounds in $CDCl_3$ are given in ppm relative to internal tetramethylsilane. EIMS were obtained with a Finnegan model 4510 at 70 V with sample introduction by GC and are reported as m/z (percentage of relative intensity). Absolute ethanol was used as the solvent for the ultraviolet spectra.

Conditions were defined for optimum yields of compounds I, II, and III. A solution of 1 g of methyl levopimarate and 2 g of *p*-toluene sulfonic acid monohydrate in $CHCl_3$ was heated at 62°C for 2 h. The solution was then extracted with 1% sodium bicarbonate and washed with water. After removal of the solvent, the reaction product (50% diethyl ether solution) was chromatographed in three portions on the same silver–resin column described in reference 4 using diethyl ether as eluant. Recycling of selected fractions provided a mixture of I and II. This mixture was chromatographed (50 μL containing 1.5 mg mixture) with a 250 mm x 10 mm Cyclobond I (bonded β-cyclodextrin, Advanced Separation Technologies Inc., Whippany, N.J.) column using 0.15% THF in hexane at a flow rate of 1.6 ml/min (UV detector set at 254 nm). Although the injection of 1.5 mg mixture overloaded

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the column capacity, isolation of the pure components was possible because of component separation (elution at 30.6 and 35.0 min under analytical conditions), column efficiency, and recycling of intermediate cuts. About 30 mg I and 10 mg II of purity >99% were eventually isolated.

Compound I

Spectral data for compound I were in accord with that previously published for methyl 13β-abieta-7,9(11)-dien-18-oate.[5] ^{1}H NMR: δ 5.45 and 5.32 (2H, br *m*, C=CH), 3.62 (*s*, OMe), 1.24 and 0.96 (2 Me *s*), 0.891 and 0.877 (*dd*, 2 Me of isopropyl). ^{13}C NMR: δ 178.8, 146.3, 133.6, 120.0, 117.9, 51.8, 47.0, 43.9, 41.0, 37.2, 36.4, 36.1, 35.6, 32.4, 30.1, 25.7, 21.1, 19.8, 19.6, 18.3, and 17.1. MS: 316 (72), 301 (8), 273 (12), 256 (30), 241 (100), 213 (30), 201 (41), 185 (31), 157 (32), 131 (40). UV: λ_{max} 240.5 nm (ε = 18,300).

Compound II

The spectral data for compound II (methyl 7,9(11)-abietadien-18-oate) were as follows. ^{1}H NMR: δ 5.54 and 5.37 (2H br *m*, C=CH), 3.63 (OMe), 1.24 and 0.97 (2 Me *s*), 0.886 and 0.879 (*dd*, 2 Me of isopropyl). ^{13}C NMR: δ 179.0, 146.9, 132.7, 121.0, 118.5, 51.8, 46.9, 44.2, 40.2, 37.1, 36.6, 36.4, 35.2, 31.2, 29.6, 25.6, 22.4, 20.2, 20.1, 18.3, 17.2. The MS was essentially identical to that for I. UV: λ_{max} 243.5 nm (ε = 15,800).

Compound III

For compound III (methyl 8,12-abietadien-18-oate), a fraction, eluting from the silver–resin column after most of the methyl abietate, was rechromatographed on the silver–resin column and then chromatographed on the Cyclobond column. The GLC retention characteristics and the ^{1}H NMR spectrum were identical to data[5] for authentic material.[8] ^{13}C NMR: δ 179.3, 140.0, 134.8, 124.2, 116.2, 51.8, 47.8, 46.1, 36.7, 36.6, 36.0, 34.2, 33.1, 31.3, 25.3, 21.5, 21.3, 21.1, 19.7, 18.3, 16.5. The MS of the isolate and that in the literature were consistent; the only difference was that the base peak for the isolate was *m/z* 146 (GC-MS) in our study but *m/z* 91 in the literature.[5]

Corresponding 7,9(11)-Pimarane and -Isopimarate Derivatives

These compounds, courtesy of Professor Bernard Delmond, provided comparison spectra. Data are provided here to complement that published.

For methyl 7,9(11),15-pimaratrien-18-oate, the spectral data were as follows. ^{1}H NMR: δ 5.9-4.8 (3 exocyclic vinyl H, see reference 13 for details), 5.38 (*m*, 2 C=CH), 3.64 (OMe), 1.25, 0.97, 0.95 (3 Me *s*). MS; 314 (72), 299 (62), 273 (36), 239 (100), 212 (50), 143 (73), 105 (47), 91 (56). UV: λ_{max} 240.0 nm (ε = 14,800). See reference 13 for comparison.

For methyl 7,9(11),15-isopimaratrien-18-oate, the data were as follows. ^{1}H NMR: δ 5.9-4.8 (3 exocyclic vinyl H, see reference 14 for details), 5.38 (*m*, 2 C=CH), 3.63 (OMe), 1.25, 0.99, 0.96 (3 Me *s*). The MS was identical to that of the 7,9(11),15-pimaratrienoate except for some minor intensity differences and *m/z* 299 (34). UV: λ_{max} 241.5 nm (ε = 16,700). See reference 15 for comparison.

ACKNOWLEDGMENT

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