R_F 0.42 (2:1 v/v ethyl acetate–benzene); $[\alpha]^{24}D$ +7.6° (*c* 0.559, water). *Anal.* Calcd for $C_{10}H_{18}O_6$: C, 51.27; H, 7.74. Found: C, 51.39; H, 7.95.

3,4-Di-*O*-methyl-D-mannitol (V) from *cis*-1,2:*trans*-5,6-Di-*O*-ethylidene-D-mannitol (III).—Sodium hydride, 0.928 g in a 55% oil dispersion, was washed with two 50-ml portions of anhydrous ethyl ether; finally, the gray powder was covered with 50 ml of ether. *cis,trans* III (0.385 g) was added, and the reaction mixture was stirred for 30 min, when methyl sulfate (1.2 ml) was added in one portion. After the mixture was stirred at room temperature for 20 hr, tlc revealed the methylation to be complete. The reaction was worked up as reported for the *cis,cis* III to give, after removal of the ether, a syrup (0.241 g). This syrup was dissolved in 10 ml of methanol, and 5 drops of concentrated hydrochloric acid was added. After 20 hr at room temperature the methanolic solution was diluted with 20–30 ml of water, neutralized to pH 7.0 ± 0.1 with 0.01 *N* sodium hydroxide, and concentrated to dryness to a granularlike solid. Trituration of this solid with three 30-ml portions of ethyl acetate–isopropyl alcohol (1:1 v/v) gave on concentration 0.172 g, mp 143–148°, of crude 3,4-di-*O*-methyl-D-mannitol. Recrystallization from a mixture of 5 ml of ethanol and 10 ml of ethyl acetate gave 96 mg, mp 145–148° (concentrating mother liquor gave 72 mg of an impure sample). The melting point of a mixture of compound V from the *cis,cis* isomer and *cis,trans* isomer was undepressed. *Anal.* Calcd for $C_8H_{18}O_6$: C, 45.70; H, 8.63. Found: C, 45.73; H, 8.63.

Registry No.—II (*cis*-1,2:*cis*-5,6-), 17288-91-4; II (*cis*-1,2:*trans*-5,6-), 17288-92-5; II (R′ = Ts; *cis*-1,2:-*cis*-5,6-), 17326-49-7; II (R = Ac; *cis*-1,2:*cis*-5,6-), 17288-93-6; II (R = Ts; *cis*-1,2:*trans*-5,6-), 17288-94-7; II (R = Ac; *cis*-1,2:*trans*-5,6-), 17288-95-8; III (*cis*-1,2:*cis*-5,6-), 17288-96-9; III (*cis*-1,2:*trans*-5,6-), 17288-97-0; V, 17288-98-1.

Acknowledgment.—Acknowledgment is made to Mrs. Clara McGrew and Mrs. Bonita Heaton for the microchemical analyses and to Mr. C. A. Glass and Mr. W. A. Boyd for the nmr data.

Novel Ring Openings in Methyl Levopimarate[1a]

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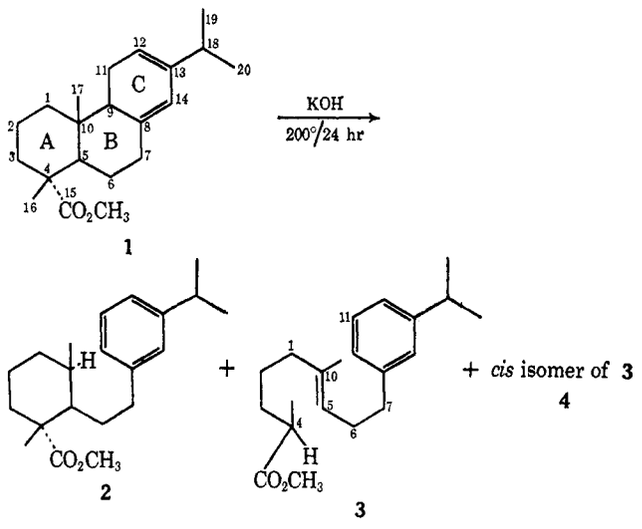
Methyl levopimarate (1) in the presence of a catalytic amount of potassium hydroxide at 200° rearranges to give four new compounds isomeric to 1, in about 57% yield. Three of these compounds (2, 3, and 4) have been isolated and their structures have been postulated. The reaction involves the opening of ring B in the formation of 2, and that of rings A and B in the formation of 3 and 4. In all three compounds ring C is aromatized. Treatment with iodine converts the *cis* isomer 4 into the *trans* isomer 3 and also closes ring A to form 2.

During the course of a systematic investigation[2-4] of the effect of heat and of heat and alkali upon the four conjugated dienoic resin acids (and their esters) found in pine gum, we have recently discovered two new ring-cleavage reactions to occur in the case of levopimaric acid methyl ester. Methyl levopimarate, in the presence of 5 mol % of potassium hydroxide at 200° for 24 hr under nitrogen was found to give a mixture of 6.2% **4**, 30% **3**, 14.6% an unknown peak, 22.9% **2**, 9.6% palustrate, 2.4% levopimarate, 2% dihydroabietate (?), 4.6% dehydroabietate, and 7.7% abietate.

The crude mixture was analyzed by means of glpc on a Versamid column.[2] Compounds **2**, **3**, and **4** were collected on a preparative glpc Versamid column and compounds **2** and **3** were rechromatographed on a SE-30 glpc column and collected.

The mass spectra confirmed the fact that **2**, **3**, and **4** were isomeric to **1** since all showed a molecular ion *m/e* 316. This was considered unusual in view of the fact that the compounds all came off the glpc columns much earlier than any of the resin acid esters. The infrared (ir) spectra indicated the presence of the ester group and of a *meta*-disubstituted aromatic ring in all cases. Similarly, all three compounds exhibited maxima in the ultraviolet (uv) absorption region of 263 mμ,

SCHEME I



typical of *meta*-disubstituted aromatic compounds.[5] The nuclear magnetic resonance (nmr) spectra of all three compounds showed multiplet peaks in the aromatic region (peaks from δ 6.85 to 7.25 ppm) equivalent on integration to four protons. The position and shape of these peaks resembled those exhibited by *m*-xylene.[6] These data would suggest that ring opening(s) had occurred in the three compounds in question.

Biemann[7] has postulated, based on mass spec-

(1) (a) Presented to the American Chemical Society, First Central Regional Meeting, Akron, Ohio, May 1968. (b) National Academy of Sciences, National Research Council postdoctoral fellow. (c) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) H. Takeda, W. H. Schuller, and R. V. Lawrence, *J. Org. Chem.*, **33**, 1683 (1968).

(3) H. Takeda, W. H. Schuller, and R. V. Lawrence, *J. Chem. Eng. Data*, in press.

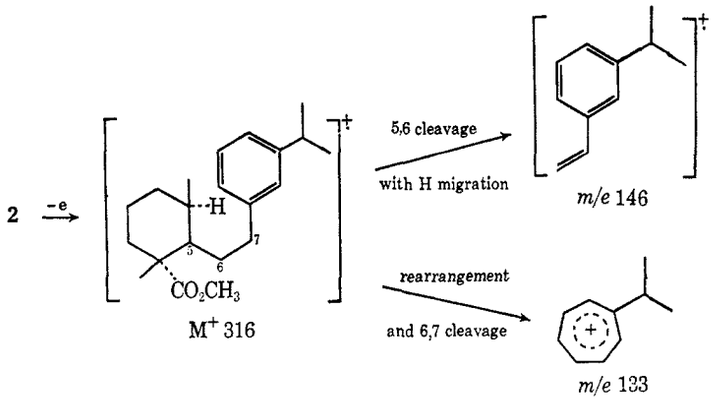
(4) H. Takeda, W. H. Schuller, and R. V. Lawrence, to be published.

(5) L. Coub and J. M. Vandenbelt, *J. Amer. Chem. Soc.*, **71**, 2414 (1949).

(6) N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Catalog," Varian Associates, Inc., Palo Alto, Calif., 1962, Spectrum No. 202.

(7) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 337.

SCHEME II



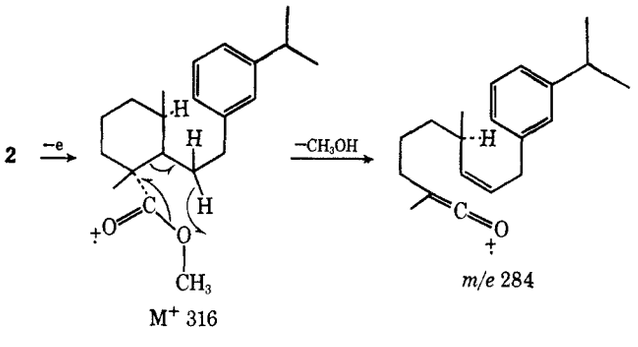
troscopic studies, that C_9–C_{10} bond cleavage commonly occurs in resin acid esters by electron bombardment provided that the C_9–C_{10} bond is located β to a double bond. Thus peaks at *m/e* 181 and 121 are found in high intensity in the mass spectra of methyl pimarate,[7,8a] methyl sandaracopimarate,[7] and methyl levopimarate.[8b] It is significant, therefore, that in the mass spectra of compounds **2**, **3**, and **4** *m/e* 181 and 121 peaks were found to be absent or in very low abundance, indicating the absence of a C_9–C_{10} bond β to a double-bond system.

Further detailed consideration of the nmr and the mass spectra led to the postulation of structure **2** for the compound of relative retention time of 0.555 (methyl dehydroabietate as 1.0).[9] This compound would appear to result from the cleavage of ring B at the 9,10 position. In the nmr spectrum, the benzyl protons appeared as a triplet (J = 6 Hz) at δ 2.62 ppm. A somewhat unresolved doublet contered at δ 1.00 ppm was assigned to the C_{10} methyl. In addition to the C_4-methyl signal at δ 1.15 and the methoxy signal at δ 3.66 ppm, the double-intensity methyl doublet of the isopropyl group at δ 1.24 ppm (J = 6.5 Hz) was also observed.

The mass spectrum provided strong evidence for the assignment of structure **2** to the compound under discussion (see Scheme II). The base peak of **2** was found at *m/e* 146 (100%) arising from bond rupture at C_5–C_6 with proton migration. Peak 133 (46%) is explained as being due to a rearrangement followed by cleavage of the C_6–C_7 bond to give a tropylium ion carrying an isopropyl group.

It has been reported[10a] by Genge that the M − 43, peak arising from a loss of an isopropyl group from the molecular ion, is a common peak in the mass spectra of rosin acid esters with the exception of methyl neoabietate and methyl dehydroabietate, where this peak is not observed. In the latter case, this is probably due to the aromatic nature of ring C (*e.g.*, toluene does not lose a methyl group on electron bombardment[10b]). Essentially no peak was observed at M − 43 in the mass spectra of **2**, **3**, and **4**. An intense peak in **2** is located at *m/e* 284, accounted for by the loss of a methanol molecule from the molecular ion (see Scheme III). The loss of methanol is considered to proceed in a similar fashion to the "McLafferty rearrangement"[11a] or the *ortho* effect,[11b] forming a six-membered ring as shown in Scheme III.

SCHEME III



The nmr and mass spectral data suggest that the compound of relative retention time 0.481 has structure **3**. The nmr spectrum shows a single proton triplet (J = 6.0 Hz) at δ 5.20 ppm assigned to the vinyl proton at C_5, an allylic proton (C_1) at δ 1.98 ppm, also as a triplet (J = 6 Hz), and the other allylic protons (C_6) at δ 2.41 ppm as two sets of triplets (J_{6-7} = 7 Hz, J_{5-6} = 6 Hz). The shielded C_{10}-methyl singlet signal at δ 1.55 ppm indicates the configuration about the double bond to be *trans*. In addition, the C_4-methyl doublet at δ 1.13 ppm (J = 7 Hz) and the isopropyl methyls centered at δ 1.25 ppm as doublets were observed.

The mass spectrum of **3** exhibited a base peak at *m/e* 146, as was observed in the case of **2**, as well as a strong peak at *m/e* 133 (70.7%) both explainable in terms of Scheme II (same cleavage of same moiety as in **2**). The low abundance of peak *m/e* 284 in the mass spectra of **3** is attributed to the absence of the C_4–C_5 bond. It is this bond which holds the ester in position for the "McLafferty rearrangement" to take place. Intense peaks of *m/e* 187, 151, and 123 were observed as well as a peak at 129 in the mass spectrum of **3**. These peaks were found to be in low abundance in the mass spectrum of **2**. The probable pathways for the

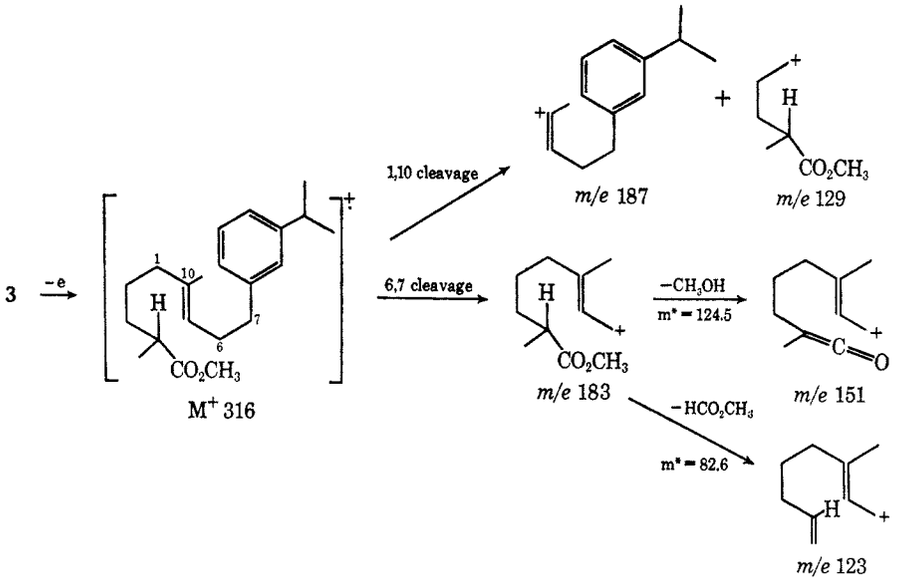
(8) (a) H. E. Audier, S. Bory, M. Fetizon, and N. T. Anh, *Bull. Soc. Chim. Fr.*, 4002 (1966); (b) H. H. Bruun and S. Gasland, *Acta Acad. Aboensis, Math. Phys.*, **22**, 24 (1960).

(9) After this work had been completed, D. F. Zinkel and J. W. Rowe described the isolation and characterization of compound **2** from a tall oil fraction at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts of Papers D No. 30. The stereochemistry of **2** at C_{10} as shown in this manuscript was felt by the present authors to be most logical based on mechanistic considerations. D. F. Zinkel as a referee on the present manuscript noted that the stereochemistry has been confirmed by him to be as shown in the present work.

(10) (a) C. A. Genge, *Anal. Chem.*, **31**, 1750 (1959); (b) see ref 7, p 85.

(11) (a) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966, p 123; (b) p 133.

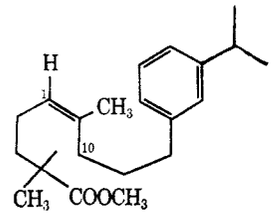
SCHEME IV



formation of these peaks are outlined in Scheme IV. Peaks *m/e* 187 and 129 are considered to be the result of C_1–C_{10} bond cleavage. Similarly, cleavage of the C_6–C_7 bond would produce the fragment *m/e* 183. The loss of neutral methanol and methyl formate from the fragment *m/e* 183 to form *m/e* 151 and *m/e* 123 peaks were confirmed by the metastable peaks at m* 124.5 and m* 82.6, respectively.

The ir, uv, and mass spectra of the compound of relative retention time of 0.428 are strikingly similar to these spectra of compound **3**. It is therefore concluded that this new material (**4**) is the *cis* isomer of **3**. If **4** were the optical isomer of **3** at C_4, the two compounds would not be expected to be cleanly separated by glpc on Versamid, while experimentally a clean separation is observed. The structure of **4** as the *cis* isomer of **3** is confirmed by the nmr spectrum although the over-all appearance of the spectrum resembled that of **3**. A deshielded C_{10}-methyl signal is observed at δ 1.66 ppm as a fine splitting doublet (J = 1.5 Hz). Consequently, the C_5-vinyl signal appears as a broad triplet at δ 5.20 ppm.

Another isomer of **3** could be considered as a candidate for the last compound under discussion (**5**).



5

The mass spectrum, however, rules out this structure. Fragments at *m/e* 187 and 129 are unlikely to occur from **5** since the formation of these fragments involve C_1–C_{10} bond cleavage.

Compounds **2**, **3**, and **4** were heated separately at 200° for 24 hr in the presence and absence of base. No change occurred in any case, indicating that the compounds are not in equilibrium with one another. The ratio of products formed from **1** must thus be kinetically determined.

Compound **4** was treated with a trace of iodine in refluxing benzene. Compound **3**, the *trans* isomer, was found (18.5% yield) as well as compound **2** (36.7% yield). The formation of compound **2** must involve the formation of a new carbon to carbon bond. Compound **3** on treatment with iodine also formed **4** (6.2%), **2** (19.7%), and an unknown material (13.5%). The closure of the C_4–C_5 bond in the presence of iodine to form compound **2** probably occurs because of radical formation α to the carboxyl.[12]

Levopimaric acid isomerized at 200° to give an equilibrium mixture of 81% abietic acid, 14% palustric acid, and 5% neoabietic acid.[2] Levopimaric acid in the presence of 5 mol % of potassium hydroxide at 200° was found to isomerize predominantly with only a trace of compounds **2**, **3**, and **4** being formed. However, levopimaric acid in the presence of 105 mol % of potassium hydroxide forms about 15% **2**, **3**, and **4** and 25% an unknown material located in the same region of the glpc curve. This unknown material was found extremely difficult to purify.

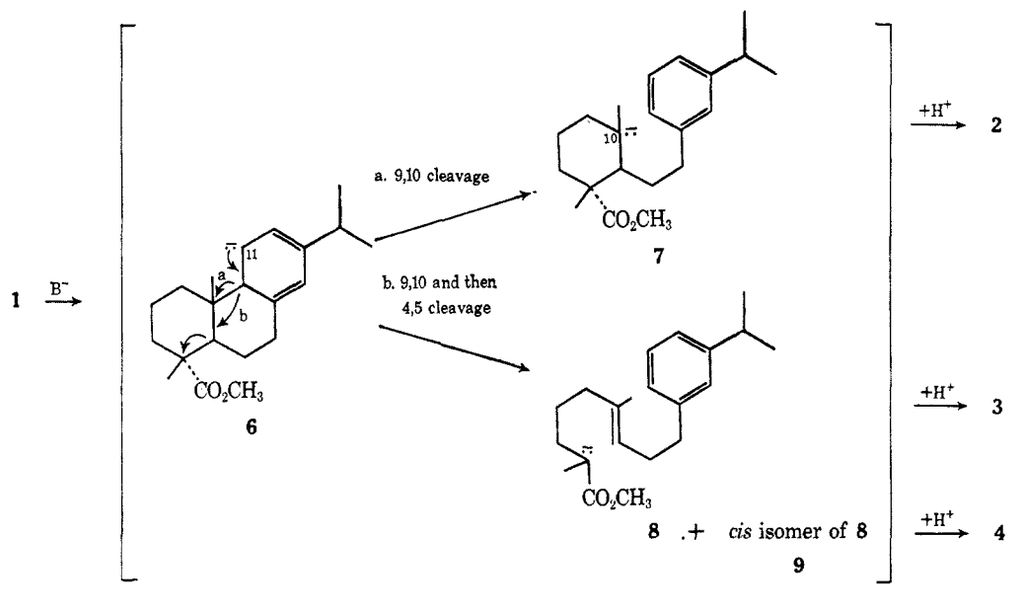
In the present work it was observed that an old Versamid column, containing amine[2] and/or potassium hydroxide from earlier injections of samples, formed **2**, **3**, and **4** in modest amounts upon injection of fresh methyl levopimarate. It has been reported that methyl levopimarate on standing for long periods of time forms small amounts of a considerable number of unidentified compounds.[13]

Compounds somewhat similar in structure to compound **2** have been reported.[14] These were prepared by the reaction of levopimaric acid with acetylenic dienophiles followed by thermal cleavage of the adducts.

Methyl levopimarate in the absence of base isomerizes very rapidly at 200° to methyl abietate, neoabietate, and palustrate.[4] Disproportionation to methyl dehydroabietate also occurs.[4] Methyl abietate,[3] palustrate,[4] and neoabietate[4] also isomerize to an equilibrium mixture of methyl abietate, methyl palustrate, and methyl neoabietate at 200°. Dispro-

(12) This fact was pointed out by a referee.
(13) F. H. Max Nestler and D. F. Zinkel, *Anal. Chem.*, **39**, 1118 (1967).
(14) W. Herz, R. C. Blackstone, and M. G. Nair, *J. Org. Chem.*, **31**, 1800 (1966).

SCHEME V



portionation of methyl abietate to methyl dehydroabietate also occurs.[3] The addition of potassium hydroxide to methyl abietate[3] strongly inhibits both isomerization and disproportionation. In addition, it was found that methyl dehydroabietate was stable at 200° in the presence of potassium hydroxide. No rearrangement to compounds **2**, **3**, and **4** was observed in any of the above cases.[3,4] Thus it would appear that, in the case of methyl levopimarate, the presence of alkali prevents isomerization and disproportionation to the other four esters which in turn are not convertible into compounds **2**, **3**, and **4** at 200°. The presence of base would appear simultaneously to catalyze the cleavage of methyl levopimarate to give compounds **2**, **3**, and **4** as is discussed below. The rearrangement reactions are observed to be considerably less kinetically favored than the isomerization reactions.

The rearrangements of **1** were found to occur in the presence of free-radical inhibitors and not to be accelerated by free-radical catalysts. On the basis of the present evidence, it would seem that the conversion of **1** into **2**, **3**, and **4** involves a carbanion intermediate as pictured in Scheme V. Abstraction of a proton from C_{11} should readily occur to give **6** followed by the electron shifts indicated. In this manner **7**, **8**, and **9** are formed. The formation of the aromatic ring would be expected to be a driving force in all three cases. Anion **7** would be expected to add a proton quite readily. The fact that **2** does not go to **3** and **4** in the presence of base is explained by the difficulty of forming **7** from **2** in the presence of potassium hydroxide. The stability of anions **8** and **9** would also be expected to be a driving force in their formation and thus in the conversion of **1** into **3** and **4**.

The isomerization of levopimaric acid in the presence of an excess of potassium *t*-butoxide in dimethyl sulfoxide has been reported.[15] The isomerization to abietic, palustric, and neoabietic acids, which do not form **2**, **3**, and **4**, is apparently so kinetically favored (reaction time 1 min) that compounds **2**, **3**, and **4** do not form to any significant extent. This shows[12] that the anion at C_{11}, although formed more readily, has a considerably longer half-life than the anion at C_7.

(15) W. H. Schuller and R. V. Lawrence, *J. Org. Chem.*, **30**, 2080 (1965).

Experimental Section[16]

The Reaction of Methyl Leovopimarate in the Presence of Potassium Hydroxide at 200°.—An ether–methanol solution of methyl levopimarate and 5 mol % of potassium hydroxide was charged in equal portions to glass Carius tubes, the solvent was removed under reduced pressure, and the tubes were sealed under nitrogen *in vacuo* in the usual manner[2] and heated to 200° in an oil bath. Tubes were opened at intervals; the reaction was followed by glpc analysis.[2] The reaction was found to be complete in 24 hr. Data are given as compound number (yield) (relative retention time based on methyl dehydroabietate as 1.0): **4** (6.2%) (0.428), **3** (30%) (0.481), unknown peak (14.6%) (0.518), **2** (22.9%) (0.555), methyl palustrate–methyl levopimarate ratio of 4:1 in peak (12%) (0.815) (peak collected and analyzed by $[\alpha]^{t}D$), dihydroabietate (?) (2%) (0.935), methyl dehydroabietate (4.6%) (1.0), and methyl abietate (7.7%) (1.165). The yields are given on the portion which is volatile on the glpc column. The total per cent volatiles was 77%. The use of 15 mol % of potassium hydroxide for 48 hr at 200° gave essentially identical results.

Methyl 2-[2′-(*m*-Isopropylphenyl)ethyl]-1,3-dimethylcyclohexane Carboxylate (2).—Compound **2** was collected from the Versamid preparative column, followed by recollection from the analytical SE-30 column. The colorless oil then gave a single peak on both SE-30 and Versamid columns: $[\alpha]^{25}D$ 0.0° (*c* 1); uv max 263 mμ (ε 380), 271 mμ (ε 316); ir (neat), 1724 (C=O), 1605 (aromatic), 1485, 1460 (CH_3), 1380 (CH), 1290, 1250, 1220, 1195, 1175 (isopropyl), 1140 (isopropyl), 1123, 1105, 1038, 982, 963, 884, 788 (*meta*-disubstituted aromatic), and 702 cm^{-1} (*meta*-disubstituted aromatic); nmr (see Scheme I for numbering system), δ 1.00 (unresolved d, 3, C_{10} CH_3), 1.15 (s, C_4 CH_3), 1.24 (d, 6, J = 6.5 Hz, isopropyl CH_3), 2.62 (t, 2, J = 6 Hz, C_7 C_6H_5-CH_2), 2.76 (septet, 1, J = 6.5 Hz, C_{18} **H**), 3.66 (s, 3, $COOCH_3$) and 7.02 (m, 4, aromatic protons); mass spectrum, *m/e* (rel

(16) Optical rotations and uv absorption spectra were determined in 95% ethanol. Nmr were obtained in deuteriochloroform on a Varian A-60 spectrometer. Frequencies are in parts per million measured downfield from the internal standard, tetramethylsilane. Preparative glpc was carried out on an Aerograph A-700 using a 20 ft × 3/8 in. o.d. aluminum column packed with 5% Versamid 900 on 60–80 mesh Chromosorb W at 250°. Analytical glpc work was carried out on an F & M 500 using a 15 ft × 1/4 in. o.d. aluminum column packed with the same materials. For further purification of compounds **2** and **3**, a 15 ft × 1/4 in. o.d. aluminum column packed with 3.8% of SE-30 on 60–80 mesh Chromosorb W was used at 215° on the F & M 500. Mass spectra were obtained on the Hitachi Perkin-Elmer RMU-6D mass spectrometer, ionizing voltage 70 eV, using the direct inlet technique. Microanalyses were carried out by Galbraith Laboratories, Inc.

intensity) 316 (parent peak) (7.5), 284 (16.5), 192 (15), 147 (16.5), 146 (100), 134 (18), 133 (46), 131 (19.5). 123 (19.5), 117 (22.4), 111 (12), 109 (24), 105 (16.5), 101 (18), 95 (19), 92 (19.5), 91 (30), 81 (16), 69 (15), 67 (13.5), 55 (27).

Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.72; H, 10.18; O, 10.11. Found: C, 79.68; H, 10.22; O, 10.31.

Methyl 9-(*m*-Isopropylphenyl)-2,6-dimethyl-*trans*-6-nonenoate (3).—Compound **3** was collected from the Versamid preparative column followed by recollection from the analytical SE-30 column. The colorless oil then gave a single peak on both SE-30 and Versamid columns: $[\alpha]^{25}D$ 0.0° (*c* 1); uv max 263 mμ (ε 442), 271 mμ (ε 380); ir (neat), 1735 (C=O), 1600 (aromatic 1460 (CH_3), 1378 (CH_3), 1360, 1190, 1170 (isopropyl), 1155, 1135 (isopropyl), 1047, 987, 885, 790 (*meta*-disubstituted aromatic), and 702 cm^{-1} (*meta*-disubstituted aromatic); nmr (see Scheme I for numbering system), δ 1.13 (d, 3, J = 7 Hz, C_4 CH_3), 1.25 (d, 6, J = 6.5 Hz, isopropyl CH_3), 1.55 (s, 3, C_{10} CH_3), 1.98 [*t*, 2, J = 6 Hz, C_1 CH_2—C(CH_3)=CH], 2.41 [two sets of t, 2, J_{6-7} = 7 Hz, J_{6-7} = 6 Hz, C_6 CH_2—CH=C(CH_3)], 2.54 (t, 2, J = 7 Hz, C_7 CH_2—C_6H_5), 2.76 (septet, 1, J = 6.5 Hz, C_{18} **H**), 3.66 (s, 3, $COOCH_3$), 5.20 [t, 1, J = 6.0 Hz, C_5 **H**—C=C(CH_3)], 7.05 (m, 4, aromatic protons); mass spectrum, *m/e* (rel intensity), 316 (parent peak) (6.5), 187 (31.5), 183 (20.6), 151 (67.3), 147 (14), 146 (100), 134 (18.5), 133 (70.7), 131 (14), 129 (5), 123 (48.9), 119 (10), 118 (12), 117 (25), 109 (14.2), 95 (45.7), 93 (12), 91 (19.6), 88 (12), 81 (35.9), 69 (13), 67 (14.2), 59 (12), 55 (30.4).

Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.72; H, 10.18; O, 10.11. Found: C, 79.82; H, 10.26; O, 10.16.

Methyl 9-(*m*-Isopropylphenyl)-2,6-dimethyl-*cis*-6-nonenoate (4).—Compound **4** was collected from Versamid preparative column as an oil: $[\alpha]^{25}D$ +5.1° (*c* 0.3); uv max 263 mμ (ε 380) and 271 mμ (ε 316); ir (neat), 1735 (C=O), 1600 (aromatic), 1460 (CH_3), 1378 (CH_3), 1360, 1190, 1155, 1135 (isopropyl), 985, 882, 788 (*meta*-disubstituted aromatic), and 700 cm^{-1} (*meta*-disubstituted aromatic); nmr (see Scheme I for numbering system), δ 1.12 (d, 3, J = 7 Hz, C_4 CH_3), 1.24 (d, 6, J = 6.5 Hz, isopropyl CH_3), 1.66 (d, 3, J = 1.5 Hz, C_{10} CH_3), 1.97 [t, 2, J = 6 Hz, C_1 CH_2—C(CH_3)=CH], 2.50 (t, 2, J = 7 Hz, C_7 CH_2—C_6H_5), 2.76 (septet, 1, J = 6.5 Hz, C_{18} **H**), 3.63 (s, 3, $COOCH_3$), 5.20 [broadened t, 1, J = 6 Hz, C_5 **CH**=C(CH_3)], 7.03 (m, 4, aromatic protons); mass spectrum, *m/e*, (rel intensity) 316 (parent peak) (12.7), 187 (39) 183 (29), 159 (15.4), 152 (10), 151 (92), 147 (15.5), 146 (100), 134 (24.6), 133 (88.2), 131 (17), 123 (64.5), 119 (14.5), 118 (16), 117 (34.6), 115 (14), 109 (20), 105 (12), 97 (10), 96 (12), 95 (64.5), 93 (15), 91 (26.4), 88 (14), 79 (10), 69 (24.4), 67 (20), 59 (19.1), 57 (13), 55 (43.5).

Anal. Calcd for $C_{21}H_{32}O_2$: C, 79.72; H, 10.18; O, 10.11. Found: C, 79.78; H, 10.24; O, 10.07.

Thermal Behavior of 2, 3, and 4 in the Presence and Absence of Base at 200°.—Pure **2**, **3**, and **4** were charged to separate Carius tubes in the presence and absence of 5 mol % of potassium hydroxide, evacuated, sealed under nitrogen, and heated at 200° for 24 hr. No change occurred in any of the samples as determined by glpc on a Versamid column.

Reaction of 4 with Iodine.—To a solution of 25 mg of **4** in 10 ml of benzene was dissolved a trace of iodine. After 9 hr of refluxing, glpc analyses showed the presence of 44.8% **4**, 18.5% **3**, and 36.7% **2**. This ratio did not change during an additional 8 hr of refluxing nor on exposure to sunlight for 5 hr.

Reaction of 3 with Iodine.—To a solution of 30 mg of **3** in 10 ml of benzene was dissolved a trace of iodine. After 24 hr of refluxing, glpc analysis showed the presence of 6.2% **4**, 60.6% **3**, 19.7% **2**, and 13.5% an unknown peak of relative retention time of 0.457.

Behavior of Methyl Dehydroabietate in the Presence of Base at 200°.—Methyl dehydroabietate in the presence of 5 mol % of potassium hydroxide was heated for 4 days at 200°. At the end of this time, glpc analysis showed only a single peak corresponding to the starting material.

Behavior of Methyl Levopimarate in the Presence of Free-Radical Inhibitors and Initiators.—Methyl levopimarate plus 5 mol % of potassium hydroxide and 1 mol % of copper resinate and 2 mol % of 2,6-di(*t*-butyl)-4-methylphenol, respectively, were heated for 24 hr at 200°. Essentially the same results were obtained as in the absence of inhibitors. Methyl levopimarate (a) in toluene, (b) in toluene plus 5 mol % of potassium hydroxide, (c) in toluene plus 5 mol % of benzoyl peroxide or 2,2′-azobis(2-methylpropionitrile), respectively, and (d) in toluene plus 5 mol % of potassium hydroxide plus 5 mol % of benzoyl peroxide or 2,2-azobis(2-methylpropionitrile), respectively, were all refluxed 8 hr. Essentially the same small amount of compounds **2**, **3** and **4** were obtained in all cases.

Reaction of Levopimaric Acid in the Presence of Potassium Hydroxide at 200°.—A mixture of levopimaric acid and 5 mol % of potassium hydroxide was prepared in methanol–ether. Equal portions were charged to Carius tubes, the solvent was removed under reduced pressure, and the tubes were evacuated, flushed with nitrogen, sealed, and heated at 200°. After 10 days, the mixture exhibited (glpc analysis) a total of 3% **2** and **3** plus 72% abietate, 15.2% palustrate, 4.4% dehydroabietate, and 5.2% neoabietate. The run was repeated in an open glass tube (attached to a long rubber tube to prevent contamination by fumes from bath) containing levopimaric acid plus 105% potassium hydroxide (Danger! Sealed tubes explode). After 3 days at 200° the mixture exhibited the following composition: **4** (1.1%) (0.428), **3** (4.2%) (0.481), unknown peak (24.8%) (0.518), **2** (9.6%) (0.555), levopimarate–palustrate (49.4%) (0.815), dehydroabietate (7.7%) (1.0), and abietate (3.2%) (1.165). The yields are based on the volatile portion of the sample; the crude material contained 62% volatile products.

Behavior Methyl Levopimarate on an Old Versamid Column.—A fresh sample of methyl levopimarate on a fresh Versamid column exhibits a total of 7% **2**, **3**, and **4** and 2% dehydroabietate. Fresh methyl levopimarate on an old column, containing considerable amine and/or potassium hydroxide from earlier injection of samples, formed a total of 13% **2**, **3**, and **4**, and 5% dehydroabietate. A sample of methyl levopimarate, after standing for 75 days, neat, at room temperature (formed a viscous solid) on a fresh column, exhibited a total 9% **2**, **3**, and **4** and 56% dehydroabietate. These compounds were collected and their identity established by ir.

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