Dimeric Components From the Dimerization of Abietic Acid

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Capillary gas-liquid chromatography of the product formed by sulfuric acid-catalyzed dimerization of abietic acid showed the presence of some 40 dimeric components. The three major components were isolated and shown to be heptacyclic dimers, two of which had a conjugated double bond system. The other component had two nonconjugated double bonds. Also isolated were three dimers consisting of monomers attached through a single carbon-carbon bond: one carboxyl group in each of these dimers was in the form of a γ-lactone.

Polymerized rosins are commercially important rosin products used in a wide variety of applications including adhesives, inks and varnishes. Rosin polymers also are expected components of tall oil pitch, a byproduct from tall oil distillation.

Rosin is polymerized with an acid or Lewis acid catalyst. Numerous patents and other publications on the subject of polymerization have appeared since the description by Grun and Winkler in 1919 (1) of the heterogenous polymerization of rosin in petroleum ether using sulfuric acid as catalyst. Generally, the commercial products were characterized by acid number, color, softening point and, occasionally, by an ultraviolet spectrum. But now GPC is being used routinely to estimate the monomer/polymer content (2). GLC with packed columns has been used to characterize the products from abietic acid dimerization (3-6).

The polymerization of rosin results primarily in the formation of dimers. On the basis of GPC data, Chang (2) postulated that small amounts of rosin trimers also form. Brus et al. (7) and Morillon (8) used spectral and chemical evidence to postulate structures for abietic acid dimers. However, Bardyshev and Strizhakov (9) assigned yet a different structure to the major dimeric component from abietic acid polymerization.

We report herein the application of capillary column GLC to the analysis of dimerized resin acids and the isolation and partial characterization of six abietic acid dimers.

EXPERIMENTAL PROCEDURES

Capillary column GLC of resin acid dimers. Polymerized products of abietic acid were analyzed as the methyl esters (prepared by adding ethereal CH_2N_2 to a solution of the acids in 9:1 diethyl ether-methanol) using the "bonded" methyl silicone DB-1 as a 15-m, 0.1 μ film, fused silica column (J & W Scientific, Inc., Rancho Cordova, California) with a Hewlett Packard 5840 gas chromatograph (split ratio of 100/1). A temperature program (1°/min for 250-290 C, temperature at 290 C for 30 min) was used in most of the work.

Preparation and isolation of abietic acid dimers. Pure abietic acid in chloroform solution was dimerized using concentrated sulfuric acid as catalyst, following the method described by Sinclair et al. (10). The heterogenous system was maintained at 35 C under N_2 and stirred vigorously for 5 hr. The chloroform solution was washed with distilled water until neutral, and the solvent then removed to give a brown resin.

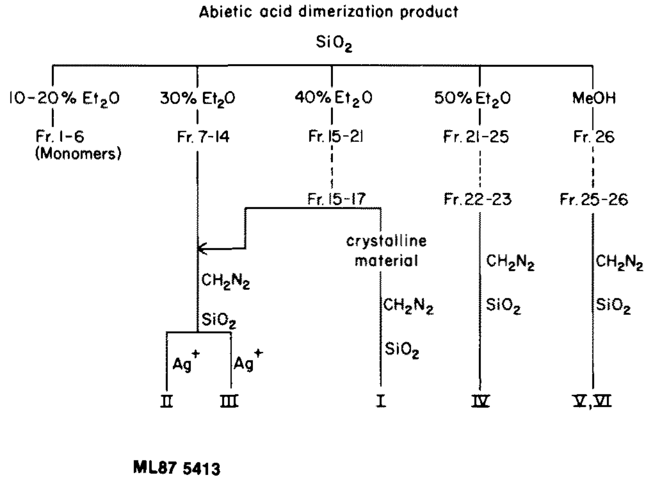

FIG. 1. General scheme for the isolation and purification of abietic acid dimer compounds.

The dimerization product was prefractionated on silica gel (Fig. 1) using 10-50% diethyl ether-petroleum ether gradients, followed by methanol. Purification of the dimeric components was accomplished by chromatography of the methyl esters (CH_2N_2) on silica gel using a series of 0-10% diethyl ether-petroleum ether gradients with supplemental argentation (resin) chromatography (11).

^1H NMR and ^{13}C NMR were determined at 250 and 62.89 MHz, respectively ($CDCl_3$ soln; TMS as internal standard) with a Bruker WM 250 spectrometer equipped with 5-mm BB probe. EIMS and CIMS were obtained with a Finnegan model 4510 mass spectrometer at 70 and 40 eV, respectively.

RESULTS AND DISCUSSION

GLC of resin acid dimers. We used the packed column system of Sinclair et al. (4), consisting of a partially oxidized SE-52 liquid phase on Gas Chrom Q, initially for gas chromatographic characterization of the dimer components in dimerized abietic acid. In our chromatograms, which were similar to those depicted by Sinclair et al. (4), it was obvious that many components were not recognized due to overlapping peaks; other components probably were undetected in the baseline. As this would prove a serious limitation in evaluating purity during isolation of components, we investigated fused silica capillary columns with bonded liquid phases. As can be seen in Figure 2, some 40 components appear in the dimer region of the chromatogram. Of particular note is that the major peak in the packed column

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[1]Maintained in cooperation with the University of Wisconsin.

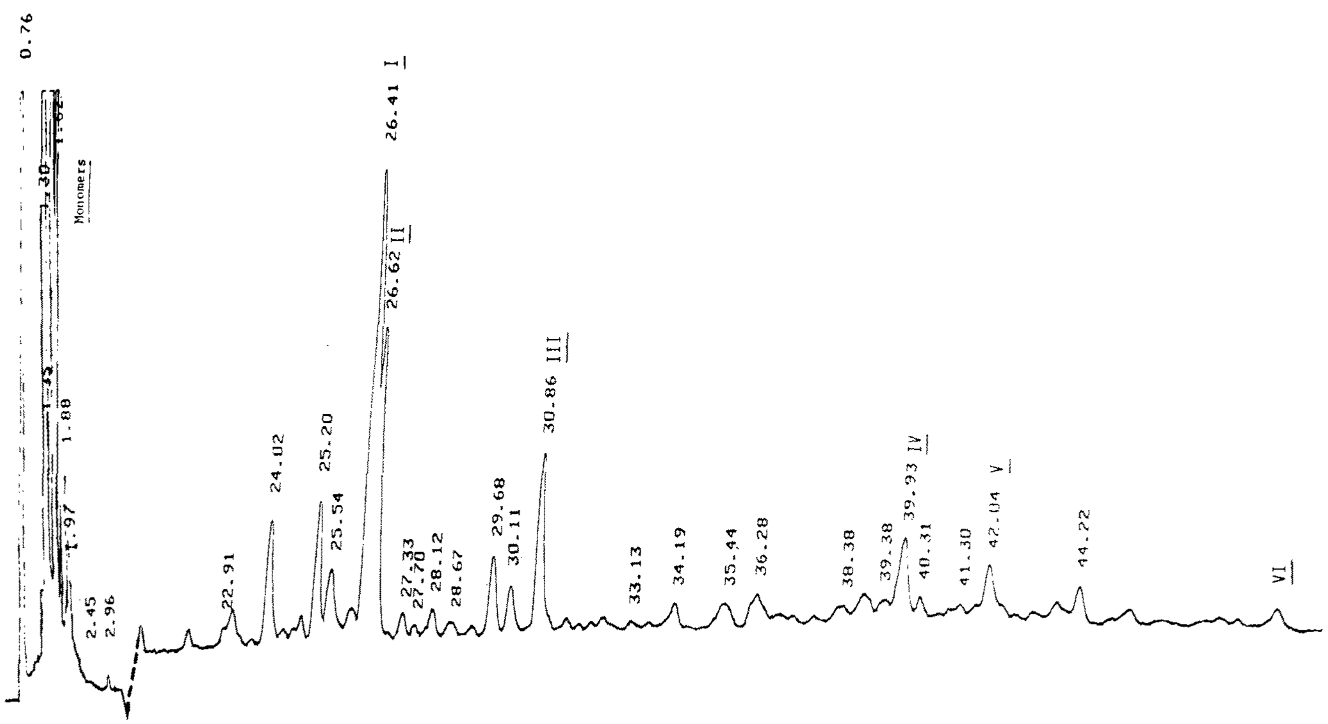


FIG. 2. GLC of dimerized abietic acid (methyl esters) on a DB-1 (15m) WCOT column (per dimer program, see text. Retention is in minutes).

chromatogram is resolved into two peaks by the capillary column.

Isolation and characterization of abietic acid dimers. The dimerization of abietic acid was carried out under conditions giving high dimer yields, but which hopefully avoided degradation reactions that would occur under more rigorous, i.e., higher temperature, conditions. Yields of dimer (ca. 70%) were slightly lower than previously reported (5,12), but were more than adequate for isolation of dimeric components.

The results of a preliminary fractionation of the dimer reaction product by chromatography on silica gel are summarized in Figure 1. The first diethyl ether-petroleum ether fraction contained most of the monomers. The other fractions were combined as appropriate, based on the GLC composition. The major dimeric component (I) was found to crystallize in some of the fractions. Because this crystalline dimer in the free acid form was poorly soluble in most solvents, it was subsequently purified by chromatography as the methyl ester, as were the other dimer fractions. Argentation chromatography (11) provided further purification of II (eluted with 25% diethyl ether-petroleum ether) and III (eluted with 50% diethyl ether-petroleum ether). Preliminary MS data indicated that dimer methyl esters I, II and III, the three major components, had molecular weights of 632 ($C_{42}H_{64}O_4$), indicative of heptacyclic dimers. The molecular weights of 616 ($C_{41}H_{60}O_4$) for components IV, V and VI indicated that one of the carboxyl groups was present as an internal ester (lactone). The spectral characteristics of dimers I, II and II are summarized in Table 1.

Dimers I and II are very similar not only in gas chromatographic retention but also in spectral characteristics. The MS of both dimers have the M^+ as the base peak; the primary differences between the spectra are the relative intensities of fragment ions. The UV characteristics were nearly identical in having molar absorptivities of ca. 20,000 (indicating one conjugated diene per dimer unit). The ^1H NMR spectra are nearly identical, the primary differences being in the chemical shift for the single vinylic proton of each dimer and for the chemical shifts of the two nonequivalent isopropyl-methyl groups (pair of doublets). Because previous studies (7-9) on the characterization of abietic acid dimers used similar preparation conditions, the major, readily crystallizable dimer would be expected to be common to their and our work. Although three structures (Fig. 3) postulated by previous workers for this dimer (I) contain a conjugated diene, none have a vinylic hydrogen as seen in our ^1H NMR spectra, thus eliminating these three structures as possibilities for both I and II. In evaluating other possible structures for these dimers, we assumed, as did the previous workers, that the conditions of the dimerization would not be conducive to skeletal rearrangements. Four spectral features were of primary importance in considering possible structures. These features were (i) MW of 632; (ii) a conjugated diene; (iii) one vinylic hydrogen with a small coupling constant, and (iv) nonequivalence of the methyls of one isopropyl group. The latter feature could well be a consequence of restricted rotation along with diamagnetic shielding by a double bond in analogy with similar observations for isopropylcyclopentenes (13) and isopropyl tartrates (14). We have observed the two doublets for the isopropyl-methyls of the 8(14)-abietenoates (ref. 15, *d,d* at δ0.90 and 0.91 for the 13β-H compound and δ0.91 and 0.87 for the 13α-H compound) and β-phellandrene (δ0.90 and 0.91, J = 6.7 Hz); there is no evidence of significant diamagnetic shielding in the 7-, 8- or 13-abietenoates (15). Thus, any diamagnetic shielding of the isopropyl-methyls of these compounds

TABLE 1

Spectral Characteristics of the Major Abietic Acid Dimers

	Spectral Characteristics[a]								
Compound	MS[Mz(%)]	UV(λ_{max}^{EtOH})	^{1}H NMR[b] (chemical shifts, δ)					^{13}C NMR	
			C=C-H[d]	COOMe	C-19(Me)	C-20(Me)	(Me)of *i*-prop.[c] C-16,C-17;C-16′,C-17′	$\underline{\underline{C}}$OO	$\underline{\underline{C}}$=$\underline{\underline{C}}$
I	632(M^+,100), 589(M^+-*i*pr,0), 573(M^+-$COOCH_3$,0), 421 (12) 315(9), 286(15), 257(26), 255(32) 211(22), 173(22), 133(27), 131(23), 121(87), 109(91), 107(45)	250nm,ε=19,900 243,257.5nm-sh.	6.01,*s*	3.64,*s*;3.63,*s*	1.24,*s*,6H	0.92,*s*; 0.87,*s*	0.98,*d*,6H;0.79*d*,0.75,*d*	179.2,178.9	144.5,132.5-131.4, 129.2-128.6,119.5
II	632(100),589(1),573(4) 421(8),315(3),286(1),257(6),255(6) 211(3),173(4),133(27),131(3), 121(16),109(16),107(7)	250nm,ε=20,100 243,258nm-sh.	5.90,*s*	3.63,*s*;3.62,*s*	1.24,*s*,6H	0.94,*s*; 0.88,*s*	0.98,*d*,6H;0.78,*d*,0.69,*d*	179.0,178.9	143.0,131.8,130.6, 119.6
III	632(25),589(1),573(4) 451(9),315(100),316(81),317(45) 257(25),255(40),211(2),207(15), 207(15),147(11),133(9),131(6), 121(15),109(10),107(8)	200nm,ε=21,600	—	3.66,*s*;3.64,*s*	1.17,*s*;1.14*s*	0.97,*s*; 0.83,*s*	1.66,*s*,3H;1.64,*s*,3H 0.85,*d*,3H;0.82,*d*,3H	179.1,179.1	135.4,134.3,133.4, 121.4
Methyl abietate	See ref. 15	See ref.15	5.77,5.36	3.63	1.25	0.82	1.01,*d*;1.00,*d*	178.7	145.0,135.4,122.6,120.6[e]
Methyl 8(14)-abieten-18-oate	See ref. 15	See ref. 15	5.32	3.65	1.19	0.78	0.86,*d*;0.83,*d*	179.2	137.9,126.0
Methyl 13β-abiet-8(14)-en-19-oate	See ref. 15	See ref. 15	5.48	3.65	1.19	0.80	0.91,*d*;0.87,*d*	179.4	137.5,125.7

[a] Spectra available from D. F. Zinkel.

[b] Compare with spectra for various abietane type resin acid methyl esters (15).

[c] Coupling constants 6.7 to 6.8 Hz.

[d] *cf.* C-6 proton of 6,8(14),15-isopimaratriene derivatives at δ 5.90 and 5.95(16).

[e] *cf.* ref. 17 and 18.

would be relatively small and similar to that seen in the 250 MHz spectrum of methyl abietate (Table 1).

Of the numerous possible dimer structures, only three (A, B and C of Fig. 4) are consistent with the primary spectral features; each has a MW of 632, a heterocyclic conjugated diene that would have an absorption maximum at 250 nm according to Woodward's rules, a vinylic hydrogen that appears as a broad singlet in the ^{1}H NMR due to the small coupling resulting from the ca. 80-90% angle between the C-5 and C-6 hydrogens, and the β, γ relationship of a double bond to the isopropyl group. Structure A is a "head-to-head" joining of two monomers, whereas B and C are "head-to-tail" configurations. Bardyshev and Strizhakov (9) reported that the infrared spectrum of an anhydride prepared from their dimer showed the anhydride to be intramolecular (cyclic), thus proving a "head-to-head" structure. Not only are these infrared data not conclusive for a macrocyclic anhydride, but molecular models indicate that intramolecular anhydride formation is not favorable. Although we do not have direct evidence to choose among structures A, B and C, the head-to-tail structure C is most plausible mechanistically in that each monomer portion retains a double bond. Numerous isomers of C can be visualized considering only the assymetric centers being established at the double bond carbons of the parent abietic acid, i.e., the resulting stereochemistry at carbon atoms 7′, 8, 14, and particularly the isopropyl substituted 13,13′ of the dimer. Of the eight possible stereochemical isomers considering just the 7′, 8 and 14 centers, only the two all-*cis* (hydrogens all α or all β) isomers can be reasonably excluded on thermodynamic grounds. Dimer I has six peaks in the C = C region of the ^{13}C NMR spectrum; we interpret the 132.5-131.4 and 129.2-128.6 pairs to be due to two closely related, e.g. C-13, isomers. Thus, dimers I and II are stereochemical isomers (of the 7′, 8, 14 centers) of structure C.

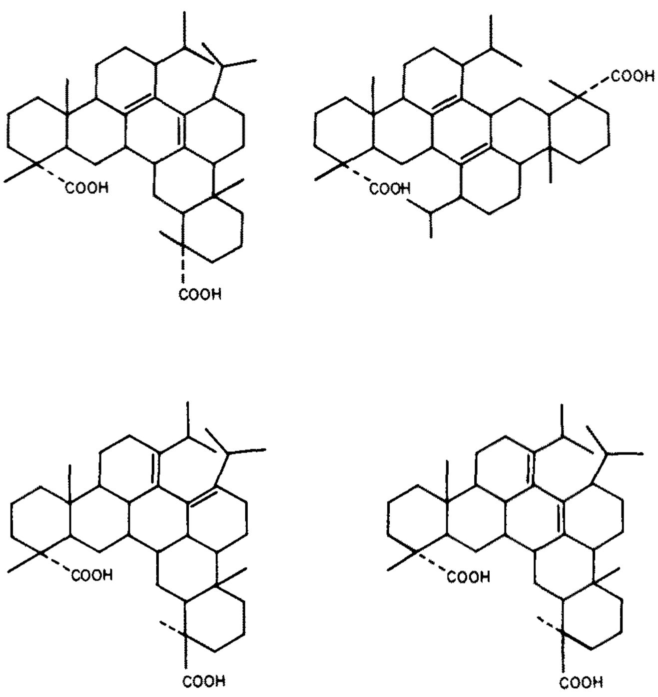


FIG. 3. Previously proposed structures for abietic acid dimers.

Dimer III differs from dimers I and II in having double bonds that are nonconjugated. The locations of these double bonds are readily deducible by the ^{1}H NMR spectrum. One double bond is clearly in the 13(15) position (i.e., an isopropenyl such as in neoabietic acid) of one monomeric fragment; the other double bond is assigned the 8′(14′) position of the second monomeric fragment based, again, on the nonequivalence of isopropyl-methyl hydrogens as discussed above. Structures D and E both satisfy these critiria. We favor E because of the

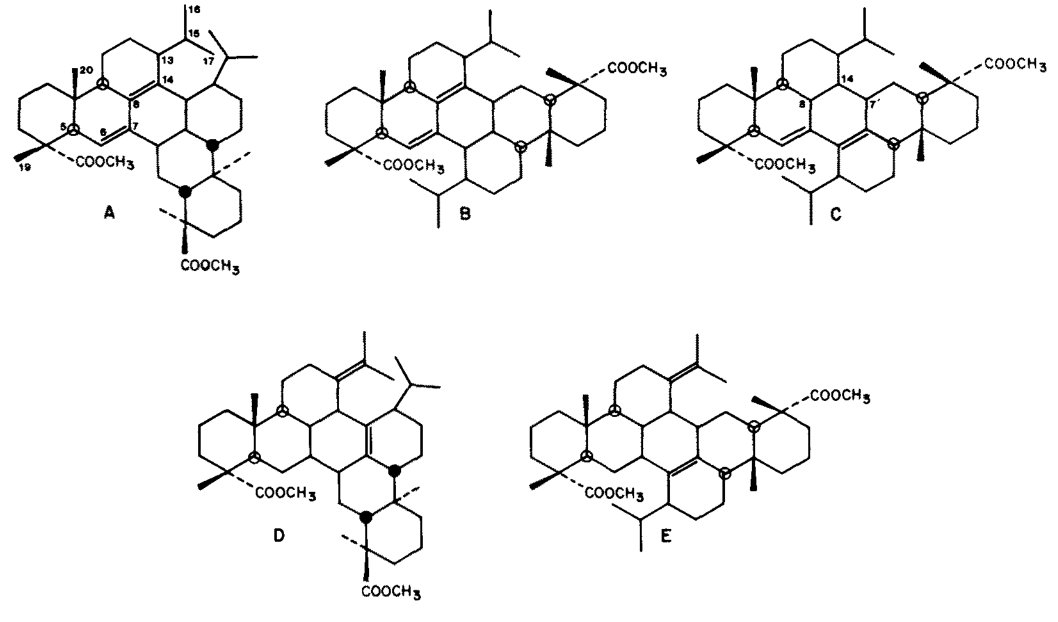


FIG. 4. Possible abietic acid dimer structures (as methyl esters) for compounds I, II and III.

TABLE 2

MS and ^1H NMR Spectral Characteristics of Abietic Acid Dimer Lactones

		^1H NMR Chemical Shifts, δ[b]						
			Methyl-H					
Compound	MS[m/z(%)][a]	Aromatic-H	C-20	C-19	C-16,17	C-20′	C-19′	C-16′,17′
IV	616(7),556(20),541(6),353(17), 326(16),313(36),289(9),*268(100)*, *253(94)*,242(27),239(8),223(6), 211(35),173(3).	7.14*d*(J=8.2) 6.98*d*(J=8.2) 7.03*s*	1.22	1.27	1.23*d*	0.94	1.10	0.89*d*
V	616(4),570(4),556(4),541(29), 353(2),326(3),317(44),313(12), *299(100)*,253(6),241(26),239(40), 223(42),211(6),173(7).	7.14*d*(J=8.2) 6.89*d*(J=8.2) 6.88*s*	1.20	1.28	1.16*d*	0.67	1.06	0.87*d* 0.89*d*
VI	616(4),556(17),541(11),353(10), 326(11),313(85),299(6),289(11), 268(42),*253(100)*,249(46),241(37), 239(13),223(6),211(27),173(30).	7.14*d*(J=8.2) 7.01*d*(J∼8) 7.01*s*	1.22	1.28	1.24*d*	0.81	1.18	0.93*d*
Methyl dehydroabietate	——— cf. ref. 15 ———	7.15*d*(J=8.2); 6.99*d*(J=8.2); 6.88*s*	1.22	1.27	1.23*d*	—	—	—
Methyl abietanoates	——— cf. ref. 15 ———	—	—	—	—	0.84[c]	1.17	0.83*d*

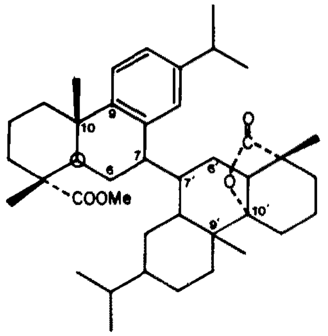
[a] Most important ions; base peak is italic. High resolution MS of IV and V: 616($C_{41}H_{60}O_4$); 570($C_{40}H_{58}O_2$); 556($C_{39}H_{56}O_2$); 541($C_{38}H_{54}O_2$); 353($C_{24}H_{33}O_2$); 326($C_{22}H_{30}O_2$); 317($C_{21}H_{33}O_2$); 313($C_{21}H_{29}O_2$); 299($C_{20}H_{27}O_2$); 293($C_{22}H_{29}$); 268($C_{20}H_{28}$); 253($C_{19}H_{25}$); 241($C_{18}H_{25}$); 239($C_{18}H_{23}$).

[b] Non-prime positions are for the aromatic (dehydroabietate) portion of dimer, prime (′) positions are for the abietane portion of dimer.

[c] δ1.05 for 8β-H compounds.

stereochemical crowding that would occur between the isopropyl groups in structure D.

Three minor dimers, IV, V and VI, (Fig. 1) were isolated in milligram quantities; IV and V were ca. 90% pure by GLC and VI was about 76%. All three are similar in having a MW of 616 (EI- and CIMS) and IR absorption at 1768-1770 cm^{-1} characteristic of a γ-lactone, in addition to absorption at 1725 cm^{-1} for the ester carbonyl. The possible presence of lactones in crude dimerized rosins has been noted by Sinclair et al. (19). Aromaticity similar to that of dehydroabietate was evident in the 1610 and 824 cm^{-1} IR absorption, the UV absorption, and the ^1H NMR spectra. (Mass and ^1H NMR spectra are summarized in Table 2.) The ^1H NMR spectra integrate for two benzylic hydrogens at ca. δ2.8. Because the isopropyl methyl groups are doublets, the 7 position of the aromatic unit has one benzylic hydrogen. Therefore, the attachment of this unit is at the 7 position. The strong m/z 313 ($C_{21}H_{29}O_2^+$) for IV and VI indicates a cleavage of the monomer-monomer bond (β to the aromatic group) resulting in a methyl dehydroabietate ion. However, formation of the m/z 268 ($C_{20}H_{28}^+$) as the base peak in IV does not appear to be consistent with the lactone being in the tetrahydroabietanyl unit, as the m/z 268 ion could be formed by cleavage of the 6,7, the 9,10, the 6′,7′ and the 9′,10′ bonds of F; the m/z 253 ion would result from a subsequent loss of CH_3. Formation of the m/z 268 ion from F would require additional rearrangements including migration of the C-9′ methyl unless the original lactoni-



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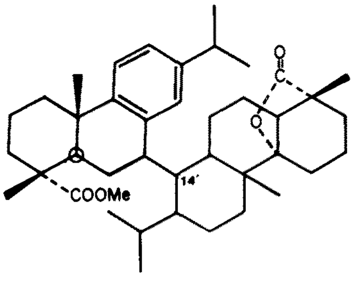

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FIG. 5. Possible structures of abietic acid dimer lactones IV, V and VI.

zation resulted in the C-10′ methyl moving to C-5′. At first glance, the m/z 317 ($C_{21}H_{33}O_2{}^+$) and 299 ($C_{20}H_{27}O_2{}^+$) of V would seem compatible with the lactone being present in the dehydroabietyl unit but this would require the shift of two hydrogens to give a protonated species of m/z 299. The lack of O-C-H multiplets in the ^{1}H NMR of IV, V and VI limits the lactonization of C-10′ with concomitant migration of the methyl to C-9′ (or possibly C-5′).

Although it is tempting to further assign structural features to the tetrahydroabietyl units of IV, V and VI based on ^{1}H NMR comparison with abietalactones (20,21) and isopimaralactone (22; structure proven by X-ray crystallography, ref. 23), the steric effects resulting from the dehydroabietyl attachment to the tetrahydroabietalactone could well result in major conformational differences, invalidating such comparisons. The dehydroabietyl unit is probably linked to the 7 or 14 positions of the abietalactones (Fig. 5) in analogy to our proposals for the heptacyclic dimers. The half-lactone dimers (IV, V and VI) could have been formed from abietyl-dihydroabietyl dimers which then undergo aromatization by either a concerted oxidation/dehydration or by disproportionation of the abietyl unit and acid catalyzed lactonization of the dihydroabietyl unit.

Since completion of this work, another abietic acid dimer has been isolated for the p-toluene sulfonic acid dimerization of levopimaric acid (24). Its structure was shown by NMR and X-ray crystallography to be a triene, consisting of a bond between the 7 position of an abietic acid monomer to the 7′ position of an 8-abieten-18-oic acid (cf 7-7′ junction of F, Fig. 5); the isolate was a mixture of two C-13′ isomers.

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