Cyclopinolenic Acids: Synthesis, Derivatives and Thermal Properties

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The two isomeric cyclopinolenic acids (CP-1 and CP-2), components of distilled tall oil, have been synthesized by means of an intramolecular Diels-Alder reaction of isomers of 5,10,12-octadecatrienoic esters, themselves synthesized in a stereocontrolled manner. The 5*cis*,10-*trans*,12*trans* isomer cyclizes at 200°C to a 1:3 mixture of esters of CP-1 and CP-2. At 200°C, the 5*cis*,10*trans*,12*cis* isomer is unreactive, but at 240°C it gives the same CP-1 + CP-2 ester mixture, presumably by way of prior isomerization to the 5*cis*,10*trans*,12*trans* isomer. A subambient thermal study of CP-1 and CP-2 and their derivatives shows that the compounds, excluding CP-1, lack crystalline structures or melting points, and display glass transitions only, below −80°C for esters and below −50°C for the carboxylic acids.

KEY WORDS: Bicyclic fatty acids, glass transition, intramolecular Diels-Alder, synthesis, tall oil.

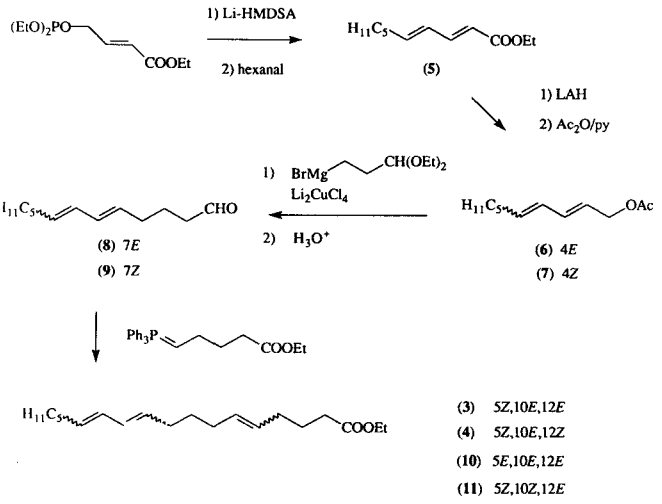
The cyclopinolenic acids (CP-1 and CP-2; formulas **1a** and **2a**, respectively) are artefact C_{18} bicyclic fatty acids, first reported in 1972 at about 3% level from distilled Finnish tall oil fatty acids (1). Later, additional mono- and bicyclic fatty acids were identified from the same source (2,3). The cyclopinolenic acids have a 4-(5-pentyl-3a,4,5,7a-tetrahydro-4-indanyl)butanoic acid structure, and arise from pinolenic acid (all-*cis*-5,9,12-octadecatrienoic acid) by thermal isomerization under alkaline sulfate pulping conditions to 5,10,12-octadecatrienoic acids, followed by an intramolecular Diels-Alder (IMDA) cyclization during tall oil distillation (4). It was assumed that CP-1 and CP-2 are stereoisomers and that their ratio depends upon the relative amounts of the conjugated 5-*cis*-10-*trans*-12-*cis*- and 5-*cis*-10-*trans*-12-*trans*-isomers initially formed.

We have earlier described the synthesis and IMDA cyclization of all-*trans* 5,10,12-octadecatrienoic acid (5). We now report the stereocontrolled synthesis of 5-*cis*-10-*trans*-12-*trans*- and 5-*cis*-10-*trans*-12-*cis*-octadecatrienoic esters (**3** and **4**, respectively; Scheme 1) and show that their IMDA cyclization leads to mixtures of CP-1 and CP-2 esters (**1** and **2**, respectively; Scheme 2). Furthermore, the subambient thermal properties of CP-1 and CP-2 and their esters and hydrogenated products are described.

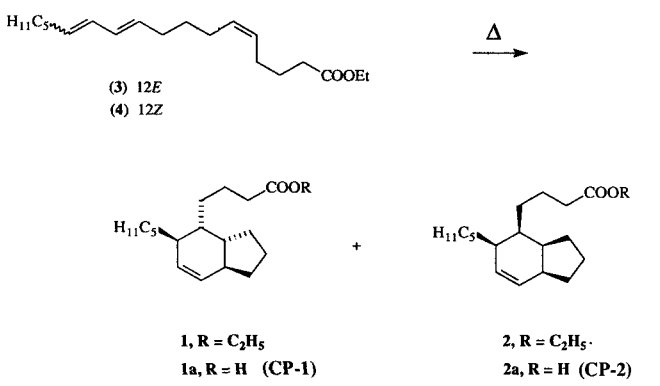
EXPERIMENTAL PROCEDURES

Chromatography. Gas-liquid chromatography (GLC) analysis was performed with a Hewlett-Packard 5890 instrument, equipped with a flame-ionization detector and a Hewlett-Packard 3396A integrator (Palo Alto, CA). The column used was a 50 m × 0.27/0.82 mm BDS glass capillary column.

For argentation chromatography we kept silica gel (60 g; Kieselgel 60, E. Merck, Darmstadt, Germany, no. 9385, 230–400 mesh ASTM) overnight in an oven at 120°C and then treated it with 100 mL of a 10% solution of $AgNO_3$ in acetonitrile, predried over 3Å molecular sieves. After the removal of acetonitrile under vacuum in a rotary evaporator at 70°C, the impregnated silica was used to fill a glass chromatography column (23 × 2.5 cm).



SCHEME 1



SCHEME 2

Spectroscopy. Nuclear magnetic resonance (NMR) spectra were run on a Varian Gemini 200 spectrometer (Sunnyvale, CA) (200 MHz for ^1H; $CDCl_3$ solvent and referenced to solvent δ $^1H = 7.29$ ppm and $^{13}C = 77.30$ ppm). High resolution mass spectra (HRMS) were run on a JEOL JMS-SX102 instrument (Tokyo, Japan). Synthetic intermediates **5–9** were characterized (and a sufficient purity ascertained) by NMR and mass spectroscopy, but the spectra are trivial and will not be presented here.

Thermal analysis. For differential scanning calorimetry (DSC), the Mettler TA 4000 thermal analyzer system was used equipped with a DSC 30S measuring cell (Mettler-Toledo AG, Greifensee, Switzerland). The instrument was calibrated with *n*-hexane (m.p. −94.0°C, standard quality for gas chromatography [GC], >99.7%, E. Merck, no. 9687), water (m.p. 0.0°C, distilled and ion exchanged), and

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indium (m.p. 156.6°C, Mettler standard ME-29749). The thermograms were analyzed by means of Mettler GraphWare TA 72AT.2 software.

Samples (2–3 mg; see below) were weighted to standard aluminum DSC pans (ME-27331) on a Mettler electrobalance with a sensitivity of 0.2 μg. The pans were sealed and scanned from −120°C to 0°C at a rate of 10°C min^{-1}. An empty DSC pan was used as a reference. The curves were analyzed for the onset temperature of glass transition and the heat capacity change. Baseline shifts, reflecting heat capacity changes upon glass transition, were determined as the difference between extrapolated baselines at the transition and were converted to $Jg^{-1}K^{-1}$. Some samples were done in duplicate, and the reproducibilities of the onset temperature of glass transition was found to be better than ±0.3°C. The standard deviation of heat capacity changes was less than 0.04 $Jg^{-1}K^{-1}$. A standard procedure (6) was thus followed except when measuring the heat of fusion, ΔH_f, for the only crystalline sample, the CP-1 acid (**1a**). The crystallization of this compound is too slow to be achieved by the standard method (6). Instead, the melting peak temperature T_m and ΔH_f were measured for samples crystallized from pentane. The samples were heated at a rate of 10°C/min starting from ambient temperature.

Samples for thermal analysis. CP-1 and CP-2 methyl esters were prepared by refluxing the corresponding ethyl esters in methanol for 22 h in the presence of a catalytic amount of *p*-toluenesulfonic acid. Evaporation of solvent and flash chromatography on silica (elution with CH_2Cl_2) gave the products in quantitative yield.

For hydrogenated derivatives, 200 mg (0.65 mmol) of a CP ester was dissolved in 10 mL of ethanol, and 20 mg of a 5% Pd/C catalyst (Johnson Matthey, type 87L) was added. The reaction vessel was rinsed five times with H_2, and the sample was then hydrogenated for 4 h at 60°C and 20 bar, followed by filtration and evaporation of the solvent. The hydrogenation of CP-1 esters was uneventful, but the CP-2 esters isomerized easily under these conditions and gave mixtures of three products in the ratio 15:35:50. The identity of these compounds is not known at present.

Synthesis. Ethyl 2-*trans*-4-*trans*-decadienoate (**5**): To a solution of lithium hexamethyldisilazide (from 30 g [0.19 mol] of hexamethyldisilazane and 0.18 mol of butyllithium [1.6 mol in hexane] in THF [250 mL]) at −78°C was added 45 g of ethyl 4-(diethylphosphono)crotonate (**7**) (0.18 mol) in 50 mL of THF. The solution was warmed to −50°C, and 21.5 mL of hexanal (0.18 mol) in 20 mL of THF was added dropwise. The reaction mixture was then warmed to room temperature, and THF was removed *in vacuo*. The residue was partitioned between 300 mL of water and 100 mL of ether, and the aqueous phase was extracted with two additional 100-mL portions of ether. The combined extracts were washed with 100 mL of 1 N HCl and dried over Na_2SO_4, and the solvent was removed to give 35 g (80%) of **5**.

2-*trans*-4-*trans*-Decadienol acetate (**6**): A solution of 20 g (0.13 mol) of **1** in 30 mL of dry ether was added dropwise at −30°C to a stirred mixture of 5.5 g (0.14 mol) of $LiAlH_4$ in 200 mL of dry ether. After 1 h, ethyl acetate (20 mL) was added followed by dilute HCl. Extraction with ether, washing of the combined organic layers with water, drying (Na_2SO_4) and removal of solvent gave 13.5 g (85%) of 2,4-decadienol. This was acetylated in the usual way with acetic anhydride and pyridine to give **6**.

5-*trans*-7-*trans*-Tridecadienal (**8**) and 5-*trans*-7-*cis*-tridecadienal (**9**): The preceding acetate (**6**, 10 g, 0.05 mol) was added to the Grignard reagent prepared from 3-bromopropanal diethyl acetal (**8**) (16 g, 0.076 mol), in the presence of dilithium tetrachlorocuprate (**9**) (5 mL of 0.1 M THF solution) in THF (200 mL) at −30°C. After 3 h, the reaction mixture was quenched with 10 mL of water, the organic phase was dried over Na_2SO_4, and the solvent was removed. Flash chromatography on silica gave 7 g (50%) of the tridecadienal diethyl acetal. This was hydrolyzed in 95% yield to the tridecadienal (**8**) by 10% H_2SO_4 (5 mL in 50 mL of acetone). Similarly, 2-*trans*-4-*cis*-decadienol acetate (**7**) (10) gave 5-*trans*-7-*cis*-tridecadienal (**9**) in 95% yield.

Ethyl 5-*cis*-10-*trans*-12-*trans*-octadecatrienoate (**3**) and ethyl 5-*cis*-10-*trans*-12-*cis*-octadecatrienoate (**4**): The phosphonium salt of ethyl 5-bromopentanoate (8.0 g, 0.017 mol), potassium carbonate (11) (3.0 g), the aldehyde **8** (3.0 g, 0.0155 mol), 1,4-dioxane (16 mL) and H_2O (0.4 mL) were stirred overnight at 95°C under argon. The solvent was evaporated under reduced pressure, and the residue was extracted several times with hexane. Flash chromatography of the concentrate in a silica column (elution with CH_2Cl_2) yielded 3.3 g (70%) of crude **3**, consisting of the 5-*cis*-10-*trans*-12-*trans* isomer (85–90%) and the 5-*trans*-10-*trans*-12-*trans* isomer **10** (10–15%). The major product was isolated in pure state for analytical purposes by argentation chromatography. ^1H NMR: δ 0.90 (3H, H-18), 1.20–1.55 (*m*, 11H), 1.69 (quintet, $J = 7.3$ Hz, 2H, H-3), 2.06 (*m*, 8H, H-4, H-7, H-9, and H-14), 2.31 (*t*, $J = 7.3$ Hz, 2H, H-2), 4.14 (*q*, $J = 7.1$ Hz, 2H, CH_2O), 5.38 (*m*, 2H, H-5 and H-6), 5.59 (*m*, 2H), 6.01 (*m*, 2H). ^{13}C NMR: δ 14.3, 14.5, 22.8, 25.1, 26.8, 27.0, 29.3, 29.6, 31.7, 32.4, 32.8, 34.0, 60.4, 129.0, 130.5, 130.8, 130.9, 132.0, 132.8, 173.9. HRMS: $C_{20}H_{34}O_2$ requires 306.2559, found 306.2545.

Similarly, the isomeric aldehyde (**9**) gave crude (**4**) in 70% yield, purified by argentation chromatography. ^1H NMR: δ 0.90 (3H, H-18), 1.20–1.55 (*m*, 11H), 1.70 (*q*, $J = 7.2$ Hz, 2H, H-3), 2.10 (*m*, 8H, H-4, H-7, H-9 and H-14), 2.30 (*t*, $J = 7.5$ Hz, 2H, H-2), 4.13 (*q*, $J = 7.2$ Hz, CH_2O), 5.38 (*m*, 3H, H-5, H-6 and H-13), 5.66 (*dt*, $J = 15.0$ Hz, 7.2 Hz, 1H, H-10), 5.95 (*t*, $J = 10.9$ Hz, 1H, H-12), 6.32 (*ddq*, $J = 15.0$ Hz, 10.9 Hz, 1.1 Hz, 1H, H-11). ^{13}C NMR: δ 14.3, 14.5, 22.8, 25.1, 26.8, 27.0, 27.9, 29.6, 29.7, 31.7, 32.7, 34.0, 60.4, 126.2, 128.7, 129.1, 130.5, 130.8, 134.3, 173.9. HRMS: $C_{20}H_{34}O_2$ requires 306.2559, found 306.2567.

Cyclopinolenic acid ethyl esters (**1** and **2**): The crude trienoic esters (**3**) and (**7**) were conveniently used for the IMDA cyclization because the unwanted isomers did not react at the temperatures used and thus did not interfere with the isolation of **1** or **2**. The trienoic ester (2.0 g, 6.5 mmol, 5% solution in decalin under Ar) was heated overnight in a sealed ampoule at 200–210°C. Flash chromatography over silica gave 1.5 g (75%) of a mixture of **1** and **2**. In a typical argentation chromatography run (elution with 5:95 ether:hexane), 200 mg of this mixture (distilled) gave 140 mg of (**2**) and 50 mg of (**1**). Data for **1**: ^1H NMR: δ 0.88 (3H), 1.05 (*m*, 2H), 1.20–1.90 (*m*, 21H), 2.01 (*m*, 2H), 2.31 (*m*, 2H), 4.14 (*q*, $J = 7.1$ Hz, 2H, CH_2O), 5.49 (*ddd*, $J = 9.9$ Hz, 4.2 Hz, 2.5 Hz, 1H, H-6), 5.77 (*dt*, $J = 9.9$ Hz, 1.4 Hz, 1H, H-7). ^{13}C NMR: δ 14.2,

14.3, 22.4, 22.8, 23.6, 26.1, 27.0, 28.0, 29.4, 32.3, 34.9, 36.4, 38.7, 38.9, 41.4, 43.8, 60.3, 129.7, 131.5, 174.2. HRMS: $C_{20}H_{34}O_2$ requires 306.2559, found 306.2539. Data for 2: ^1H NMR: δ 0.88 (3H), 1.05–1.85 (*m*, 21H), 1.94 (*m*, 2H, H-4 and H-5), 2.22 (*m*, 1H, H-3a), 2.33 (*t*, $J = 7.3$ Hz, 2H), 2.58 (*m*, 1H, H-7a), 4.13 (*q*, $J = 7.1$ Hz, 2H, CH_2O), 5.45 (*ddd*, $J = 10.2$ Hz, 3.0 Hz, 0.8 Hz, 1H, H-7), 5.82 (*ddd*, $J = 10.2$ Hz, 4.6 Hz, 2.1 Hz, 1H, H-6). ^{13}C NMR: δ 14.1, 14.3, 22.8, 23.3, 24.8, 26.9, 28.9, 31.1, 31.7, 32.3, 33.0, 34.7, 37.4, 38.0, 39.8, 41.3, 60.2, 130.6, 131.1, 174.1. HRMS: $C_{20}H_{34}O_2$ requires 306.2559, found 306.2549.

Free CP-1 and CP-2 acids (**1a** and **2a**, respectively) were obtained by refluxing **1** or **2** in 1:2 aqueous 0.5M NaOH:ethanol for 2 h. Removal of the ethanol, acidification (dil. HCl), extraction (ether), and washing and drying of the extracts gave the free acids. On prolonged standing at −20°C, **1a** became crystalline and was recrystallized from pentane, m.p. 69–70°C.

RESULTS AND DISCUSSION

Formation of cyclopinolenic acids. It would seem reasonable to assume that when pinolenic acid (all-*cis* or all-*Z* 5,9,12-octadecatrienoic acid) is isomerized, under alkaline pulping conditions, it does so by being first converted to the 5-*cis*-10-*trans*-12-*cis*-trienoic system (4), which can then undergo another isomerization to the thermodynamically more stable 5-*cis*-10-*trans*-12-*trans* system (3). To obtain fully defined substrates to study the IMDA reaction, the octadecatrienoic acid esters **3** and **4** were synthesized (Scheme 1) by employing stereocontrolled methods for the construction of polyunsaturated alkene systems. The esters **3** and **4** are obtainable from commercially available starting materials in five steps in about 20% overall yield.

The two esters differ to some extent in their IMDA reaction (Scheme 2 and Fig. 1). The cyclization of the pure 5-*cis*-10-*trans*-12-*trans* isomer **3** proceeds at 200–210°C to give cleanly a 1:3 mixture of the cyclopinolenic esters (**1** and **2**). Other bicyclic isomers are formed at about 5% level (Fig. 1, B1–B3) from the other trienoic isomers that are present in crude samples of **3**. The structures of the two main products were assigned by precedent (5,12) and from the NMR spectra. In our experience (5), the main product distribution and stereochemical outcome are typical of an IMDA reaction were there are no activating substituents in either the dienophile or the diene moiety. On the other hand, the cyclization of the 5-*cis*-10-*trans*-12-*cis* isomer **4** proved more sluggish, requiring heating at 240–250°C to proceed at a reasonable rate. It is noteworthy that **4**, which according to theory is the initial conjugated isomer to be formed from pinolenic acid, does not cyclize efficiently but rather undergoes further isomerization to a new compound (**X**, see Fig. 1, A1–A3), different from the 5-*cis*-10-*trans*-12-*trans* triene **3** and the 5-*cis*-10-*cis*-12-*trans* triene **11**. Compound **X** appears to be in equilibrium with the other trienes and slowly disappears, and it is possible that **X** is the 5-*cis*-11-*cis*-13-*trans* triene, a 1,5-hydrogen shift product from **4**. This would probably be slow to cyclize unless further isomerized to 11-*trans* form; it is interesting to note that the ring system (an octahydronaphthalene) resulting from this cyclization has also been reported (3) in tall oil fatty acids. In the final product (after 15 h at 245°C; not shown in Fig. 1) a number of cyclic and acyclic by-products are present at about 10–15% combined level but **1** and **2** again predominate in the ratio 1:3. This means that also triene **3** must be formed from **4** at

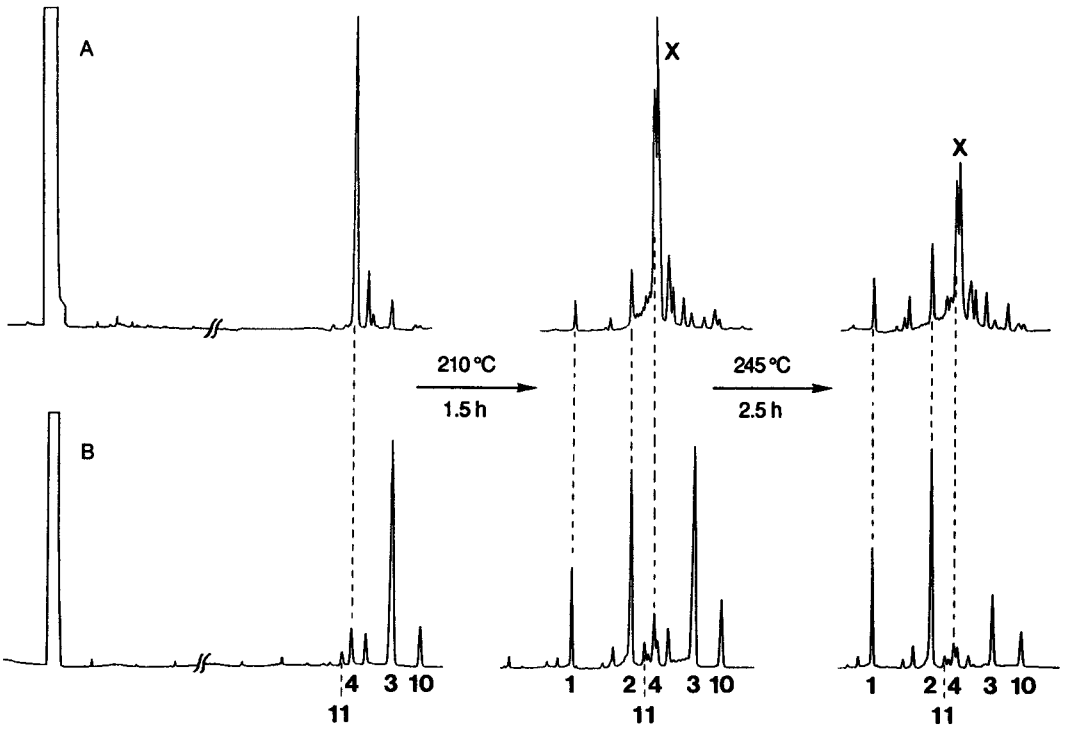

FIG. 1. Cyclization of preparative samples of ethyl 5*cis*,10*trans*,12*cis*-octadecatrienoate (4) (A) and ethyl 5*cis*,10*trans*,12*trans*-octadecatrienoate (3) (B).

some stage, but if the former arises from X is not known; 3 is absent from the reaction-monitoring chromatograms A1–A3 because at 240–250°C it is being cyclized to 1 and 2 as fast as it is formed. We conclude that the formation of cyclopinolenic acids in the distillation of tall oil is preceded and accompanied by much interconversion of the various 5,10,12-trienoic systems, and the ratio of formation of 1 and 2 is thus not a simple consequence of the relative rate of formation of the initially formed octadecatrienoic acid isomers.

Thermal properties of cyclopinolenic acid and derivatives. The onset points T_g (T_f) (6) of the glass transition and the change in thermal capacity of the cyclopinolenic acid and ester samples are summarized in Table 1. Representative DSC scans for some samples appear in Figure 2 and Figure 3. Excluding the CP-1 acid, none of the samples show a true melting point but only a glass transition. The transition ranges are at low temperatures (−56°C to −89°C) for compounds having molecular weights as high as these (278 to 308). Specific changes in thermal capacity values fall within a range of 0.49 to 0.62 $Jg^{-1}K^{-1}$ for all esters and a little lower, 0.40 to 0.45 $Jg^{-1}K^{-1}$, for the carboxylic acids.

All factors that restrict the freedom of molecular movement increase the glass transition temperature. For polymers and oligomers, the glass transition temperatures rise with the chainlength, and there are several factors affecting the dependence of Tg on the molecular weight, *e.g.*, crystallinity, molecular weight distribution, stiffness and flexibility of the backbone chain, polarity and end group or chain association effects (13–15).

Table 1 shows that Tg is lower for cyclopinolenic acid ethyl esters than for the methyl esters (entries 6, 8 and 10 *vs.* entries 1, 3 and 5). A similar effect has been observed for phthalic acid esters (16) where Tg decreases from dimethyl to dibutyl phthalate but then increases from dibutyl to dinonyl phthalate. The former phenomenon is thought to be caused by the increasing shielding effect of the ester group, as it becomes larger, on the interactions between the polar carbonyl groups (and the aromatic ring). With alkyl groups larger than butyl, the increase in molecular weights is mainly responsible for the increased Tg values. The net effect is at a minimum Tg value with dibutyl phthalates. In lactones, 1-alkanols and cycloalkanols, the minimum Tg values occur at other alkyl chainlengths (16,17). As for the cyclopinolenic acids, the alkyl group causing minimum Tg values was not identified because only methyl and ethyl esters were studied. It

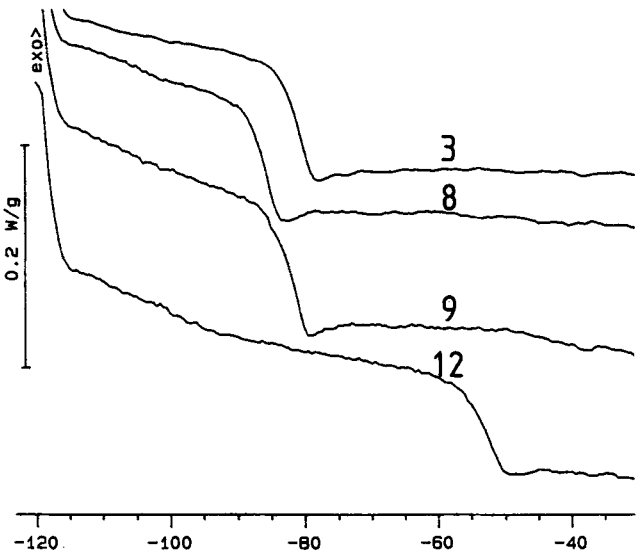

FIG. 2. Differential scanning calorimetry scans of CP-1 and CP-2 esters. Glass transition energy per weight unit (W/g) *vs.* temperature (°C).

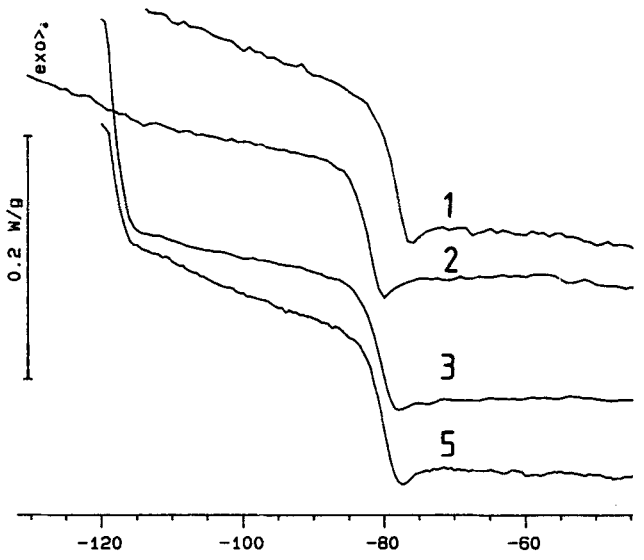

FIG. 3. Differential scanning calorimetry scans of CP-1 and CP-2 methyl esters and of a 1:1 mixture of these esters. Glass transition energy per weight unit (W/g) *vs.* temperature (°C).

TABLE 1

Thermodynamic Properties of Cyclopinolenic Acids and Derivatives[a]

Entry	Sample	Glass transition onset point Tg (°C)	Change in thermal capacity ΔCp ($Jg^{-1}K^{-1}$)
1	1/Me	−79.2	0.49
2	1/Me-H	−85.6	0.58
3	2/Me	−84.4	0.57
4	2/Me-H	−83.1	0.56
5	1 + 2/Me	−83.1	0.62
6	1/Et	−83.9	0.62
7	1/Et-H	−89.3	0.60
8	2/Et	−88.7	0.53
9	2/Et-H	−85.2	0.57
10	1 + 2/Et	−85.6	0.60
11	1	−47.3	0.40[b]
12	2	−56.8	0.45

[a]Coding of samples and product purities (by gas-liquid chromatography [GLC]): 1/Me, CP-1 methyl ester (99%); 1/Me-H, hydrogenated CP-1 methyl ester (73%); 2/Me, CP-2 methyl ester (99%); 2/Me-H, hydrogenated CP-2 methyl ester; 1 + 2/Me, 1:1 mixture of CP-1 and CP-2 methyl esters; 1/Et, CP-1 ethyl ester (85%); 1/Et-H, hydrogenated CP-1 ethyl ester (78%); 2/Et, CP-2 ethyl ester (99%); 2/Et-H, hydrogenated CP-2 ethyl ester; 1 + 2/Et, 1:1 mixture of CP-1 and CP-2 ethyl esters; 1, free CP-2 acid (99%); 2, free CP-2 acid (99%).

[b]Heat of fusion ΔH_f = 99.7 J/g, melting peak temperature T_m = 71.4°C.

seems, however, that alkyl groups larger than ethyl will diminish the Tg value, although the size of the alkyl group has less effect here than in dialkyl phthalates.

The glass transition temperatures are much higher for the carboxylic acids than for the esters, as can be expected because of the high polarity and the strong hydrogen bond effect. The effect of hydrogenation (which would stabilize the compounds for potential use) on the Tg values is not pronounced. There is, however, an unexpected discrepancy in that the hydrogenation of CP-1 methyl or ethyl ester decreases the Tg value by 6.4 and 5.4°C, respectively, whereas a similar saturation of the ring double bond in CP-2 esters increases the Tg values by 1.3 and 3.5°C, respectively. This we ascribe to the fact that CP-2 undergoes isomerization reactions easily on hydrogenation under various conditions and with various catalysts. Even in our best cases, the hydrogenated CP-2 samples were mixtures of three major compounds, and it is clear that Tg values from such samples cannot be reliably compared with those from nonisomerized compounds. We have at present insufficient spectral or mechanistic information to suggest chemical structures for the components of hydrogenated CP-2 samples.

Mixtures (1:1) of CP-1 and CP-2, either as methyl or as ethyl esters (Table 1, entries 5 and 10), show the effect of the composition of a regular binary solution on Tg values (18,19). The concentration effect is not linear because the theoretical linear Tg value is −83.2°C and the measured value for the methyl ester mixture is −81.8°C. For the ethyl esters, a linear 1:1 concentration dependence would give Tg = −86.3°C, whereas the measured value is −85.6°C.

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