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## PHOTODIMERIZATION OF AROMATIC RESIN ACIDS

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**ABSTRACT.**—Structural assignment of dimers obtained during irradiation of methyl dehydroabietate [3], methyl deisopropyldehydroabietate [2], and 10 $\alpha$ -methyl-13-deisopropyldehydroabietate [1] was achieved by using a combination of nOe difference spectroscopy, 3-D molecular modelling, and X-ray crystallography. The configuration of the A/B ring junction appears to be crucial in the stereochemical outcome of the dimerization reaction.

The acid-catalyzed dimerization of resin acids of the abietic acid type is a subject which has aroused the interest of chemists for many years because of its industrial importance (1). Photodimers, apart from an isolated instance (2), have never been found (3), so we became interested in the mechanism for their formation and therefore undertook a detailed study of the photodimerization of aromatic resin acids derived from abietic acid.

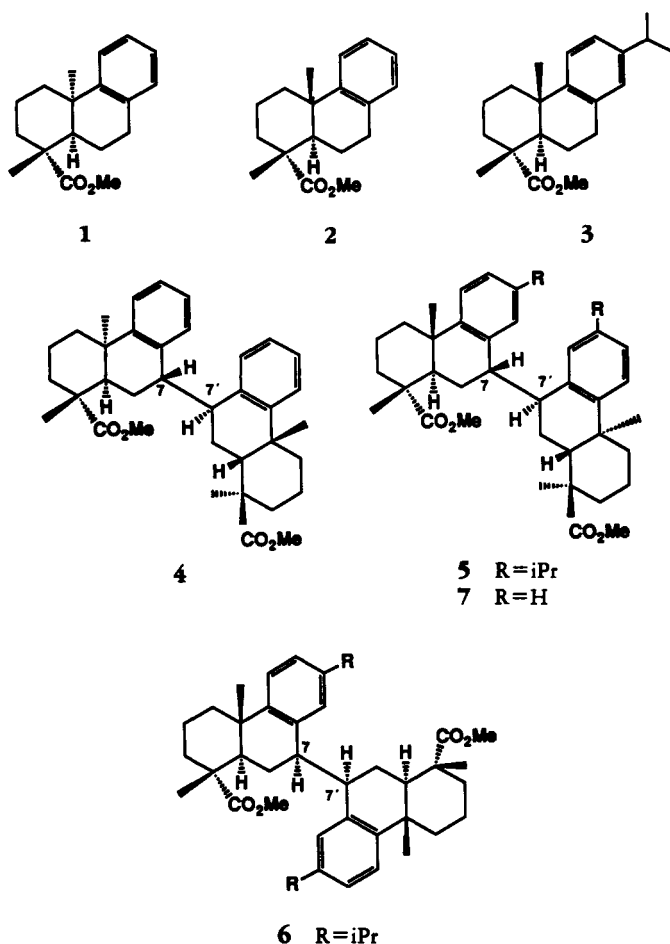
### RESULTS AND DISCUSSION

When the methyl esters of the aromatic resin acids **1**, **2** [easily obtained by AlCl<sub>3</sub> deisopropylation of methyl dehydroabietate [3] (4)] and methyl dehydroabietate [3] were irradiated (17–20 h) with a mercury vapor lamp in a deaerated Me<sub>2</sub>CO solution in a quartz vessel, several dimeric compounds were isolated and characterized.

Interestingly, while **1** gave rise to a single dimeric compound **4**, dimers **5** and **6** were the products arising from the irradiation of **3**. Only one dimer **7** was isolated from a complex mixture resulting from the irradiation of **2**.

**NMR SPECTROSCOPY.**—A common feature of the <sup>1</sup>H-nmr spectra (Table 1) of all four systems is the effective C<sub>2</sub> symmetry observed via the integration, which reveals only half the number of protons assigned on the basis of mass spectral molecular weights.

**COMPOUND 4.**—A strong mutual nOe between the lowfield aromatic proton ( $\delta$  7.3) and the methyl resonance at  $\delta$  1.35 supports a cis ring fusion in this system, these peaks being assigned to H-11 and 10-Me, respectively. The remaining aromatic peaks are similarly assigned to H-12, H-13, and H-14 (Table 2). Molecular models (Figure 1) reveal that the chemical shift of H-14 is particularly low because of shielding by the aromatic ring current from the aromatic ring in the other half of the dimer. A further nOe from H-14 to  $\delta$  3.12 enables assignment of the benzylic proton H-7. There is also a noticeable nOe from H-14 to 10'-Me, supporting the relative orientation of the two components of the dimer shown in Figure 1. Irradiation at H-7 confirms the  $\beta$  stereochemistry of this proton, since in addition to H-14, peaks at  $\delta$  2.1 (d) and  $\delta$  1.85 (dd) are enhanced. These are assigned to H-6 $\alpha$  and H-6 $\beta$ , respectively, the peak multiplicities corresponding to geminal and trans vicinal couplings. A doublet at  $\delta$  2.8 was



assigned to H-5 $\alpha$  on the basis of a difference decoupling experiment showing this peak to be trans coupled to H-6 $\beta$ . A prominent nOe from H-7 $\beta$  to H-5 $\alpha$  could not be expected directly and must therefore be from H-7 $\beta$  to H-5' $\alpha$ , thus providing further evidence for the specific relative orientation of the two components of the dimer. No nOe is observed from H-7 $\beta$  to 10-Me, supporting the  $\alpha$  configuration of 10-Me. We also note that since H-7 $\beta$  is a broad singlet with no trans coupling visible, it must be gauche

TABLE 1.  $^1\text{H-nmr}$  Data of Compounds 4–7 ( $\text{CDCl}_3/\text{TMS}$ ).<sup>a</sup>

Proton	Compound			
	4	5	6	7
Me-10 . . . . .	1.319	1.215	1.101	1.210
Me-4 . . . . .	1.202	1.318	1.228	1.317
COOMe . . . . .	3.711	3.677	3.507	3.677
H-11 . . . . .	7.231 d(7)	7.063 d(8)	7.179 d(9)	7.242 d(8)
H-12 . . . . .	7.018 t(15)	6.784 dd(8, 1.5)	7.009 dd(8, 1.5)	6.958 t(16)
H-13 . . . . .	6.627 t(15)	—	—	6.488 t(16)
H-14 . . . . .	5.894 bd(7)	5.732 d(1.5)	7.215 d(1.5)	5.754 bd(8)
H-7 . . . . .	3.082 bs	2.976 bs	3.817 dd(9,6)	2.973 bs

<sup>a</sup>Data are  $\delta$  (ppm), multiplicity, and  $J$  (in parentheses) in Hz.

TABLE 2. Observed nOe Enhancements in Compounds 4-6.

Compound	Irradiated peak	$\delta$ /ppm	Observed nOe <sup>a</sup>
4	H-11	7.30	10 $\alpha$ -Me, H-12 [2.44]
	H-12	7.08	H-11, H-13 [2.50]
	H-13	6.68	H-12, H-14 [2.48]
	H-14	5.94	H-13, H-7 $\beta$ [2.39], 10'-Me [2.61]
	H-7 $\beta$	3.12	H-14, H-6 $\alpha$ [2.47], H-6 $\beta$ [2.36], H-5' [2.06]
	H-5 $\alpha$	2.80	H-6 $\alpha$ [2.53], 10 $\alpha$ -Me [2.41], 4 $\beta$ -Me [2.69]
5	H-11	7.05	10 $\beta$ -Me, H-12 [2.43], H-1 $\beta$ [2.15]
	H-12	6.75	H-11, isopropyl
	H-14	5.73	isopropyl, H-7 $\beta$ [2.42], H-5' $\alpha$ [2.41]
	H-7 $\beta$	2.95	H-14, H-6 $\alpha$ , H-6 $\beta$ , H-5' $\alpha$ [2.16], 4'OMe
	H-5 $\alpha$	2.55	H-7' $\beta$ , H-14'
6	H-7 $\alpha$	3.82	H-14' [2.30], H-5 $\alpha$ [2.35], H-6 $\alpha$ [2.56]
	H-15	2.83	H-12, H-14, 15-Me <sub>2</sub>
	H-1 $\beta$	2.30	H-11 [2.17], H-1 $\alpha$ [1.79]
	H-5 $\alpha$	2.22	H-7 $\alpha$ , H-6 $\alpha$ [2.60]
	H-6 $\alpha$	0.93	H-14' [2.82], H-7 $\alpha$ , H-5 $\alpha$ , H-6 $\beta$ [1.76]

<sup>a</sup>Proton-proton distance as calculated from molecular models constructed using MacroModel. Distances to methyl groups are the closest contact.

with respect to both H-6 protons, and indeed equal nOe's from H-7 $\beta$  to both H-6 protons are observed. Finally, the nOe from H-5 $\alpha$  is only observed to H-6 $\alpha$  and not to H-6 $\beta$ , with an additional strong effect visible to 10-Me and a weaker one to 4 $\beta$ -Me, confirming again the *cis* stereochemistry of the ring junction.

Single crystal analysis of this compound confirmed all of the stereochemical assignments based on the nmr studies (Figure 2).

COMPOUND 5.—The *trans* configuration of the A/B ring junction of this dimer (Figure 3), though being chemically the expected one, was further confirmed on the following basis. Irradiation of H-11 at  $\delta$  7.05 enhances H-12 at 6.75, the high field methyl singlet at  $\delta$  1.20, and a doublet at  $\delta$  2.3. These last two are assigned to 10 $\beta$ -Me

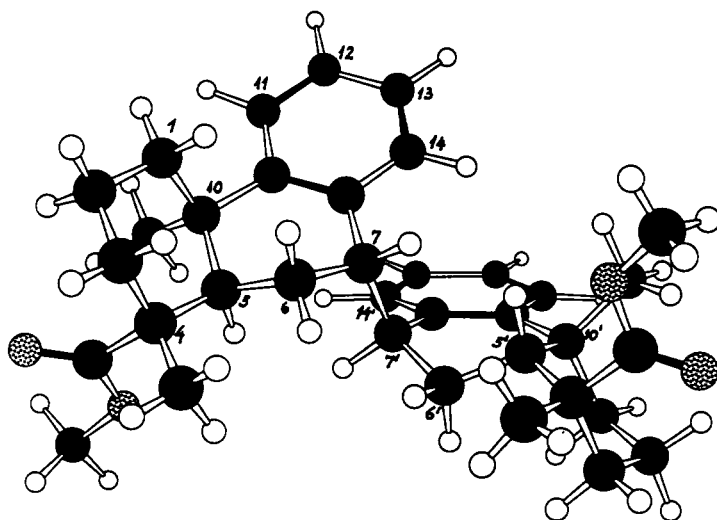


FIGURE 1. Stereochemical formula of dimer 4.

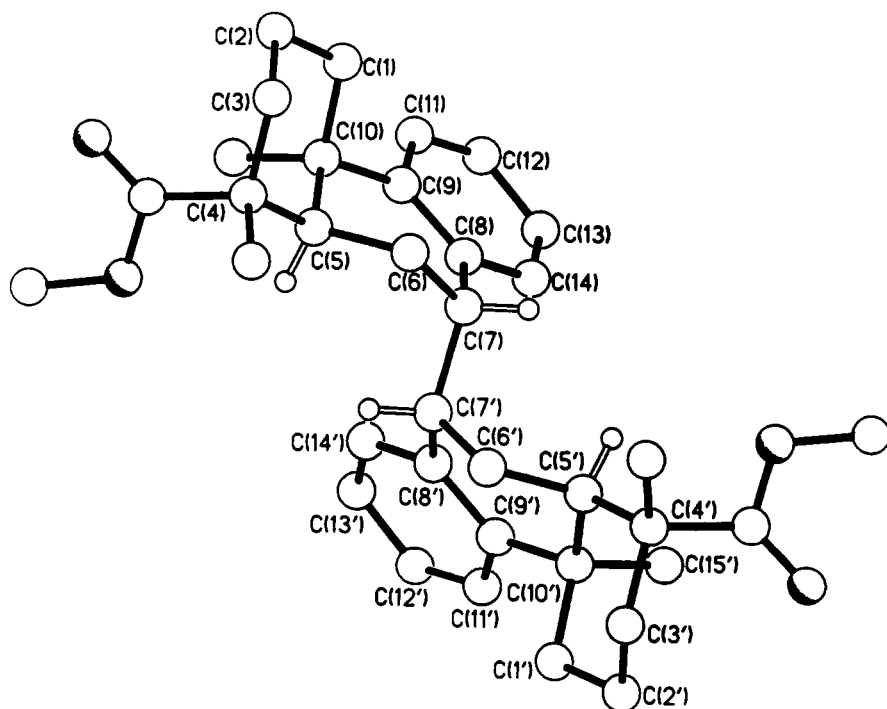


FIGURE 2. 3D Structure of **4** obtained by X-ray analysis with atomic labeling; oxygen atoms appear as shaded circles.

and to H-1 $\beta$ . Molecular models (Figure 3) show the latter to be shifted downfield by the aromatic ring current of the adjacent benzene ring. Irradiation at H-12 shows the expected enhancement of both H-11 and the isopropyl group, while H-14 similarly enhances the isopropyl group, together with H-7 $\beta$  and H-5' $\alpha$  (Table 2). Noteworthy is the upfield shift of H-14, which again implies shielding from a nearby aromatic ring. The benzylic proton H-7 $\beta$  is a broad singlet showing no diaxial coupling, and must therefore be gauche with respect to both H-6 $\alpha$  and H-6 $\beta$ . Irradiation of H-7 $\beta$  shows enhancements of H-5' $\alpha$ , H-14, H-6 $\alpha$ , H-6 $\beta$ , and 4'-OMe. The peak at  $\delta$  2.55 assigned to H-5 $\alpha$  is a doublet with trans coupling to H-6 $\beta$  and shows the expected nOe effects to both H-7' $\beta$  and H-14'.

**COMPOUND 6.**—The most prominent differences in the  $^1\text{H}$ -nmr spectrum of **6** compared with **4** or **5** are the small shift range for the aromatic signals (0.2 compared with 1.4 ppm), the high field shift at  $\delta$  0.93 of one aliphatic proton, and the downfield shift of ca. 0.9 ppm of the benzylic proton H-7 at  $\delta$  3.82. This suggests an entirely different shielding pattern induced from the aromatic rings, consistent with the conformation and configuration shown in Figure 4. The following assignments were made on the basis of nOe and coupling data. Proton H-7 is deshielded by the adjacent benzene ring, and strong nOe's from it are felt in the aromatic singlet, which we assign as being H-14', to the double doublet at  $\delta$  0.9 assigned as H-6 $\alpha$ , and to the doublet at  $\delta$  2.22 assigned as H-5 $\alpha$ . The triplet multiplicity of H-7 $\alpha$  suggests that both syn and anti vicinal coupling are present and therefore confirms the configuration shown. Irradiation at H-5 $\alpha$  shows an effect only to H-7 $\alpha$  and to H-6 $\alpha$ . Finally, irradiation at H-6 $\alpha$  shows an nOe to H-14', to H-7 $\alpha$ , to H-5 $\alpha$ , and to the H-6 $\beta$  quartet at  $\delta$  1.42.

**COMPOUND 7.**—From Table 1 it is obvious that there is a structural analogy between this dimer and **5**. Worthy of notice is the broad singlet attributed to H-7 $\beta$  with

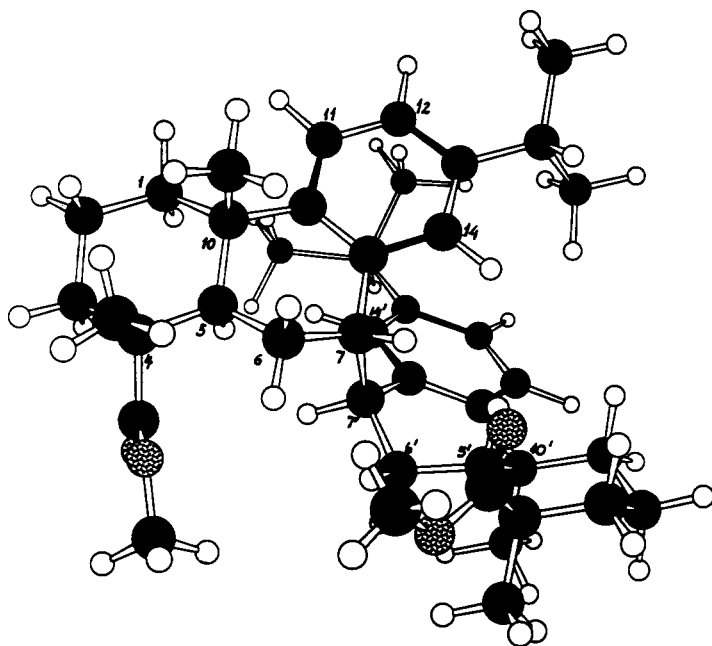


FIGURE 3. Stereochemical formula of dimer 5.

no trans coupling visible and the high field aromatic H-14 resonance appearing at  $\delta$  5.75, suggesting a similar relative conformation of the two aromatic rings.

Two aspects deserve special mention. One refers to the mass spectral data. While all dimers showed a strong  $[M - 2]^+$  ion, the rest of the spectra being dominated by ions derived from this one, the molecular ion always appeared weak or even absent. For com-

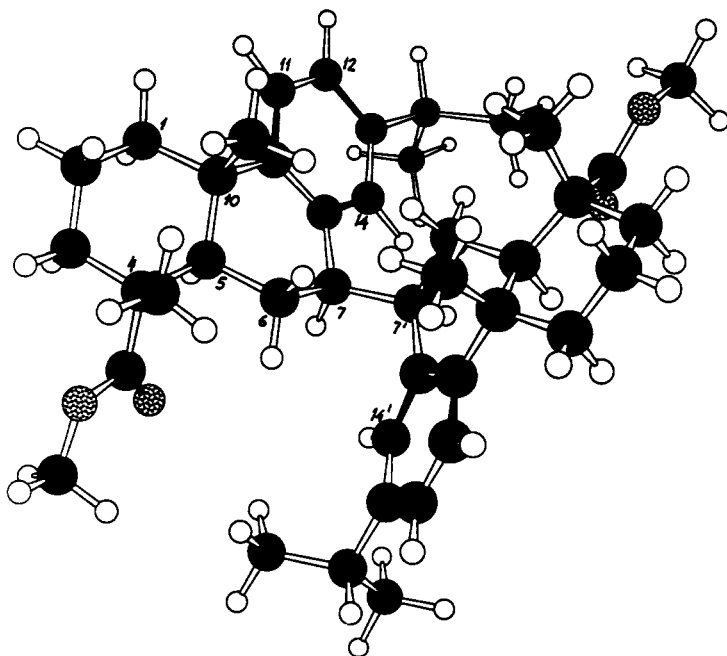


FIGURE 4. Stereochemical formula of dimer 6.

pound **5**, for example, only the  $[M - 2]^+$  ion was apparent, and care must be taken in assigning molecular formulae based solely on mass spectral data.

The other aspect relates to the stereochemical outcome of the dimerization. While aromatic resin acid derivatives possessing the trans A/B ring junction give rise to complex mixtures of dimers, the aromatic acid derivative with the corresponding cis junction yields only one dimeric product. This seems to point out the existence in the latter of a severe stereochemical constraint for photodimerization imposed upon the benzylic radical precursor at the coupling position 7.

## EXPERIMENTAL

**GENERAL EXPERIMENTAL PROCEDURES.**—The procedure for irradiation has been previously described (5), except that in this work the reaction vessel was flushed in the beginning with  $N_2$ . The reaction mixtures were analyzed by gc using a Carlo Erba HRGC 5160 gas chromatograph equipped with a flame ionization detector and a capillary column ("bonded" methyl silicone DB-1 as a 15 m, 0.1  $\mu$  film, fused silica) from J & W Scientific, Rancho Cordova, California. A temperature program, heating between 210° and 285° at a rate of 25°/min followed by an isothermic at 285° for 20 min, was used, with He as the carrier gas (split ratio of 100/1). The gc-ms analysis was done using a Carlo Erba HRGC 5160 associated with a mass spectrometer Kratos MS 25 RF, equipped with a capillary column (CP Sil 5, 26 m length, 0.12  $\mu$  thickness). Nmr spectra were recorded on a GE 300 MHz instrument in  $CDCl_3$  solution. The nOe spectra were recorded on a Bruker WM250 spectrometer in  $CDCl_3$  solution. NOE's were measured as previously (6). All nOe effects were assigned on the basis of quantitative computer models using the MacroModel (V2.5) program system<sup>1</sup>, employing the MM2(85) molecular mechanics force field and a Vax station 3200 computer system with an Evans and Sutherland PS390 stereoviewing system. For each nOe assigned, the proton-proton distance was measured as less than 3.0 Å from computer models. Diagrams were generated from MacroModel by transferring coordinates and connectivity data to an Apple Macintosh running the program Chem3D.

All other experimental details are as previously recorded (5).

**CRYSTAL DATA FOR COMPOUND 4<sup>2</sup>.**— $C_{36}H_{46}O_4$ ,  $M = 542.8$ , monoclinic,  $a = 13.805(4)$ ,  $b = 8.152(2)$ ,  $c = 15.714(5)$  Å,  $\beta = 122.38(2)^\circ$ ,  $V = 1493$  Å<sup>3</sup>, space group  $C2$ ,  $Z = 2$  (the molecule is disposed about a 2-fold axis),  $D_c = 1.21$  g·cm<sup>-3</sup>,  $\mu$  (CuK $\alpha$ ) = 6 cm<sup>-1</sup>,  $F(000) = 588$ . Data were measured on a Nicolet R3m diffractometer (graphite monochromator) using  $\omega$  scans. Independent reflections (1092) were measured, of which 1068 had  $|F_o| > 3\sigma(F_o)$ ,  $2\theta \leq 116^\circ$  and were considered to be observed. The data were corrected for Lorentz and polarization factors; no absorption correction was applied. The structure was solved by direct methods, with non-hydrogen atoms refined anisotropically. The position of the hydrogen atoms was idealized, C-H = 0.96 Å, and they were assigned isotropic thermal parameters,  $U(H) = 1.2 U_{eq}(C)$ , and allowed to ride on their parent carbon atoms. The methyl groups were refined as rigid bodies. Refinement was by block cascade full-matrix least-squares to  $R = 0.034$ ,  $R_w = 0.037$  [ $w^{-1} = \sigma^2(F) + 0.00079 F^2$ ]. The maximum and residual electron densities in the final  $\Delta F$  map were 0.13 and  $-0.16$  eÅ<sup>-3</sup>, respectively. The mean and maximum shift/error in the final refinement were 0.002 and 0.009, respectively. Calculations were carried out on an Eclipse S140 computer using the SHELXTL program system.

**PHOTODIMERIZATION OF 10 $\alpha$ -METHYL-13-DEISOPROPYLDEHYDROABIETATE [1].**—A 0.6 M solution of **1**, mp 92–93° [lit. (7) 93–94°] (599 mg, 2.2 mmol), in deaerated  $Me_2CO$  (3.5 ml) was irradiated with 2 mercury lamps, HPR 125 W, at a distance of 5 cm. After ca. 20 h, a white crystalline precipitate of **4** (58.7 mg, 10%) was collected: mp 169–170° (EtOAc/ $Me_2CO$ );  $[\alpha]_D + 61^\circ$  ( $c = 0.34$ ,  $CHCl_3$ );  $\lambda$  max ( $\epsilon$ ) (EtOH) 265 (1050), 276 (750) nm;  $\nu$  max ( $CHCl_3$ ) 1725 (C=O, ester) cm<sup>-1</sup>; <sup>1</sup>H nmr (proton numbering and integration refer only to one half of the dimer) ( $CDCl_3$ )  $\delta$  1.202 (3H, s, 4-Me), 1.319 (3H, s, 10-Me), 1.546 (3H, m), 1.780 (1H, d,  $J = 6.6$ ), 1.824 (1H, dd,  $J_1 = 7$  and  $J_2 = 2$ , Hax-6), 2.124 (2H, m, Heq-1 and Heq-6), 2.775 (1H, d,  $J = 12$ , H-5), 3.082 (1H, bs, H-7), 3.711 (3H, s, COOMe), 5.894 (1H, bd,  $J = 7$ , H-14), 6.627 (1H, t,  $J = 15$ , H-13), 7.018 (1H, t,  $J = 15$ , H-12), 7.231 (1H, d,  $J = 7$ , H-11) ppm;  $m/z$   $[M - 2]^+$  540 (0.1%),  $[M - 60 - 2]^+$  480 (0.2%), 424 (0.4%),

<sup>1</sup>Courtesy of W. C. Still, Department of Chemistry, Columbia University, New York.

<sup>2</sup>Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from Dr. Olga Kennard, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

$[M-2]^+$  271 (30%),  $[M-2-1]^+$  270 (67%),  $[M-2-60]^+$  211 (100%),  $[M-2-116]^+$  155 (39%). *Anal.* found C 79.55, H 8.40%; calcd for  $C_{36}H_{46}O_4$ , C 79.67, H 8.54%. The filtrate showed by gc-ms analysis the presence of starting material (55%) and the respective 7-oxo derivative (28%).

**IRRADIATION OF METHYL DEISOPROPYLDEHYDROABIETATE [2].**—Irradiation of **2**, mp 109–110° [lit. (7) 108–109°] (20 mg, 0.07 mmol), under similar conditions revealed by gc-ms analysis the formation of several dimers ( $m/z$   $[M]^+$  542), in yields ranging from 0.1 to 6%, together with starting material (48%) and the respective 7-oxo derivative (20%). By preparative tlc the major dimer **7** was isolated (0.9 mg) (4.5%) as a glass:  $[\alpha]_D + 55^\circ$  ( $c = 0.03$ , MeOH);  $\lambda$  max ( $\epsilon$ ) (EtOH) 265 (1000), 276 (900) nm;  $\nu$  max (CHCl<sub>3</sub>) 1726 (C=O, ester)  $cm^{-1}$ ;  $^1H$  nmr (proton numbering and integration refer only to one half of the dimer) (CDCl<sub>3</sub>)  $\delta$  1.210 (3H, s, 10-Me), 1.317 (3H, s, 4-Me), 2.545 (1H, bd,  $J = 12$ , H-5), 2.973 (1H, bs, H-7), 3.677 (3H, s, COOMe), 5.754 (1H, bd,  $J = 8$ , H-14), 6.488 (1H, t,  $J = 16$ , H-13), 6.958 (1H, t,  $J = 16$ , H-12), 7.242 (1H, d,  $J = 8$ , H-11) ppm;  $m/z$   $[M]^+$  542.3446 (5%) (calcd for  $C_{36}H_{46}O_4$ , 542.3396),  $[M-1]^+$  541 (8%),  $[M-2]^+$  540 (10%),  $[M-60-2]^+$  480 (12%),  $[M-2]^+$  271 (52%),  $[M-2-60]^+$  211 (100%),  $[M-2-116]^+$  155 (47%).

**IRRADIATION OF METHYL DEHYDROABIETATE [3].**—Irradiation of **3** (300 mg, 0.48 mmol), under similar conditions, revealed by gc-ms analysis the presence of starting material (58%), methyl 7-oxo-dehydroabietate (10%), and a mixture of dimers,  $m/z$   $[M]^+$  626 (14%). By preparative tlc the two major dimers **5** and **6** were isolated.

**Compound 5.**—Glass (3 mg) (1%):  $[\alpha]_D + 57^\circ$  ( $c = 0.11$ , MeOH);  $\lambda$  max ( $\epsilon$ ) (EtOH) 268 (1300), 276 (1200) nm;  $\nu$  max (CHCl<sub>3</sub>) 1726 (C=O, ester)  $cm^{-1}$ ;  $^1H$  nmr (proton numbering and integration refer only to one half of the dimer) (CDCl<sub>3</sub>)  $\delta$  0.762 and 0.831 (6H, 2d,  $J = 7$ , 15-Me<sub>2</sub>), 1.215 (3H, s, 10-Me), 1.318 (3H, s, 4-Me), 2.554 (1H, d,  $J = 12$ , H-5), 2.976 (1H, bs, H-7), 3.677 (3H, s, COOMe), 5.732 (1H, d,  $J = 1.5$ , H-14), 6.784 (1H, dd,  $J_1 = 8$ ,  $J_2 = 1.5$ , H-12), 7.063 (1H, d,  $J = 8$ , H-11) ppm;  $m/z$   $[M]^+$  626.4323 (0.3%) (calcd for  $C_{42}H_{58}O_4$ , 626.4335),  $[M-60]^+$  566 (11%), 485 (0.7%),  $[M-2]^+$  313 (100%),  $[M-2-60]^+$  253 (98%), 197 (17%), 154 (19%).

**Compound 6.**—Compound **6** (6 mg) (2%): mp 220–221° (Et<sub>2</sub>O/MeOH),  $[\alpha]_D + 15^\circ$  ( $c = 0.34$ , CHCl<sub>3</sub>),  $\lambda$  max ( $\epsilon$ ) (EtOH) 269 (1040), 277 (1070) nm;  $\nu$  max (CHCl<sub>3</sub>) 1726 (C=O, ester)  $cm^{-1}$ ;  $^1H$  nmr (proton numbering and integration refer only to one half of the dimer) (CDCl<sub>3</sub>)  $\delta$  0.931 (1H, ddd,  $J_1 = 13$ ,  $J_2 = 6$ ,  $J_3 = 2$ , Heq-6), 1.101 (3H, s, 10-Me), 1.228 (3H, s, 4-Me), 1.238 (2  $\times$  3H, d,  $J = 7$ , 15-Me<sub>2</sub>), 1.382 (1H, ddd,  $J_1 = 13$ ,  $J_2 = 12$ ,  $J_3 = 9$ , Hax-6), 2.212 (1H, dd,  $J_1 = 12$ ,  $J_2 = 2$ , H-5), 2.292 (1H, d,  $J_1 = 13$ , Heq-1), 2.830 (1H, m,  $J = 7$ , H-15), 3.817 (1H, dd,  $J_1 = 9$ ,  $J_2 = 6$ , H-7), 3.507 (3H, s, COOMe), 7.215 (1H, d,  $J = 1.5$ , H-14), 7.009 (1H, dd,  $J_1 = 8$ ,  $J_2 = 1.5$ , H-12), 7.179 (2H, d,  $J = 8$ , H-11) ppm;  $m/z$   $[M]^+$  626.4364 (0.2%) (calcd for  $C_{42}H_{58}O_4$ , 626.4335),  $[M-59]^+$  567 (2%), 485 (0.7%),  $[M-2]^+$  313 (31%),  $[M-2-60]^+$  253 (100%), 197 (17%), 154 (19%).

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