min at room temperature (the temperature increased slightly during the initial mixing). Water was added until the mixture was homogeneous, and the solution was poured into 80 ml of 6 *N* hydrochloric acid. When no crystallization occurred in 7 hr, the solution was adjusted to pH 2 and was extracted with four 65-ml portions of $CHCl_3$. Drying ($MgSO_4$) and evaporation of the combined extracts under reduced pressure gave a thick syrup. This material was crystallized from CH_2Cl_2–cyclohexane (1:1, v/v) to provide 0.70 g of product, mp 225–232° dec [second crop, 0.16 g, mp 217–226° dec (49% total)]. Recrystallization of the combined crude product from CH_2Cl_2–methanol gave 0.56 g (65% recovery) of ketophosphonic acid **12**: mp 224–230° dec; ir (Nujol) 1700 (C=O), 1200 (very broad, ≡PO), 1000, and 925 cm^{-1}; nmr (MeOH) δ 1.36 (s, CCH_3).

Anal. Calcd for $C_{11}H_{19}O_4P$: C 53.65; H, 7.78; P, 12.58; mol wt, 246. Found: C, 53.47; H, 7.86; P, 12.50; neut equiv, 252.

2,4-Dinitrophenylhydrazone had mp 203–208°.

Anal. Calcd for $C_{17}H_{23}N_4O_7P$: C, 47.89; H, 5.44; N, 13.14; P, 7.26. Found: C, 47.70; H, 5.60; N, 12.92; P, 7.19.

Dimethyl *trans*-[Octahydro-8a-methyl-3-oxo-4a(2H)-naphthyl]-phosphonate (13).—Diazomethane prepared from 5.80 g (27.2 mmol) of N-methyl-N-nitroso-*p*-toluenesulfonamide[24] was distilled into a solution of 2.00 g (8.12 mmol) of ketophosphonic acid **12** in 75 ml of a $CHCl_3$–dioxane–DMF mixture. The resulting solution was washed successively with dilute H_2SO_4, water, and saturated aqueous NaCl. Drying ($MgSO_4$) and evaporation of the solution under reduced pressure gave a yellow oil, the ir spectrum of which indicated was a mixture of the desired dimethyl ester and **10**. Distillation of this oil gave 0.65 g of product: bp 145–150° (1 mm); ir (neat) 1720 (C=O), 1675, 1620, 1235 (≡PO), 1180 (POMe), 1055–1035 (d, PO-alkyl), 815, and 775 cm^{-1}. Glpc analysis (Micro-Tek GC 2000-R, twin SE 30 columns, column temperature 210°, flame ionization detector) indicated that the product was contaminated with *ca.* 5% of the unsaturated ketone **10**.

Since no satisfactory separation of these compounds could be accomplished, the 2,4-dinitrophenylhydrazone, mp 124–127°, of **13** was prepared from the mixture by the usual procedure.

Anal. Calcd for $C_{19}H_{27}N_4O_7P$: C, 50.22; H, 5.99; N, 12.33; P, 6.82. Found: C, 50.02; H, 6.12; N, 12.12; P, 6.54.

Registry No.—**2**, 18554-19-3; **3**, 18554-20-6; **3** (2,4-dinitrophenylhydrazone derivative), 18554-21-7; **4**, 18554-22-8; **4** (2,4-dinitrophenylhydrazone derivative), 18554-23-9; **5**, 18554-24-0; **6**, 18554-25-1; **7**, 18554-26-2; **8**, 18554-27-3; **9**, 18554-28-4; **9** (2,4-dinitrophenylhydrazone derivative), 18554-29-5; **11**, 18554-30-8; **12**, 18554-31-9; **12** (2,4-dinitrophenylhydrazone derivative), 18554-32-0; **13**, 18554-33-1; **13**, (2,4-dinitrophenylhydrazone derivative), 18554-34-2; phosphorus trichloride, 7719-12-2.

Photochemical Reactions of Resin Acids. Photochemically Initiated Addition of Methanol to Abietic Acid[1a]

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Received June 24, 1968

Irradiation of abietic acid or methyl abietate in methanol or benzene–methanol mixture gave rise to two epimeric ethers **6** and **7** along with products of decarboxylation, disproportionation, isomerization and polymerization. The structures of the two photoadducts **6** and **7** were proved by chemical degradation and nmr and mass spectra. The addition is nonstereospecific at C_{13} and seems to be a bimolecular process,[2c] in which a photoexcited polar species abstracts a proton from methanol to give an intermediate carbonium ion, which then coordinates with solvent. No bicyclobutane intermediate could be isolated under the conditions used for photolysis.

Photochemical transformations of the diene systems in the steroids have been extensively studied[2] but only a few reports have been made on the diterpene resin acids. Photolytic valence isomerizations of levopimaric and palustric acids have been reported.[3,4] Irradiation of abietic acid in ethanol has been reported to give hydroxy acids.[5] The purpose of the present investigation was to study the photolysis of abietic acid and methyl abietate in methanol.

In contrast to the results in ethanol,[5] irradiation (2537 Å) of abietic acid or methyl abietate in absolute methanol or in benzene–methanol gave little if any alcoholic product. The major monomeric products (35% by glpc) were two ethers, photoadducts I and II, obtained in a 9:1 ratio. Isomerization, disproportionation, and, in the case of the acid, decarboxylation products were also obtained. Both ethers could be isolated by preparative glpc of the methyl esters. Thick layer or column chromatography separated the methyl esters of the adducts from the other products but not from each other. Fractional crystallization of the mixed ethers gave pure photoadduct I.

Reduction of photoadduct I with lithium aluminum hydride followed by dehydrogenation with palladium

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[1] (a) Presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 8–13, 1968. (b) Resident Postdoctoral Research Associate under the auspices of the National Academy of Sciences, National Research Council. (c) One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

[2] (a) J. Pusset and R. Beugelmans, *Tetrahedron Lett.*, 3249 (1967); (b) P. G. Gassman and W. E. Hymans, *Chem. Commun.*, 795 (1967); *Tetrahedron*, **24**, 4437 (1968), and the references cited therein; (c) G. Just and V. Di Tullio, *Can. J. Chem.*, **42**, 2153 (1964); G. Bauslaugh, G. Just, E. Lee-Ruff, *Can. J. Chem.*, **44**, 2837 (1966), and the references cited therein; (d) W. G. Dauben and W. T. Wipke, *Pure Appl. Chem.*, **9**, 539 (1964); W. G. Dauben, *Chem. Weekbl.*, **60**, 381 (1964), and the references cited therein; (e) G. J. Fonken, "Organic Photochemistry" Vol. 1, O. L. Chapman, Marcel Dekker, Inc., New York, N. Y. 1967, p 197, and the references cited therein.

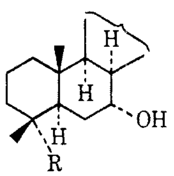
[3] W. H. Schuller, R. N. Moore, J. E. Hawkins, and R. V. Lawrence, *J. Org. Chem.*, **27**, 1178 (1962).

[4] W. G. Dauben and R. M. Coates, *J. Amer. Chem. Soc.*, **86**, 2490 (1964); *J. Org. Chem.*, **29**, 2761 (1964).

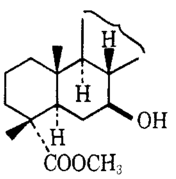
[5] R. F. Brown, G. B. Bachman, and S. J. Miller, *J. Amer. Chem. Soc.*, **65**, 623 (1943).

on charcoal gave retene, indicating that the abietic carbon skeleton was retained in the adduct. This was also supported by the pyrolysis of photoadduct I, which gave mainly methyl abietate. The nmr spectrum of photoadduct I showed a broad one-proton vinyl signal at 315 cps similar in shape and position to the C_7 proton signal of methyl abietate, a three-proton methoxyl signal at 189 cps, no **HCO** signal, and a two-proton singlet at 133 cps. This suggests that photoadduct I has a C_7–C_8 double bond and a methoxyl group at C_{13}.

Hydroboration-oxidation[6,7] of isopimaric and related $\Delta^{7,8}$ resin acids is known to give predominantly C_7 alcohols. Hydroboration–oxidation of photoadduct I by the LAH–BF_3 method[8] gave as the major product a diol (**1**) which was isolated in 65% yield as its *p*-nitrobenzoate. Attempts to analyze the crude diol by glpc were unsuccessful. Use of the sodium borohydride–BF_3 method[6] with limited reagent gave a product containing 93% **2** and 6% of another hydroxy ester, presumably **3**. The C_7-α assignment for the hydroxyl in **1** and **2** is confirmed by the position and shape of the carbinol proton band. In each case it is a one-proton peak, at 226 cps (calcd[9a] 220 cps) with a half-height[10] width of 6 cps characteristic of an equatorial carbinol proton.[6,7,9,10] In the *p*-nitrobenzoate of **1** it shifts to 307 cps. The α assignment for the C_8 proton follows from the known *cis* hydroboration[11] and is confirmed by the deshielding of the C_{17} protons.[12]



1, R = CH_2OH
2, R = $COOCH_3$



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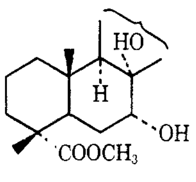
The final proof of the C_7–C_8 double bond position was obtained by the osmium tetroxide-oxidation[8b,13] reaction sequence to give the ketoaldehyde (**5**). The intermediate diol (**4**) showed a clean one-proton triplet at 210 cps ($J_{e,e}$ = 2.5 cps and $J_{a,e}$ = 3.5 cps)[14a] for the equatorial C_7-β proton, and the C_{10} methyl (C_{17} protons) was deshielded. The *cis* mode of addition[13] for osmium tetroxide is known, so the diol is **4**. The ketoaldehyde showed a triplet at 581 cps (J = 1.8 cps) characteristic of aldehydes[14b] having two protons in the α-carbon atom. An aldehyde derived from C_{14} could not have two α protons so the aldehyde proton must be at C_7 coupled with the two C_6 protons.



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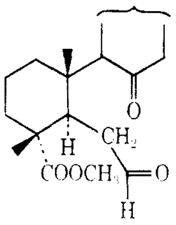

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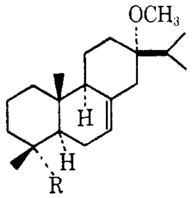
With the double bond position fixed the methoxyl must be at C_{13} giving either **6** or **7** as the structure of photoadduct I. As shown in Table I, photoadduct II has an nmr spectrum which is very similar to that of photoadduct I. In particular, the position and shape of the olefinic proton signal and deshielded methylene (C_{14}) proton signal together with the absence of an **HCO** signal strongly suggests that photoadduct II is the C_{13} epimer of photoadduct I.



6, R = $COOCH_3$
6a, R = CH_2OH

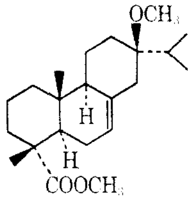


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TABLE I
CHEMICAL SHIFTS[a] (CPS) OF PHOTOADDUCT I (**6**) AND PHOTOADDUCT II (**7**)

Protons at	Photoadduct I (**6**)	Photoadduct II (**7**)
C_7	315 (diffused d, 1 H)	321 (b, 1 H)
C_{15}-OCH_3	216 (s, 3 H)	219 (s, 3 H)
C_{13}-OCH_3	189 (s, 3 H)	185 (s, 3 H)
C_{14}	133 (s, 2 H)	127 (s)
C_{16}	76 (s)	76 (s)
C_{19} and C_{20}	52 (d, J = 6.5)	52 (s, J = 6.5)
C_{17}	51 (s)	54 (s)

[a] Downfield relative to TMS as internal standard taken in $CDCl_3$.

Photolysis of 3-methylcholesta-3,5-diene in ethanol is reported[2c] to yield the unsaturated ether which would result from attack by the ethoxyl group on the less hindered side of the diene molecule. In the case of the resin acids the α side is less hindered;[7,15] therefore

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[6] E. Wenkert, P. W. Jeffs, and J. R. Mahajan, *J. Amer. Chem. Soc.*, **86**, 2218 (1964).

[7] W. Herz, D. Melchior, R. N. Mirrington, and P. J. S. Pauwels, *J. Org. Chem.*, **30**, 1873 (1965).

[8] (a) S. Wolfe, M. Nassium, Y. Mazur, and F. Sondheimer, *ibid.*, **24**, 1034 (1959); (b) D. K. Black and G. W. Hedrick, *ibid.*, **32**, 3758 (1967).

[9] (a) E. L. Eliel, M. H. Gianni, Th. H. Williams, and J. B. Stothers, *Tetrahedron Lett.*, 741 (1962); (b) J. C. Sircar and A. I. Meyers, *J. Org. Chem.*, **32**, 1248 (1967).

[10] B. E. Cross and P. L. Myers, *J. Chem. Soc., C*, 471 (1968).

[11] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, pp 145, 146.

[12] J. W. Huffman, T. Kamiya, L. H. Wright, J. J. Schmid, and W. Herz, *J. Org. Chem.*, **31**, 4128 (1966).

[13] L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 759.

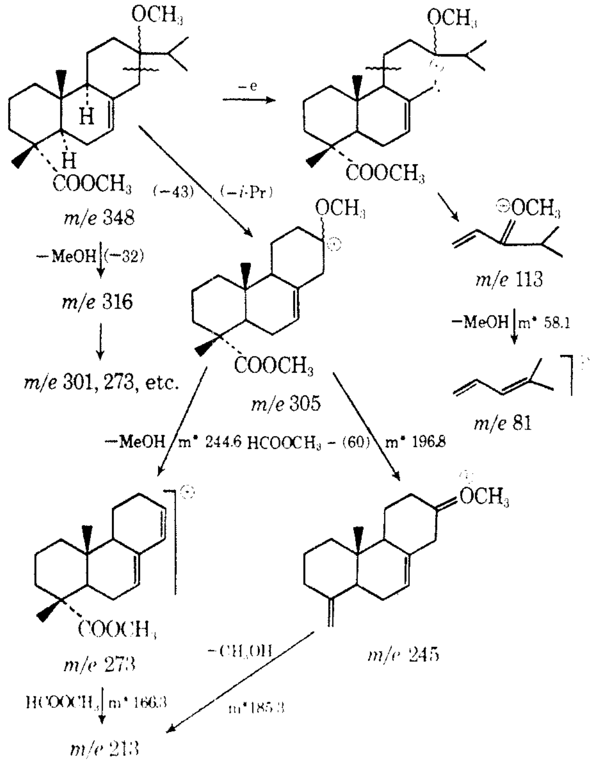
[14] (a) N. S. Bhacca and D. H. Williams, "Application of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 77; (b) *ibid.*, p 76.

[15] H. Kanno, W. H. Schuller, and R. V. Lawrence, *J. Org. Chem.*, **31**, 4138 (1966), and the references cited therein.

photoadduct I, being the major product, should have the α-methoxy structure (6).

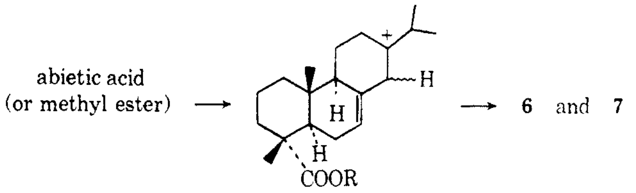
Further proof of the epimeric relationship of the two photoadducts and strong support for the structural assignments is provided by the mass spectra of the adducts. The two spectra are qualitatively identical (*i.e.*, all major peaks are common to both spectra) but differ significantly in the relative abundance of certain fragments. Origin of the major ions is outlined in Scheme I. In each case only one possible contributing structure is indicated. Formation of *m/e* 316 ions ($M - 32$) by α cleavage with rearrangement[16a] and further fragmentation to give the same ions obtained from the resin acids[16b] is to be expected regardless of the position of the methoxyl so these fragments have no qualitative significance. Ions arising from loss of an isopropyl group ($M - 43$) are not very abundant in the mass spectra of resin acid methyl esters[16b] unless the loss is facilitated by some neighboring group. Hence, the appearance of the *m/e* 305 as a major peak in the adduct spectra strongly supports the C_{13} position for the methoxyl in both adducts. Final proof that both have C_{13} methoxyls is provided by the *m/e* 113 ions which loses methanol to give the *m/e* 81 ion (metastable ion peak (m*) observed at *m/e* 58.1). The initial C_{13}–C_{14} and the final C_9–C_{11} cleavages are favored because they are β to the double bond.

SCHEME I



Bieman[17] has pointed out that when epimers differ in steric crowding, the intensity of the molecular ion is higher for the less crowded isomer. Furthermore, in the case of alcohols and their acetates the intensity of the $M^+ - ROH$ ion is lower for the less crowded isomer. Examination of molecular models of 6 and 7 shows that 7 is less crowded than 6 even if the C ring in 6 has a twist-boat conformation. Since photoadduct II gives five times as much M^+ as photoadduct I and only one-third as much $M^+ - CH_3OH$ and derived fragments, it has structure 7.

Since no cyclopropyl ring protons were evident in the nmr of the crude irradiation product, the formation of 6 and 7 probably takes place *via* the intermediate 8, nonstereospecifically by a bimolecular process.[18] The isolation of both the C_{13}-epimeric ethers 6 and 7 lends support to this mechanism and is in agreement with the results reported for 3-substituted cholest-3,5-dienes.[2c,2d,18]



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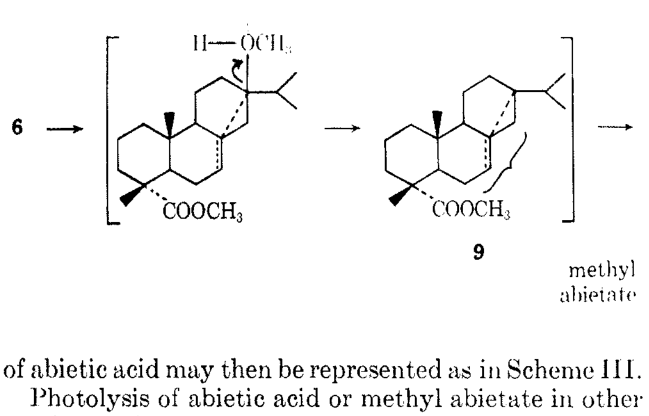
In an attempt to enhance the reaction and to avoid poly(di?)merization of the abietic acid or methyl abietate, the irradiation was carried out in methanol containing 0.1 equiv of perchloric acid.[18] No photoadduct I could be detected in the glpc. The treatment of the photoadduct I with a solution of methanol–perchloric acid at room temperature for 10–15 min resulted in the regeneration of the methyl abietate (60%). This probably occurs by protonation of the methoxyl group followed by the elimination of methanol *via* the homoallylic carbonium ion,[18b] 9, which rearranges to methyl abietate (Scheme II). The whole photochemical transformation of abietic acid may then be represented as in Scheme III.

SCHEME II



Photolysis of abietic acid or methyl abietate in other protic media is currently under active investigation and the results will follow soon. Neoabietic acid and

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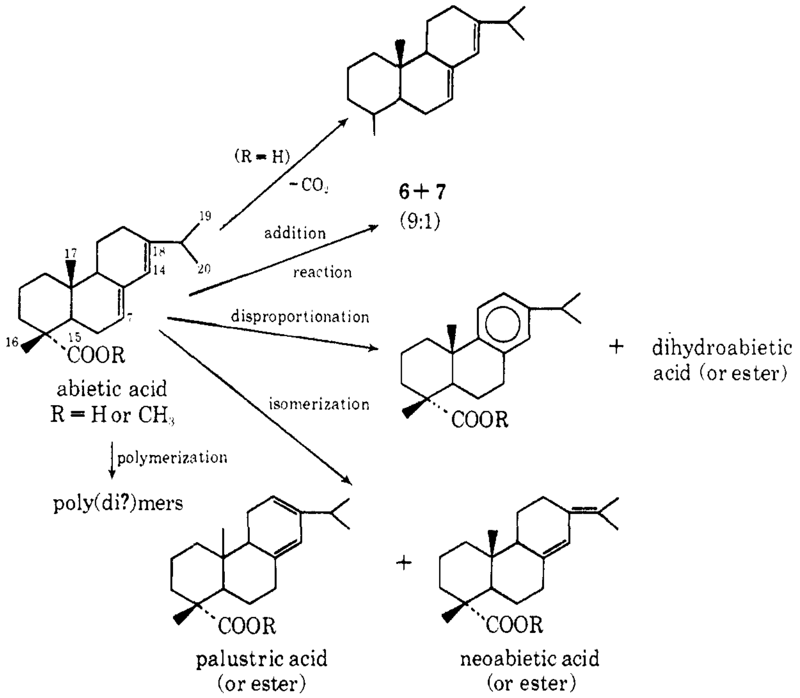
(16) (a) F. W. McLafferty, *Anal. Chem.*, **29**, 1782 (1957); (b) C. A. Genge, *ibid.*, **31**, 1751 (1959).

(17) K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 144.

(18) (a) G. Bauslaugh, G. Just, and E. Lee-Ruff, *Can. J. Chem.*, **44**, 2837 (1966), and the references cited therein. (b) G. Just and C. C. Lezoff, *ibid.*, **42**, 79, 2801 (1964).

SCHEME III



the other resin acids are also being investigated and the results will be published at a later date.

Experimental Section[19]

13-β-Isopropyl-13-α-methoxypodocarp-7-en-15-oic Acid Methyl Ester (6) and 13-α-Isopropyl-13-β-methoxypodocarp-7-en-15-oic Acid Methyl Ester (7).—Abietic acid[20,21] (9.15 g, $[\alpha]^{26}\mathrm{D}$ −105–106°) was dissolved in absolute methanol (AR, 450 ml) and the solution degassed five times alternately introducing dry nitrogen in the quartz vessel. The solution was photolyzed with 2537-Å light[22] until the absorption went down to 10–15% of the original value. Analyses were also done by glpc,[23a] converting the acids to methyl esters with tetramethylammonium hydroxide (TMAH). When the photoadduct peak was the only major peak, the reaction was stopped (138 hr). The methanol was removed under vacuum and the residue analyzed as follows: (a) neutral volatile products, 4%[23b]; (b) total volatile products, 51%; (c) photoadducts, 28.5%, (d) other products such as dehydroabietic, abietic, etc., 22.5%. The neutralization equivalent (383.2) indicated polymerization and decarboxylation.

The product was esterified with diazomethane and chromatographed over Woelm neutral alumina (activity I, 210 g). Elution with hexane (400 ml) and 5% ether–hexane (200 ml) gave the resin–acid mixtures (1.62 g) containing methyl palustrate, methyl dehydroabietate, methyl abietate, two unknown peaks and the early peaks (the decarboxylated products). All known compounds were identified by glpc and the ir. Further elution with 5% ether–hexane (200 ml), 7.5% ether–hexane (200 ml) and 10% ether–hexane (400 ml) gave the solid photoethers (3.99 g, 37%) which were recrystallized from methanol to give the photoadduct I (6): 2.0635 g, 18.5%; mp 81–83°. One additional recrystallization gave the analytical sample: mp 84°; $[\alpha]^{26}\mathrm{D}$ +12.1°; ir ($CHCl_3$) 5.84 (C=O), 7.25, 7.35 (isopropyl), 8.10, 8.45 and 8.76 (COC ester), 9.28 (COC ether) and 12.10 μ (>C=CH); nmr (see Table I); mass spectrum m/e (%Σ 40) 348 (0.1), 316 (11.6), 305 (9.1), 301 (10.5), 273 (22.4), 257 (3.0), 256 (2.1), 245 (1.0), 241 (1.1), 213 (2.8), 113 (2.7), 81 (1.1).

Anal. Calcd for $C_{22}H_{36}O_3$; C, 75.86; H, 10.34. Found: C, 76.04; H, 10.56.

The mother liquor, concentrated in the photoadduct II, and the resin acid esters were used in the preparative gas chromatography (5% Versamid-900; 20 ft × $^3/_8$ in., 120 ml/min, 245°). The unknown peak (α 1.70) ahead of palustric was collected: ir (film) 5.80, 7.25, 8.10, 8.80, and 9.10 μ; no uv max. The other resin acid esters were also collected and identified by ir.

The photoadduct II (7) was collected separately as a viscous oil: ir (film) 5.81 (C=O), 7.25, 7.35 (isopropyl), 8.10, 8.46, 8.76 (COC ester), 9.26 (COC ether), 12.10 μ (>C=CH); nmr (see Table I); mass spectrum m/e (%Σ 40) 348 (0.5), 316 (3.8), 305 (9.2), 301 (1.9), 273 (6.3), 257 (1.4), 256 (1.1), 245 (0.8), 241 (3.0), 213 (2.2), 113 (6.9), 81 (2.3).

Anal. Calcd for $C_{22}H_{36}O_3$; C, 75.86; H, 10.34. Found: C, 75.68; H, 10.27.

Photolysis of Abietic Acid in Methanol–Benzene.—Abietic acid (0.807 g) in methanol (64 ml, AR) and benzene (16 ml, AR) was irradiated for 33 hr with 2537-Å light and the reaction was followed by glpc. Evaporation of the solvent gave a brown oil which was esterified with diazomethane solution and the photoproducts 6 and 7 were isolated together by preparative gas chromatography (20% S.E.-30 on Chromosorb W at 255°; 12 ft × $^3/_8$ in. helium flow, 120 ml/min; retention time, 16 min).

Photolysis of Methyl Abietate in Methanol.—A solution of methyl abietate [prepared from abietic acid (0.5 g) with excess diazomethane in ether] in methanol (50 ml, AR) was irradiated with 2537-Å light for 26 hr and the reaction followed quantitatively both by uv and glpc. No early peaks, *i.e.*, decarboxylated abietic acid, were evident and the formation of the photoadducts

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[19] Melting points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer Infrared spectrophotometer, Model-21. Ultraviolet spectra and rotations were determined in 95% ethanol. Analytical gas chromatographic analyses were performed on a Varian Aerograph Model 1200 using $^3/_{16}$-in. columns of specified length packed with 5–10% Versamid-900 on 60–80 mesh Chromosorb W. Methyl arachidate was used as an internal standard for determination of relative retention times (α) and for quantitative analyses. Nuclear magnetic resonance spectra were determined in deuteriochloroform, unless otherwise stated, with a Varian A-60A spectrometer, using tetramethylsilane as an internal standard. The multiplicities are s = singlet, d = doublet, t = triplet, m = multiplet and b = broad. Mass spectra were measured on an A.E.I. M.S.-9 spectrometer at 70 eV, using a direct inlet system. Analyses were carried out by Galbraith Laboratories, Inc., Knoxville, Tenn. The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over others not mentioned.

[20] Prepared from levopimaric acid, kindly supplied by Dr. W. H. Schuller of our laboratory, after initial purification.

[21] W. H. Schuller, H. Takeda, and R. V. Lawrence, *J. Chem. Eng. Data*, **12**, 283 (1967).

[22] Rayonet preparative photochemical reactor, Type RS, was used, having four 15-W modules as light source, available from the Southern New England Ultraviolet Co., Middletown, Conn. 06457.

[23] (a) N. M. Joye, Jr., and R. V. Lawrence, *J. Chem. Eng. Data*, **12**, 279 (1967); (b) analyzed without TMAH.

6 and **7** increased with time; but at the same time, considerable amounts of disproportionation products were formed. After 27 hr the sample analyzed as follows: volatile matter (57.8%), composed of palustrate, dihydroabietates, etc. 6.6%, dehydroabietate 27.6%, abietate 20%, neoabietate 0.66%, and photoadducts, 45.8%.

13-β-Isopropyl-13-α-methoxypodocarp-7-en-15-ol (6a).—To a solution of photoadduct I (**6**, 195 mg) in dry ether (12 ml) was added lithium aluminum hydride (117 mg) in ether (25 ml). The mixture was then refluxed for 4 hr, cooled, decomposed with a saturated solution of sodium sulfate (0.5 ml) and the ether solution filtered, dried (Na_2SO_4) and the solvent removed to give a solid (**6a**, 192 mg), mp 88–90°. This was recrystallized from *n*-pentane and had mp 91–93°. It showed a single peak in glpc: ir (film) 3.02, 7.27, 7.32, 8.0, 8.95 and 9.25 μ.

Anal. Calcd for $C_{21}H_{36}O_2$: C, 78.75; H, 11.25. Found: C, 78.79; H, 11.32.

Heating of **6a** with Pd–C for 4 hr at 220–245° yielded retene which was identified by its glpc retention time and uv spectrum.

7α-Hydroxy-13β-isopropyl-13α-methoxy-8α-podocarpan-15-ol (1).—To the stirred ice-cold solution of the photoadduct I (**6**, 525 mg) in dry ether (20 ml) was added slowly in installments the powdered LAH (216 mg). After stirring for 30 min at 0°, freshly distilled boron trifluoride etherate (0.7 ml) in dry ether (10 ml) was added slowly during a period of 1 hr and the mixture left at room temperature for 16 hr. It was decomposed with a saturated solution of sodium sulfate (1.2 ml) and the ether layer was filtered off. Removal of solvent gave a solid residue which was dissolved in 80% aqueous alcohol (40 ml) containing sodium hydroxide (0.6 g), followed by the slow addition of 30% hydrogen peroxide (4 ml). The mixture was stirred at room temperature for 2 hr and then refluxed on a steam bath for 4 hr, before diluting with brine and extracting with ether. The total ether extract was washed thoroughly with brine and was dried (Na_2SO_4) and the solvent stripped off to give (532 mg) of **1**: mp 60–75°; ir (Nujol) 3.02, 9.30, 9.65, 9.95 and 11.85 μ; nmr 226 (b, 1, $W_{1/2}$ = 6 cps, equatorial C_7-β proton), 191 (two d, center of C_{15} AB system, 2, J = 11 cps, $\delta_B - \delta_A$ = 34 cps, δ_A = 173 cps and δ_B = 208 cps), 186 (s, 3, CH_3O), 203 cps (b, 2, exchangeable with D_2O and unmasked the other peaks on addition of D_2O, 2 OH; in DMSO-d_6, C_7-α-OH appeared at 240 (d, 1, J = 2 cps) and C_{15}-OH appeared at 193 (b, $W_{1/2}$ = 5 cps), 65 (s, C_{17} protons), 51 (d, J = 6.5 cps, C_{19} and C_{20} protons), and 43 cps (s, C_{16} protons). This could not be recrystallized from many solvents.

***p*-Nitrobenzoate of Diol 1.**—To the ice-cold solution of diol **1** (440 mg) in dry pyridine (3 ml) was added in several installments the recrystallized *p*-nitrobenzoyl chloride (1.0 g, mp 73°) with constant shaking. After the addition was over, the lumps were broken with a spatula and the mixture was allowed to stand at room temperature for 2 more hr, occasionally shaking the mixture. It was heated on a steam bath for 10 min, then poured onto the ice–sodium bicarbonate mixture. The benzoate crystallized out as the trihydrate. It was filtered, washed thoroughly with sodium bicarbonate solution and water and dried. The crude product was recrystallized from 95% ethanol to give 525 mg (65%) of the ester, mp 218–222°. It was further recrystallized from chloroform–alcohol to give the analytical sample, mp 225°.

Anal. Calcd for $C_{35}H_{44}O_9N_2 \cdot 3H_2O$; C, 60.87; H, 7.25; N, 4.06. Found: C, 60.79; H, 7.27; N, 4.06.

Recrystallization and redrying of the sample at 100° (0.2 mm) over Drierite for 14 hr gave the monohydrate: mp 225°; ir ($CHCl_3$) 5.82, 6.23, 6.56, 7.44, 7.85, 8.98, 9.10 and 9.35 μ; nmr 480 (m, 8, aromatic), 307 (b, 1, $W_{1/2}$ = 6.5 cps, equatorial C_7-β proton), 240 (two d-AB type, J = 10 cps, $\delta_B - \delta_A$ = 20 cps, C_{15} protons), 187 (s, 3, CH_3O), 73 (s, C_{17} protons), 61 (s, C_{16} protons), 53 cps (d, J = 6.5 cps, C_{19} and C_{20} protons); integrated protons ≃ 44.

Anal. Calcd for $C_{35}H_{44}O_9N_2 \cdot H_2O$: C, 64.22; H, 7.03; N, 4.24. Found: C, 64.69; H, 6.70; N, 4.18.

7α-Hydroxy-13β-isopropyl-13α-methoxy-8α-podocarpan-15-oic Acid Methyl Ester (2).—Freshly distilled boron trifluoride etherate (1.25 g) was added dropwise at 0° with stirring to a solution of the photoadduct I (**6**, 1.012 g) and sodium borohydride (330 mg) in dry tetrahydrofuran (AR, 16 ml) over a period of 40 min. Stirring was continued at 0° for a further period of 2 hr. Excess borane was destroyed by stirring for 20 min with a saturated sodium sulfate solution (1 ml). Sodium hydroxide solution (3 *N*, 2 ml) was added slowly followed by 30% hydrogen peroxide (1.4 ml) and the mixture stirred at room temperature for 2 more hr. The reaction mixture was diluted with brine and extracted thoroughly with ether. The ether layer was washed successively with 10% ferrous sulfate solution, 5% sodium carbonate solution and water and then dried over sodium sulfate. Removal of the solvent gave an oil (1.19 g) which was chromatographed over alumina (21 g) with *n*-hexane, benzene and ether as eluent. Fraction 7, eluted with 25% ether–benzene mixture, gave 658 mg (62%) of a solid, mp ~45°, which could not be further purified by crystallization. The analysis by glpc showed **2** to be 93% pure; the impurities were unreacted photoadduct I (**6**, 1.5%) and the epimeric alcohol (**3**, 6%): ir (film) 2.95, 5.81, 8.10, 8.45, 8.65 and 9.33 μ; nmr 226 (b, 1, $W_{1/2}$ = 6.0 cps, equatorial C_7-β proton), 220 (s, 3, CH_3O ester), 186 (s, 3, CH_3O–), 106 (b, 1, exchangeable with D_2O, C_7-α-OH) [in DMSO-d_6 it appeared at 246 (d, 1, J = 3 cps)], 72 (s, C_{16} protons), 65 (s, C_{17} protons), 51 cps (d, J = 6.5 cps, C_{19} and C_{20} protons). Here also we see only one type of C_7 proton and C_7-OH proton corroborating the glpc results.

The alcohol was rechromatographed over alumina to give a solid, mp 44–48°, which could not be purified by recrystallization, and analyzed.

Anal. Calcd for $C_{22}H_{38}O_4$: C, 72.09; H, 10.45. Found: C, 72.27; H, 10.49.

7α,8α-Dihydroxy-13β-isopropyl-13α-methoxypodocarpan-15-oic Acid Methyl Ester (4).—To a solution of the photoadduct I (**6**, 542 mg) in pyridine (AR, 10 ml) and dry ether (10 ml) was added a solution of osmium tetroxide (0.5 g) in dry ether (10 ml). When the solution was left at room temperature for 6 days covered with aluminum foil, dark crystals gradually separated. A solution of sodium bisulfite (1.024 g) in water (15 ml) and pyridine (5 ml) was added with continuous stirring. The complex cleared to give a brown solution which was extracted with 300 ml of chloroform (five times). The extract was washed with water thoroughly (three times) and dried (Na_2SO_4). Evaporation of the solvent gave 590.6 mg of an oil (**4**): ir (film) 2.96, 5.80, 8.02 and 9.38 μ; nmr 363 (b, exchangeable with D_2O, $C_{7,8}$-α-OH), 222 (s, CH_3O ester), 210 (t, 1, J = 3 cps, equatorial C_7-β proton), 190 (s, CH_3O ether), 72 (s, C_{16} protons), 61 (s, C_{17} protons), 52 cps (d, J = 6.5 cps, C_{19} and C_{20} protons); in DMSO-d_6, C_7-α-OH appeared at 288 (d, J = 5 cps) and C_8-OH at 339 cps (s).

Oxidation of Diol 4, to Ketoaldehyde 5.—The crude diol **4** (0.55 g) was dissolved in glacial acetic acid (50 ml) and the lead tetraacetate (511 mg) was added to it slowly. The mixture was left at room temperature overnight (21 hr) and then the excess lead tetraacetate was decomposed by stirring at room temperature for 30 min with ethylene glycol (0.2 ml). The mixture was diluted with aqueous sodium chloride solution and then extracted with ether, washed with aqueous $NaHCO_3$ solution, water and dried (Na_2SO_4). Evaporation of the solvent gave an oil (459.5 mg). The crude ketoaldehyde was chromatographed twice over alumina (1.5 g) and eluted with *n*-hexane, and ether. *n*-Hexane fraction gave the ketoaldehyde **5** (258 mg) as an oil: ir (film) 5.80, 5.83, 8.08 and 9.35 μ; nmr 582 (t, 1, J = 1.8 cps, CH_2CHO) 218 (s, 3, CH_3O ester), 180 (s, 3, CH_3O ether), 145 (s, 2, C_{14} protons), 74 (s, C_{16} protons), 63 (s, C_{17} protons), 56 cps (d, J = 6.5 cps, C_{19} and C_{20} protons).

Product **5** (258 mg) was rechromatographed over alumina (2.5 g) and eluted with *n*-pentane and analyzed.

Anal. Calcd for $C_{22}H_{36}O_5$: C, 69.59; H, 9.47. Found: C, 69.41; H, 9.54.

Treatment of Photoadduct I (6) with Methanolic Perchloric Acid.—Photoadduct I (**6**, 25 mg) was dissolved in methanolic perchloric acid (2.5 ml, containing about 1 mg of 72% $HClO_4$) and its decomposition was followed by glpc. The decomposition was complete in 1 hr, giving methyl abietate, palustrate and dehydroabietate.

Registry No.—**1**, 18508-94-6; *p*-nitrobenzoate of **1**, 18508-95-7; **2**, 18508-96-8; **4**, 18508-97-9; **5**, 18508-98-0; **6**, 18508-99-1; **6a**, 18509-00-7; **7**, 18509-01-8.

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