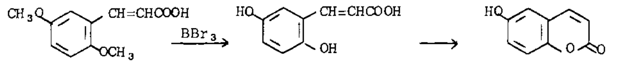
was cleanly obtained in a 77% yield. When the reaction was interrupted after 20 hours 2,5-dihydroxycinnamic acid was the major product, 89% yield, accompanied by a little 6-hydroxycoumarin. Excess boron trichloride failed to give any reaction with 2,5-dimethoxycinnamic acid under similar conditions. The use of hydrogen bromide in acetic acid alone gave only decarboxylation to polymeric material; when combined with mercuric chloride, no definable product was obtained.



The procedure may have broad utility for the synthesis of coumarins from both *o*-hydroxy- and *o*-methoxycinnamic acids, and would be especially valuable for the preparation of hydroxylated coumarins. Methoxycinnamic acids are in general more readily obtainable than the hydroxy acids, usually from the Dobner condensation of appropriate benzaldehydes with malonic acid.

EXPERIMENTAL

6-Hydroxycoumarin. To an ice-cold solution of 26.7 grams (0.128 mole) of 2,5-dimethoxycinnamic acid (Research Organic Chemicals) in 1 liter of chloroform was added 100 grams (0.4 mole) of boron tribromide, dropwise, with stirring. The yellow solution underwent a series of color changes, eventually becoming orange-red. After one hour, the ice bath was removed and the mixture was allowed to stand for 48 hours at room temperature. The mixture was cooled in ice, and 500 ml. of ice water was added cautiously with stirring. After 30 minutes, the mixture was extracted with ethyl acetate. The organic extract was dried over magnesium sulfate and evaporated in vacuo. The solid residue was stirred with 150 ml. of 5% sodium bicarbonate for 2 hours. The product was collected, washed with water and ether, and dried to leave 16.0 grams (77%) of pale yellow crystals, m.p. 247–48° C.; lit. (*1*) m.p. 248–50° C. The infrared spectrum was identical with material prepared by the method of Sastri *et al.* (*3*).

2,5-Dihydroxycinnamic Acid. The reaction was conducted at twice the scale described above, but was worked up after 20 hours. After treatment with ice water, the resulting solid material was collected by filtration. The chloroform layer from the filtrate yielded only a trivial amount of 6-hydroxycoumarin. The filter cake was extracted with several portions of ethyl acetate, dried over magnesium sulfate, and evaporated in vacuo to leave 41.5 grams (89%) of 2,5-dihydroxycinnamic acid, m.p. 197–9° C.; lit. (*2*) m.p. 207° C.

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Oxidation Reactions of Methyl 12,14-(2-Oxapropano)-abiet-8,9-enoate

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Interesting new resin acid chemistry was developed from oxidation studies of recently reported resin acid derivatives. Methyl 12-α-hydroxymethylabiet-7,8-enoate in an acetic acid–sulfuric acid mixture was esterified and isomerized, giving methyl 12-α-acetoxymethylabiet-8,9-enoate. This was converted to the 7-keto enone by chromic acid oxidation. 7-Keto-12,14-(2-oxapropano)-abiet-8,9-enoate reported previously was converted with *m*-chloro perbenzoic acid to its -8,9-epoxides and to a 1,6-diketone and a 1,2-diol by ruthenium tetroxide oxidation of the 8,9 double bond. Characterization was achieved by infrared, ultraviolet, nuclear magnetic resonance, and mass spectra.

As PART of a program for the preparation of polyols from resin acids (*2*), methyl 12,14-(2-oxapropano)-abiet-8,9-enoate (**1**) was obtained by the reaction of formaldehyde with methyl 12α-hydroxymethylabiet-7,8-enoate (**2**) (*3*). The fundamental aspects concerning the stereochemistry and structure of **1** are reported elsewhere (*4*). The present paper describes some hitherto unpublished oxidation reactions of **1** and **3** which have produced valuable resin acid chemistry and may lead to potentially useful diterpene intermediates.

EXPERIMENTAL SECTION

Methyl 12-Acetoxymethylabiet-8,9-enoate (3). Methyl 12-hydroxymethylabiet-7,8-enoate (20.8 grams) in glacial acetic acid (420 cc.), water (50 cc.), and concentrated sulfuric acid (35 cc.) was heated at 70° C. for 2 hours. Addition to water, ether extraction, washing with aqueous $NaHCO_3$ and water until neutral, concentration, and distillation gave methyl 12-acetoxymethylabiet-8,9-enoate, b.p. 218–20° C./1.5 mm. (20 grams, 85%), NMR signal at 0.75, 0.86 (isopropyl, J = 6.5 c.p.s.), 0.97 (C-10 Me), 1.15 (C-4 Me), 1.96 (acetate Me), and 3.56 (ester Me). Chemical shift for C-10 Me given in an earlier paper (2) is in error.

Chromic Acid Oxidation of Methyl 12-Acetoxymethylabiet-8,9-enoate (3). A mixture of methyl 12-acetoxymethylabiet-8,9-enoate (10 grams) in 85% acetic acid (150 cc.) and chromic acid (2.6 grams) was stirred at 50° C. for 30 minutes. Addition of methanol (50 cc.) followed by addition to water, ether extraction, and washing with aqueous $NaHCO_3$ and water gave the crude ene-one (12.0 grams), λ_{max} 248 mμ; g.l.p.c. (a 6-foot × ⅛-inch column of OV-1 5%, $T = 250°$ C.)

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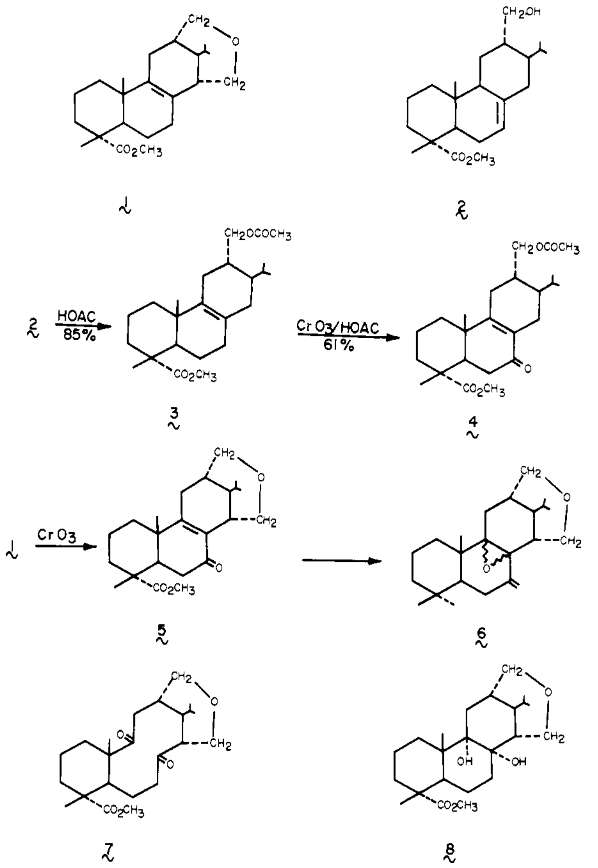

showed major components at t = 8.0 and 14.0 minutes. Chromatography over alumina (250 grams) and elution with hexane-ether (3 to 1) gave a forerun of starting material followed by methyl 12-acetoxymethyl-7-ketoabiet-8,9-enoate (**4**) (6.0 grams, 61%), b.p. 265-70° C./1.0 mm., λ_{max} 248 mμ (ϵ = 13,600), λ_{max} 1650 and 1625 cm.$^{-1}$, NMR signals at 0.79, 0.90 (isopropyl J = 6.5 c.p.s.), 1.11 (C-10 Me), 1.23 (C-4 Me), 1.98 (acetate Me), 3.60 (ester Me), and signals in the 2.0-2.5 p.p.m. region (C-6 protons) and centered at 3.90 p.p.m. (5 α-proton).

Epoxidation of Methyl-7-keto-12,14-(2-oxapropano)-abiet-8,9-enoate (5). A mixture of **5** (1.0 gram), m-chloroperbenzoic acid (2.0 grams), and dry chloroform (100 cc.) was refluxed 24 hours, the resulting solution washed with aqueous potassium iodide solution, aqueous sodium thiosulfate solution, water, cold 5% aqueous NaOH solution, and water. After drying ($MgSO_4$), concentration in vacuo gave a resinous solid (1.0 gram). G.l.p.c. showed three major components at t = 7.0 (~45%), t = 10.5 (~25%), and t = 13.8 minutes (~10%) having longer retention times. Chromatography of the mixture (1.0 gram) over alumina (30 grams) and elution with dichloromethane gave a small forerun of unreacted **5** (0.1 gram) followed by methyl 7-keto-8,9-epoxy-12,14-(2-oxapropano)-abietate (**6**) as a colorless crystalline solid (0.36 gram); m.p. 167-8° C., γ_{max} (CH_2Cl_2), 1720 (ester C=O), 1695 (ketone C=O) and 893 cm.$^{-1}$ (epoxide); g.l.p.c. gave a single peak, t = 7.0 minutes; NMR signals appeared at 0.99, 0.89 and 0.92, 0.82 (doublets for isopropyl group, J = 6.5 c.p.s.), 1.19 (C-4 Me), 1.02 (C-10 Me), 3.64 (ester Me), doublets centered at 3.76 and 3.98 (J = 12 c.p.s., 5 α-proton), doublets centered at 1.97, 2.15 (J = 12 c.p.s.) and 2.36 p.p.m. (J = 10 c.p.s.) (6 α- and 6 β-protons).

Anal. Calcd. for $C_{23}H_{34}O_5$: C, 70.73; H, 8.78. Found: C, 70.59; H, 8.73.

Further elution with dichloromethane gave a mixture of components with t = 10.5 and 13.8 minutes. Concentration of these fractions and addition of dry ether afforded a second epoxide as colorless plates (0.21 gram); m.p. 177-9° C., γ_{max} 1725 (ester C=O), 1695 cm.$^{-1}$; no absorption in the ultraviolet region; g.l.p.c. showed a major peak (~ 95%) at t = 10.5 minutes; NMR signals at 0.97, 0.87 and 0.90, 0.82 (isopropyl doublets), 1.17 (C-4 Me), 0.99 (C-10 Me), 3.63 (ester Me), a broad six-proton signal centered at 1.66 p.p.m. (ring methylenes), two doublets centered at 4.00 and 3.76 p.p.m. (J = 12 c.p.s., 5 α-protons) and three doublets in region of 1.90 to 2.60 p.p.m. (6 α- and 6 β-protons).

Anal. Calcd. for $C_{23}H_{34}O_5$: C, 70.73; H, 8.78. Found: C, 70.64; H, 8.71.

Mother liquors after separation of **6** showed infrared bands at 1770, 1775, and 1725 cm.$^{-1}$.

Ruthenium Tetroxide Oxidation of 1. Ester **1** (1.0 gram) in carbon tetrachloride (100 cc.) was treated with a solution of ruthenium tetroxide in carbon tetrachloride (*5, 7*) (~10% excess) at room temperature for 2 hours. Excess ruthenium tetroxide was destroyed by addition of n-propanol. The mixture was filtered, concentrated in vacuo, ether (20 cc.) and n-propanol (1 cc.) added, and the solution passed through a column (2- × 20-cm.) of activated carbon to remove finely divided ruthenium dioxide. Elution with ether (200 cc.) and concentration of the combined, dried eluates gave a solid (0.9 gram), m.p. ~ 200° C. Gas liquid chromatography (6-foot × ⅛-inch W-98, T = 270° C., He flow 60 cc. per minute) showed a major peak at t = 6.0 minutes (~60%), with additional peaks at t = 5.2, 6.8, 8.4, and 10.0 minutes. Recrystallization of the crude solid from acetone-carbon tetrachloride gave colorless needles (0.5 gram), m.p. 196-7° C., identified as the diketone (**7**), γ_{max} ($CHCl_3$) 1725 (ester C=O), 1695 cm.$^{-1}$ (ring ketone C=O); g.l.p.c. showed a single peak, t = 6.0 minutes; NMR ($CDCl_3$) signals at 0.99, 0.88 and 0.94, 0.84 (doublets for isopropyl group, J = 6.5 c.p.s.), 1.27 (C-4 Me), 1.48 (C-10 Me), and 3.66 p.p.m. (ester Me).

Anal. Calcd. for $C_{23}H_{36}O_5$: C, 70.36; H, 9.25. Found: C, 70.25; H, 9.20.

The above mother liquors were concentrated and chromatographed on neutral alumina (20 grams). Elution with carbon tetrachloride-ether (9 to 1) followed by carbon tetrachloride-ether (4 to 1) gave only mixtures of components. Elution with ether gave a mixture of components with t = 5.2 and 8.4 minutes. Recrystallization from acetone-ether gave the diol (**8**) as colorless needles (0.1 gram), m.p. 231-4° C., g.l.p.c. gave a single peak, t = 8.4 minutes, γ_{max} ($CHCl_3$) 3400 (H), 1725 (ester C=O); NMR ($CDCl_3$) signals at 0.87, 0.76 and 0.95, 0.84 (doublets for isopropyl group, J = 6.5 c.p.s.), 1.26 (C-4 Me), 1.38 (C-10 Me), and 3.66 (ester Me).

Anal. Calcd. for $C_{23}H_{38}O_5$: C, 70.01; H, 9.71. Found: C, 70.11; H, 9.69.

Lead Tetraacetate Oxidation of Diol 8. Diol **8** (0.2 gram) was left at room temperature overnight with lead tetraacetate (0.2 gram) in acetic acid (10 cc.). Addition of ethylene glycol (0.2 cc.), standing 30 minutes, dilution with water, ether extraction, concentration, and recrystallization from acetone-carbon tetrachloride gave the 1,6-diketone **7** (0.1 gram), m.p. 196-7° C.

DISCUSSION

To study the steric effects imposed by the pyran ring on the reactivity of the 8,9-double bond in methyl 12,14-(2-oxapropano)-abiet-8,9-enoate (**1**), a comparison was made of the chromic acid oxidation of **1** and methyl 12α-acetoxymethylabiet-8,9-enoate (**5**). Treatment of **1** with chromic acid in acetic acid (*10*) gave methyl 7-keto-12,14-(2-oxapropano)-abiet-8,9-enoate (**5**) as major product (*4*), oxidation occurring at the less hindered C-7 site. Under similar conditions, chromic acid oxidation of **3** gave methyl 7-keto-12-acetoxymethylabiet-8,9-enoate (**4**) in 61% yield.

Table I. Mass Spectral Data of Resin Acid Derivatives—Major Ions

3		4		5		6		7	
m/e	% Base Peak	m/e	% Base Peak	m/e	% Base Peak	m/e	% Base Peak	m/e	% Base Peak
390	6	404	6	374	100[a]	390	8	392	28
375	7	361	7	356	10	372	23	374	22
347	5	344	60	329	26	331	21	346	22
330	100[a]	331	46	314	21	301	18	332	27
315	86	301	22	298	28	259	23	267	33
287	42	262	27	223	28	241	28	211	16
271	40	241	39	187	18	209	100[a]	180	16
255	45	202	36	171	18	181	10	147	18
227	43	199	31	158	36	160	20	135	28
199	21	185	30	145	40	138	19	123	90
185	18	171	39	135	23	121	32	121	100[a]
173	15	159	60	119	38	107	36	109	69
159	19	145	88	105	39	91	37	93	42
145	35	134	62	91	54	81	35	91	38
131	36	131	58	81	17	77	39	81	46
121	54	121	53	77	21	67	32	67	40
105	95	119	68	69	20	55	53	55	57
91	49	109	64	55	35	43	96	43	37
81	28	105	89	43	45	41	85	41	52
74	54	95	48	41	46				
69	26	91	100[a]						
59	93	81	57						

[a] Base peak.

In this report, **3** was obtained by reaction of **2** with aqueous acetic acid–sulfuric acid mixture; the preparation was somewhat different than the method reported previously (*3*).

The $\alpha\beta$-unsaturated ketone **4** was characterized by its infrared, ultraviolet, nuclear magnetic resonance, and mass spectra. It showed infrared spectral bands at 1650 and 1625 cm.$^{-1}$ and an ultraviolet maximum at 248 mμ. The NMR spectrum showed superimposed doublets at 0.90 and 0.79 p.p.m. (isopropyl group, $J = 6.5$ c.p.s.) and singlets at 1.11 (C-10 Me), 1.23 (C-4 Me), 1.98 (acetate Me), and 3.60 p.p.m. (ester Me). Major ions found in the mass spectrum of **4** are given in Table I.

Oxidation of $\alpha\beta$-unsaturated ketones with peracids is known to give enol and/or epoxy esters or lactones, depending on the reaction conditions and on whether the ene-one is alicyclic or acyclic (*8*). Epoxidation of **5** afforded a mixture which, on chromatography (aluminum oxide) and recrystallization, gave two solid products. The major product was methyl 7-keto-8,9-epoxy-12,14-(2-oxapropano)-tetrahydroabietate (**6**). Its NMR spectrum showed methyl singlets at 1.19 (C-4 Me), 1.02 (C-10 Me), 3.64 (ester Me), a broad six-proton signal centered at 1.68 p.p.m. (ring A methylene), and signals of an ABX pattern in the regions 1.90 to 2.60 and 3.70 to 4.10 p.p.m. (C-5 and C-6 protons). The mass spectrum showed a molecular ion at 390 and the base peak at *m/e* 209, resulting from fission to the oxirane ring. The second product was not completely identified, but it is believed to be a stereoisomer of the above 8,9-epoxide.

Oxidation of **1** with ruthenium tetroxide (*9*) in carbon tetrachloride gave the 8,9-diketone (**7**) as major product, together with the *cis*, 8,9-diol (**8**). Some oxidation of the pyran ring (*1*) was evidenced by the presence of a δ-lactone absorption in the infrared spectra of the intermediate chromatographic fraction. A Dreiding model of **7** shows a preferential di-axial orientation of the C-10 Me group with the adjacent carbonyl group. This is supported by the observed deshielded C-10 methyl group at 1.48 p.p.m. Lead tetracetate fission of the 1,2-diol **8** gave the same 1,6-diketone.

The NMR spectrum of the diol **8** showed two pairs of doublets at 0.95, 0.87 and 0.87, 0.76 p.p.m. (isopropyl group, $J = 6.5$ c.p.s.), singlets at 3.66 (ester Me), 1.26 (C-4 Me), and a strongly deshielded singlet at 3.66 (ester Me), 1.26 (C-4 Me), and a strongly deshielded singlet at 1.38 p.p.m. (C-10 Me), consistent with the 1,3-diaxial configuration of that methyl group and the C-8 hydroxyl (*11*). The alternative *cis*-diol, having α-OH groups, would not be expected to give rise to such deshielding of the C-10 methyl groups. Herz and Wahlborg (*6*) have reported 9α-hydroxy resin acids which show C-10 methyl signals in the region 0.92 to 0.97 p.p.m. and 8α,9α-diols which show C-10 methyl signals in the region 1.10 to 1.15 p.p.m. (*6*). Clark *et al.* (*5*) have found that an 8β-OH group in a steroid nucleus causes a 0.18 p.p.m. downfield shift of the C-10 methyl signal.

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