plates and developed with 1:1 ether in benzene. The major band was removed from the plates and eluted with chloroform to afford acetyleupaserrin (**2**) as a viscous colorless glass. Various attempts at crystallization of **2** were unsuccessful and so it was characterized as a foam: $[\alpha]^{25}D$ +83° (*c* 0.95, $CHCl_3$); ir λ_{max}^{KBr} 5.68, 5.78, 5.82, 6.10, 8.10, 8.62, and 8.77 μ; mass spectrum *m/e* 446.1931 (M^+, calcd for $C_{24}H_{30}O_8$, 446.1939), 386, 246, 228, 213, and 141; R_f 0.70.

Acetylation of Deacetyleupaserrin (5).—To a solution of deacetyleupaserrin (**5**, 300 mg) in acetic anhydride (10 ml), powdered potassium carbonate (20 mg) was added and the mixture stirred at room temperature for 2 hr. The reaction mixture was poured into ice–water, stirred for a further 3 hr, and extracted with chloroform. The organic extract was washed with aqueous sodium bicarbonate and then water, dried over sodium sulfate, and evaporated to give a colorless residue (300 mg), which yielded two major components on preparative tlc. The band of higher R_f, eluted with 10% methanol in chloroform, was crystallized from methanol to yield eupaserrin (**1**, 85 mg): mp 153–154° (mixture melting point, tlc, ir, and nmr identical with those of the material described above). The lower R_f band was extracted in the same manner to give acetyleupaserrin (**2**, 122 mg) as a colorless foam (tlc, ir, and nmr identical with those of the material described previously).

Hydrolysis of Deacetyleupaserrin (5).—Deacetyleupaserrin (**5**, 300 mg) was dissolved in 5 *N* aqueous sodium hydroxide (25 ml) and heated under nitrogen at 60° for 30 min. The reaction mixture was then acidified with concentrated hydrochloric acid, saturated with sodium chloride, and extracted with ether (6 × 80 ml). The ether layer was extracted with 5% sodium carbonate solution (3 × 10 ml), which was acidified, saturated with sodium chloride, and extracted with ether (3 × 30 ml). The final ether layer was washed with saturated sodium chloride solution, dried over sodium sulfate, and evaporated to give a foam (84 mg). This material was applied to ten Cellulose F precoated plates (20 × 20 cm × 0.2 mm) and developed with 20:80 2 *N* aqueous ammonia in *sec*-butyl alcohol. The acidic band (visualized with bromophenol blue) was scraped from the plates and extracted with methanol. Evaporation of the methanol afforded 16 mg of oily crystals which were recrystallized from ether–petroleum ether to give sarracinic acid, mp 51.4–52.1°. The infrared spectrum of this sample was identical with that of an authentic sample and the mixture melting point was undepressed.

Methanolysis of Deacetyleupaserrin (5).—To a solution of sodium methoxide (65 mg) in 4 ml of anhydrous methanol was added deacetyleupaserrin (**5**, 200 mg). The reaction mixture was stirred for 1 hr at room temperature, heated for 10 min at 60°, cooled and acidified with dilute hydrochloric acid, and then extracted with chloroform. The chloroform extract was dried over magnesium sulfate and evaporated to give 200 mg of yellow foam. This material was applied to eight ChromAR 7GF plates (20 × 20 cm × 0.25 mm) and developed with 5% MeOH in chloroform. The major band was removed and eluted with chloroform to afford 86 mg (50%) of the methanol adduct **4** as a viscous oil: $[\alpha]^{25}D$ +72.5° (*c* 0.99, $CHCl_3$); ir $\lambda_{max}^{CHCl_3}$ 2.78, 2.90, 5.70, 6.05, 8.55, 8.85, 9.00, and 10.30 μ; mass spectrum *m/e* 296.1614 (M^+, calcd for $C_{16}H_{24}O_5$, 296.1617), 278, 264, 246, 233, 195, 152, 122, 113, 107, 95; R_f 0.31.

Pyrolysis of Deacetyleupaserrin (5).—Pyrolysis of deacetyleupaserrin (**5**, 85 mg) at 180–200° for 3 min under aspirator pressure gave quantitatively a yellow glass. This material was separated on four silica gel plates (20 × 20 cm × 0.25 mm) using 5% methanol in chloroform to give 69 mg (81%) of the aldehyde lactone **6** as a colorless foam: $[\alpha]^{25}D$ +9.3° (*c* 0.71, $CHCl_3$); ir $\lambda_{max}^{CHCl_3}$ 2.90, 3.68, 5.67, 5.83, 6.12, 8.70, and 9.90 μ; mass spectrum *m/e* 362.1719 (M^+, calcd for $C_{20}H_{26}O_6$, 362.1722), 347, 344, 300, 298, 264, 246, 202, 163, 135, 107, 99; R_f 0.59.

Pyrolysis of Acetyleupaserrin (2).—Pyrolysis of acetyleupaserrin (**2**, 90 mg) at 200° for 4 min under aspirator pressure gave an approximately 1:1 mixture of starting **2** and the enol acetate **3**. The crude product was applied to five silica gel plates (20 × 20 cm × 0.25 mm) and eluted with 1:1 ether in benzene giving in the band of higher R_f enol acetate **3** as a colorless foam (31 mg, 34%). The lower R_f band, corresponding to acetyleupaserrin (**2**), was eluted to give **2** as a pale yellow glass (28 mg, 31%), which was shown to be identical with **2** described above. The enol acetate **3** was unstable and was characterized by nmr (see Table I); ir λ_{max}^{KBr} 2.90, 3.25, 5.67, 5.75, 5.82, 6.00, 6.08, 8.15, and 8.65 μ; mass spectrum *m/e* 446.1942 (M^+, calcd for $C_{24}H_{30}O_8$, 446.1939), 386, 288, 246, 213, 141, 99, and 81; R_f (ChromAR, 1:1 ether–benzene) 0.25.

Registry No.—**1**, 38456-36-9; **2**, 38400-51-0; **3**, 38456-37-0; **4**, 38456-38-1; **5**, 38456-39-2; **6**, 38456-40-5; sarracinic acid, 7689-64-7.

Novel Tricyclic Compounds from Alkylated Hydroquinones and C-10 Terpenes

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The novel hydroxylated 7-oxatricyclo[6.4.0.$1^{2,6}$]trideca-8,10,12-trienes **9** and **10** and the spiro[cyclohexane-1,2′-chroman] **11** have been synthesized in 5–31% yields *via* the acid-catalyzed condensation of alkylated hydroquinones with linalool **6** and myrcene **7**. Their structures were assigned on the basis of nmr and mass-spectral data and were mechanistically rationalized. Yields of the type **9** structures were substantially increased with *d*-limonene (**15**) or α-phellandrene (**16**), supporting the idea that a cyclized monoterpene is involved in the formation of both **9** and **10**.

The acid-catalyzed condensation of open-chain monoterpenes with phenolic compounds in general leads to alkenyl-substituted chromans, but in several cases tricyclic compounds have been reported as a result of further cyclization under the acidic conditions. Green and McHale cited the formation of tricyclic chromanols[1] from trimethylhydroquinones and geraniol and linalool, but their materials were not characterized unequivocally. More recently, Ichikawa and Kato[2] isolated the tricyclic compound **1** as a by-product in the synthesis of chromanol **2**, and Kane[3] characterized the product from phloroglucinol dimethyl ether and citral (mixture of neral and geranial) as the tetracyclic **3a**. Tricyclic chromanols **3b**, **3c**, and **3d** have also been synthesized in cannabinoid studies. Mechoulam and Yagen[4] prepared **3b** from olivetol and geraniol *via* the stereoselective cyclization of cannabigerol, while Crombie and Ponsford[5] obtained

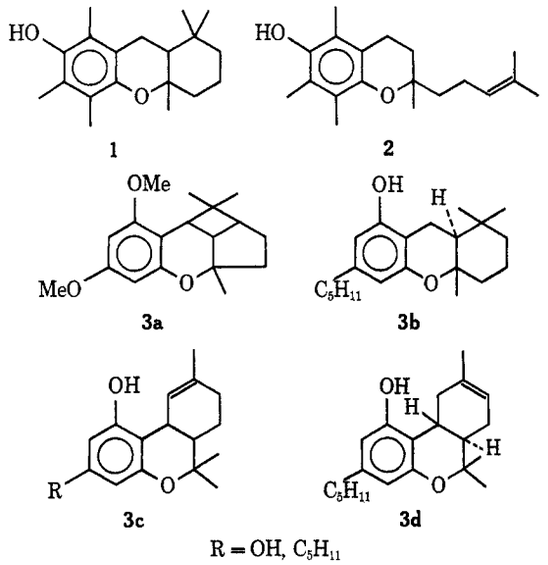
(1) J. Green and D. McHale, British Patent 949,715 (1964).
(2) T. Ichikawa and T. Kato, *Bull. Chem. Soc. Jap.*, **41**, 1224 (1968).
(3) V. V. Kane, *Tetrahedron Lett.*, 4101 (1971).
(4) R. Mechoulam and B. Yagen, *ibid.*, 5349 (1969).
(5) L. Crombie and R. Ponsford, *J. Chem. Soc. C*, 788, 796 (1961); *Tetrahedron Lett.*, 4557 (1968).

TABLE I

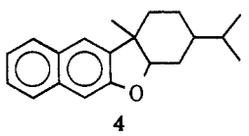
CONDENSATIONS WITH OPEN-CHAIN TERPENES IN ACETIC ACID (ZINC CHLORIDE CATALYST) OR NEAT (BORON TRIFLUORIDE ETHERATE)

Reactants and conditions	Crystalline product	Yield,[a] %	Mp, °C	$E^{1\%}_{1\,cm}$ (λ_{max})
TOHQ,[b] 6, reflux, 7 hr	10e	5 (10)	154–155	146 (301)
TOHQ, 7, 50–60°, 2 hr	11e	7 (15–20)	151–153	129 (300)
TBHQ, 6, reflux, 7 hr	9d	5 (10–15)	172–173	170 (300)
TBHQ, 7, 50–60°, 4 hr[c]	9d	4 (10–15)	173–174	170 (300)
TBHQ, 7, 50–60°, 4 hr[c]	11d	8 (15–20)	127–136	153 (298)
Methyl HQ, 7, neat	9b	3 (16)	154–156	182 (298)
Trimethyl HQ, 7, neat	11c	31 (80)	100–102	110 (292)
Trimethyl HQ, 7[d]	10c	(50)[e]	80–81[e]	72 (284)[e]
Hydroquinone, 7, 90°, 1 hr, neat	11a	10 (15)	113–115	141 (298)

[a] Estimated overall yields, including filtrate residues, are given in parentheses. [b] TOHQ = *tert*-octylhydroquinone; TBHQ = *tert*-butylhydroquinone. [c] Comparable yields were obtained at 20°, 3 days (exothermic rise to 50°), when BF_3 etherate was substituted for zinc chloride. [d] Compound 7 was used as the HCl adduct with $SnCl_2 \cdot 2H_2O$ as catalyst; product **10c** was estimated to have 75% purity based on its $E^{1\%}_{1\,cm}$ value. [e] These data are on the acetate of **10c** prior to saponification.



related *cis*- and *trans*-**3c** from citral and olivetol or phloroglucinol. Petrzilka, *et al.*,[6] obtained (−)-Δ^8-6a,10a-*trans*-tetrahydrocannabinol (**3d**) from *p*-mentha-2,8-dien-1-ol and olivetol. Much earlier Salfield[7] had reported the preparation of the tetracyclic **4** from the condensation of β-phellandrene with β-



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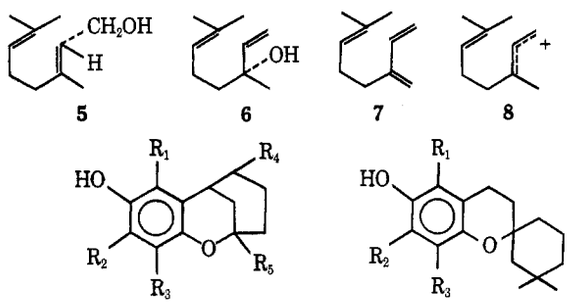
naphthol. In the absence of nmr data, particularly concerning the presence or absence of the angular H adjacent to oxygen, this structure assignment is in doubt.

In an attempt to prepare some alkenyl-substituted chromanols of type **2** *via* the zinc chloride catalyzed condensation of geraniol **5** with various alkyl-substituted hydroquinones in hot glacial acetic acid, only glasses were obtained, which were unresolvable by molecular distillation, chromatographic, or fractional crystallization techniques. Thin layer chromatograms of these glasses on silica gel were streaked, indicating the presence of many components. In the presence of acidic catalysts, geraniol (and the cis isomer, nerol) can generate linalool **6**, myrcene **7**, and a variety of monocyclic monoterpenes[8] (including α-terpineol, *dl*-limonene, terpinenes, and phellandrenes), all of which are potentially condensable with hydroquinones. Accordingly, linalool **6** and myrcene **7** were used as starting materials, since these should generate the likely reactive intermediate, carbonium ion **8**, more readily.



Condensations of various alkyl-substituted hydroquinones (Table I) gave small yields (5–31%) of products isolated by chromatography which have been assigned structures **9**, **10**, and **11** on the basis of their spectral properties. All of the compounds have nmr spectra devoid of olefinic absorption; *i.e.*, they are tricyclic.

The characteristic nmr features of type **9** and **10** compounds are the presence of a 1 H multiplet at ~2.5–2.9 and a 6 H triplet (at 60 MHz) centered at ~0.9–1.0 ppm. The triplet is transformed into a double doublet at 100 MHz and is assigned as an isopropyl group whose methyls are anisochronous by virtue of adjacent dissymmetry. Type **10** compounds have in addition a 3 H doublet at ~1.0 ppm, whereas type **9** compounds have a 3 H singlet at ~1.3 ppm. The *tert*-butyl, *tert*-octyl, and aromatic methyl absorptions appear in characteristic positions when present (see Table II).

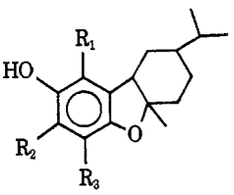
The nmr evidence led to the consideration of two possible tricyclic structures, namely, **9** and **12**, and **10** and **13**.

Distinction between the two possibilities was made on the basis of their mass spectral fragmentation (Scheme I). The loss of the fragments C_5H_8 and C_5H_{10}

(6) T. Petrzilka, *et al.*, *Helv. Chim. Acta*, **52**, 1102 (1969).
(7) J. Salfield, *Ber.*, **73**, 376 (1940).
(8) "The Terpenes," Vol. I, J. L. Simonsen, Ed., Cambridge University Press, New York, N. Y., 1931, pp 40–43, 55, 144–147.

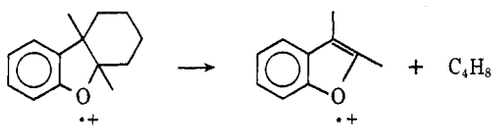
TABLE II
CHEMICAL SHIFTS (δ) OF TRICYCLIC COMPOUNDS

Compd	R_1	R_2	R_3	α-CH	Ang Me	*gem*-diMe	*i*-Pr	Ar-*t*-Bu	ArCC-*t*-Bu	$ArCMe_2$	MeCH	ArMe
9b	H	CH_3	H	2.90 (1 H)	1.30		0.92 + 1.03 (d)					2.17
9d	H	*tert*-Butyl	H	2.88 (1 H)	1.33		0.93 + 1.03 (d)	1.36				
9e	H	*tert*-Octyl	H	2.90	1.32		0.93 + 1.02 (d)		0.72	1.41		
10c	CH_3	CH_3	CH_3	2.83 (1 H)			0.99 + 1.11 (d)				0.99 (d)	2.14
												2.16
10e	H	*tert*-Butyl	H	2.55 (1 H)		0.86 + 1.04 (s)	0.99 + 1.10 (d)		0.78	1.43	0.98 (d)	
11a	H	H	H	2.69 (2 H)								
11c	CH_3	CH_3	CH_3	2.68 (2 H)		0.89 + 1.12 (s)						2.14
												2.16
11d	H	*tert*-Butyl	H	2.62 (2 H)		0.87 + 1.06 (s)		1.36				
11e	H	*tert*-Octyl	H	2.65 (2 H)		0.85 + 1.03 (s)			0.73	1.39		



12 **13**

for **9** and C_3H_6 and C_7H_{12} for **10**[9] follows a reasonable mechanistic path; it is hard to imagine a path whereby **12** and **13** could yield these fragments. Furthermore, **12** and **13** would be expected to fragment in a fashion similar to that found[10] for **14**; there are, however, no analogous fragment ions in the spectra of **9** and **10**.



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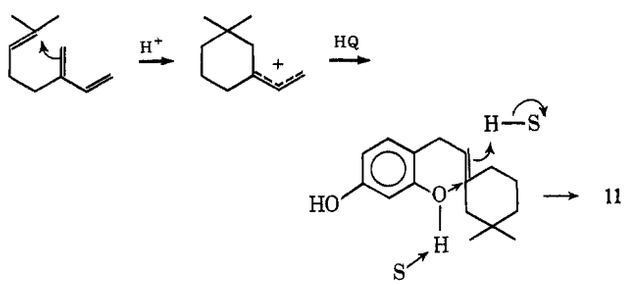
The formation of **9** and **10** are rationalized as shown in Scheme II. Reaction of the cyclized intermediate ion at the secondary carbon is reasonable from a consideration of steric factors.[11]

In products of type **11** structure, the relevant nmr data are the presence of a 2 H skewed triplet at ~2.6 ppm, whose peak separations do not change at 100 MHz, two 3 H singlets at 0.9–1.1 ppm, and the conspicuous absence of any signal for a methyl group analogous to the singlet in type **9** compounds and the doublet in type **10**. For type **11** compounds, we propose the structure given and rationalize its formation *via* the following scheme.



S = solvent

The mass spectral fragment ions of these molecules are consistent with this structure, as indicated in Scheme I and Table III.

When the condensation was carried out using *d*-limonene (**15**) and α-phellandrene (**16**) (precyclized monoterpenes, so to speak) the yield of **9** was increased substantially and the product had retained at least part of the original optical activity (Table IV). Both these results support the idea that a cyclized monoterpene is an intermediate in the reaction.

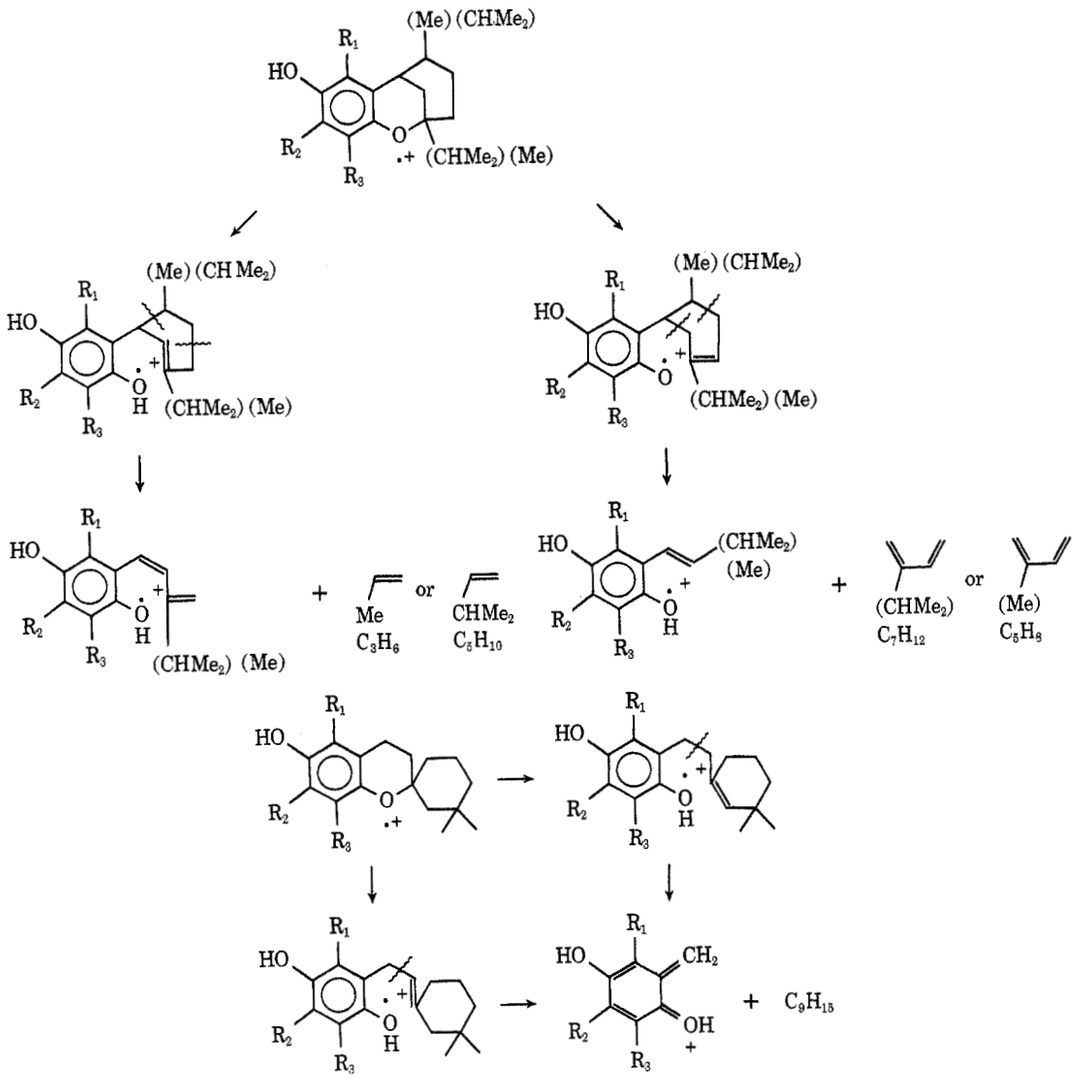
The retained optical activity argues that the carbonium ion rearrangement in Scheme II labeled step 1

(9) The loss of the appropriate fragment does not always occur from the parent ion. Prior fragmentations occur more readily when the alkyl substituents are *tert*-butyl or *tert*-octyl or when the hydroxyl is acetylated

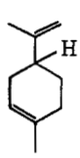
(10) S. Yamamura and Y. Hirata, *Tetrahedron*, **19**, 1485 (1963).

(11) W. S. Johnson, P. J. Neustaedter, and K. K. Schmiegel, *J. Amer. Chem. Soc.*, **87**, 5148 (1965).

SCHEME I



must be a 1,3-hydride shift (or concerted 1,2 shifts), since 1,2-stepwise shifts should lead to racemization of the intermediate and thus the product.



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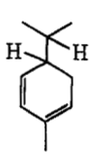

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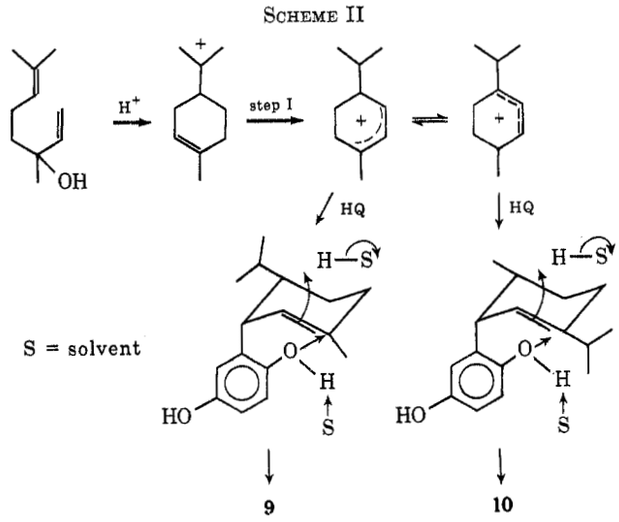
Experimental Section

Melting points (Hoover apparatus) are uncorrected. Chemical shifts are reported in parts per million downfield from tetramethylsilane in chloroform-*d* solution. Mass spectra were obtained from either a Du Pont 21-110B or Hitachi RMS 4 mass spectrometer operating at 70 eV. Uv spectra were determined in ethanol solution.

Column chromatography (hexane development) was accomplished on Doucil (sodium aluminum silicate, 60–100 mesh, Philadelphia Quartz Co.), Florisil (60–100 mesh, Floridin Co.), and MDA. The latter is our descriptive term for Merck's acid-washed alumina deactivated in the column prior to use by successive washes with equal volumes of 5% aqueous acetone and hexane. Elutions of Doucil and MDA, after hexane development, were done, respectively, with benzene, diethyl ether and 95:5 diethyl ether–ethanol.

SCHEME II



Thin layer chromatography (tlc) was effected with silica gel on glass plates and spots were detected after benzene development by spraying with aqueous rhodamine 6G solution and exposing to uv radiation.

A. Condensations with Linalool (6) in Acetic Acid Containing Zinc Chloride.—Solutions of TBHQ or TOHQ, linalool (Eastman Chemical 861), and freshly fused zinc chloride (0.1:0.13:0.14 mol) in glacial acetic acid (300 ml) were refluxed for 4–7 hr in an

TABLE III

PARTIAL MASS SPECTRA OF TRICYCLIC COMPOUNDS AND RELATIVE INTENSITY OF FRAGMENT ION RESULTING FROM THE LOSS OF R

Compd	R_1	R_2	R_3	Base peak	R: C_9H_{15}	C_8H_6	C_7H_{12}	C_5H_8	C_5H_{10}
9b	H	CH_3	H	260				43.4[a]	21.1[a]
9d	H	*tert*-Butyl	H	302				37.0	8.3
								24.6[b]	66.1[b]
9e	H	*tert*-Octyl	H	287				11.0[a,c]	4.7[c]
10c	CH_3	CH_3	CH_3	288		0	5.4[a,d]		
10e	H	*tert*-Octyl	H	287		1.7[c]	6.9[c]		
11a	H	H	H	123	100[a]				
11d	H	*tert*-Butyl	H	179	100[a]				
11e	H	*tert*-Octyl	H	287	3.9				

[a] Cleavage supported by appropriate metastable peak. [b] Cleavage takes place after loss of CH_3 from *tert*-butyl. [c] Cleavage takes place after loss of C_5H_{11} from *tert*-octyl. [d] Cleavage takes place after loss of CH_2CO from acetyl.

TABLE IV

PRODUCTS FROM CONDENSATIONS WITH CYCLIC C-10 TERPENES IN CHLOROFORM–CARBON TETRACHLORIDE–ETHER (BORON TRIFLUORIDE ETHERATE CATALYST)[a]

Crystalline product	Conditions	Yield,[b] %	Mp, °C	$E^{1\%}_{1\,cm}$ (λ_{max})	$[\alpha]^{25}D$
9d (racemic)	TBHQ, 15[c]	46.8	174–175	166 (300)	−1.32
(levo)	5°, 4 days	4.3 (20)	141–142	172 (300)	−14.9
9d (racemic)	TBHQ, 16[d]	8.1	175–176	165 (300)	+0.17
(dextro)	5°, 4 days	10.0 (17)	141–142	165 (300)	+16.1
9e (racemic)	TOHQ, 15[c]	12 (18)	139–140	156 (301)	+0.18
(levo)	20°, 4 days	11.6 (48)	136–136.5	152 (301)	−3.41

[a] Subsequent experiments demonstrated that carbon tetrachloride is unnecessary and that a 4:1 mixture of chloroform–ether is just as effective. [b] Estimated overall yields, including filtrate residues, are given in parentheses. [c] *d*-Limonene; $[\alpha]^{25}D$ +97.3°. [d] α-Phellandrene; $[\alpha]^{25}D$ −93.3°.

atmosphere of nitrogen, cooled, and poured into a mixture of ice and hexane. The organic phase was washed four times with 1 *N* sodium hydroxide and with water to neutrality and dried. After partial concentration and cooling to remove unreacted hydroquinone, the filtrate residue was distilled in a molecular still using stripped lard carrier.

Compound 10e (0.1-mol Run; from TOHQ).—The distillate paycut [11.6 g, bp 140–175° (90 μ)] with *E* (1%, 1 cm) (300 mμ) 122, gave two main spots on tlc. Crystallization from hexane gave **10e** (1.6 g), mp 141–148°, in 4.4% yield. Recrystallization from acetonitrile gave white platelets: mp 154–155°; *E* (1%, 1 cm) (301 mμ) 146; ir (Nujol) 2.93 (OH) and 8.4 μ (CO); M^+ *m/e* 358.

Anal. Calcd. for $C_{24}H_{38}O_2$: C, 80.39; H, 10.8; mol wt, 358. Found: C, 80.1; H, 10.8; mol wt, 347.

Chromatography of the filtrate residues on Doucil followed by crystallization of the hexane filtrate fraction gave additional **10e** (0.5% yield).

Compound 9d (0.2-mol Run; from TBHQ).—Two distillate paycuts were obtained [16 g, bp 113° (3 μ), and 13 g, bp 150° (4 μ)] having *E* (1%, 1 cm) (296–297 mμ) values of 141 and 117, respectively, and similar infrared spectra. Chromatography of the higher boiling fraction (five spots on tlc) on Doucil (300 g) and crystallization of the resulting filtrate fraction (8.1 g) from petroleum ether (bp 30–60°) at −20° gave **9d**: mp 172–173° (3% yield); ir (Nujol) 2.95 (OH) and 8.37, 8.42 μ (CO); M^+ *m/e* 302. Recrystallization from acetonitrile raised the melting point to 174–175°.

Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.4; H, 9.99; mol wt, 302. Found: C, 79.0; H, 10.0; mol wt, 275.

Chromatography of the filtrate residue from **9d** on Brockmann neutral alumina (175 g) and then elution of the top zone with ether gave mixed chromanol-like products, *E* (1%, 1 cm) (300 mμ) 152, with nmr different from nmr of both **9** and **11**.

B. Condensations with Myrcene (7) in Acetic Acid–Zinc Chloride.—Myrcene (0.22 mol, Aldrich) in acetic acid (20 ml) was added, with stirring, to a heated (50–60°) solution of the substituted hydroquinone (0.2 mol) and zinc chloride (0.3 g) in acetic acid (64 ml). After stirring at 50–55° for 3.5 hr, the crude product was isolated as described above.

Compounds 9d and 11d (from TBHQ).—Chromatography of the glass (56.8 g) obtained from myrcene and TBHQ on MDA (1.2 kg) gave three column-held fractions eluted separately with 95:5 ether–ethanol. Crystallization (from hexane) of the fraction from the bottom zone gave **9d** (2.2 g), mp 173–174°, *E* (1%, 1 cm) (300 mμ) 170, in 3.6% overall yield.

Similar crystallization of the middle-zone fractions gave spiran **11d** (4.8 g), mp 127–136°, *E* (1%, 1 cm) (298 mμ) 153, in 8% yield. Recrystallization from acetonitrile gave platelets (2.5 g, mp 145–147°) having the same uv spectrum, ir (Nujol) 2.98 (OH) and 8.35, 8.5 μ (CO); M^+ *m/e* 302.

Anal. Calcd for $C_{20}H_{30}O_2$: C, 79.42; H, 9.99; mol wt, 302. Found: C, 79.1; H, 10.0; mol wt, 304.

Compound 11e (from TOHQ).—The viscous oil was separated from excess TOHQ (12 g) by crystallization from hexane at 5° and then chromatographed on MDA (2 kg). Elution of the column-held material gave a glass (40.9 g) that crystallized (hexane) to give the spiran **11e** (5.1 g), mp 141–150°, in 7% yield (recrystallization from acetonitrile raised the melting point to 151–153°): ir (Nujol) 2.95 (OH) and 8.5 μ (CO); M^+ *m/e* 358.

Anal. Calcd for $C_{24}H_{38}O_2$: C, 80.39; H, 10.68; mol wt, 358. Found: C, 80.2; H, 10.3; mol wt, 301.

Compound 11a (from Hydroquinone).—The reaction mixture was cooled, diluted with ethyl ether, and washed successively with 0.52 *M* KOH solution and water. After the extract had been dried and the solvent evaporated, the residue (19 g) was purified by solvent distribution (Skellysolve F–80% ethanol). The alcohol-soluble fraction (10 g) was crystallized from Skellysolve F–ether (5:1) at −20° to give a crop of crystals (2.1 g) of **11a**, mp 110–113° (recrystallization raised the melting point to 113–115°), *E* (1%, 1 cm) (298 mμ) 141. An additional 1.3 g of crystals was recovered from the filtrates.

C. Condensations (Neat) with Myrcene and Boron Fluoride Etherate.—Compounds **9b**, **11a**, and **11c** were prepared by condensing myrcene with the appropriate hydroquinone in a slurry containing a catalytic quantity of boron trifluoride etherate. The reactions were highly exothermic. Purification was accomplished by solvent distribution (Skellysolve F–83% ethanol), an additional reductive cyclization step (zinc–alcoholic sulfuric acid), chromatography on Florisil, and finally *via* formation of crystalline piperazine complexes.

Compound 9b (from Monomethylhydroquinone).—The chromatographed product (8.1 g) from a 0.16-mol run was dissolved in ether and mixed with a solution of piperazine (1.6 g) in acetone (40 ml). After evaporation, the residue was dissolved in Skellysolve F (65 ml), filtered, and cooled to −20° to give 1.4 g of solid

piperazine complex, mp 127–135°. A sample (1.2 g) of this complex in ether was washed successively with dilute sulfuric acid and water to regenerate the tricyclic compound **9b** (0.99 g), which was crystallized from Skellysolve F, mp 154–156°, E (1%, 1 cm) (298 mμ) 182.

Anal. Calcd for $C_{17}H_{24}O_2$: C, 78.5; H, 9.25. Found: C, 78.7; H, 9.5.

Compound 11c (from Trimethylhydroquinone).—The chromatographed product (14 g) from an 0.08-mol run was treated with piperazine (2.6 g) as above to give a solid complex (7.7 g), mp 123–133°. A sample (2 g) of the complex gave 1.8 g of the regenerated compound **11c**, which crystallized from Skellysolve F, mp 100–102°, E (1%, 1 cm) (292 mμ) 110.

Anal. Calcd for $C_{19}H_{28}O_2$: C, 79.2; H, 9.7. Found: C, 79.3; H, 10.0.

D. Compound 10c from Trimethylhydroquinone and Myrcene–HCl Adduct.—A solution of trimethylhydroquinone (15.2 g, 0.1 mol) and $SnCl_2 \cdot 2H_2O$ (22.5 g) in 200 ml of glacial acetic acid was stirred at reflux (N_2 atmosphere) while the myrcene–HCl adduct (21.4 g, 87% estimated purity of mixed neryl geranyl chlorides) was added over 3 hr. After 90 min of additional reflux, the product mixture was cooled and filtered and the filtrate was diluted with water. The pentane extract was washed with water, dried, and chromatographed on Florisil. The middle fraction (22 g, 75% purity, 50% estimated yield) was acetylated (pyridine–acetic anhydride) and the actate was crystallized from hexane at −30°, mp 80–81°, mol wt 330, E (1%, 1 cm) (284 nm) 72. This was then saponified to give **10c**.

E. Condensations with *d*-Limonene and α-Phellandrene in Chloroform–Carbon Tetrachloride–Ether Containing Boron Fluoride Etherate.—Solutions of the appropriate hydroquinone and cyclic terpene (0.1-mol runs) in a 4:2:1 mixture of $CHCl_3$:CCl_4:ether were cooled to 5–10°, treated with 4 ml (0.032 mol) of boron fluoride etherate, and stored at 5 or 20°. The products were isolated from the organic layer after washes with ice water, 1 N sodium hydroxide, and water.

Compound 9e (from TOHQ and *d*-Limonene, 4 Days, 20°).—The glassy product (tlc showed mainly one component other than unreacted TOHQ) was crystallized from acetonitrile to give 4.15 g of **9e** (6.4 g, 18% weight yield): mp 139–140°; E (1%, 1 cm) (301 mμ) 156; $[\alpha]^{25}D$ +0.18°; ir (Nujol) 2.98 (OH) and 8.42 μ (CO); M^+ m/e 358.

Anal. Calcd for $C_{24}H_{38}O_2$: C, 80.39; H, 10.60; mol wt, 358. Found: C, 80.5; H, 10.7; mol wt, 323.

A second portion of the original filtrate residue was chromatographed on MDA (700 g) using 1:1 benzene–hexane for development. Evaporation of the filtrate gave material (17.4 g, 48.5% crude yield, one component by tlc) that crystallized from acetonitrile in 11.6% overall yield to give an optical isomer of **9e** (4.15 g), mp 135–136°, with $[\alpha]^{25}D$ −3.41. Recrystallization raised the melting point only slightly to 136–136.5°; the mixture melting point with **9e** was 136.5–138°. Its ir and uv absorption spectra were identical with those of **9e**.

Compound 9d (from TBHQ and *d*-Limonene, 4 Days, 20°).—Trituration of the glassy product with hexane gave 11.6 g of solids, mp 174–175°, E (1%, 1 cm) (300 mμ) 166, with nmr and mass spectra identical with those of **9d** prepared from linalool or myrcene. Two more crops of crystalline **9d** were obtained from the hexane mother liquor, giving a total 46.8% yield, $[\alpha]^{25}D$ −1.32°.

The filtrate residue, E (1%, 1 cm) (296 mμ) 138, was chromatographed on MDA (300 g). Elution of the bottom 50% of the column with ether containing 5% ethanol, followed by recrystallization of the eluate residue from hexane at 5°, gave 1.3 g (4.3% yield) of a lower melting (mp 141–142°) optical isomer having $[\alpha]^{25}D$ −14.9°; its nmr, infrared, and uv spectra were identical with those of **9d**. An overall 20% yield of the lower melting isomer was estimated on the basis of tlc analyses of the filtrate residue.

Compounds 9d (from TBHQ and α-Phellandrene, 7 Days, 5°).—The glassy product crystallized after several days from hexane to give solids (6.75 g), mp 113–117°, and mother liquor (A). A benzene solution of the solid was chromatographed on MDA and the nonadsorbed fraction was crystallized to give crude **9d** (2.5 g), mp 167–170°, in 8.1% yield. Recrystallization from hexane gave purified **9d** (1.48 g), mp 175°, E (1%, 1 cm) (300 mμ) 165, having only slight optical activity ($[\alpha]^{25}D$ +0.17°).

Chromatography of the filtrate residue from mother liquor (A) on MDA (400 g) followed by elution of the lower 60% of the column gave a glass (7.3 g) that crystallized from hexane. The product (3 g, 10% yield), mp 141–142°, E (1%, 1 cm) (300 mμ) 165, $[\alpha]^{25}D$ +16.1°, proved identical by nmr with the levorotatory isomer isolated from TBHQ and *d*-limonene, but gave a mixture melting point of 141–175°.

Registry No.—**6**, 78-70-6; **7**, 123-35-3; **9b**, 38359-57-8; **9b** (piperazine complex), 38359-63-6; **9d**, 38359-58-9; **9e**, 39050-42-5; **10c**, 38359-59-0; **10e**, 39050-43-6; **11a**, 31130-21-9; **11c**, 38359-61-4; **11c** (piperazine complex), 38359-64-7; **11d**, 38359-62-5; **11e**, 39050-44-7; **15**, 5989-27-5; **16**, 99-83-2; TOHQ, 719-03-9; TBHQ, 1948-33-0; methyl HQ, 95-71-6; trimethyl HQ, 700-13-0; hydroquinone, 123-31-9.

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