Derivatives of 1,8(9)-p-Menthadien-10-yl-carbinol

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In the previous paper[1], the preparation of a limonenylcarbinol and the determination of its structure as 1,8(9)-*p*-menthadien-10-yl-carbinol (I) were reported. The present paper describes various derivatives of the limonenylcarbinol.

When a mixture of I and paraformaldehyde was heated at 130~150°C for several hours, a pale yellow viscous oil was obtained. Analysis ($C_{12}H_{20}O_2$) and the molecular weight (192) indicated that the product was an adduct of one mole of formaldehyde to I. The presence of a primary hydroxyl group was proved by a qualitative analysis and an infrared absorption spectrum (9.6 μ). Quantitative acetylation with pyridine and acetic anhydride[2] showed that it was a monohydric alcohol. The infrared absorption spectrum showed characteristic absorption bands of the acetal type at 8.05, 8.6 and 9.0 μ (Fig. 1). From the above results, it was concluded that the structure of the substance is formaldehyde mono-1,8(9)-*p*-menthadien-10-yl-carbinyl acetal (II).

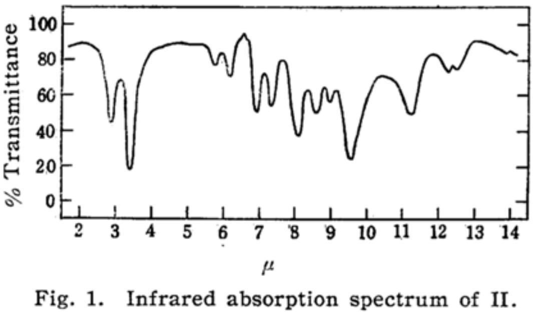


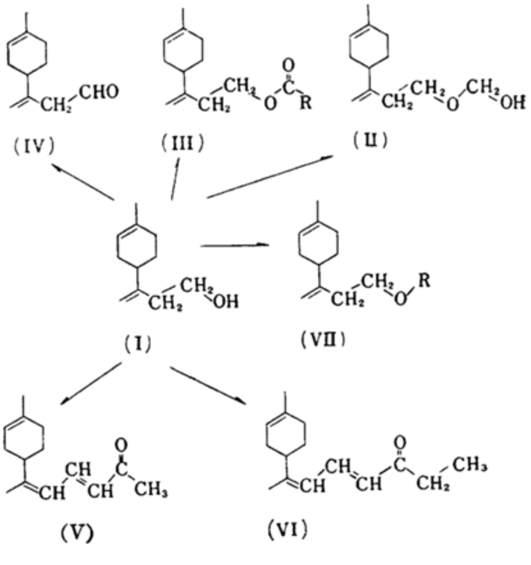
Fig. 1. Infrared absorption spectrum of II.

Various esters (III) were prepared from I. The monoesters of maleic acid, phthalic acid and succinic acid were prepared. The sodium salt of the acid maleate shows remarkable surface activity, and the foaming force is equal to that of the cetylsulfate (Table I). By the action of palmitoyl chloride, capryloyl chloride, isovaleryl chloride, phenylacetyl chloride and cinnamoyl chloride, I gave the esters of the corresponding acids (Table II). The caprylate and the phenylacetate are fragrant.

TABLE I. THE FOAMING FORCE OF SODIUM LIMONENYLCARBINYL MALEATE

%	Numbers of foams after (min.) 2	5	Quantities of foams after (min.) 2	5
Na limonenylcarbinyl maleate				
0.50	25.5	13.8	216	184
0.25	19.8	12.3	195	173
0.10	14.0	10.0	114	90
Na laurylsulfate (SO_3: 27.2%)				
0.24	7.4	2.2	857	852
0.15	8.4	2.7	758	753
Na cetylsulfate (SO_3: 22.1%)				
0.30	24.8	16.2	265	256
0.15	19.8	13.4	180	173

By the action of chromic anhydride in glacial acetic acid, a limonenylformaldehyde, 3-(4-methyl-3-cyclohexen-1-yl)-3-buten-1-al (IV) was obtained. Its odor is more fragrant than that of I. It gives positive reactions with Schiff's reagent and Tollen's reagent. The composition was confirmed from those of the 2,4-dinitrophenylhydrazone and semicarbazone.



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[1] K. Suga, J. Ishii and S. Watanabe, This Bulletin, 32, 711 (1959).

[2] N. Sugiyama, "Micro Identification of Organic Compounds (Yukikagobutsu no Biryo Kakuninho)", Baifukan Co, Ltd., Tokyo (1957), p. 60.

TABLE II. MONO-BASIC ACID ESTERS OF THE LIMONENYLCARBINOL

	Refining procedure	Physical constants	Molecular weight	
			Found	Calcd.
Palmitate	Chromatography	n_D^{19} 1.4794	378	404
Caprylate	Chromatography	n_D^{18} 1.4797 $[\alpha]_D^{15}$ +11.7	301	320
Isovalerate	Chromatography	n_D^{19} 1.4884	244	250
Phenylacetate	Vacuum distillation	n_D^{17} 1.5270 b. p. 150C°/4 mmHg $[\alpha]_D^{15}$ +26.0	279	284
Cinnamate	Chromatography	n_D^{11} 1.4822 $[\alpha]_D^{15}$ +15.1	290	296

TABLE III. LIMONENYLCARBINYL ETHERS

	Boiling point °C/mmHg	Refractive index	Specific gravity	Molecular refraction		Yield %
				Found	Calcd.	
Methyl	85～86/12	n_D^{25} 1.4870	$d_4^{24.5}$ 0.9317	55.39	52.61	80
Ethyl	96～97/4～5	n_D^{23} 1.4921	d_4^{23} 0.9353	59.98	59.64	90
Allyl	115～118/17	n_D^{23} 1.4927	$d_4^{24.5}$ 0.9293	64.26	63.79	80
Benzyl	175～179/10	n_D^{23} 1.5300	d_4^{23} 0.9885	80.17	79.13	90

Action of a large excess of acetone and aluminum isopropoxide on I gave a limonenylmethyleneacetone, as a viscous oil with burning odor. The structure of 6-(4-methyl-3-cyclohexen-1-yl)-3,5-heptadien-2-one(V) was demonstrated as follows: The substance gave a 2,4-dinitrophenylhydrazone and a positive iodoform reaction, which showed that it was a methyl ketone. The major absorption peaks at 295 and 223 mμ in the ultraviolet spectrum (Fig. 2) suggested the presence of a conjugated dienone grouping.

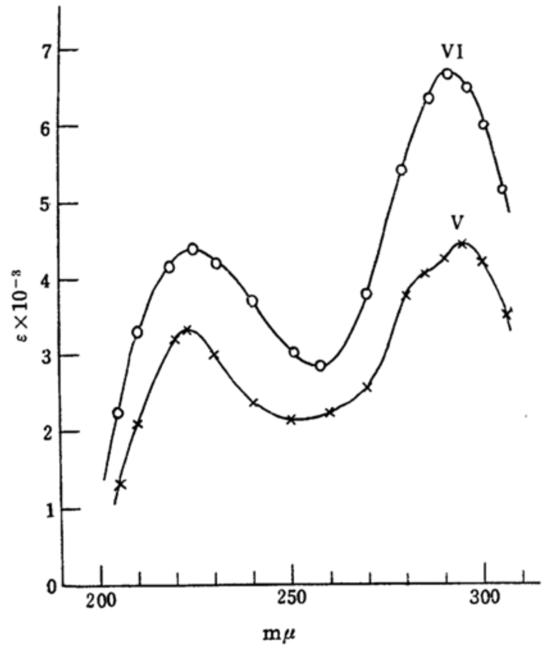

Fig. 2. Ultraviolet absorption spectra of V and VI.

Similarly, 7-(4-methyl-3-cyclohexen-1-yl)-4,6-octadien-3-one(VI) was prepared from I and methyl ethyl ketone. It is more viscous than V and also possesses a burning odor. The composition was confirmed by an elementary analysis of its 2,4-dinitrophenylhydrazone. It showed absorption peaks at 291 and 225 mμ (Fig. 2) corresponding to the conjugated dienone structure(VI). The iodoform reaction was negative.

Some ethers of I were also prepared. I was converted into the sodium compound by the action of sodamide in benzene. The ethyl limonenylcarbinyl ether VII ($R=C_2H_5$) was obtained in a yield of 90% from ethyl bromide and the sodium compound. Its ethoxyl radical was detected by Zeisel's method[3]. Similarly, methyl, ethyl, benzyl and allyl ethers were prepared (Table III).

Experimental

1,8(9)-*p*-Menthadien-10-yl-carbinol(I).—Prepared from *d*-limonene and paraformaldehyde as reported previously[1]: b. p. 102～106°C/4 mm.; d_4^{17} 0.9603; n_D^{17} 1.5020; $[\alpha]_D^{10}$+37.2; phenylurethan, m. p. 56～57°C.

Formaldehyde Mono-1,8(9)-*p*-menthadien-10-yl-carbinyl Acetal.—In a glass tube, 4 g. of I and 0.8 g. of paraformaldehyde were sealed and heated

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[3] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds", 4th Ed., John Wiley & Sons, Inc., New York; Maruzen Co., Ltd., Tokyo (1956), p. 116.

at 150∼170°C for 6 hr. By fractional distillation, 1.5 g. of II was given: b. p. 155∼162°C/5 mm.; $n_D^{20.5}$ 1.5066; $d_4^{20.5}$ 1.0306; molecular refraction 56.64 (calcd. for $C_{11}H_{17}OCH_2OH$: F_2, 57.65); hydroxyl group, 6.03% (calcd. for monohydric alcohol, 8.68%); molecular weight, 192 (calcd. for $C_{12}H_{20}O_2$: 196.2).

Anal. Found: C, 72.17; H, 9.41. Calcd. for $C_{12}H_{20}O_2$: C, 73.40; H, 10.27%.

The Limonenylcarbinyl Monoesters of Dibasic Acids.—*1,8(9)-p-Menthadien-10-yl-carbinyl hydrogen maleate.*—A mixture of 2 g. maleic anhydride and 2 g. of I was heated at 100°C for 3 hr. The reaction mixture was thoroughly washed with water of 60°C, dried in vacuo, and 3 g. of a pale yellow monoester was obtained, n_D^{12} 1.4921. Molecular weight, 264.25[4] (calcd. for $C_{15}H_{20}O_4$: 264.2). The silver salt was prepared by adding silver nitrate solution to the sodium salt of the acid maleate.

Anal. Found: Ag, 29.75; Calcd. for $C_{15}H_{19}O_4Ag$: Ag, 29.08%.

The foaming force of the sodium salt solution was measured by Nakajima's method[5] (Table I).

Acid phthalate and acid succinate of I.—They were prepared similarly.

The Limonenylcarbinyl Esters of Monobasic Acids. — *1, 8(9) - p - Menthadien - 10 - yl - carbinyl palmitate.*— To a mixture of 1.5 g. of I and 20 cc. of anhydrous ether, a dry ethereal solution of 3.0 g. of palmitoyl chloride was added with stirring. The reaction mixture was left overnight at room temperature. The crude palmitate was extracted with ether and the extract was washed three times with 30% aqueous methanolic solution containing 5% potassium hydroxide, and several times with water, and dried over anhydrous sodium sulfate. The crude palmitate, obtained by evaporation of the solvent, was chromatographed on active alumina and the pale yellow part in the middle of the chromatogram was eluted with methanol. By removing the methanol, 2.0 g. of the palmitate was obtained.

Caprylate, phenylacetate and cinnamate.—They were prepared similarly (Table II).

3-(4-Methyl-3-cyclohexen-1-yl)-3-buten-1-al(IV). —To a mixture of 4 g. of chromic anhydride, 5 cc. of water and 100 cc. of glacial acetic acid, a mixture of 9 g. of I, 30 cc. of acetone and 20 cc. of glacial acetic acid was added in 25 min. at 50∼55°C with vigorous agitation, and the mixture was stirred for 4.5 hr. Then this was poured into a large amount of water and extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulfate. By fractional distillation, 3.5 g. of IV was obtained: b. p. 88°C/4 mm.; n_D^{8} 1.5045. It gave a positive reaction with Schiff's reagent and reduced an ammoniacal silver nitrate solution.

2, 4-Dinitrophenylhydrazone.—It was prepared as usual and recrystallized twice from a mixture of pyridine and methanol. Fine red crystals, m. p. higher than 220°C.

Anal. Found: N, 16.14. Calcd. for $C_{17}H_{20}O_4N_4$: N, 16.27%.

Semicarbazone.— A mixture of IV, semicarbazide hydrochloride, sodium acetate and methanol was allowed to stand for about a month, and the crystals produced were collected and recrystallized twice from methanol. Colorless needles, m. p. 192°C.

Anal. Found: N, 18.35. Calcd. for $C_{12}H_{19}ON_3$: N, 18.98%.

6-(4-Methyl-3-cyclohexen-1-yl)-3, 5-heptadien-2-one(V).—A mixture of 5 g. of I, 18.5 g. of aluminum isopropoxide, 150 g. of refined acetone and 150 g. of anhydrous benzene was refluxed for 40 hr. Then 300 g. of benzene was added to the reaction mixture, and the benzene solution was separated, washed with 30% sulfuric acid three times and with water several times, and dried over anhydrous sodium sulfate. After benzene was evaporated, 1.0 g. of V was obtained by fractional distillation: b. p. 125∼133°C/3 mm.; n_D^{10} 1.5271; λ_{max} 295 mμ, ε 4480; λ_{max} 223 mμ, ε 3340. The substance gave a positive iodoform reaction.

2, 4-Dinitrophenylhydrazone.—This was prepared as usual and recrystallized from ethylacetate. Red needles, m. p. 179∼180°C.

Anal. Found: N, 14.50. Calcd. for $C_{20}H_{24}O_4N_4$: N, 14.50%.

7-(4-Methyl-3-cyclohexen-1-yl)-4, 6-octadien-3-one-(VI).—A mixture of 7 g. of I, 24 g. of aluminum isopropoxide, 200 g. of refined methyl ethyl ketone and 200 g. of dry benzene was refluxed for 60 hr. It was poured into 30% sulfuric acid and extracted with ether. The extracts were washed with water and dried over anhydrous sodium sulfate. By fractional distillation, 2.0g. of VI was obtained: b. p. 125∼132°C/2 mm.; n_D^{23} 1.4806; λ_{max} 291 mμ, ε 6650; λ_{max} 225 mμ, ε 4340. It did not give a positive iodoform reaction.

2, 4-Dinitrophenylhydrazone.—This was prepared as usual and recrystallized twice from a mixture of ethyl acetate and ethanol. Red needles, m. p. 203°C.

Anal. Found: N, 14.11. Calcd. for $C_{21}H_{26}N_4O_4$; N, 13.99%.

The Ethers of the Limonenylcarbinol(VII). — *Ethyl 1, 8(9)-p-menthadien-10-yl-carbinyl ether* ($R=C_2H_5$).—To a benzene solution (100 cc.) of 4.3 g. of sodamide, 12.4 g. of I was added gradually at 60∼65°C with vigorous agitation. When ammonia gas was no more generated, 13.3 g. of ethyl bromide was added in drops and the mixture was stirred for three hours. After leaving it overnight, the benzene solution was washed with water, and dried over anhydrous sodium sulfate. By fractional distillation 13.1 g. of VII was given.

Anal. Found: C, 80.04; H, 11.61. Calcd. for $C_{13}H_{22}O$: C, 80.34; H, 11.41%.

The ethoxyl radical was detected by Zeisel's method.

Methyl, benzyl and allyl ethers.—These were prepared similarly.

Absorption Spectra. — Infrared absorption spectra were measured by using a Perkin-Elmer spectrophotometer and ultraviolet absorption

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[4] It was measured by using 0.3971 N sodium hydroxide solution.

[5] H. Nakajima, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **56**, 611 (1953).

spectra by a "Shimadzu" photometric spectrophotometer Type QB-50 using isopropyl alcohol as a solvent.

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