

# Acetals and Ketals of 3 $\beta$ , 4 $\beta$ -caranediol—New Odoriferous Compounds from (+)-3-carene

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The interest in (+)-3-carene as an intermediate for synthesis of pesticides,<sup>1</sup> odoriferous substances<sup>2</sup> and other products had grown in recent years. It follows from the fact that (+)-3-carene (*1*) became an easily accessible and relatively cheap raw material isolated, together with  $\alpha$ -pinene, from turpentine of *Pinus silvestris*. However, contrary to  $\alpha$ -pinene which found broad application for synthesis of odoriferous compounds, practical utilization of carene is small as yet.

Studying oxidation of (+)-3-carene (*1*), we obtained four stereoisomeric diols, in which the positions of the hydroxy groups in relation to the cyclopropane ring, determining also position of the methyl group at the carbon atom C-2, depended on the oxidizing agent used (see figure 1). (-)-3 $\beta$ , 4 $\alpha$ -Caranediol (*4*) was formed by oxidation of *1* with hydrogen peroxide in acetic or formic acid.<sup>3</sup> (+)-3 $\alpha$ , 4 $\beta$ -Caranediol (*5*) was obtained by a sequence of reactions: diol *4*, monotosylate of diol (*6*),  $\beta$ -epoxycarene (*7*) and its solvolysis resulting in opening the epoxide ring with inversion on the carbon atom C-3.<sup>4</sup> The third isomer, (+)-3 $\alpha$ , 4 $\alpha$ -caranediol (*3*) was isolated from a multi-component reaction mixture after oxidation of *1* with KMnO<sub>4</sub>.<sup>4,5</sup> The fourth diol,

most interesting for us, (+)-3 $\beta$ , 4 $\beta$ -caranediol (*2*), was obtained by oxidation of *1* with iodine in the presence of silver acetate.<sup>6</sup> This method is relatively expensive but silver salt can be regenerated almost quantitatively. All stereoisomeric diols are odorless.

The preservative oxidation of diols *4* and *5* by means of various methods delivered expected hydroxyketones<sup>7</sup> but oxidation of diol *2* (3 $\beta$ , 4 $\beta$ -caranediol) by the Jones method<sup>8</sup> gave an unknown compound (yield 73%) with very intensive odor. Its IR spectrum exhibited the presence of ether as the only functional group. Analysis of the NMR spectrum showed that this compound had retained the cyclopropane ring (2H,  $\delta$ =0.78 ppm), two gem-dimethyl groups (2x6H,  $\delta$ =1.35, 1.60 ppm) and one methyl group bounded with the tetra-substituted carbon atom C-3 (3H,  $\delta$ =1.63 ppm). Determination of molecular weight by means of mass spectrometry gave indeed a result:  $m/e$  = 195 at ionization energy 70 eV but ion with  $m/e$  = 210 appeared apart from it at 15 eV. This fact supported our supposition that the unknown compound was ketal, therefore diol *2* was not oxidized but reacted in acidic medium with acetone used as the solvent in the Jones

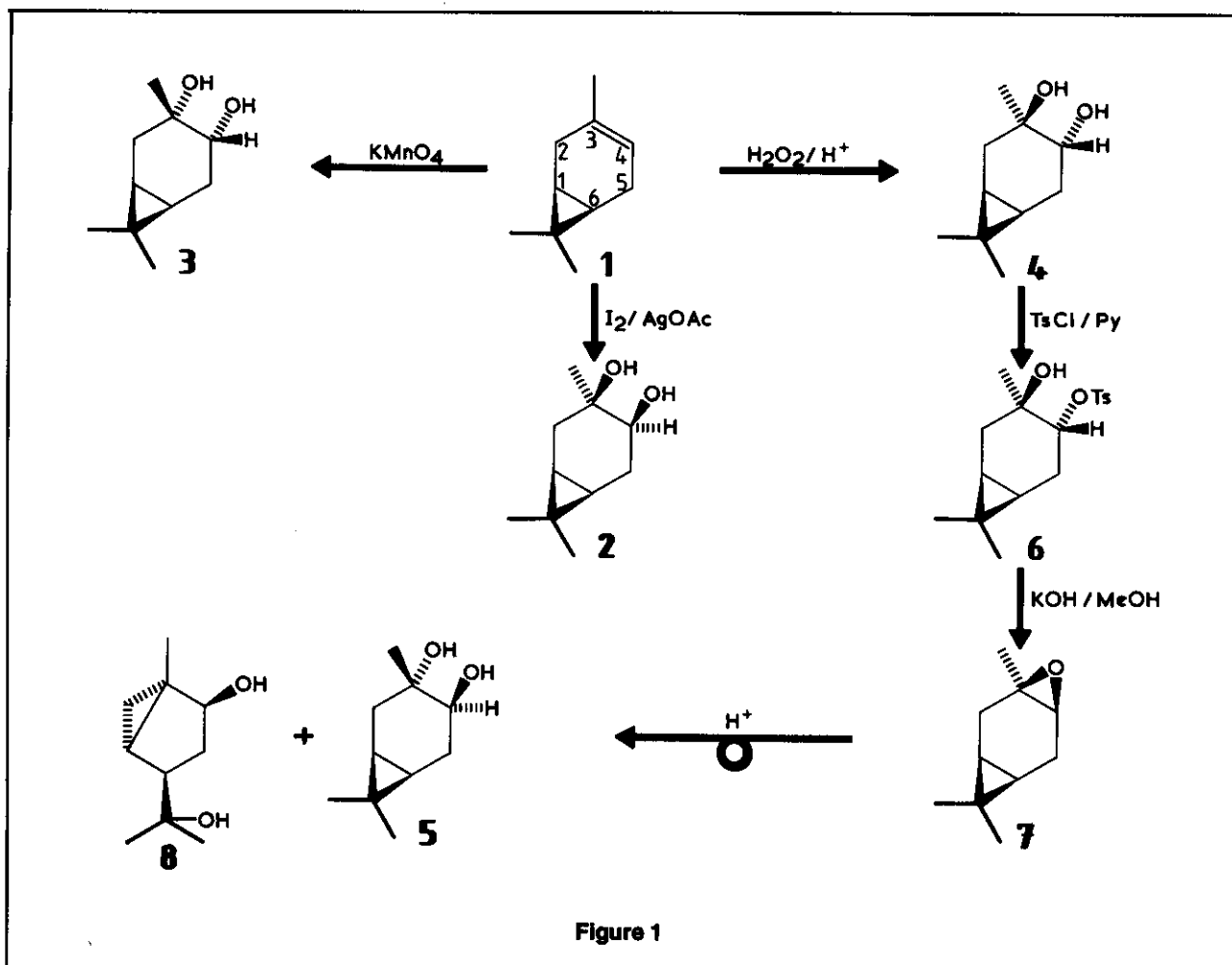


Figure 1

method. Ketal 9, (+)-1 $\alpha$ ,3,3,8,8-pentamethyl-2,4-dioxo-cis-tricyclo (5.3.0<sup>1,5</sup>.0<sup>7,8</sup>) decane, was stable compound which could be distilled and stored for a longer time at room temperature without change of properties.

Isomeric 3 $\alpha$ ,4 $\alpha$ -caranediol (3) yielded ketal 10, hydroxyketone 11 and trans-diol 4 in reaction with the Jones reagent (figure 2). Ketal 10 was a less stable compound with a rather unpleasant odor.

The structures of compounds 9 and 10 were confirmed by their synthesis from diols 2 and 3, respectively, and acetone in the presence of catalytic amounts of *p*-toluenesulfonic acid.

Discovery of the interesting odor of ketal 9 inspired us to carry out syntheses of homologous ketals of 3 $\beta$ ,4 $\beta$ -caranediol with 2-butanone, 2-pentanone, and of acetals with propanal and isobutanal. These syntheses were performed by allowing (+)-3 $\beta$ ,4 $\beta$ -caranediol (2) with appropri-

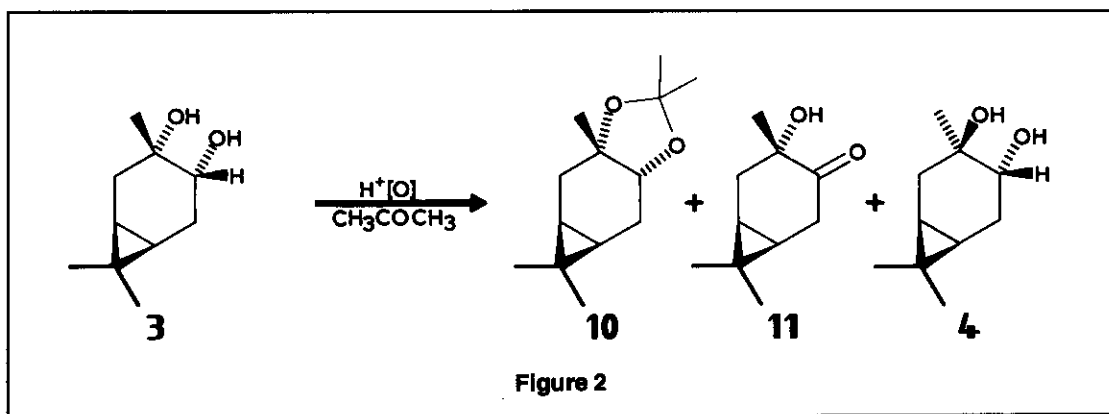


Figure 2

Table I. Acetals and Ketals—Physicochemical Constants and Odor Characteristics

	Ketals of (+)-3 beta,4 beta-caranediol	Yield (from GC)	MS m/e	n <sub>D</sub> <sup>20</sup>	(α) <sub>D</sub> <sup>20</sup> (CHCl <sub>3</sub> , c=3)	Odor
1. dimethyl-	<u>9</u>	73%	210	1.4668	+11.50°	intensive, pleasant, sweet, floral-rose-pinky
2. methylethyl-	<u>13</u>	72%	224	1.4666	+ 6.25°	intensive, pleasant, green, floral with fir-cedar note
3. diethyl-	<u>12</u>	72%	238	1.4710	+15.30°	intensive, sweet, floral- woody with absinthine note
4. methylpropyl-	<u>14</u>	74%	238	1.4614	+11.90°	intensive, pleasant, floral- balsamic with ambergris note
	Acetals of (+)-3 Beta,4 Beta-caranediol					
5. -propanal	<u>15</u>	76%	210	1.4603	- 7.60°	intensive, sharp, resembling that of marsh tea (Ledum palustris)
6. -isobutanal	<u>16</u>	72%	224	1.4662	- 8.30°	weak, woody-floral

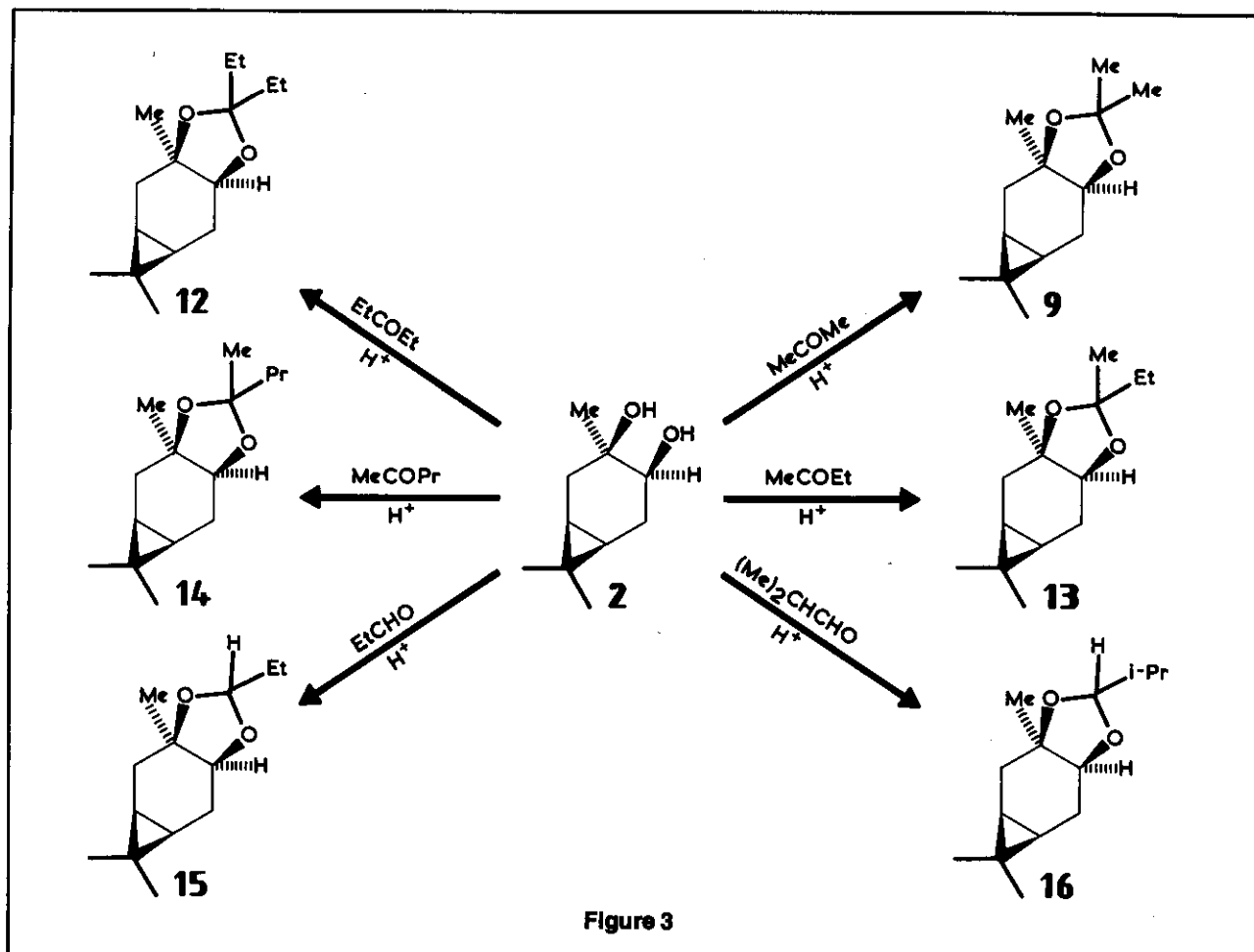


Figure 3

ate ketone or aldehyde in the presence of catalytic amounts of sulfuric or p-toluenesulfonic acid to stand for 24 hours at room temperature. Yields of ketals amounted to 70-75%; of acetals, to 72-76%. (See figure 3.)

The structures of compounds obtained were supported by the physicochemical studies, especially the IR and NMR spectra. The physicochemical constants and odor characteristics of acetals and ketals are listed in Table I.

The comparative analysis of the odor of synthesized acetals and ketals of (+)-3β,4β-caranediol indicated the significant role of the gem-dialkyl group in the dioxolane ring in creating pleasant, floral-balsamic or floral-woody odor of ketals. Acetals, which do not have this group, exhibited markedly less pleasant odor, more penetrating with the retained woody note.

In summary, it is noteworthy that the odor characteristics of acetals and ketals of bicyclic terpenic diols have been absent in the literature. Our discovery of interesting odors of ketals of (+)-3β,4β-caranediol indicates further potential possibilities of synthesis of new odoriferous

compounds in the series of bicyclic terpenic diols.

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