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**Registry No.**—**4b,** 67382-63-2; **4c,** 67382-64-3; **5b,** 67382-65-4; **5c,** 54781-19-0; **7b,** 67382-66-5; **7c,** 67382-67-6; **8b,** 67382-68-7; **8c,** 6651-36-1; **12,** 67382-69-8; **16,** 3839-48-3; triethylsilyl phenyl ether, 5888-66-4; tetrachloroethylene, 127-18-4.

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## Solvolysis of Virescenol B 19-Tosylate

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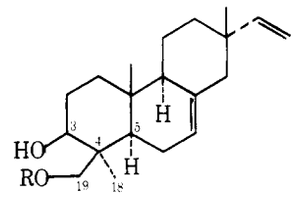
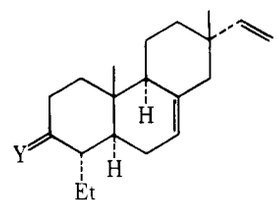
In continuation of a study of the chemistry of virescenol B (**1a**),[1] the aglycon of several of the fungal, virescenoside metabolites,[3] the solvolysis of the 19-tosylate (**1b**)[4] in dimethyl sulfoxide was investigated. It produced two carbonyl-containing substances whose structures are the subject of this note.

One of the products could be shown to be ketone **2a** on the basis of the following facts. Its infrared absorption at 1708 $cm^{-1}$ revealed it to be a cyclohexanone. The disappearance of the oxymethine, oxymethylene, and 4-methyl $^1H$ NMR signals normally associated with the C(3) and C(4) substitution pattern of the virescenol B skeleton and the exhibition of a methyl triplet ($J$ = 6 Hz) in the $^1H$ NMR spectrum of the product suggested the latter to be an $\alpha$-ethyl ketone. Finally,

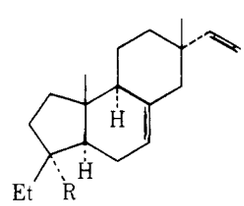


**1a,** R = H
**b,** R = Ts

its $^{13}C$ NMR spectra confirmed the structural changes at C(3) and C(4), showed rings B and C of virescenol B (**1a**)[5] to be affected only minimally, and ring A reminiscent of a 3-keto-steroid.[6] Sodium borohydride reduction of the ketone yielded a ca. 2:1 mixture of alcohols, whose $^1H$ NMR spectra indicated them to be equatorial and axial isomers, respectively. The low equatorial–axial isomer ratio, in contrast to the high ratio resulting from the hydride reduction of a 3-ketosteroid,[7] was in accord with the presence of a 4$\alpha$-ethyl-3-keto system whose ethyl group offered resistance to the normal $\alpha$ attack by borohydride. The $^{13}C$ NMR spectra of the alcohols confirmed fully structures **2b** and **2c** for the reduction products.

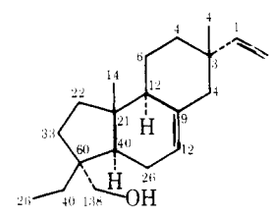


**2a,** Y = O
**b,** Y = $\alpha$-H, $\beta$-OH
**c,** Y = $\alpha$-OH, $\beta$-H

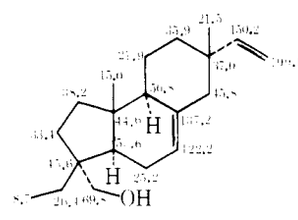


**3a,** R = CHO
**b,** R = $CH_2OH$

The minor product of the solvolysis of **1b** was shown by its infrared absorption bands of 2670 and 1722 $cm^{-1}$ to be an aldehyde and by its $^1H$ NMR spectrum to have its carboxaldehyde unit in an equatorial orientation[8] next to a nonprotonated carbon center. Once again the structural change at C(3) and C(4) was revealed not only by the new carbonyl group, but also by a methyl triplet ($J$ = 5 Hz) indicative of the presence of an ethyl group. Sodium borohydride reduction of the aldehyde yielded an alcohol whose $^1H$ NMR spectral characteristics revealed the presence of an equatorial hydroxymethyl group[8,9] next to a nonprotonated carbon and an ethyl group. The $^{13}C$ NMR spectra of the alcohol exhibited virescenol B-like ring B and C carbon signals and a homoneopentyl carbon signal customary for a methyl group on an ethyl function terminating on a nonprotonated carbon site. A Yb(DPM)$_3$ shift study (cf. $\Delta\delta$ values on formula **4**) permit-



**4**



**5**

ted a carbon signal assignment and structure analysis as depicted by formula **5** (**3b**), thus showing the aldehyde to possess structure **3a.**

The simplest explanation for the production of the two carbonyl compounds, **2a** and **3a,** on solvolysis of tosylate **1b** involves the migration of the 4$\alpha$-methyl group to the site of the departing tosylate group with concommitant O–C(4) bond formation by the neighboring 3$\beta$-hydroxy group. Hydride migration from C(3) to C(4) of the resultant conjugate acid of a 3$\beta$,4$\beta$-epoxide (**6**) leads to an O-protonated 4$\beta$-ethyl 3-

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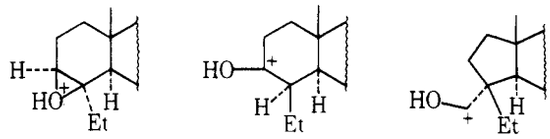
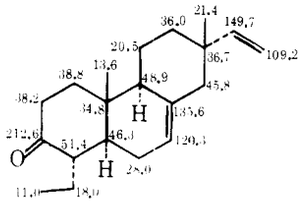


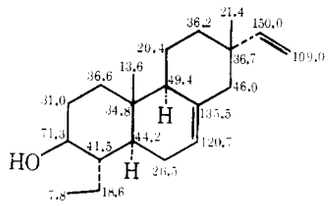
6 7 8

ketone (7), whose enolization and reketonization gives ketone **2a**, whereas C(2)–C(3) bond migration to C(4) of **6** yields the conjugate acid (8) of aldehyde **3a**.

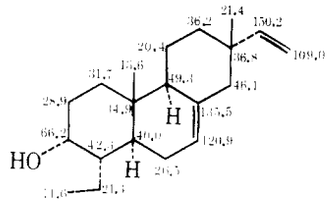
The carbon shifts of ketone **2a** are outlined on formula **9**. The similarity of the C(2) shift of 38.2 ppm with that of 5α-androstan-3-one (38.1 ppm)[6] shows the ethyl group to be equatorial and hence 4α oriented. The assignment of the chemical shifts of the alcohols **2b** and **2c** is portrayed on formulas **10** and **11**, respectively.



9



10



11

The migration of C(18) from C(4) to C(19) in the solvolysis of virescenol B 19-tosylate (**1b**) may be of biogenetic significance. Whereas many one-carbon rearrangements abound in the pimaranic diterpene field, none of the aforementioned type has been observed heretofore. Nevertheless, an ethano unit attachment to C(4) of diterpene rings A, such as in ketone **2a**, appears in the form of a furan ring in some constituents of the coffee bean.[10]

## Experimental Section

Melting points were determined on a Reichert micro-hotstage and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 167 spectrophotometer. $^1H$ NMR spectra ($Me_4Si$, $\delta = 0$) were recorded on a Jeol H-60 spectrometer and the $^{13}C$ NMR spectra were produced on a Varian XL-100-15 spectrometer operating at 25.2 MHz in the Fourier transform mode.

**Solvolysis of Virescenol B Tosylate (1b).** A solution of 600 mg of tosylate **1b** in 7 mL of dimethyl sulfoxide was heated at 95 °C under nitrogen with stirring for 7 h. After the addition of 50 mL of saturated brine solution the mixture was extracted thoroughly with chloroform. The extract was washed with water, dried ($Na_2SO_4$), and evaporated under vacuum. Chromatography of the residual oil, 330 mg, on silica gel and elution with benzene yielded 60 mg (16%) of liquid aldehyde **3a:** IR ($CCl_4$) 2670 (CHO), 1722 (C=O) $cm^{-1}$; NMR ($C_6D_6$) $\delta$ 0.68, 0.86 (s, 3 each, $Me_2$), 0.73 (t, 3, $J$ = 6 Hz, Me of Et), 8.96 (s, 1, CHO).

Anal. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56. Found: C, 83.70; H, 10.72.

Elution with 20:1 benzene–ethyl acetate gave 185 mg (50%) of solid whose crystallization from pentane led to crystalline ketone **2a:** mp 92–94 °C; IR ($CCl_4$) 1708 $cm^{-1}$ (C=O); NMR ($C_6D_6$) $\delta$ 0.76, 0.90 (s, 3 each, $Me_2$), 0.96 (t, 3, $J$ = 6 Hz, Me of Et).

Anal. Calcd for $C_{20}H_{30}O$: C, 83.86; H, 10.56. Found: C, 83.92; H, 10.54.

**Alcohols 2b and 2c.** A solution of 60 mg of sodium borohydride in 5 mL of ethanol was added dropwise to a stirring solution of 600 mg of ketone **2a** in 15 mL of ethanol at 0 °C. The mixture then was stirred at room temperature for 1 h and poured into ice water. It was extracted with chloroform and the extract dried ($Na_2SO_4$) and evaporated. Chromatography of the oily residue, 550 mg, on silica gel and elution with 20:1 benzene–ethyl acetate afforded 180 mg (30%) of semisolid alcohol **2c:** IR ($CCl_4$) 3625 $cm^{-1}$(OH); NMR ($CCl_4$) $\delta$ 3.86 (m, 1 OCH).

Anal. Calcd for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.42; H, 11.02.

Further elution with the same solvent pair gave 310 mg (51%) of solid whose crystallization from pentane–benzene yielded crystalline alcohol **2b:** mp 120–125 °C; IR ($CCl_4$) 3620 $cm^{-1}$(OH); NMR ($CCl_4$) $\delta$ 3.20 (m, 1, OCH).

Anal. Calcd. for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.38; H, 11.00.

**Alcohol 3b.** A solution of 15 mg of sodium borohydride in 5 mL of ethanol was added dropwise to a stirring solution of 50 mg of aldehyde **3a** in 3 mL of ethanol at 0 °C. The mixture then was stirred at room temperature for 1 h. Workup as above, chromatography of the curde product, 40 mg, on silica gel, and elution with 30:1 benzene–ethyl acetate led to 35 mg (80%) of semisolid alcohol **3b:** NMR $\delta$ 3.25, 3.45 (AB dd, 2, $J$ = 11 Hz, $OCH_2$).

Anal. Calcd for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.05; H, 11.31.

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**Registry No.**—**1b,** 67393-59-3; **2a,** 67393-60-6; **2b,** 67393-61-7; **2c,** 67393-62-8; **3a,** 67393-63-9; **3b,** 67393-64-0.

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# Novel Applications of the Potassium Chlorate–Osmium Tetroxide Oxidizing System. Synthesis of α-Dicarbonyl Derivatives from Acetylenic Compounds. Synthesis of a 2,3-Dihydroxy-1,4-dione from a 2,5-Dialkylfuran

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The cis hydroxylation of olefins to α-diols by metal chlorates in aqueous solution containing catalytic amounts of osmium tetroxide has found wide use.[1] This method is especially useful when the oxidation of other organic functions present in the substrate has to be avoided; most of these functions are, in fact, unaffected by the said oxidizing system. The reaction of acetylenic compounds with this oxidizing

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