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TWO NEW TRITERPENES HAVING A TRANS-DIOL FUNCTION OBTAINED FROM RHODODENDRON LINEARIFOLIUM

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In the previous paper (1) we reported the structures of five triterpenoids obtained from Rhododendron Linearifolium Sieb. et Zucc. Further investigation of this plant led to the isolation of two new triterpenes having a trans-diol function, i.e. fernenediol (I), $C_{30}H_{50}O_2$, m.p. 204°, $[\alpha]_D$ -34°, and epigermanidiol (II), $C_{30}H_{50}O_2$, m.p. 221°, $[\alpha]_D$ -1.4°. In this communication structural studies of fernenediol and epigermanidiol are presented.

A 1,2-glycolic function in fernenediol (I) was shown by consumption of lead tetraacetate. Acetylation of I with acetic anhydride and pyridine gave a diacetate (III), $C_{34}H_{54}O_4$, m.p. 240°, $[\alpha]_D$ -65°, ν_{max}^{KBr} 1740cm^{-1}, a vinyl proton signal at 5.35ppm. Reaction of I with acetone and sulfuric acid at room temperature gave an acetonide (IV), $C_{33}H_{54}O_2$, m.p. 229°. Tosylation of I with p-toluenesulfonyl chloride and pyridine, followed by reduction with lithium aluminum hydride afforded a monohydroxy compound (V), $C_{30}H_{50}O$, m.p. 188°, $[\alpha]_D$ -17° (2). V gave an acetate, $C_{32}H_{52}O_2$, m.p. 221°, $[\alpha]_D$ -10°. Chromium trioxide oxidation of V afforded a ketone (VI), $C_{30}H_{48}O$, m.p. 196°, $[\alpha]_D$ -60°, ν_{max}^{KBr} 1708cm^{-1}, which on reduction by the

Huang-Minlon condition, afforded a hydrocarbon (VII), $C_{30}H_{50}$, m.p. 171°, $[\alpha]_D$ -27°. The hydrocarbon (VII) was shown to be identical with fern-9(11)-ene (3) by mixed m.p. determination and by comparison of IR spectra with authentic species.

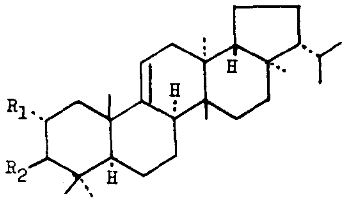
That V has 3β-hydroxyl group is shown by derivation of V into arundoin (4). Thus, V was methylated with potassium and methyl iodide to give the methyl ether (VIII), $C_{31}H_{52}O$, m.p. 238°, ν_{max}^{KBr} 1105, 815, 795cm^{-1}, which was shown to be identical with authentic species by mixed m.p. determination and by comparison of IR spectra.

Action of chromium trioxide in glacial acetic acid on the diacetate III gave an αβ-unsaturated ketone (IX), $C_{34}H_{52}O_5$, m.p. 214°, $[\alpha]_D$ -52°, ν_{max}^{KBr} 1740, 1670cm^{-1}, λ_{max}^{EtOH} 241mμ(ε 10,140). The optical rotatory dispersion curve of IX exhibited a positive Cotton effect $[\phi]_{362m\mu}^{peak}$ +2122°, $[\phi]_{320m\mu}^{trough}$ -2263°, which is the same sign with that of 13α,14β-methylfernen-12-one (3).

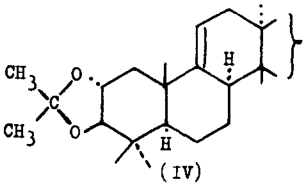
The mass spectra of diacetate (III), monohydroxy compound (V), and ketone (VI) have a significant peak at M^+-167m/e, which supports the fern-9(11)-ene skeleton (2,4).

The NMR spectrum of the acetonide (IV) has signals of protons attached to the carbon atoms bearing oxygen function at 3.09ppm (1 H, doublet J_{ab}=10c/s) and at 3.76ppm (1 H, quartet of doublets J_{ab}=10c/s, J_{ax}=8.5c/s, J_{ay}=4c/s). These coupling constants suggest that the 1,2-glycolic function has a trans-configuration (5), and hence fernenediol must be 2α,3β-dihydroxy-fern-9(11)-ene.

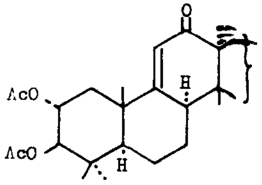
Epigermanidiol (II) also has a trisubstituted double bond (4.86ppm 1 H, doublet J=1.8c/s) and a 1,2-glycolic function (periodate consumption). Acetylation of II with acetic anhydride and pyridine gave a diacetate (X), $C_{34}H_{54}O_4$, m.p. 171°, $[\alpha]_D$ -13°. The diol II was converted to a monohydroxy compound (XI), $C_{30}H_{50}O$, m.p. 180°, $[\alpha]_D$ +9°. by a series of reactions



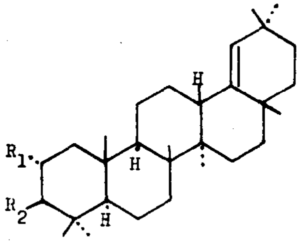
(I) : $R_1=R_2=OH$
(III) : $R_1=R_2=OAc$
(V) : $R_1=H$, $R_2=OH$
(VII) : $R_1=R_2=H$
(VIII): $R_1=H$, $R_2=OMe$



(IV)



(IX)



(II) : $R_1=R_2=OH$
(X) : $R_1=R_2=OAc$
(XI) : $R_1=H$, $R_2=OH$

applied to the diol I. The monohydroxy compound (XI) was shown to be identical with germanicol (6) by mixed m.p. determination and by comparison of IR spectra with authentic specimen. Melting points of the derivatives of XI; the ketone 188°, and the acetate 278°; are substantially identical with the melting points of germanicone 189°, and germanicol acetate 280°, respectively.

The NMR spectrum of II in $CDCl_3$ containing D_2O shows signals at 2.97ppm (1 H, doublet J=10.5c/s) and at 3.66ppm (1 H, multiplet), indicating that the 1,2-glycolic function has a trans-configuration, and hence the diol II is 2α-hydroxygermanicol.

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