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Short Communications

Totarolone, a New Diterpene Ketophenol from *Tetraclinis articulata* *

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A mixture of two new ketones, totarolone and totarolenone, has recently been isolated from the heartwood extract of *Tetraclinis articulata* (Vahl, Masters).[1] Hydrogenation of the mixture over Pd/C in ethanol gave pure totarolone, $C_{20}H_{28}O_2$, m.p. 188–189°, $[\alpha]_D + 102°$. The empirical composition, the U.V. absorption of totarolone [λ_{max}] 208 mμ (ε 37 700), 281 (1 900), and 286 (1 900)] and the I.R. absorption [3 380, 1 685 (1 705 in CCl_4), 1 590, and 810 cm^{-1}] suggests that totarolone is a new diterpene ketophenol containing a keto group that is not conjugated with the aromatic ring. This is supported by the physical properties of totarolone acetate, $C_{22}H_{30}O_3$, m.p. 113–115°, $[\alpha]_D + 96.6°$ ν_{max} at 1 755, 1 704 and 1 210 cm^{-1}, λ_{max} 207 mμ (ε 5 600), 266 (470).

Totarolone, now shown to be Ia, gave on Clemmensen reduction a good yield of totarol[2] (IIIa). Reduction of totarolone with potassium borohydride gave a diol, totaradiol (IIIb), $C_{20}H_{30}O_2$, m.p. 100–102°, $[\alpha]_D + 38.5°$, ν_{max} 3 610, 1 002 and 3 380 cm^{-1}. Acetylation (pyridine-acetic anhydride) furnished a diacetate (IIIc): $C_{24}H_{34}O_4$, $[\alpha]_D + 41°$, ν_{max} 1 766 and 1 725 cm^{-1}. The molecular rotation shift between totaradiol and its diacetate, m.p. 120–122°, $\Delta[M]_D + 43°$ is very similar to that between hinokiol (IIa) and its diacetate (IIb) $\Delta[M]_D + 47°$[3] suggesting that the environments of the assymetric centres are similar in both cases. Confirmation of structure Ia for totarolone was obtained as follows.

Totarolone benzyl ether, m.p. 169–171°, (Ib) was reduced with lithium aluminium hydride to totaradiol benzyl ether, (IIId) m.p. $C_{27}H_{36}O_2$, 192–193°, ν_{max} 3 420, 1 032, and 1 264 cm^{-1}. The ether (IIId) was treated successively with phosphorus pentachloride, osmium tetroxide and lead tetraacetate as recently described for hinokiol[3]; acetone and the trisnor-ketone (IV), ν_{max} (in CCl_4) at 1 740 and 1 260 cm^{-1}, [2,4-dinitrophenylhydrazone (amorphous), $C_{30}H_{32}O_5N_4$, λ_{max} 363 mμ (ε 20 200)] were obtained. The optical rotatory dispersion curve of IV was very similar to that of a 5β-A-norsteroid[4] indicating that inversion had occurred at C_5 during the reactions[5].

Furthermore the large positive Cotton effect shown by totarolone (and also by hinokione) is similar to that shown by lanost-8-en-3-one[6]. The A/B ring junction in totarolone, and consequently that in totarol, must therefore possess the conventional steroid absolute configuration, namely 5α,10β. The correctness of this assignment was also demonstrated by a direct correlation of totarol with dehydroabietic acid *etc.* in the following manner. Ozonisation, or better chromic acid oxidation, of totarol acetate (IIIe) gave 7-ketototarol acetate (V), $C_{22}H_{30}O_3$, m.p. 169–170°, λ_{max} at 213 mμ (ε 23 900), 252 (8 100), and 297 (2 600), ν_{max} at 1 758 and 1 676 cm^{-1}, $[\alpha]_D + 43.3°$ (in $CHCl_3$). Successive treatment of V with trifluoroperacetic acid, ozone and alkaline hydrogen peroxide afforded the dicarboxylic acid VI[7], m.p. 160–163° (identified by mixed

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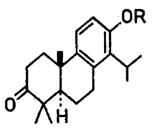
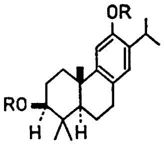
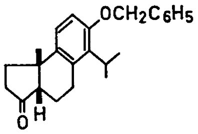


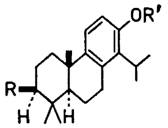
Ia: R = H
Ib: R = $-CH_2C_6H_5$



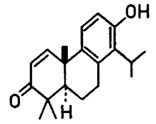
IIa: R = H
IIb: R = Ac



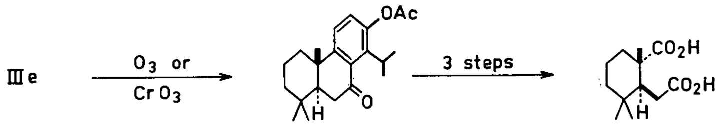
IV



IIIa: R = R' = H
IIIb: R = OH; R' = H
IIIc: R = OAc; R' = Ac
IIId: R = OH; R' = $-CH_2C_6H_5$
IIIe: R = H; R' = Ac



VII



V VI

melting point and its I.R. spectrum). A racemic totarolone methyl ether having the structure I (R = CH_3) has recently been synthesised by Taylor[8] and its I.R. spectrum was shown to be identical with that of the methyl ether of the natural product (m.p. 98—100°).

Since the original mixture of totarolone and totarolenone has a U.V. absorption at 223 mμ and an I.R. band at 1 652 cm^{-1} in addition to those of totarolone, it follows that the unisolated totarolenone must be 1,2-di-dehydrototarolone (VII).

Infrared spectra were taken in KBr discs and optical rotations in ethanol unless otherwise specified. All ultraviolet spectra were taken in ethanol solution. Satisfactory analyses were obtained for all the compounds described. We thank Dr. W. Klyne for the rotatory dispersion data and valuable discussions and Professor O. Jeger for an authentic specimen of the dicarboxylic acid VI.

1. Work done in this laboratory. To be published shortly.
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