Constituents of Labiatae.[1] Anagadiol, a New Triterpene from *Salvia Broussonetii* Benth.

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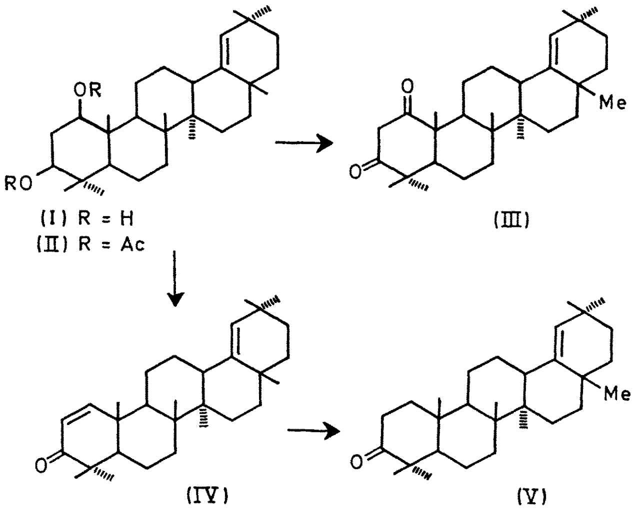
Summary Chemical and spectral evidence for the 1β,3β-dihydroxyolean-18-ene structure of anagadiol (I), a new triterpene isolated from the aerial parts of *Salvia Broussonetii* Benth., are reported.

IN connection with our work on the chemical components of Labiatae we have investigated *Salvia Broussonetii* Benth., endemic to the Canary Islands.[2] The concentrated ethanolic extract of the aerial parts of this plant was percolated through silica gel. The fractions eluted with $CHCl_3$ showing positive Liebermann–Burchard test were acetylated and chromatographed on a dry column. Elution with benzene gave several triterpenes. One of them has the empirical formula $C_{34}H_{54}O_4$ (M^+ 526), m.p. 247—255°. Its n.m.r. spectrum shows the presence of eight angular Me groups (τ 8·92—9·25), one vinyl hydrogen (5·18), two Me–CO (8·00, 8·04), and two hydrogen atoms on carbon bearing oxygen (5·31, 5·42, q). Hence, this substance (II) is a diacetate. Its mass spectrum shows the characteristic pattern[3] of the triterpenes of the Δ^{18}-oleanene series (peaks at *m/e* 205, 204 base peak, 190, 189, 177). The corresponding alcohol was named anagadiol (I), $C_{30}H_{50}O_2$, m.p. 212—214°, $[\alpha]_D$ +5° ($CHCl_3$).

Jones oxidation of (I) yielded a diketone (III), $C_{30}H_{46}O_2$, m.p. 112—114°, $[\alpha]_D$ +61° ($CHCl_3$); i.r. ($CHCl_3$) 1720, 1703 cm^{-1}; u.v. (EtOH) 260 nm. By adding alkali the u.v. maximum suffers a bathochromic shift to 293 nm. This behaviour is typical of the enolizable $O{=}C{-}CH_2{-}C{=}O$ group.[4] The presence of a β-diketone system as shown in (III) is supported by examining its n.m.r. spectrum: it shows a doublet (probably a degenerated quartet, 2H) at τ 6·60, 6·64 which disappears by equilibration with D_2O.[5]

Oppenauer oxidation of (I) gave an $\alpha\beta$-unsaturated ketone (IV), $C_{30}H_{46}O$, m.p. 163—164°, $[\alpha]_D$ +29° ($CHCl_3$); i.r. ($CHCl_3$) 1670, 1620 cm^{-1}; u.v. (EtOH) 232 nm; n.m.r. τ 4·14 and 2·77 (2d, *J* 10 Hz). Catalytic reduction of (IV) yielded germanicone (V), m.p. 189—190°, $[\alpha]_D$ +40° ($CHCl_3$). Hence, anagadiol possesses structure (I).



Its stereochemistry at C-1 and C-3 was deduced from the n.m.r. spectrum of (II) at 100 MHz. The two protons geminal to the acetyl groups give rise to partially superimposed quartets, part X of two independent ABX systems, whose $J_{AX} + J_{BX}$ are 16 and 17 Hz, respectively. This suggests axial–axial and axial–equatorial couplings which are compatible only with a 1β-OH,3β-OH configuration. From all these results we conclude that anagadiol must be 1β,3β-dihydroxyolean-18-ene (I). This is the first time that a natural product of the oleane series has been found to be oxidized at C-1.

Satisfactory analyses were obtained for all the compounds mentioned. The n.m.r. spectra were recorded in $CDCl_3$ with Me_4Si as internal reference.

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