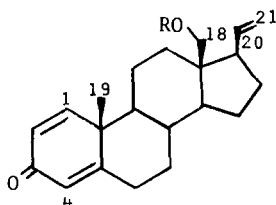


18-ACETOXY- AND 18-HYDROXYPREGNA-1,4,20-TRIEN-3-ONE FROM THE
TELESTACEAN OCTOCORAL TELESTO RIISEI (DUCHASSAING & MICHELOTTI)¹

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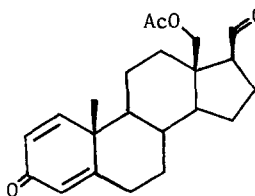
Abstract -- Two new pregnane derivatives were isolated from a telestacean octocoral Telesto riisei. The structures were deduced spectrally and confirmed by inter-conversion and by transformation to a ketone of known structure.

In contrast to extensive chemical research on soft (Alcyonacea) and horny (Gorgonacea) corals,² the order Telestacea, to which T. riisei belongs,³ has not previously been examined chemically. T. riisei, which lacks symbiotic zooxanthellae,⁴ also appears to be the only known octocoral that is significantly fouling.^{5,6} In fact, T. riisei was collected in shallow water off dock pilings at Enewetak Atoll in the Marshall Islands. The structures were deduced spectrally and confirmed by relating 1 to 2 and to dione 3, which was identical with a sample which we synthesized from progesterone.



1, R = Ac

2, R = H



3

The methylene chloride soluble portion of a methanol extract of T. riisei was chromatographed on silica gel to yield a fraction (40% EtOAc/CH₂Cl₂) rich in 1, which was further purified by two successive preparative TLC's (silica gel, 15% EtOAc/CHCl₃, R_f 0.45) to yield pure 18-acetoxypregna-1,4,20-trien-3-one (1) as a pale yellow oil, C₂₃H₃₀O₃ (m/e 354.2191, calcd 354.2195), in 0.02% yield from dry animal weight. The minor component was eluted with 60% EtOAc/CH₂Cl₂ and yielded after successive preparative TLC's on silica gel (10% EtOAc/CHCl₃ in two developments, R_f 0.3) and a C₁₈ reversed phase support (10% H₂O/MeCN, R_f 0.45), 18-hydroxypregna-1,4,20-trien-3-one (2) as a pale yellow oil.

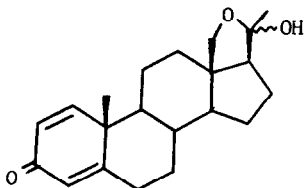
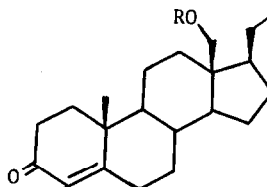
The C-18 acetate of 1 was characterized by IR absorption at 1745 cm⁻¹, a sharp 3H NMR singlet at δ 2.06 (CDCl₃), a ¹³C NMR singlet at δ 171.2, and a major peak in the mass spectrum

at m/e 294, which corresponds to a loss of 60 mass units (AcOH) from the molecular ion at m/e 354. Attachment of the acetate to $-\text{CH}_2-\text{C}\equiv$ was evidenced by a ^2H NMR singlet at δ 4.08 ppm, a major mass peak at m/e 281 corresponding to loss of 73 mass units from M^+ , and a triplet at δ 62.3 in the off resonance ^{13}C NMR spectrum.

The C-20,21 terminal olefin was deduced following irradiation of the allylic spectral region (δ 2.4), which collapsed a multiplet at δ 6.0-5.65 to a double doublet centered at δ 5.84 ($J = 18, 10$ Hz) and a δ 4.95 broad multiplet to a pair of double doublets centered at 5.01 ($J = 18, 2$ Hz) and δ 4.96 ($J = 10, 2$ Hz), constituting an ABX system. Infrared bands at 1000 and 935 cm^{-1} and ^{13}C NMR absorptions at δ 138.3 (d) and 114.2 (t) support this assignment.

The ring A dienone gave rise to a UV maximum at 242 nm (ϵ 12,400) and an intense IR band at 1675 cm^{-1} . ^1H NMR signals at δ 7.06 (1H, d, $J = 10$ Hz) for C-1 and 6.25 (1H, dd, $J = 10, 2$ Hz) for C-2 are coupled (10 Hz) as confirmed by irradiation experiments. Collapse of a broad singlet at δ 6.09 (C-4) to a doublet ($J = 2$ Hz) following irradiation of the allylic region (δ 2.4) suggested that this signal was coupled to the C-2 proton by 2 Hz. These data are compatible with a ring A dienone, where the C-2 and C-4 protons are W -coupled and the C-4 proton is also coupled allylically. A 3H NMR singlet at δ 1.24 is assigned to the C-19 methyl. ^{13}C NMR absorptions for five sp^2 carbons at δ 186.3 (s) for C-3, 168.9 (s) for C-5, 155.8 (d) for C-1, 127.6 (d), and 124.0 (d) for C-2 and C-4 are compatible with this assignment. Assuming a steroidal nucleus we arrive at 1, which on the basis of ^1H NMR data is preferred over 19-acetoxypregna-1,4,20-trien-3-one.

While exploring synthetic routes to 1, we obtained methyl ketone 3 by forced acetylation ($\text{Ac}_2\text{O}/\text{pyr}$, 100° , 10 h)^{7,8} of cyclic hemiketals 4, available in six steps from progesterone (Aldrich).⁹ Natural 1 was converted by selective catalytic oxygenation [$(\text{Ph}_3\text{P})_3\text{RhCl}$, benzene, 12 h ambient temperature, pressure]^{10,11} in high yield to 3, which was identical with the synthetic sample. Superimposable CD curves of synthetic and naturally-derived 3 indicated the absolute configuration of 1 as shown with all-trans ring junctures.

45, R = Ac6, R = H

The minor pregnane of I. riisei was shown to be 2. Comparison of ^1H NMR data of 2 revealed an upfield chemical shift to δ 3.64 of C-18 protons (δ 4.08 in 1) and absence of an acetate methyl resonance. Basic hydrolysis (1% KOH/MeOH, 1 h reflux) of 1 furnished 2, identical with natural 2. Selective catalytic hydrogenation [$(\text{Ph}_3\text{P})_3\text{RhCl}$, 1:1 benzene/

ethanol, 16 h, ambient temperature, pressure] of 1 and 2 gave the expected¹² 5 and 6, respectively, both characterized in the ¹H NMR spectrum by a sole low field proton (H-4) at δ 5.75 (bs).

These previously undescribed pregnanes represent as far as we know the first chemical investigation of a telestacean octocoral. They belong to a growing number of marine-derived non-glycosidic pregnanes which have been reported from North Atlantic¹³ and South Pacific¹⁴ soft corals (Alcyonacea), from sponges,¹⁵ and from a Mediterranean gorgonian.¹⁶

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