mp, and infrared (IR)) with 2-hydroxy-6-pentyl-1,4-benzoquinone (VII), PMR: 0.88 (3H, t, J=6, -CH₂), 1.05—1.90 (6H, br., -CH₂×3), 2.45 (2H, t-like, J=6, -C=C-CH₂-), 6.10, 6.46 (1H each, s, ring H×2), prepared analogously from I via physodone (V). Consequently, the structure of oxyphysodonic acid has been established as II.

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Neridione A, a C₂₁-Stesoid in Neriurn odorum

Concerning the constituents of Neriurn odorum, we have previously reported the isolation of pregnenolone glucosides from its root bark. This communication deals with the isolation and the structural elucidation of neridione A, a pregnane compound in the same source.

The methanol percolate of the root bark was extracted with benzene, and through successive column chromatography of the benzene extractives followed by crystallization from acetone—hexane, a substance, sensitive to 2,4-dinitrophenylhydrazine reagent on thin—layer chromatography, was obtained as prisms and named neridione A (NA). NA, (mp 210—211°, [α]D +71.5°, Mass. Caled. for C₃₉H₃₈O₃ m/e 326.1875; Found 326.1882), shows nuclear magnetic resonance (NMR) signals at δ (ppm) 0.98 (3H, s), 1.16 (3H, s), 2.43 (3H, s), 3.71 (1H, dd), 5.67 (1H, s), 5.81 (1H, s), 6.12 (2H, s) and 6.99 (1H, dd). Two oxygens in NA were found to belong to the unsaturated ketones, 4,6-dien-3-one and 16-en-20-one of steroid system, according to the ultraviolet absorptions at 283 nm (ε 24100) and 245 nm (ε 12900), infrared (IR) bands at 1665, 1640, 1612 and 1580 cm⁻¹, and NMR signals at 5.67 (C₄-H), 6.12 (C₆-7-H) and 6.99 ppm (C₁₆-H). The IR bands at 3420 and 3320 cm⁻¹ as well as the disappearance of the peak at δ 5.81 ppm with D₂O exchange indicated that the remaining oxygen function forms a hydroxyl group. NA, on reduction with NaBH₄ gave three products, dihydro--, tetrahydro- and hexahydro-compounds, the first of which, (Caled. for C₃₉H₃₈O₃ 328.2038; Found 328.2079) bears no 16-en-20-one system in its molecule, and afforded a diacetate (Caled. for C₅₁H₄₆O₆ 412.2249; Found 412.2233) on acetylation, whereas NA was unreactive with Ac₂O and pyridine. The above results suggested that the hydroxyl group is oriented in the position under the influence of 16-en-20-one, and the location and the configuration were determined as C₁₆-β-OH...

1) This forms Part IV of "Neriurn." Part III: T. Yamauchi, Y. Môri and Y. Ogata, Phytochemistry, 12, 2737 (1973).
by the double-doublet lines at 3.71 ppm with coupling constants of 5 and 10 Hz, due to a carbinoil methine proton.

When NA was subjected to catalytic hydrogenation over Pd charcoal, two hexahydro derivatives, NA-I (mp 173–175°, Calcd. for C₁₇H₃₃O₃ 332.2351; Found 332.2334) and NA-II (mp 157–160°, Found 332.2324) were obtained. NA-II, on oxidation with CrO₃, gave a triketone compound (mp 208–212°, [α]₅ + 174°, Calcd. for C₁₇H₃₃O₃ 330.2195; Found 330.2161), which was identified as 5α-pregnane-3,12,20-trione on direct comparison with the authentic sample synthesized from hecogenin. The structure of NA, therefore, was elucidated as 12β-hydroxyprogna-4,6,16-triene-3,20-dione.

Recently, 12β-hydroxyprogna-4,6-diene-3,20-dione, the dihydro-derivative of NA, and the several C₂ₙ steroids have been known to possess the peculiar effect against fish as the defence substance of the water beetles. In our experiments on NA, goldfishes were observed to go down to the bottom of the vessel and keep their bodies static within 10 min at the concentration of ca. 10 mg/liter.

In the early studies on the cardiac glycosides of Nerium by Reichstein and his associates, the presence of the substances having the absorptions at ca. 280 and 240 nm was noted as "Substance 1" in the bark of N. odoratum and "Substance A" in the seeds of N. oleander, respectively, although no further investigations have been provided. NA is most likely the same or the closely related substance as those obtained by them.

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Odorous Metabolites of Aquatic Actinomycetes. Identification of 1-Phenyl-2-propanone and 2-Phenylethanol

Investigations on odorous metabolites produced by actinomycetes have been greatly advanced in the last decade by the use of gas chromatography (GC) and mass spectrometry combined with GC (GC–MS). In 1965, Gerber, et al. isolated a strongly earthy-smelling substance, geosmin, from seventeen strains of Streptomyces, Nocardia, and Microbispora

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