mp, and infrared (IR)) with 2-hydroxy-6-pentyl-1,4-benzoquinone (VII), PMR: 0.88 (3H, t, J=6, $-CH_3$), 1.05—1.90 (6H, br., $-CH_2-\times 3$), 2.45 (2H, t-like, J=6, $-C=C-CH_2-$), 6.10, 6.46 (1H each, s, ring H×2), prepared analogously from I *via* physodone (V).[6]

Consequently, the structure of oxyphysodic acid has been established as II.

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Neridienone A, a C_{21}-Steroid in *Nerium odorum*[1]

Concerning the constituents of *Nerium odorum*, we have previously reported the isolation of pregnenolone glucosides[2] from its root bark. This communication deals with the isolation and the structure elucidation of neridienone 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 neridienone A (NA). NA, (mp 210—211°, $[\alpha]_D$ +71.5°, Mass. Calcd. for $C_{21}H_{26}O_3$ 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 (C_4-H), 6.12 ($C_{6,7}$-H) and 6.99 ppm (C_{16}-H). The IR bands at 3420 and 3320 cm^{-1} as well as the disappearance of the peak at δ 5.81 ppm with D_2O exchange indicated that the remaining oxygen function forms a hydroxyl group. NA, on reduction with $NaBH_4$, gave three products, dihydro-, tetrahydro- and hexahydro-compounds, the first of which, (Calcd. for $C_{21}H_{28}O_3$ 328.2038; Found 328.2079) bears no 16-en-20-one system in its molecule, and afforded a diacetate (Calcd. for $C_{25}H_{32}O_5$ 412.2249; Found 412.2233) on acetylation, whereas NA was unreactive with Ac_2O 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 C_{12}-β-OH

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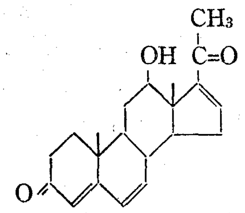
[1] This forms Part IV of "*Nerium*." Part III: T. Yamauchi, Y. Mōri and Y. Ogata, *Phytochemistry*, **12**, 2737 (1973).

[2] T. Yamauchi, M. Hara and K. Mihashi, *Phytochemistry*, **11**, 3345 (1972).

by the double-doublet lines at 3.71 ppm with coupling constants of 5 and 10 Hz, due to a carbinol methine proton.

When NA was subjected to catalytic hydrogenation over Pd/charcoal, two hexahydro derivatives, NA-I (mp 173—175°, Calcd. for $C_{21}H_{32}O_3$ 332.2351; Found 332.2334) and NA-II (mp 157—160°, Found 332.2324) were obtained. NA-II, on oxidation with CrO_3, gave a triketone compound (mp 208—212°, $[\alpha]_D+$ 174°, Calcd. for $C_{21}H_{30}O_3$ 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.[3] The structure of NA, therefore, was elucidated as 12β-hydroxypregna-4,6,16-triene-3,20-dione.



neridienone A

Recently, 12β-hydroxypregna-4,6-diene-3,20-dione,[4] the dihydro-derivative of NA, and the several C_{21}-steroids[5] 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. odorum*[6] and "Substance A" in the seeds of *N. oleander*,[7] 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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[5] V. Herout, "Progress in Phytochemistry 2," ed. by Reinhold and Y. Liwschitz, Interscience Publishers, Inc., New York, 1970, p. 143.
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[7] H. Jäger, O. Schindler and T. Reichstein, *Helv. Chim. Act.*, **42**, 976 (1959).

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

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.*[2] isolated a strongly earthy-smelling substance, geosmin, from seventeen strains of *Streptomyces*, *Nocardia*, and *Microbispora*

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[2] N.N. Gerber and H.A. Lechevalier, *Appl. Microbiol.*, **13**, 935 (1965). As to the structure determination, see N.N. Gerber, *Tetrahedron Letters*, **1968**, 2971.