lactone ring − 60), 295 (43.4) (M − lactone ring − 60 − 18), 239 (94.8) (lactone ring + C_{16} − C_{17} − C_{20} − C_{21}), 225 (100) (lactone ring + C_{17} − C_{20} − C_{21}), 183 (49.6) (lactone ring), 125 (51.2) ($C_7H_9O_2$, McLafferty on ring A). (Found: C, 69.13; H, 8.14. $C_{32}H_{44}O_8$ requires: C, 69.04; H, 7.97%).

Preparation of acnistoferin from jaborosalactone A. Compound **1** (60 mg) was dissolved in Me_2CO (43 ml), treated with 8 N H_2SO_4 (0.33 ml) and the soln was stirred for 4 hr at room temp. It was then poured into dil $NaCO_3H$ soln and extracted with $CHCl_3$. Evapn of the solvent gave a residue that was crystallized from EtOH. The product (45 mg) was identical (mp, IR, ^{1}H NMR) to natural acnistoferin.

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29-HYDROXYLUPEOL FROM *GYMNOSPORIA WALLICHIANA**

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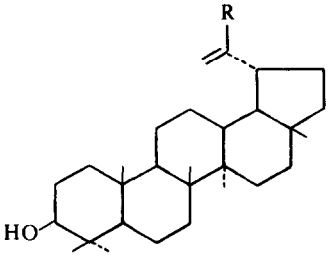
Key Word Index—*Gymnosporia wallichiana*; Celastraceae; wallichianol; wallichenol; 29-hydroxylupeol; triterpenoids.

A chemical investigation of *Gymnosporia wallichiana* reported [1] that the mixture of compound F_1 (wallichianol) and compound F_2 (hereafter referred to as wallichenol), could not be resolved by any chromatographic means. However, it was observed that MS of the mixture of wallichianol and wallichenol contained M^+, M − 15 and M − 18 peaks of wallichianol as well as the corresponding peaks due to wallichenol, two mass units lower than those of wallichianol and it was anticipated that wallichenol had a double bond in the molecule. Wallichianol was therefore isolated by Br_2 oxidation of wallichenol to a mixture of products of higher R_f value followed by chromatography. The structure of wallichianol was elucidated as (20*S*)-lupan-3β,29-diol.

The present paper deals with the structure elucidation of wallichenol. The mixture of wallichianol and wallichenol was silylated and subjected to GC–MS, which furnished separate MS for silylated wallichianol and wallichenol. Both the MS showed common fragment ions involving rings A and B at *m/e* 279, 202, and 189 whereas M^+, M − Me, M − $(Me)_3SiOH$ and M − $(Me)_3$-SiOH − Me peaks of silylated wallichenol were two mass units lower than the corresponding peaks of wallichianol. This indicated a skeletal similarity between the two compounds.



1 R = CHO
2 R = CH_2OH

The ^{1}H NMR spectrum of the wallichianol and wallichenol mixture showed a pair of broad singlets at δ 4.13 and 4.93 ppm, whereas these signals were absent in the ^{1}H NMR spectrum of wallichianol. These signals were therefore assigned to the olefinic protons of wallichenol. On addition of trichloroacetyl isocyanate (TAI) [2], the olefinic signals suffered a downfield shift to δ 4.76 and 5.05 ppm, indicating the presence of an allylic OH group in wallichenol. This inference was confirmed by MnO_2 oxidation of the mixture of wallichianol and wallichenol which resulted in the formation of a product of higher R_f value (TLC) leaving wallichianol intact. The new product was separated from wallichianol by chromatography over Si gel. This product (1), $C_{30}H_{48}O_2$ (M^+ 440), mp

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240° (lit. mp 225–26° and 232–33°), λ_{max} 226 nm (log ε 3.9) yielded a monoacetate, mp 224°, λ_{max} 225 nm (log ε 3.8). It was identified as 3β-hydroxylup-20(30)-en-29-al (**1**) by its co-chromatography, superimposable IR and mmp, and those of its acetate with the authentic samples. The authentic sample of **1**-acetate was obtained by SeO_2 oxidation of lupeol acetate [3]. The alkaline hydrolysis of the latter yielded **1**.

Since 3β-hydroxylup-20(30)-en-29-al was formed by allylic oxidation of wallichenol, the structure of wallichenol was established as lupan-20(30)-en-3β,29-diol (**2**)†. This assignment was further confirmed by the catalytic hydrogenation of the mixture of wallichianol and wallichenol which yielded a completely homogeneous product identical with wallichianol in all respects.

EXPERIMENTAL

All mps are uncorr. The ^1H NMR spectra were recorded at 60 MHz in $CDCl_3$ unless otherwise stated. A 3% OV-1 column was used for GC at 262° and He was the carrier gas. R_f values refer to TLC on Si gel plates in C_6H_6–MeOH (96:4).

MnO_2 *oxidation of wallichianol–wallichenol mixture.* The mixture of wallichianol and wallichenol (100 mg) was dissolved in $CHCl_4$ (10 ml) and stirred with MnO_2 (100 mg) for 24 hr, then filtered. The filtrate was evapd. The product showed 2 spots of R_f 0.47 and 0.68 on TLC. The product was chromatographed over Si gel. The $CHCl_3$ eluate yielded the product of higher R_f (**1**, 45 mg), mp 240°, λ_{max} 225 nm (log ε 3.9). (Found: C, 81.9; H, 10.65. $C_{30}H_{48}O_2$ requires: C, 81.9; H, 10.9%).

On acetylation with C_6H_5N–Ac_2O **1** yielded an acetate mp 224°, λ_{max} 225 nm (log ε 3.8).

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† Lupan-20(30)-en-3β,29-diol obtained by reduction of 3β-acetoxylup-20(30)-en-29-al has a mp 231–2° [4].

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PREGNANES OF *ANODENDRON AFFINE*

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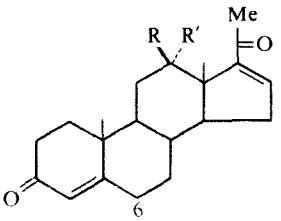
Key Word Index—*Anodendron affine*; Apocynaceae; pregnane derivatives; neridienone A homologs; steroids.

Anodendron affine Druce is indigenous to the southern part of Japan. Previously, the constituents of the trunk were investigated by Inagaki *et al.* [1] and pyrrolizidine alkaloids were isolated from the leaves by Sasaki and Hirata [2]. Cardenolides bearing a 4,6-dideoxyhexosone were isolated from the same genus, and the structures were determined by Lichti *et al.* [3]. We now report the identification of four pregnanes with 4,16-dien-3-one and 4,6,16-trien-3-one functions.

Four compounds (**1**–**4**) were obtained as crystals from the MeOH percolate of the trunk with bark by partitioning the MeOH extractives with benzene followed by silica gel chromatography.



1 R = OH, R′ = H, Δ^6
2 R = OH, R′ = H
3 R,R′ = = O, Δ^6
4 R,R′ = = O

1 was identified as neridienone A, a pregnane derivative previously isolated from the root bark of *Nerium indicum* [4], by direct comparison with an authentic sample. **2** shows a lower M^+ than **1** by 2 mass units, and neither an absorption maximum at 284 nm nor the 2H resonance at δ 6.13, due to the C-6 and C-7 olefinic protons in a 4,6-dien-3-one system. Since an absorption due to the Δ^{16}-20-one was observed at 245 nm, and a C-16 olefinic proton at δ 7.00 as in **1** in lower field than a 12-deoxy derivative, the structure of **2** was determined as 12β-hydroxy-4,16-pregnadien-3-one.