bonds, viz. one out of the 3 possible in α-residues, three out of the 6 possible in β- and γ-residues, and two out of the 3 possible in δ-residues (cf. structure 2).

This at least suggests that reduction of the postulated precursor tri-*O*-geranylgeranylglycerol occurs progressively from the oxygenated end of the isoprenoid chains. Unfortunately the structures of these very minor triethers do very little to clarify the biogenesis of the ω,ω'-biphytanyl skeleton in the major cyclic diether lipids of *Caldariella*.

EXPERIMENTAL

Culture methods and lipid extraction procedures are described elsewhere [1,3]. Direct extraction of the total lipid (25 g) with hexane gave a soluble fraction (540 mg) which was subjected to chromatography on Merck Kieselgel (70–230 mesh) in hexane with increasing proportions of Et_2O. The triethers eluted with 20% Et_2O and were further separated into (**1**) and (**2**) by TLC (Merck Kieselgel 60-F254) in hexane–ether (7:3) (R_f 0.5 and 0.4 respectively).

Hydrogenation of (**2**). The triether (10 mg) was treated with H_2 on Pd–C (5%; 15 mg) in MeOH (3 ml) for 24 hr; chromatography of the product, as above, gave (**1**) (NMR, IR) which was subsequently converted as for the natural saturated triether.

Ether cleavage etc. Treatment of (**1**) (15 mg) with 57% HI (1 ml; 24 h reflux) and work-up (extraction into hexane, washing with H_2O, aq. K_2CO_3, aq. $NA_2S_2O_3$, and H_2O, partition with hexane and 90% aq. MeOH, and TLC in hexane) gave phytanyl iodide, $C_{20}H_{41}I$ (MS and NMR). The product (10 mg) was refluxed with AgOAc (20 mg) in AcOH (2 ml) for 24 hr. The reaction mixture was taken up in Et_2O, centrifuged, washed (H_2O, aq. NaCl, aq. $NaHCO_3$, aq. $Na_2S_2O_3$, H_2O) and purified by TLC in hexane–ether (17:3). The product R_f 0.75, was identified as phytanyl acetate by comparison with authentic material [MS, NMR, and GLC (on a 2m × 3mm glass column packed with 1% OV-1 on Gas-Chrom Q 100/120 with 40 ml/min N_2 at 200°; retention time 6.24 min)]. Alternatively, the triether (10 mg) was treated with BCl_3 (1 ml with 1 ml $CHCl_3$; 14 hr at R.T.). Excess reagent was removed at reduced pressure and the alkyl chloride taken up in hexane for purification by TLC as above (phytanyl chloride, $C_{20}H_{41}Cl$ by MS and NMR). The undissolved residue was taken up in methanol and identified as glycerol by TLC (in $CHCl_3$–MeOH, 4:1 on Si gel, R_f 0.40, visualised with Ag–NH_3).

Spectra. All IR spectra were measured in CCl_4; NMR spectra at 100 MHz in CCl_4 with TMS standard; MS on the AEI MS-30.

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6β,22-DIHYDROXYHOPANE, A NEW TRITERPENE FROM THE FERN *CHEILANTHES MARANTAE*

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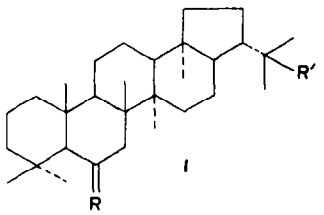
Key Word Index—*Cheilanthes marantae*; Sinopteridaceae; doradilla acanalada; fern; triterpenes, steroids; diplopterol; fernenol; 6β,22-dihydroxyhopane; sitosterol; sitosterol-*o*-β-D-glucoside.

Plant. Cheilanthes marantae L. local name doradilla acanalada. Specimen no. 322 deposited in the Herbarium of the Botany Department, University of La Laguna. *Source.* Monte de las Mercedes, Tenerife, Canary Islands. Collected in June. *Previous work.* None.

Present work. In addition to *saccharose, diplopterol, fernenol, sitosterol* and *sitosterol-*O-β-D-glucoside, the new natural triperpene *6β,22-dihydroxyhopane* (**1a**), characterized by its IR, PMR and MS spectra, was isolated from the stems and leaves of *Cheilanthes marantae*. The hopane framework of (**1a**) was deduced from its MS which showed the same fragmentation pattern as that of zeorin (**1d**) and related compounds [1]. The large downfield shifts of the methyl groups at C-4β, C-8β and C-10β observed in the PMR spectrum (*ca* 0.35 ppm) compared with 22-hydroxyhopane are compatible only with the presence of a C-6β hydroxyl group [2]. These assumptions were chemically confirmed by partial synthesis of (**1a**) from zeorin.



1

1a R = H; β-OH R' = OH
1b R = H; β-OAc R' = OAc
1c R = O R' = OH
1d R = H; α-OH R' = OH

EXPERIMENTAL

Mp's determined on a Koffler hot-stage apparatus, are uncorr. Optical rotations were measured in $CHCl_3$ and PMR spectra in $CDCl_3$ with TMS as internal reference.

Extraction. Leaves and stems were extracted with hot EtOH and conc *in vacuo*. Saccharose was separated by crystallization from the concentrate and the residue was chromatographed on Si gel and eluted with C_6H_6, C_6H_6–AcOEt, AcOEt, giving: diplopterol (2.7×10^{-3}% of plant dry wt.), fernenol (3.4×10^{-3}%), sitosterol, the new natural triterpene 6β,22-dihydroxyhopane (**1a**, 4.8×10^{-4}%) and sitosterol-*o*-β-D-glucoside.

Diplopterol. Mp 234–236° (MeOH–Me_2CO), $[\alpha]_D$ + 42° (*c* 0.262). IR ν_{max}^{KBr} cm^{-1}: 3450 (OH). PMR δ: 0.79 (3H, *s*, C-28), 0.84 (6H, *s*, C-23, C-24), 0.86 (3H, *s*, C-25), 0.98 (6H, *s*, C-26, C-27), 1.21 (6H, *s*, C-29, C-30). MS (70eV), *m/e* (rel. int.): 428 (M^+, 5), 207 (21), 191 (59), 189 (49), 149 (54), 121 (21), 95 (71), 59 (100).

Fernenol. Mp 198–200° (MeOH) $[\alpha]_D$ − 23° (*c* 0.216) [3]. IR ν_{max}^{KBr} cm^{-1}: 3610 (OH). PMR δ: 0.72, 0.76, 0.83, 0.88, 0.95, 1.06 (24H, eight Me groups), 3.15 (1H, *m*, $W_{1/2}$ = 18 Hz, C-3), 5.35 (1H, *m*, $W_{1/2}$ = 10 Hz, C-11). MS (70eV), *m/e* (rel. int.): 426 (M^+, 50), 411 (100), 393 (20), 273 (12), 255 (12), 259 (94), 241 (30), 95 (34). *Acetate.* Mp 218° (Me_2CO), $[\alpha]_D$ − 6° (*c* 0.246). (Found: C, 81.61; H, 11.15. Calc. for $C_{32}H_{52}O_2$: C, 81.99; H, 11.18%.) On chromic acid oxidation, fernenol furnished the corresponding *ketone.* Mp 197° (MeOH), $[\alpha]_D$ − 47° (*c* 0.254). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1700 (CO). MS (15eV), *m/e* (rel. int.: 424 (M^+. 18), 410 (12), 409 (34), 271 (20) 258 (20), 257 (100), 246 (15), 245 (22). To our knowledge, this is the first reported instance of fernenol in ferns.

6β,22-*Dihydroxyhopane.* Mp 238–242° (MeOH), $[\alpha]_D$ + 19° (*c* 0.194). (Found: C, 81.09; H, 11.42. $C_{30}H_{52}O_2$ requires: C, 81.02; H, 11.79%.) IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3605 (OH). PMR δ: 0.79 (3H, *s*, C-28), 0.92 (3H, *s*, C-24), 0.96 (3H, *s*, C-27), 1.19 (3H, *s*, C-23), 1.21 (6H, *s*, C-25, C-26), 1.30 (6H, *s*, C-29, C-30), 4.55 (1H, *m*, $W_{1/2}$ = 10 Hz, C-6). MS (70eV), *m/e* (rel. int.): 444 (M^+, 4), 426 (3), 411 (1), 207 (21), 191 (16), 189 (52), 149 (34), 59 (100). Attempts to acetylate and oxidize **1a** under mild conditions were unsuccessful, giving unchanged starting material.

6β, 22-*diacetoxyhopane* (**1b**). Acetylation of **1a** by refluxing for 30 min. with isopropenyl acetate and *p*-toluenesulfonic acid as catalyst gave (**1b**): mp 146–150° (MeOH). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720, 1260 (OAc). PMR δ: 0.79 (3H, *s*, C-28), 0.94 (6H, *s*, C-24, C-27), 1.42 (3H, *s*, C-29 or C-30), 1.50 (3H, *s*, C-30 or C-29), 0.99, 1.15, 1.19 (9H, *s*, C-23, C-25, C-26 not respectively), 1.95 (3H, *s*, OAc), 2.02 (3H, *s*, OAc), 5.53 (1H, *m*, $W_{1/2}$ = 10 Hz, C-6).

6β,22-*Dihydroxyhopane* (**1a**) from *zeorin* (**1d**). Zeorin was oxidized with CrO_3–AcOH–H_2O to zeorinone (**1c**) [4] which was reduced with $LiAlH_4$ to epizeorin (**1a**) [5], identical to the natural product (**1a**) (mmp, TLC, IR, PMR).

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6-METHOXYBENZOXAZOLINONE AND TRITERPENOIDS FROM ROOTS OF *SCOPARIA DULCIS*

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Key Word Index—*Scoparia dulcis*; Scrophulariaceae; 6-methoxybenzoxazolinone; betulinic acid; ifflaionic acid.

INTRODUCTION

Scoparia dulcis L. (Scrophulariaceae), known as a folk-medicinal plant, has been used as a cure for diabetes mellitus in India and for hypertension in Taiwan [1]. To date, only common constituents; sitosterol, hexacosanol, D-mannitol, tritriacontane [2,3] and some unidentified compounds: dulciol, scropanol, dulciolone [3] and an alkaloid [4] have been isolated from this plant. The biologically active substance has been found, although the Indian drug "amellin" [5], which was obtained from the fresh plant, has been used as the antidiabetic principle [6]. The present report deals with the isolation of three compounds; 6-methoxybenzoxazolinone, betulinic acid and ifflaionic acid from the plant material which was collected at Hsinchu, Taiwan and identified at the Herbarium of National Taiwan University.

RESULTS AND DISCUSSIONS

Dried powdered root of *Scoparia dulcis* was extracted with Et_2O. Subsequent separation of the Et_2O extract was achieved by repeated column chromatography using Si gel to give three crystalline compounds designated as compound A, B and C respectively.

Compound A (**1**), colourless needles from Me_2CO–petrol, mp 157–8°, IR ν_{max} cm^{-1}: 3350–3000 (N-H), 1770 (C=O, carbamate), 1620, 1490 (C=C, aromatic) and 1300 (C–N), UV λ_{max}nm (log ε): 209(4.01), 232(4.05) and 290 (3.80), had the molecular formula $C_8H_7NO_3$, as indicated by its molecular ion peak at *m/e* 165 and the elemental analysis. The NMR spectrum of compound A in $(CD_3)_2CO$ showed a three-protons singlet at 3.75 ppm corresponding to a methoxy group, and three aromatic protons at 6.62 (*dd*, J_1 = 9, J_2 = 3 Hz), 6.8 (*d*, *J* = 3 Hz) and 6.93 ppm (*d*, *J* = 9 Hz) indicating the presence of the 1,2,4-trisubstituted benzene ring. Compound A could be acetylated with Ac_2O–Py to give an acetyl derivative (**2**), mp 151–2° and methylated with CH_2N_2 to give a N-methyl derivative (**3**), mp 97–9°. More detailed NMR studies led to the structure of **1** as 6-methoxybenzoxazolinone which was isolated from maize and wheat plants [7]. This identification was confirmed by direct compari-