mp 187–188°; λ_{max}^{EtOH} 358 nm (ε, 37 980). composé **3** (= isosuccutalal) rendement (0.014%). Liquid; $[\alpha]_D$ −142° (c, 0.5 dans $CHCl_3$); ν_{max} 2710, 1720, 1680 (aldéhydes), 1650, 840 cm^{-1} (double liaison trisubstituée); RMN (90 mHz, $CDCl_3$) 0.93 et 0.98 (chaque, *s*, 3H, 1.59 et 1.67 (*s*, large, chaque 3H, diméthyles allilıques, 1.77 (*m*, H-16), 2.2–2.3 (*m*, H-5), 2.4–2.6 (*m*, H-6), 3.22 (*s*, large, H-8), 5.02 (*t*, large, H-17) et 7.04 (*q*, *J* − 5 Hz, H-7).

Reduction du composé **1** *avec* $LiAlH_4$ donnant un diol pur mp 91–92°; $[\alpha]_D$ + 15° (*c*, 0.66 dans $CHCl_3$); ν_{max} 3300, 1035, 990 cm^{-1} (OH), 1660, 830 cm^{-1} (double liason trisubstituée); δ 0.78 et 0.88 (chaque *s*, 3H), 1.58 et 1.68 (chaque *s*, large 3H), 2.0 (*m*, 5H), 3.16 (*s*, large, 2H, OH), 3.5–4.5 (*m*, 4H), 5 03 (*t*, large, 1H), 5.78 ppm (*m*, 1H).

Lactonization du composé **2**. avec 2NNaOH (2 ml) à 100° pendant 1 hr est chromatographié CM préparative fourni un γ-lactone en petite quantité: ν_{max} 1760 cm^{-1}, δ 0.84 (*s*, 6H), 1.58 et 1.66 (chaque *s*, large, 3H, diméthyle allilique), 3.90 et 4.34 (chaque *t*, *J* = 9 Hz, 2H) et 6.84 ppm (*m*, 1H).

Transformation du composé **2** *au composé* **3**. L'aldéhyde **1** est chauffée avec AcOEt et H_2SO_4 concentré (80:1) pendant 30 min reflux sous azote. Après refroidissement le résidue est chromatographié CM préparative (*n*-héxane–AcOEt, 4:1) donnant un aldéhyde. Les spectres des UV, IR et SM sont identique au ceux du composé **3**.

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ISOMOTIOL, A NEW TRITERPENE FROM *STRYCHNOS POTATORUM*

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Key Word Index—*Strychnos potatorum*; Loganiaceae, pentacyclic triterpene, new fernane derivative; sterols

Abstract—Isomotiol (fern-8-en-3β-ol) was isolated from the leaves of *Strychnos potatorum*; it was not known previously as a natural product, but it has been obtained by acidic isomerization of compounds with a fern-7-ene or a fern-9(11)-ene skeleton. From the leaves and the bark mixtures of sitosterol, stigmasterol and campesterol were also isolated.

INTRODUCTION

Strychnos potatorum. (Loganiaceae) is a much-branched medium sized tree distributed in Central and South India, Sri Lanka and Burma, and also in East and northern South Africa [1]. In India the various parts of the plant are used in both the Ayurvedic and Yunani systems of medicine for a number of ailments [2]. The occurrence of diaboline as the main alkaloid in the seeds, leaves and bark of *S. potatorum* has been reported [3]. Pharmacological studies made on the alkaloids indicated a marked hypotensive and convulsive activity [4]. The seeds have been found to contain triterpenoids of the amyrin and lupeol series and sitosterol and stigmasterol [5]. The fatty acid composition of the seed oil has also been reported [6]. We now report the structure elucidation of a new triterpenoid, isolated from the leaves of *S. potatorum*.

RESULTS

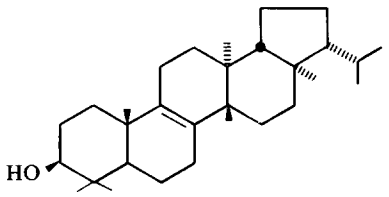
The isolated triterpenoid (**1**) mp 197–199°, $[\alpha]_D^{20°}$ + 17° had the formula $C_{30}H_{50}O$. Its IR spectrum had only a significant band at 3500 cm^{-1} for a hydroxyl group; no absorption was present in its UV spectrum. The NMR spectrum showed a complex pattern of six tertiary methyls and two secondary methyls, and a quartet (*J* = 10.5 and 4.5 Hz) at δ3.25, attributed to a CHOH proton, whereas no vinyl proton was present. Conclusive information on the skeleton was given by the MS which showed strong peaks (see

Experimental) characteristic of a fernane or arborane skeleton [7–13].

Compound **1** gave an acetyl derivative mp 226–227°, and a ketone, mp 210–211° by Jones oxidation at 0°. The above data and results were consistent with fern-8-en-3β-ol (**1**). Both fern-7-en-3β-ol (motiol) and fern-9(11)-en-3β-ol (fernenol) have been reported as natural products [10, 14, 15], while fern-8-en-3β-ol (**1**) has been obtained in laboratory only by isomerization of motiol [14] (and hence named isomotiol) and by a two-step transformation of arundoin [9–10]. Physical constants reported for synthetic isomotiol were in good agreement with those of our product. Therefore, we prepared synthetic isomotiol from a sample of natural motiol; direct comparison with our natural product proved the identity (mmp, crossed injection on GLC, NMR and MS). The same identity was confirmed by the acetate and the ketone which were identical by the above criteria to the corresponding synthetic standards.

Comparison of the NMR spectra (100 MHz, expanded run in the δ0.70–1.20 region) showed identical patterns for the methyl groups in natural and synthetic isomotiol, while motiol and fernenol gave quite different patterns.

Two minor discrepancies were observed; we found $[\alpha]_D^{20°}$ + 17° for natural isomotiol (reported [10] + 24.5°), and C<u>H</u>OH at δ3.25 in both natural and synthetic isomotiol (reported [10] δ3.62). Sterol fractions isolated from the leaves and the bark were found by GLC to contain the ubiquitous sitosterol, stigmasterol and campesterol (see Experimental).



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EXPERIMENTAL

Extraction of the leaves. Air-dried leaves (850 g) were powdered and extracted (Soxhlet) with petrol (bp 60–80°). Evapn of the solvent under red. pres. gave a dark green mass (40 g) which was chromatographed over Al_2O_3 (S. Merck, according to Brockmann, 400 g): petrol eluted 1.6 g of a crude product, which was rechromatographed over Al_2O_3 and yielded isomotiol (310 mg), homogeneous on TLC and GLC, violet colour on Liebermann–Burchard test. Elution of the column with petrol–C_6H_6 (9:1) gave a mixture of sterols (1.43 g, green colour on Liebermann–Burchard test). GLC proved the occurrence of campesterol (24%), stigmasterol (43%) and sitosterol (33%) (crossed injection with a mixture of the three sterols). Pure isomotiol, mp 197–199° (from MeOH), reported 195–197° [9]. 199–200° [10]; $[\alpha]_D^{20°}$ + 17° ($CHCl_3$; *c*, 0.32), reported [10] + 24.5°. IR ν_{max}^{Nujol} cm^{-1}. 3500. NMR (100 MHz, $CDCl_3$): δ3.25 (*q*, *J* = 10.5 and 4.5 Hz, 3α-H). MS (70 eV) *m/e* (rel. int.): 426 (M^+, 48), 411 (100), 393 (27), 273 (17), 259 (96), 247 (16), 241 (48), 189 (29). Found: C, 84.59; H, 11.96. Calc. for $C_{30}H_{50}O$: C, 84.44; H, 11 81%. Acetylation of **1** with Ac_2O in Py at room temp. gave an acetate, mp 226–227° (from Me_2CO), reported [10] 226–227° for isomotiyl acetate. Jones oxidation of **1** at 0° gave a ketone, mp 210–211° (from EtOH), reported 200–202° [16], 209 [14], 214–216° [17]. The possibility that chromatography on Al_2O_3 could have isomerized motiol or fernenol to isomotiol was ruled out, as it was checked that both products were recovered unchanged from percolation over this and other commercial aluminium oxides.

Synthetic isomotiol. A sample of motiol was isomerized to isomotiol as reported [14]. The product, its acetate and its ketone, had the identical mp reported here for natural isomotiol and its derivatives. Mmp showed no depression. GLC (crossed injections with natural isomotiol and derivatives) proved the identity of the products.

Extraction of the bark. Air-dried bark (2 kg) was powdered and extracted with petrol. The extract (20 g) was chromatographed on Al_2O_3. C_6H_6 and then C_6H_6–$CHCl_3$ (39 1) eluted a mixture of sterols (550 mg, green colour on Liebermann–Burchard test), which was examined by GLC and found to contain campesterol (20%), stigmasterol (25%) and sitosterol (55%).

GLC analyses. Analyses of the triterpenes and sterols were performed on a FID instrument, N_2 flow rate 20 ml/min, column packed with 3% OV-1 on Varaport 30 80–100 mesh, 1.5 m × 3 mm, isothermal 250°

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