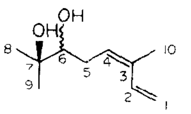
p-toluenesulfonic acid afforded the acetonide, **2** The absolute stereochemistry could not be determined.



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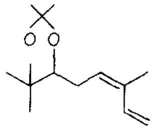

2

EXPERIMENTAL

The air-dried plant material (from the Garden of the Botanic Research Institute, Pretoria, voucher 81/247) was extracted with Et_2O-petrol (1 2), and the resulting extracts were separated by CC (Si gel) and further by repeated TLC (Si gel) Known compounds were identified by comparing the ^1H NMR spectra with those of authentic material The roots (280 g) gave 10 mg *ent*-kaurenic acid, 10 mg *ent*-kauren-19-al, 6 mg friedelin, 5 mg euphone and further triterpenes, while the aerial parts (50 g) gave 20 mg squalene and 4 mg **1**, colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3640, 3590 (OH), MS *m/z* (rel int) 170 $[M]^+$ (1), 152 120 $[M - H_2O]^+$ (16) ($C_{10}H_{16}O$), 137 $[152 - Me]^+$ (3), 119 $[137 - H_2O]^+$ (2), 82 $[C_6H_{10}]^+$ (58), 59 $[Me_2C - OH]^+$ (100) To 2 mg **1** in 1 ml Me_2CO 10 mg *p*-toluenesulfonic acid was added After 12 hr standing at 20° TLC (Et_2O-petrol, 1 10) afforded 2 mg **2**, colourless oil ^1H NMR see Table 1

Acknowledgements—We thank Dr B de Winter and Miss M Welman, Botanic Research Institute, Pretoria, for their help during plant collection and E T thanks the UNESCO project BUL 77/009 for the stipendium

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PIPTOCARPHOL ESTERS FROM *PIPTOCARPHA OPACA*

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Key Word Index—*Piptocarpha opaca*, Compositae, Vernonieae, piptocarphol esters; sesquiterpene lactones

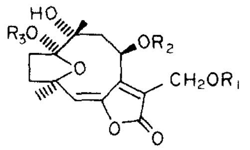
Abstract—Isolation of two new piptocarphol esters from *Piptocarpha opaca* is reported.

INTRODUCTION

Piptocarpha (Compositae, Vernonieae) is a widespread neotropical genus of *ca* 45 species [1] Six sesquiterpene lactones **1a**–**1f*** (piptocarphins A–F) which are derivatives of the unknown piptocarphol **1i** have been isolated from *P chontalensis* Pall [2] and flavonoids and triterpenes, but no lactones, were reported from *P. oblonga* (Gardn.) Baker [3] We now describe isolation of small amounts of two new lactones **1g** and **1h** from the Amazonian species *P opaca* Baker Other constituents were vanillin, various triterpenes, plant sterols and their glucosides

RESULTS AND DISCUSSION

The new lactones occurred as a mixture from which a small quantity of **1h** was isolated in relatively pure form.



1a R_1 = Ac , R_2 = MeAcr , R_3 = H
1b R_1 = Ac , R_2 = Tigl , R_3 = H
1c R_1 = H , R_2 = MeAcr , R_3 = H
1d R_1 = Ac , R_2 = R_3 = H
1e R_1 = Ac , R_2 = MeAcr , R_3 = Et
1f R_1 = Et, R_2 = MeAcr, R_3 = H
1g R_1 = Tigl , R_2 = R_3 = H
1h R_1 = MeAcr , R_2 = R_3 = H
1i R_1 = R_2 = R_3 = H

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*Lactones **1e** and **1f** may have been artefacts of the isolation procedure [2]

Table 1 ^{1}H NMR spectra*

	1g	**1h**†
H-2a	2 43 *dt* (7, 12)	—
H-2b	2 16 *dd* (12, 7)	—
H-3a H-3b	2 07–1 78 *c*	—
H-5	5 87	5 89
H-8	5 48 *br d* (11)	—
H-9a	2 51 *dd* (15, 11)	—
H-9b	2 07–1 78 *c*	—
H-13‡	4 96	4 99
H-14§	1.21 *br*	—
H-15§	1 66 *br*	—
H-3′	6.90 *br q* (7)	6 15 *br*, 5 63 *br*
H-4′§	1 81 *br d* (7)	1 95 *br*
H-5′§	1 84 *br*	—

*Run in $CDCl_3$ at 270 MHz Frequencies in Hz Unmarked signals are singlets.

†Signals identical with those listed for **1g** except where indicated

‡Intensity of two protons, center of AB system

§Intensity of three protons

^{1}H NMR spectra are listed in Table 1 Comparison of chemical shifts and coupling constants with those of the piptocarphins [2] showed that the free secondary hydroxyl group of the new compounds was located at C-8 and that the ester function was on C-13. The relative stereochemistry at C-1 and C-10 shown in the formulae was assigned [2] on the basis of the strong intramolecular hydrogen bonding between the C-1 and C-10 hydroxyl groups which we have also found in **1g** and **1h** The C-10 stereochemistry, which is the same as that of the rolandrolides [4], differs from that postulated earlier [5–9] for similar compounds from *Vernonia* and related species although the correct C-10 stereochemistry was depicted in some other papers [10, 11].

The meagre evidence available at this time suggests that 7,11-unsaturated-13-acylated germacranolides, characteristic of certain sections of the large genus *Vernonia* and some species of allied genera, may also be typical of *Piptocarpha*. Study of other members of the genus is clearly desirable

EXPERIMENTAL

Above-ground parts of *P opaca* Baker, wt 4 5 kg, collected on 11 August 1978 by Dr S McDaniel and Mr Manuel Rimachi Y on the Río Momon (tributary of the Río Nanay) below Balcón near Iquitos, Loreto, Peru (voucher McDaniel and Rimachi 21982 on deposit in the Herbarium of Mississippi State University), was extracted with $CHCl_3$ and worked-up as usual [12] The crude gum (16 5 g) was preadsorbed on 30 g silicic acid (Mallinckrodt, 100 mesh) and chromatographed over 300 g silicic acid set in C_6H_6, 250 ml portions of eluate being collected as follows 1–8 (C_6H_6, 2 l), 9–16 (C_6H_6–$CHCl_3$, 1 1, 2 l), 17–24 ($CHCl_3$, 2 l), 25–32 ($CHCl_3$–MeOH, 99 1, 2 l), 33–36 ($CHCl_3$–MeOH, 49 1, 1 l), 37–40 ($CHCl_3$–MeOH, 19 1, 1 l) and 41–48 ($CHCl_3$–MeOH, 9 1, 2 l)

Purification of fractions 7, 10 and 12 gave a mixture of lupeol, α-amyrin and β-amyrin (160 mg), a mixture of stigmasterol and β-sitosterol (22 mg) and a mixture of stigmasterone and β-sitosterone (12 mg) Fractions 20 and 21, upon purification and crystallization, gave 130 mg vanillin Purification of fraction 29 by TLC ($CHCl_3$–MeOH–EtOAc, 9 0 25 0 75) and further TLC (EtOAc–hexane, 3 2, developed twice) gave two bands The upper band (36 mg) was a 7 3 mixture of **1g** and **1h** (^{1}H NMR analysis) The lower band (45 mg) was a 1 1 mixture of **1g** and **1h** Further purification afforded a mixture of **1g** and **1h** and 6 mg 90% pure **1h** which had IR bands ($CHCl_3$) at 3470, 3340, 1760, 1715 and 1650 cm^{-1}, MS (CI) *m/z* 395 (MH$^+$ of **1g**), 381 (MH$^+$ of **1h**), 377 (MH$^+$ of **1g** $-$ H_2O, 58%), 363 (MH$^+$ of **1h** $-$ H_2O, 100%), 295 (MH$^+$ $-$ C_5H_8O or C_4H_6O, 15%), 277 (32%) and 259 (12%) ^{1}H NMR spectra are listed in Table 1 Fraction 46 on trituration with MeOH gave 45 mg of a mixture of stigmasterol and sitosterol β-D-glucosides

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