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A MONOTERPENE FROM *ASTER BAKERANUS**

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Key Word Index—*Aster bakeranus*, Compositae, monoterpene.

Abstract—The aerial parts of *Aster bakeranus* afforded 6,7-dihydroxy-6,7-dihydro-*cis*-ocimene.

So far chemical investigations of representatives of the large genus *Aster* (Compositae, tribe Astereae) have shown that, in addition to acetylenic compounds [1], umbelliferone derivatives [2] and a variety of other constituents are present We now have studied a South African species, *Aster bakeranus* Burtt Davy ex C A Smith The roots afforded only *ent*-kaurenic acid and the corresponding aldehyde, γ-humulene, friedelin, euphone and some further triterpenes which have not been identified. The aerial parts contained squalene and a monoterpene diol; its structure followed from the spectroscopic data, especially from the ^{1}H NMR spectrum which displayed signals for an olefinic methyl (δ1.87 *dt*, J = 1, 1 Hz), two tertiary methyls (1.23 *s* and 1.18 *s*), a vinylic end group (6.75 *ddd*, 5 26 *br d* and 5.14 *ddd*) and an olefinic proton (5.48 *br t*). Furthermore, a lowfield double doublet at δ 3.43 and a broadened triplet at 2.35 were visible. These data indicated the presence of a monoterpene with two conjugated double bonds. The chemical shifts of the olefinic signals corresponded to those of *cis*-ocimene. In agreement with the IR spectrum, the double doublet at δ 3.43 was assigned as a proton adjacent to a hydroxyl group. As the chemical shifts of the singlets at δ1.23 and 1.18 required an oxygen function, the presence of the diol, **1**, was very likely Accordingly, reaction with acetone and

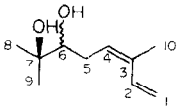
Table 1 ^{1}H NMR spectral data of **1** and **2** (400 MHz, $CDCl_3$, TMS as int standard)

	1	**2**
H-1*t*	5 26 *br d*	5 25 *br d*
H-1*c*	5 14 *ddd*	5 14 *ddd*
H-2	6 75 *ddd*	6.75 *ddd*
H-4	5 48 *br t*	5.48 *br t*
H-5	2 35 *br t*	2 43 *br dt* 2.37 *br dt*
H-6	3 43 *dd*	3 75 *dd*
H-8	1.18 *s*	1 10 *s*
H-9	1 23 *s*	1.22 *s*
H-10	1 87 *dt*	1 84 *dt*
Acetonide	—	1 32 *s*
Me	—	1 41 *s*

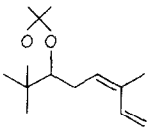
J(Hz) 1*t*, 2 = 17, 1*c*, 2 = 11, 1*t*, 1*c* = 1*c*, 4 = 2, 4 = 4, 10 = 5, 10 ~ 1, 4, 5 = 5, 6 = 7 5, 5′, 6 = 6 (compound **2** 4, 5 = 8, 4, 5′ = 6)

*Part 468 in the series "Naturally Occurring Terpene Derivatives" For Part 467 see Omar, A A., Sarg, T. M, Khafagy, S. M, Ibrahim, Y E, Zdero, C. and Bohlmann, F (1983) *Phytochemistry* **22**, 779

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



1



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.

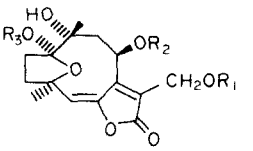
INTRODUCTION

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.

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



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