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SESQUITERPENE LACTONES FROM *OLDENBURGIA ARBUSCULA* AND *PLEIOTAXIS RUGOSA*

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Key Word Index—*Oldenburgia arbuscula*; *Pleiotaxis rugosa*; Compositae, sesquiterpene lactones; guaianolides; bisabolene derivatives.

Abstract—The aerial parts of *Oldenburgia arbuscula* gave desacylcynaropicrin and three bisabolene derivatives while from *Pleiotaxis rugosa* in addition to janerin and 19-desoxyjanerin further guaianolides were isolated, including a new one. The chemistry of the *Oldenburgia* species supports its placement in the Mutisieae, subtribe Gochnatiinae, but that of *Pleiotaxis* may indicate that this genus is better placed in the Cynareae.

The small South African genus *Oldenburgia* (Compositae, tribe Mutisieae) has always been placed in the subtribe Gochnatiinae [1]. As nothing was known on characteristic constituents we have investigated *O. arbuscula* E. Mey., a large woody shrub with leather like leaves, thick branches and large flower heads at the end of them. While the roots gave no typical compounds [2], the aerial parts afforded the guaianolide **1** [3] and the bisabolene derivatives **8** [4], **9** [5] and **10** [6]. The isolation of these compounds agrees with the placement of *Oldenburgia*, as derivatives of zaluzanin C are present in several genera of the subtribe Gochnatiinae (*Dicoma* [7], *Cnicothamnus* [8], *Pleiotaxis* [9], *Gochnatia* [6, 8, 10–12], *Macroclinium* [13], *Pertya* [14], *Diaspananthus* [15]). Furthermore, bisabolene derivatives such as **6**–**10** are reported from *Gochnatia* [6, 10] and *Onoseris* [16]. A further species, *O. onoserioides* (H.B.K.) B. L. Robinson, also gave bisabolene derivatives (see Experimental).

The genus *Pleiotaxis* with 26 species in tropical Africa is also placed in the subtribe Gochnatiinae next to *Oldenburgia* [17], however, the position is somewhat in doubt. *Pleiotaxis rugosa* O. Hoffm. has been investigated previously [9] and the chemistry, especially the isolated acetylenes, indicated a relatioship to members of the tribe Cynareae. A reinvestigation of the polar parts gave, in addition to two guaianolides isolated previously (**4** and **5**) [17], four further ones, the known guaianolides **2** [18], **3** [19] and **7** [20] as well as a new one, the isobutyrate **6**. The structure of the latter clearly followed from its ^{1}H NMR spectrum (see Experimental) which of course was very close to that of **4**. The nature of the ester group could be easily deduced from the typical signals (2.61 *qq*, 1.22 *d* and 1.21 *d*).

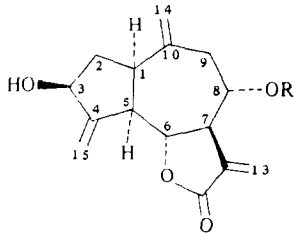
The new results give no clear decision for the placement of *Pleiotaxis*. The presence of desacylcynaropicrin derivatives shows relationships to *Oldenburgia* and *Gochnatia*, while the acetylenic compounds so far have not been observed in any member of the Mutisieae.

EXPERIMENTAL

The air-dried plant material was extracted and the extracts obtained were separated as reported previously [21]. The aerial parts of *Oldenburgia arbuscula* (680 g, collected in September 1986 near Grahamstown, R.S.A., voucher 86/66, deposited in the Herbarium of Rhodes University, Grahamstown) gave by TLC 10 mg **1**, 20 mg **8**, 15 mg **9** and 10 mg **10**.

The aerial parts of *Onoseris onoserioides* (1 kg collected and investigated by V. Castro, University of Costa Rica, voucher 102898) gave by CC and TLC 50 mg lupeol, 30 mg stigmasterol, 20 mg α-humulene, 20 mg β-sesquiphellandrene, 30 mg α-zingiberene, 50 mg α-curcumene and 30 mg 2-hydroxy-α-curcumene.

The aerial parts of *Pleiotaxis rugosa* (380 g, from the garden of the Botanical Research Institute, Pretoria, R.S.A.) gave by CC in addition to triterpenes and acetylenes [9] two polar fractions (1, Et_2O; 2, Et_2O–MeOH, 9:2). Fraction 2 gave 2 g **5** while HPLC (RP 8, MeOH–H_2O, 7:3, flow rate 3 ml/min) of fraction 1 gave 20 mg **2** (R_t 4.1 min) and three mixtures (1/1 R_t 0.7 min, 1/2 R_t 0.9 min, 1/3 R_t 2.7 min). TLC ($CHCl_3$–C_6H_6–Et_2O–MeOH, 30:30:30:1 = T1) of fraction 1/1 gave 10 mg **7** (R_f 0.50) and 20 mg **5** (R_f 0.35). TLC of 1/2 (T1) gave 10 mg **3** (R_f 0.35) and TLC of 1/3 (T1) 60 mg **4** and 5 mg **6** (R_f 0.65); colourless oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1760 (γ-lactone), 1730 (CO_2R); MS *m/z* (rel. int.): 260.105 $[M-RCO_2H]^+$ (6) (calc. for $C_{15}H_{16}O_4$: 260.105), 242 $[260-H_2O]^+$ (2), 230 $[260-CH_2O]^+$ (2.5), 148 (6), 71 $[C_3H_7CO]^+$ (100); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.96 (*br dd*, H-3), 4.63 (*dd*, H-6), 3.09 (*tt*, H-7), 5.11 (*ddd*, H-8), 2.75 and 2.35 (*dd*, H-9), 6.20 and 5.58 (*d*, H-13), 5.17 and 4.92 (*br s*, H-14), 1.98 (*br s*, H-15), 2.61 (*qq*, H-17), 1.22 and 1.21 (*d*, H-18, H-19); *J* [Hz]: 2,3 = 7 and 4; 5,6 = 11; 6,7 = 7,8 = 9; 7,13 = 3.5; 7,13′ = 3; 8,9 = 5; 8,9′ = 3.5; 9,9′ = 14; 17,18 = 17,19 = 7.



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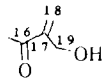
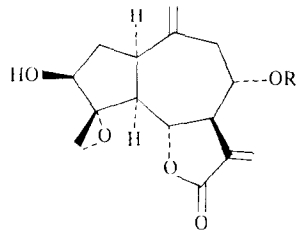
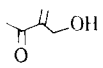
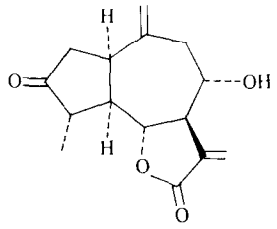
3 R = 



4 R = Meacr **5** R = 

6 R = *i*Bu



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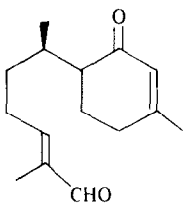

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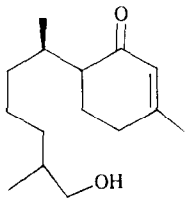

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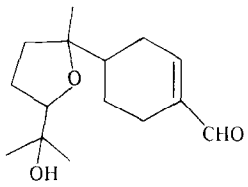

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