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SESQUITERPENE LACTONES AND OTHER CONSTITUENTS OF *CENTAUREA NICAENSIS*

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Key Word Index—*Centaurea nicaensis*; Compositae; Cardueae; sesquiterpene lactones; germacradienolides; elemadienolide.

Abstract—Aerial parts of *Centaurea nicaensis* furnished germacradienolides, commonly found in *Centaurea* species, as well as a new elemadienolide which was identified as (5*R*,6*R*,7*R*,8*S*,10*S*,11*S*)-15-hydroxy-8-(1,2-dihydroxyethyl)-acryloxyelema-1,3-dien-6,12-olide.

INTRODUCTION

In continuation of our study of *Centaurea* species found in Sicily [1–4] we examined *Centaurea nicaensis* All. Isolated from the aerial parts were cnicin (**1a**), the main sesquiterpene lactone constituent, onopordopicrin (**1b**), **2a** previously found in *Centaurea pullata* [5], dihydroamarin **2b** [6], amarin (**1c**) [6] admixed with **2b**, and the new elemadienolide **3**. Also present was a mixture of lappaol A (**4**) and its isomer of uncertain structure found previously in *C. sphaerocephala* ssp. *polyacantha* [7] and *C. napifolia* [4]. A previous article mentions isolation from *C. nicaencis* of an unknown lactone $C_{20}H_{28}O_5$ from *C. nicaensis* but supplies no further details [8].

The structure of the new elemadienolide (**3**) was evident from the mass spectrum and the ^{1}H NMR spectrum (see Experimental). Spin decoupling allowed identification of all signals; the value of $J_{7,11}$ (12 Hz) showed that the methyl group on C-11 was α-orientated.

EXPERIMENTAL

Above-ground parts (530 g) of *C. nicaensis* collected in June 1992 near Campobello di Marza (TP), Sicily (voucher on deposit in the herbarium of the Palermo botanical garden) were extracted with $CHCl_3$. Work-up in the usual fashion [9] gave 65 g of crude gum which was absorbed on 100 g of silica gel (Merck No. 7734, deactivated with 15% H_2O) and subjected to CC over 1 kg of the same adsorbent, 150 ml fractions being collected as follows: frs 1–2 (petrol), frs 3–14 (petrol:EtOAc, 9:1), frs 15–22 (petrol:EtOAc, 4:1), frs 23–37 (petrol:EtOAc, 7:3), frs 38–44 (petrol:EtOAc 3:2), frs 45–52 (petrol:EtOAc, 2:3), frs 53–61 (petrol:EtOAc, 3:7), 62–71 (petrol:EtOAc, 1:4), 72–93 (EtOAc), frs 94–120 (EtOAc:MeOH, 9:1).

Frs 55–67 were rechromatographed over silica gel ($CHCl_3$:MeOH, 49:1) to give two main fractions. The first was purified by radial chromatography ($CHCl_3$:MeOH, 49:1) to give 6 mg of impure and 19 mg of pure **1b** identified by ^{1}H NMR spectrometry. The second fraction, containing three components, was subjected to radial chromatography ($CHCl_3$:MeOH, 97:3) to give 5 mg of the mixture of lappaol A and its isomer, 18 mg of **2b** and 6 mg of a mixture of **1c** and **2b**.

Frs 62–92 were subjected to CC over silica gel ($CHCl_3$:MeOH, 49:1) to give 6 mg of **3** and 192 mg of **2a**. Frs 93–100 of the original chromatogram were recrystallized from EtOAc to give 1 g of **1a** identified by comparison with an authentic sample.

(5R,6R,7R,8S,10S,11S-15-*Hydroxy*-8-(1,2-*dihydroxyethyl*)-*acryloxyelema*-1,3-*dien*-6,12-*olide* (**3**). Gum; MS PCI (NH_3) *m/z* (rel. int.): 399 $[M + NH_4]^+$ (100); ^{1}H NMR ($CDCl_3$, 500 MHz): δ6.36 (*brs*, H-5'a), 6.05 (*brs*, H-5'b), 5.77 (*dd*, *J* = 18, 11 Hz, H-1), 5.41 (*s*, H-3a), 5.20 (*ddd*, *J* = 11, 11, 4 Hz, H-8), 5.06 (*d*, *J* = 11 Hz, H-2 cis), 5.01 (*d*, *J* = 18 Hz, H-2 *trans*), 4.98 (*s*, H-3b), 4.62 (*dd*, *J* = 7, 3.5 Hz, H-3'), 4.26 (*dd*, *J* = 11.5, 11 Hz, H-6), 4.09 (*br d*, *J* = 13.5 Hz, H-15a), 3.99 (*br d J* = 13.5 Hz, H-15b), 3.85 (*dd*, *J* = 11, 3.5 Hz, H-4'a), 3.60 (*dd*, *J* = 11, 7 Hz, H-4'b), 2.64 (*dq*, *J* = 12, 7 Hz, H-11), 2.46 (*d*, *J* = 11.5 Hz, H-5), 2.02 (*ddd*, *J* = 12, 11, 11 Hz, H-7), 1.93 (*dd*, *J* = 13.5, 4 Hz, H-9a), 1.72 (*dd*, *J* = 13.5, 11.5 Hz, H-9b), 1.24 (*d*, 3H, *J* = 7 Hz, H-13), 1.18 (*s*, 3H, H-14).

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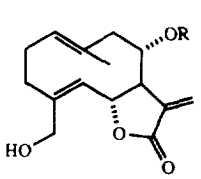

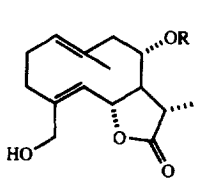

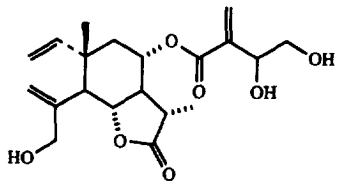

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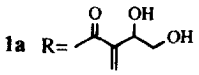

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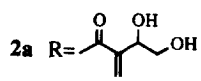

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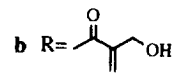

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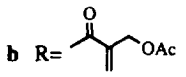

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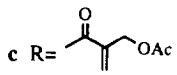

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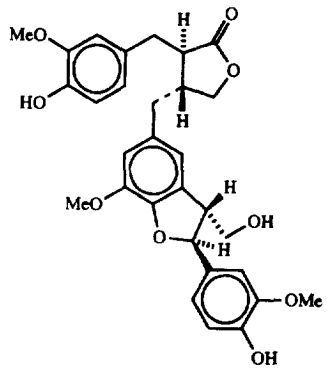

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