C-3), 39 0 (*s*, C-5), 40 1 (*t*, C-8), 59 3 (*d*, C-6), 62 5 (*d*, C-2), 77 1 (*d*, C-7), 85 1 (*s*, C-11), 133 4 (*d*, C-1), 142 1 (*s*, C-10), 197 1 (*s*, C-9)

Dehydration of kanshone A with phosphorus oxychloride To a stirring soln of kanshone A (**1**) (10 mg) in pyridine (1 ml), $POCl_3$ (0 04 ml) was added and the reaction was continued for 30 min at room temp The reaction was arrested by addition of ice H_2O and the mixture extracted with *n*-hexane The *n*-hexane layer was washed with H_2O, dried and chromatographed over silica gel (10 g) Elution with C_6H_6 afforded **5** as an oil, $[\alpha]_D$ −217 8° ($CHCl_3$, *c* 0 12), EIMS (direct inlet) 70 eV, *m/z* 216 $[M]^+$, 201, 173, 161, 160, 134, 119, 93, 79, 77, ^{1}H NMR (100 MHz $CDCl_3$) δ 0 92 (3H, *d*, J = 6 4 Hz, H-15), 1 08 (3H, *s*, H-14), 1 54 (3H, *s*, H-13), 2 15 (1H, *m*, H-4), 3 15 (1H, *dd*, J = 6 6 and 1 0 Hz, H-6), 4.90 (2H, *m*, H-12), 6.15 (1H, *dd*, J = 10.0 and 1.0 Hz, H-8), 6.70 (1H, *dd*, J = 10.0 and 6.5 Hz, H-7), 6.88 (1H, *t*, J = 4.0 Hz, H-1).

Hydrogenation of nardosinone followed by dehydration with phosphorus oxychloride A soln of nardosinone (**3**) (50 mg) in MeOH (5 ml) was stirred at room temp in an atmosphere of H_2 and in the presence of $Pd/CaCO_3$ (10 mg) for 1 hr After usual work-up, it yielded nardosinone diol (**4**) (50 mg), ($[\alpha]_D$-4 2° ($CHCl_3$, *c* 0 50), the ^{1}H NMR spectrum (100 MHz, $CDCl_3$) was identical to that of the reported nardosinone diol (**4**) [5]) Nardosinone diol (**4**) (20 mg) was dehydrated in the same manner as described above to afford **5**, $[\alpha]_D$-355 4° ($CHCl_3$, *c* 0 44), whose mass and ^{1}H NMR spectra were superimposable on those of **5** prepared from kanshone A (**1**)

^{13}C *NMR* (25 *MHz*, $CDCl_3$) *of nardosinone* (**3**). δ 16 0 (*q*, C-15), 22 0 (*q*, C-12), 23 7 (*q*, C-13), 25 8 (*t*, C-2 and C-3), 26 8 (*q*, C-14), 33 0 (*d*, C-4), 39 9 (*t*, C-8), 39 9 (*s*, C-5), 59 6 (*d*, C-6), 77 9 (*d*, C-7), 85 0 (*s*, C-11), 137 6 (*d*, C-1), 140 0 (*s*, C-10), 196.3 (*s*, C-9)

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EUDESMANOLIDES FROM *PICRIS ACULEATA*

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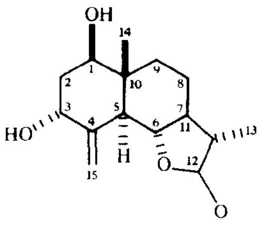
Key Word Index—*Picris aculeata*, Compositae, Lactuceae; sesquiterpene lactones, eudesmanolides, scopoletin

Abstract—Extraction of the aerial parts of *Picris aculeata* afforded two new eudesmanolides, 1-epierivanin and 1-epialkhanol.

Previous studies of two representatives of the Old World genus *Picris* (Compositae, Lactuaceae) have furnished guaianolides such as lactucin, 8-deoxylactucin, jaquilenin and glycosides thereof [1, 2]. We now report the isolation from *Picris aculeata* Vahl [syn *Helminthia aculeata* (Vahl)DC], a plant of southern Italy and central Sicily, of two new eudesmanolides 1-epierivanin (**1**) and 1-epialkhanol (**2**). Scopoletin (**3**) was also found

The structures assigned to **1** and **2** are based on the ^{1}H NMR spectra and extensive decoupling experiments (Table 1) Thus in the case of **1**, irradiation at the frequency of the H-13 methyl doublet (δ1 24) collapsed the *dq* of H-11 at δ2.35 to a doublet Irradiation at the latter frequency in turn identified a multiplet at δ1 65 as that due to H-7 Subsequent irradiation at the frequency of H-7 located H-6 as a triplet at δ4 07 and H-8α and H8β as a *dq* at δ. 1.90 and as a multiplet at δ1 50, while further irradiation at the frequencies of H-8α, β identified the signals of H-9α, β

Irradiation at the frequency of H-6 collapsed a broadened doublet at δ2 45 (H-5) to a broad singlet The broadening was shown to be due to allylic coupling to



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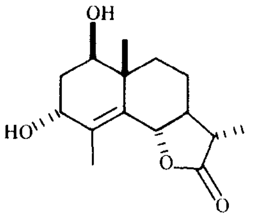

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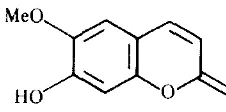

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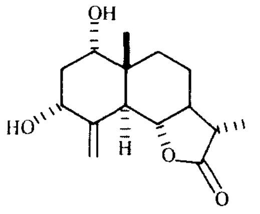

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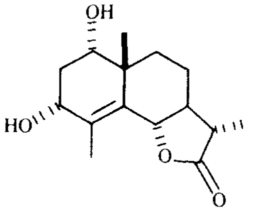

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Table 1 ^{1}H NMR spectra of compounds **1** and **2** (270 MHz, $CDCl_3$)

	1	**2**
H-1α	3 70 *dd* (11, 5)	3 79 *dd* (12, 4)
H-2α	2 14 *ddd* (14, 5, 2)	2 32 *ddd* (14, 4, 2)
H-2β	1 80 *ddd* (14, 11, 4)	1 48 *ddd* (14, 12, 3)
H-3β	4 46 *dd* (4, 2)	4 28 *dd* (3. 2)
H-5α	2 45 *br d* (11)	—
H-6β	4 07 *t* (11)	4 58 *br d* (11)
H-7α	1 65 *m*	1 78 *m*
H-8α	1 90 *dq* (12, 3)	1 90 *m*
H-8β	1 50 *m*	1 55 *qd* (12, 4)
H-9α	1 31 *m*	1 28 *m*
H-9β	2 05 *m*	2 10 *m*
H-11β	2 35 *dq* (11, 7)	2 27 *dq* (11, 7)
H-13*	1 24 *d* (7)	1 23 *d* (7)
H-14*	0 85 *s*	1 11 *s*
H-15a	5 32 *brs*	2 00 *br s**
H-15b	5 22 *brs*	

*Intensity three protons

two vinylic protons (H-15a, b) at δ5.32 and δ5 22 which were also coupled allylically to a slightly broadened *dd* at δ4 46 (H-3) The latter was coupled to two geminally coupled signals at −δ2 14 and 1 80 (H-2α and H-2β, respectively), each of which was in turn coupled to a *dd* at δ3 70 (H-1) The remaining signal, a methyl singlet at δ0 85, required attachment to a quaternary carbon (C-10) between C-1 and C-9, i e a eudesmanolide structure, while the chemical shifts of H-1 and H-3 and the empirical formula from the mass spectra required attachment of two hydroxyl groups to C-1 and C-3 The coupling constants involving H-5 through H-9 and that involving H-7 and H-11 were in accord only with the stereochemistry depicted in the formula, while the coupling constants involving H-1, H-2α, H-2β and H-3 required that the hydroxyls at C-1 and C-3 be β- and α-orientated, respectively Hence the substance was the C-1 epimer of erivanin (**4**) [3]

The structure and stereochemistry of **2**, obviously an isomer of **1** with a 4,5-double bond, were determined in a similar manner In this instance, H-6 at δ4 58 was allylically coupled to the vinylic methyl at δ2 00 Substance **2** is the C-1 epimer of alkhanol **5** [4]

EXPERIMENTAL

Above-ground parts (350 g) of *Picris aculeata* Vahl, collected in June 1986 near Bivona, Sicily (voucher specimen deposited in the herbarium of the Botanical Garden of Palermo, Sicily) were extracted with $CHCl_3$ and worked-up in the usual manner [5] The crude gum (2 g) was adsorbed on 6 g of silica gel (Merck No 7734 dactivated with 15% H_2O) and subjected to CC over 200 g of the same adsorbent, 250 ml fractions being collected as follows 1–4 (petrol), 5–8 (petrol–EtOAc 4 1), 9–12 (petrol–EtOAc 3 2), 13–16 (petrol EtOAc 2 3), 17 20 (petrol–EtOAc 1 4), 21 24 (EtOAc), 25–28 (EtOAc), 25-28 (EtOAc–MeOH 9 1)

Fr 10–17 were combined and rechromatographed over 60 g of silica gel packed in petrol Elution with petrol–FtOAc (4 1) gave a mixture of **1** and **2** which was separated by radial chromatography ($CHCl_3$–MeOH 49 1) Pure **1**, 2 mg was a colourless gum, IR ν^{CHCl_3} 3580, 3540, 1770, 1660 cm^{-1}, MS (Cl) *m/z* (rel int) 267 ($[M+1]^+$, 100), 249 (25), 231 (4), 147 (10) The ^{1}H NMR spectrum is listed in Table 1 Pure **2**, 8 mg, was also a colourless gum, IR ($CHCl_3$) 3560 3530, 1770 cm^{-1}, MS (Cl) *m/z* (rel int) 267 ($[M+1]^+$, 100), 249 (94), 231 (5) The ^{1}H NMR spectrum is listed in Table 1 Fr 13 on rechromatography over silica gel gave 10 mg of scopoletin (**3**) [6] identified by mp, ^{1}H NMR and mass spectrum

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GUAIANOLIDES FROM *SAUSSUREA CANDICANS*

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Key Word Index—*Saussurea candicans*, Compositae, Cynareae, sesquiterpene lactones, guaianolides

Abstract—*Saussurea candicans* afforded three new highly oxygenated guaianolides along with several known guaianolides The structures were elucidated by high field ^{1}H NMR spectroscopic methods.

INTRODUCTION

The large genus *Saussurea* (Compositae, tribe Cynareae) with more than 300 species [1] has been investigated chemically for acetylenes [2] as well as for sesquiterpene lactones So far lactones are reported from nine species [3–11] Guaianolides related to cynaropicrin are characteristic of this genus Some other types of lactones are also reported from *S. lappa* [4] We have now examined *S candicans* C. B Clarke Previous work on this plant led to the isolation of acetylenes [2] The results of the present investigation will be discussed in this paper

RESULTS AND DISCUSSION

The aerial parts of *S. candicans* gave arctigenin and matairesinol [12], guaianolides cynaropicrin (**1**) [5], desacyl cynaropicrin (**2**) [13], aguerin-B (**3**) [14], janerin (**4**) [14], 19-desoxychlorojanerin (**5**) [15], chlorojanerin (**6**) [16], centaurepensin (**7**) [17, 18], repdiolide triol (**8**) [19] as well as tetrol (**9**) and its 15-methoxy (**10**) and 15-acetoxy (**11**) derivatives. As the polarity of these lactones were similar and comparatively high, their separation could be achieved by repeated prep TLC and HPLC. The structure of (**9**) was deduced from ^{1}H NMR spectral data (Table 1) which indicated that this compound only differed from repdiolide triol (**8**) in the nature of the ester moiety at C-8 position Methacrylate signals were replaced by its 3-hydroxy derivative, and subsequently the methyl signal was replaced by a broad singlet at δ4.39 integrated for two protons The chemical shifts of the other protons remained as such. A similar compound with a 4-hydroxy tiglate ester function at C-8 position was reported earlier from *Centaurea imperialis* [20]. Its data were completely identical with (**9**) except an ester part. On acetylation it gave two tetra acetates (**9a**) and (**9b**) In the former case all the four hydroxyl groups acetylated and accordingly H-3, H-15, H-15′ and ester protons were shifted downfield. In (**9b**), 3-hydroxymethacrylate ester moiety hydrolysed prior to acetylation and replaced by an acetate peak at δ2 19.

The ^{1}H NMR spectral data of (**10**) and (**11**) were very similar to that of (**9**) with additional peaks for a methoxy (δ3 45) and an acetoxy (δ2 18) functions respectively. The H-15, H-15′ doublets were shifted slightly upfield at δ3.98 and 3.67 in former and shifted downfield at δ5.03 and 4.22 in the latter case Chemical shifts of the rest of the protons remain unchanged The structures of the known lactones were established by comparison with literature data or by rigorous spin decoupling experiments

EXPERIMENTAL

The air-dried aerial parts (1 kg, supplied by M/s United Chemicals and Allied Products, Calcutta, voucher deposited at RUBL, Herbarium Jaipur, India) were extracted with Et$_2$O-petrol-MeOH (1 1 1) at room temp for 24 hr Evaporation of the solvent at red pres gave a greenish semi-solid mass which was dissolved in 200 ml MeOH and left overnight at 2° After filtration, the filtrate was concd and chromatographed over silica gel and gave the following fractions Fraction 1 (petrol), 2 (petrol–Et$_2$O, 4 1), 3 (petrol–Et$_2$O, 1 1), 4 (Et$_2$O) and 5 (Et$_2$O–MeOH, 4 1) Fractions 1 and 3 gave negligible amount hence were not investigated further, while fraction 2 afforded 50 mg of phytol, 15 mg of taraxasteryl acetate, 20 mg of lupeyl acetate and 25 mg of lupeol on TLC over petrol–Et$_2$O (9 1) Fraction 4 was yellowish solid mass and separated on TLC