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GUAIANOLIDES FROM SAUSSUREA CANDICANS

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

Abstract—*Saussurea candicans* afforded three new highly oxygenated guianolides along with several known guianolides. The structures were elucidated by high field ^1H 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]. Guianolides 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

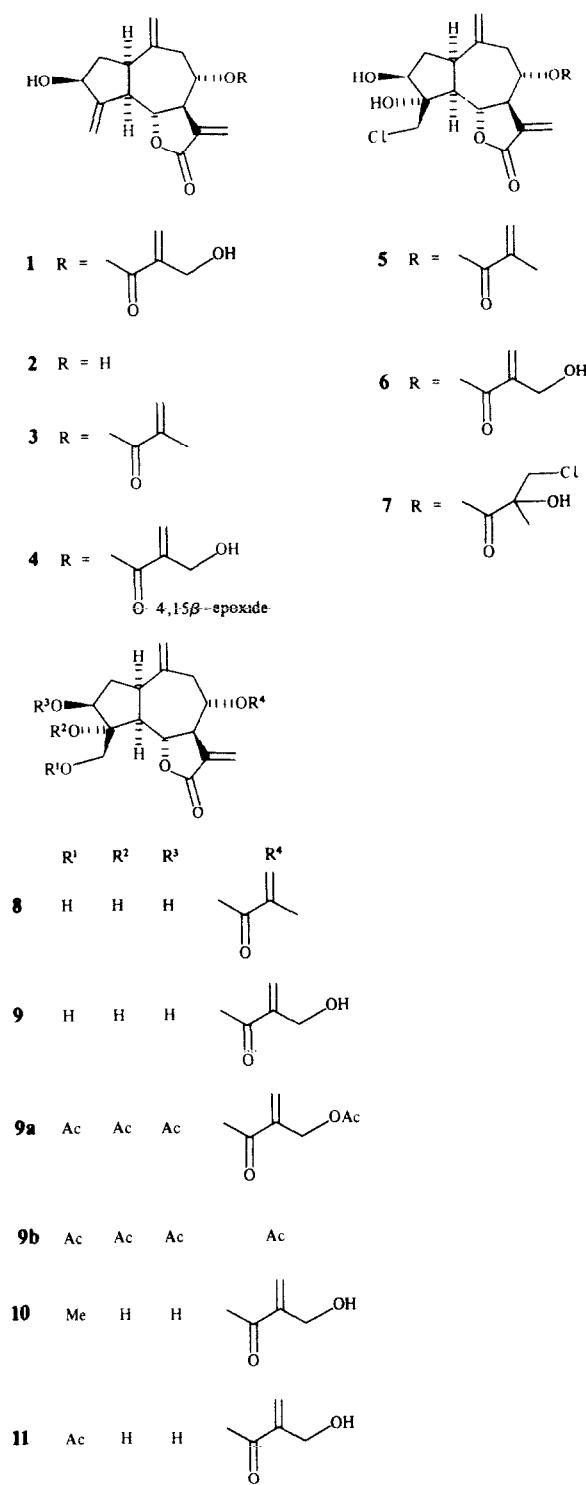
The aerial parts of *S. candicans* gave arctigenin and matairesinol [12], guianolides cynaropicrin (1) [5], de-sacyl cynaropicrin (2) [13], aguerin-B (3) [14], janerin (4) [14], 19-desoxychlorojanerin (5) [15], chlorojanerin (6) [16], centaurepensin (7) [17, 18], repdiolide triol (8) [19] as well as 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 ^1H 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 δ 4.39 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 δ 2.19.

The ^1H NMR spectral data of (10) and (11) were very similar to that of (9) with additional peaks for a methoxy (δ 3.45) and an acetoxy (δ 2.18) functions respectively. The H-15, H-15' doublets were shifted slightly upfield at δ 3.98 and 3.67 in former and shifted downfield at δ 5.03 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_2O -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_2O , 4:1), 3 (petrol- Et_2O , 1:1), 4 (Et_2O) and 5 (Et_2O -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 lupeol acetate and 25 mg of lupeol on TLC over petrol- Et_2O (9:1). Fraction 4 was yellowish solid mass and separated on TLC



($C_6\text{H}_5\text{--CH}_2\text{Cl}_2\text{--Et}_2\text{O}$, 1:1:1), yielding 20 mg of archigenin and 100 mg of a mixture of closely related halogenated guaianolides which was further separated by HPLC (RP 18, $\text{MeOH--H}_2\text{O}$, 7:3, *ca* 100 bar), giving 50 mg of chlorojanerin (6) (R_f 4.5 min), 12 mg of centaurepensin (7) (R_f 5.4 min), 10 mg of 19-desoxy-chlorojanerin (5) (R_f 8.1 min) and 15 mg of aguerin-B (3) (R_f

10.9 min). Fraction 5 was a gummy mass and on TLC over ($C_6\text{H}_5\text{--CH}_2\text{Cl}_2\text{--Et}_2\text{O}$, 1:1:3), yielded 13 mg of mataresinol (R_f 0.7), 30 mg of cynaropicrin (1) (R_f 0.65), 7 mg of a methoxy lactone (10) (R_f 0.53), 5 mg of janerin (4) (R_f 0.45), 5 mg of desacylcynaropicrin (2) (R_f 0.42), 7 mg of repdiolide triol (8) (R_f 0.40), 5 mg of an acetate (11) (R_f 0.38) and 30 mg of a tetrol (9) (R_f 0.25).

15-Deschloro-15-hydroxychlorojanerin (9). Colourless solid. IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} 3400 *br* (OH), 1770 (γ -lactone), 1715 ($\text{C}=\text{CCO}_2\text{R}$), MS (rel int) 349 128 [$M-\text{CH}_2\text{OH}$]⁺ (15) (calc for $C_{18}\text{H}_{21}\text{O}_7$ 349 128), 247 [349- RCOOH]⁺ (4), 229 [247- H_2O]⁺ (5), 201 [229- CO]⁺ (4), 85 [$\text{C}_4\text{H}_8\text{O}_2$]⁺ (28), 84 [$\text{C}_4\text{H}_4\text{O}_2$]⁺ (80), 66 [84- H_2O]⁺ (100). On heating with *p*N,N-dimethylamino pyridine and acetic anhydride at 70 for 1 hr a subsequent separation on TLC gave tetraacetates (9a) and (9b), $[\alpha]_D^{24} = 20.3$ (CHCl_3 , *c* 0.60).

15-Deschloro-15-methoxychlorojanerin (10). Colourless gum, IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} 3520 (OH), 1780 (γ -lactone), 1720 ($\text{C}=\text{CCO}_2\text{R}$), MS (rel int) 349 129 [$M-\text{CH}_2\text{OMe}$]⁺ (16) (calc for $C_{18}\text{H}_{21}\text{O}_7$ 349 129), 247 [349- RCOOH]⁺ (16), 229 [247- H_2O]⁺ (14), 201 [229- CO]⁺ (12), 85 [RCO]⁺ (100), 57 [85- CO]⁺ (40), $[\alpha]_D^{24} = 25.0$ (CHCl_3 , *c* 0.85).

15-Deschloro-15-acetoxychlorojanerin (11). Colourless gum, IR $\nu_{\text{max}}^{\text{CHCl}_3}$, cm^{-1} 3500-3600 *br* (OH), 1780 (γ -lactone), 1740 (OAc), 1720 ($\text{C}=\text{CCO}_2\text{R}$), MS (rel int) 349 129 [$M-\text{CH}_2\text{OAc}$]⁺ (4) (calc for $C_{18}\text{H}_{21}\text{O}_7$ 349 129), 247 [349- RCOOH]⁺ (12), 229 [247- H_2O]⁺ (14), 201 [229- CO]⁺ (12), 85 [RCO]⁺ (100), 57 [85- CO]⁺ (54), $[\alpha]_D^{24} = 13.0$ (CHCl_3 , *c* 0.43).

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Table 1 ^1H NMR data of compounds 9–11 (400 MHz, CDCl_3 , TMS as int standard)

H	9	9a*	9b†	10‡	11§
1	3.37 <i>ddd</i>	3.34 <i>ddd</i>	3.33 <i>ddd</i>	3.43 <i>ddd</i>	3.50 <i>ddd</i>
2 α	1.71 <i>m</i>	1.60 <i>m</i>	1.60 <i>m</i>	1.64 <i>ddd</i>	1.66 <i>ddd</i>
2 β	2.43 <i>ddd</i>	2.51 <i>ddd</i>	2.51 <i>ddd</i>	2.45 <i>ddd</i>	2.50 <i>ddd</i>
3	4.18 <i>t</i>	5.50 <i>dd</i>	5.49 <i>dd</i>	4.15 <i>dd</i>	3.84 <i>dbr</i>
5	2.32 <i>dd</i>	2.05 <i>m</i>	2.06 <i>m</i>	2.34 <i>dd</i>	2.35 <i>dd</i>
6	4.58 <i>dd</i>	4.49 <i>dd</i>	4.45 <i>dd</i>	4.60 <i>dd</i>	4.83 <i>dd</i>
7	3.17 <i>dddd</i>	3.19 <i>d,dd</i>	3.10 <i>ddd</i>	3.16 <i>ddd</i>	3.18 <i>ddd</i>
8	5.13 <i>ddd</i>	5.17 <i>ddd</i>	5.02 <i>ddd</i>	5.16 <i>ddd</i>	5.18 <i>ddd</i>
9 α	2.36 <i>dd</i>	2.43 <i>dd</i>	2.43 <i>dd</i>	2.38 <i>dd</i>	2.44 <i>dd</i>
9 β	2.79 <i>dd</i>	2.51 <i>dd</i>	2.51 <i>dd</i>	2.76 <i>dd</i>	2.75 <i>dd</i>
13	6.22 <i>d</i>	6.26 <i>d</i>	6.25 <i>d</i>	6.22 <i>d</i>	6.22 <i>d</i>
13'	5.68 <i>d</i>	5.66 <i>d</i>	5.65 <i>d</i>	5.65 <i>d</i>	5.64 <i>d</i>
14	5.18 <i>s(br)</i>	5.18 <i>s(br)</i>	5.13 <i>s(br)</i>	5.18 <i>s(br)</i>	5.17 <i>s(br)</i>
14'	4.98 <i>s(br)</i>	4.90 <i>s(br)</i>	4.92 <i>s(br)</i>	4.90 <i>s(br)</i>	4.86 <i>s(br)</i>
15	4.03 <i>d(br)</i>	4.98 <i>d</i>	4.97 <i>d</i>	3.98 <i>d</i>	5.03 <i>d</i>
15'	3.97 <i>d(br)</i>	4.75 <i>d</i>	4.74 <i>d</i>	3.67 <i>d</i>	4.22 <i>d</i>
OCOR	6.33 <i>s(br)</i> 5.97 <i>q</i> 4.39 <i>s(br)</i>	6.45 <i>s(br)</i> 6.10 <i>s(br)</i> 4.84 <i>s(br)</i>		6.34 <i>s(br)</i> 5.97 <i>q</i> 4.40 <i>s(br)</i>	6.34 <i>s(br)</i> 5.96 <i>s(br)</i> 4.40 <i>s(br)</i>

*OAc: 2.06 *s*, 2.09 *s*, 2.12 *s*, 2.13 *s*, †OAc: 2.06 *s*, 2.09 *s*, 2.12 *s*, 2.19 *s*, ‡OMe: 3.45 *s*; §OAc: 2.18 *s*
 $J[\text{Hz}]$: 1,2 α =8, 1,2 β =10.5, 1,5=8, 2 α ,2 β =14.5, 2 α ,3~1.5, 2 β ,3=6.5, 5,6=11, 7,8=7; 7,13=3.5, 7,13'=3, 8,9 α ~2, 8,9 β =5, 9 α ,9 β =14.5, 15,15'=12, compound 10: 15,15'=10, OCOR: 3',4'=1.5

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