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# STRUCTURAL DETERMINATION OF CLEMENTEIN, A NEW GUAIANOLIDE ISOLATED FROM *CENTAUREA CLEMENTEI*[1]

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Summary: The structure of clementein was deduced on the basis of I.R., M.S. and N.M.R. spectra.

Sesquiterpene lactones commonly present a C-11 $\alpha$-methylene-$\gamma$-lactone moiety, which is related with the biological activity[2,3] of this group of natural products. Any other kind of functionalization at C-11 is infrequent[4,5].

As part of an ongoing project to elucidate the secondary metabolites from species of the Compositae Family, we now report the isolation and structure elucidation of clementein 1, the first reported oxetane-containing sesquiterpene lactone.

The air-dried whole plant (12 Kg) was extracted with hot EtOH and further concentration yielded a dark-green residue (380 g). Silica gel column chromatography (EtOAc/petrol) gave a colorless solid (0.120 g) which upon recrystallization afforded pure clementein 1 [m.p. 193-195° (EtOAc/petrol)].

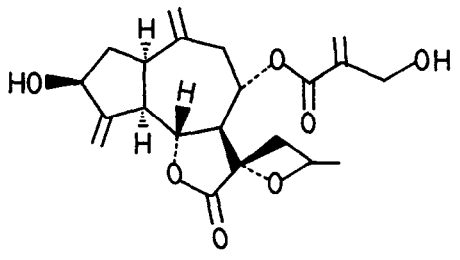
The molecular formula $C_{21}H_{26}O_7$ was derived from MS m/z 390 ($M^+$,0.8%) and confirmed by combustion analysis [calc. for $C_{21}H_{26}O_7.H_2O$, %C 61.81, found 61.43; %H 6.91, found 7.40]. Examination of spectral data indicated the presence of an $\alpha$-hydroxymethylacrylate moiety [IR (BrK) 1.720 $cm^{-1}$], [m/z 288 ($M^+$-102, 6%), 306 ($M^+$-84, 2.3%), and 85 ($C_4H_5O_2^+$,base)]; [NMR $\delta$ 6.33 and 5.89 (Table)], two terminal methylene double bonds, IR, 1.640 $cm^{-1}$; [NMR ( $\delta$ 5.39 and 5.31), ( $\delta$ 5.08 and 4.89)], a $\gamma$-lactone moiety IR 1.765 $cm^{-1}$; [NMR $\delta$ 4.38], a secondary OH, IR 3.450 and 3300 $cm^{-1}$; [NMR $\delta$ 4.48] and a secondary Me group, [NMR $\delta$ 1.12]. These NMR data are in part very similar to those of cynaropicrin 2[6], a guaianolide which was also found in C. clementei.

The above functionalities in a guaianolide skeletal type, contribute $C_{19}H_{24}O_6$ towards the molecular formula and account for eight of the nine degrees of insaturation inherent in the formula.

Finally, the ABX system (signals centered at $\delta$ 1.86,1.92 and 3.92) is assigned to the methyl oxetane moiety. Its orientation is inferred from the chemical shift of H-6 because a $\beta$ configuration for the oxetane oxygen would produce a deshielding effect

upon the lactonic proton[7].

Clementein 1 is an acetaldehyde adduct of the co-occurring lactone cynaropicrin 2 and could be considered as an artefact formed during the extraction procedure. However, when several species of Centaurea[8,9] which contained cynaropicrin were submitted to different extraction procedures, only C. clementei afforded compound 1. Compound 3[10], is also present in C. clementei.



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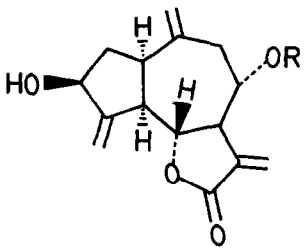

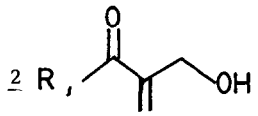

2 R,

3 R, H

TABLE

NMR data ( $\delta$ ,$CDCl_3$-$CD_3OD$ 1:1, 400 MHz)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| H-1 | 2.90 ddd(br) | H-8 | 5.45 ddd | H-15 | 5.39 s(br) | H-4$'_2$ | 5.89 ddd |
| H-2 | 1.69 ddd | H-9 | 2.61 dd | H-15' | 5.31 s(br) | J(Hz): 1,2=7; 1,2'=9; 2,2'=13; | |
| H-2' | 2.16 dt | H-9' | 2.37 dd | H-16 | 3.92 ddq | 2,3=7; 2',3=9; 3,15=1.5; 5,6= | |
| H-3 | 4.48 dddd | H-13 | 1.92 dd | H-17 | 1.12 d | =6,7=10; 7,8=9.5; 8,9=4.5; | |
| H-5 | 2.77 dd(br) | H-13' | 1.86 dd | H-3$'_1$ | 4.32 d(br) | 8,9'=5; 9,9'=14; 13,13'=15; | |
| H-6 | 4.38 dd | H-14 | 5.08 s(br) | H-3$'_2$ | 4.25 d(br) | 13,16=8; 13',16=3.5; 16,17=6.5; | |
| H-7 | 2.89 dd | H-14' | 4.89 s(br) | H-4$'_1$ | 6.33 s(br) | $3'_1,3'_2$=14.5; 3',4=$4'_1,4'_2$=1. | |

## REFERENCES AND NOTES


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