

(*t*), 24.4 (*q*), 24.1 (*d*), 23.3 (*q*), 21.8 (*t*), 21.2 (*q*), 20.5 (*q*), 20.0 (*q*), 17.2 (*s*); mass spectrum  $m/z$  464 ( $M - H_2O$ ), 325, 265, 239; high-resolution mass measurement, observed  $m/z$  464.1563,  $C_{24}H_{33}^{79}BrO_4$  requires 464.1562.

**Acetylation of diacetate 2.** A soln of the diacetate **2** (10 mg, 0.021 mmol) in  $Ac_2O$  (0.56 ml) and pyridine (1.0 ml) was allowed to stand at room temp. overnight. The reagents were evapd under high vacuum and the residue dissolved in  $Et_2O$  and passed through a short plug of Si gel to obtain the triacetate **4** (11 mg, quantitative), having spectral data, particularly  $^1H$  NMR, identical with those of a sample prepared by Schmitz *et al.* [2] from the monoacetate **3**.

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## PHLOROGLUCINOL DERIVATIVES FROM *LEUCANTHEMOPSIS PULVERULENTA*

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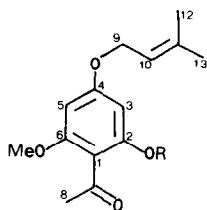
(Revised received 31 May 1981)

**Key Word Index**—*Leucanthemopsis pulverulenta*; Compositae; roots; phloroglucinol derivatives.

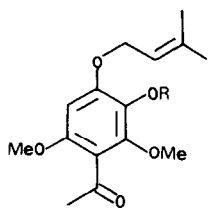
**Abstract**—From roots of *Leucanthemopsis pulverulenta*, two new phloroglucinol derivatives and (+) sesamin, have been isolated. The new compounds were identified as 1 - acetyl - 4 - isopentenyl - 6 - methylphloroglucinol and 1 - acetyl - 3 - hydroxy - 2,6 - dimethyl - 4 - isopentenylphloroglucinol.

*Leucanthemopsis* is a small genus, belonging to the Anthemideae tribe (Compositae) with only 6 species, most of them, widely distributed in Spain and Portugal. They have not as yet been examined for chemical constituents and we are now beginning their study with *Leucanthemopsis pulverulenta*, collected at the end of May, near Ledesma (Salamanca, W. Spain).

From the roots of *L. pulverulenta*, we have isolated (+)sesamin [1, 2] and two new phloroglucinol derivatives, **2** and **3**.



**2** R=H  
**2a** R=Ac



**3** R=H  
**3a** R=Ac

Compound **2**, shows a  $M^+$  in the mass spectrum, at  $m/z$  250, in agreement with the formula  $C_{14}H_{18}O_4$ . Its UV spectrum is characteristic of a polyhydroxy-acetophenone derivative (see Experimental). Acetylation of **2** yields the monoacetate **2a**. The bathochromic shift (20 nm) induced in the UV of **2**, by addition of  $AlCl_3-HCl$  to the ethanolic solution, is indicative of an OH *ortho* to a COMe group [3]. The substituents were identified by  $^1H$  NMR, which showed the presence of a 1,2,4,6-tetrasubstituted aromatic ring, with -COMe, -OH, -OMe and *O*-isopentenyl groups as substituents (Table 1). The signal at 3.75 ppm for the -OMe group on C-6, so that the *O*-isopentenyl group must be on C-4 [4, 5].

Compound **3**, had a  $M^+$  at  $m/z$  280, in agreement with the formula  $C_{15}H_{20}O_5$ . Its UV spectrum was similar to that of **2**, but there was no induced shift on addition of  $AlCl_3-HCl$ , although the acetylation yields a monoacetate, **3a**. Thus, the free hydroxyl group is not at C-2 or C-6 [3]. The  $^1H$  NMR spectrum of **3** confirms the presence of a 1,2,3,4,6-pentasubstituted aromatic ring, with -COMe, -OH, -*O*-isopentenyl

Table 1.  $^1\text{H}$  NMR data for **2**, **2a**, **3**, and **3a** (60 MHz, TMS,  $\text{CDCl}_3$ )

H	<b>2</b>	<b>2a</b>	<b>3</b>	<b>3a</b>
H-3	5.68 <i>d</i>	6.00 <i>d</i>	—	—
H-5	5.82 <i>d</i>	6.17 <i>d</i>	6.06 <i>s</i>	6.21 <i>s</i>
H-8	2.48 <i>s</i>	2.32 <i>s</i>	2.57 <i>s</i>	2.32 <i>s</i>
H-9	4.40 <i>d</i>	4.38 <i>d</i>	4.45 <i>d</i>	4.50 <i>d</i>
H-10	5.34 <i>brt</i>	5.35 <i>brt</i>	5.35 <i>brt</i>	5.35 <i>brt</i>
H-12	1.72 <i>brs</i>	1.72 <i>brt</i>	$\left. \begin{array}{l} 1.73 \text{ brs} \\ 1.85 \text{ brs} \end{array} \right\}$	
H-13	1.78 <i>brs</i>	1.80 <i>brs</i>	—	—
—OH	13.75 <i>s</i>	—	7.95 <i>s</i>	—
Ph-OMe	3.75 <i>s</i>	3.78 <i>s</i>	3.69 <i>s</i>	3.75 <i>s</i>
Ph-OMe	—	—	3.90 <i>s</i>	3.85 <i>s</i>
Ph-OAc	—	2.12 <i>s</i>	—	2.11 <i>s</i>

$J(\text{Hz})$ : 3.5 = 2; 9, 10 = 7.

and two —OMe groups as substituents (Table 1). The two —OMe groups must be in the *o/o'* positions relative to the —COMe group [3]. The chemical shift due to the unique aromatic proton in the  $^1\text{H}$  NMR of **3** and **3a**, at 6.06 and 6.21 ppm respectively, show that in both, the only aromatic proton is between two ether groups, on C-5, so that the free hydroxyl group must be on C-5 [4, 5].

The mass spectra of **2** and **3** are both very characteristic, with fragmentation of the benzoyl carbanion with the loss of the fragment  $\text{C}_5\text{H}_8^+$ .

#### EXPERIMENTAL

Mps are uncorr. and UV spectra were recorded in EtOH.  $^1\text{H}$  NMR spectra were recorded at 60 MHz using TMS as int. standard. Analytical TLC was performed on Si gel G (Merck 7731), prep. TLC on Si gel PF<sub>234-336</sub> (Merck 7748) and a CC on Si gel 60 (Merck 7734).

**Extraction.** Roots (500 g) of *L. pulverulenta* (Lag.) Heywood\* were air-dried, ground and extracted with hot  $\text{C}_6\text{H}_6$ . The extract was concd *in vacuo* and the residual syrup was extracted with 50% aq. EtOH. The alcoholic soln was extracted with  $\text{CHCl}_3$ , the solvent distilled off and the residue chromatographed on Si gel ( $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_6\text{--Et}_2\text{O}$ , 99:1;  $\text{C}_6\text{H}_6\text{--Et}_2\text{O}$ , 9:1) giving (+) sesamin **1** (100 mg), **2** (60 mg) and **3** (40 mg).

**1-Acetyl-4-isopentenyl-6-methylphloroglucinol (2).** Mp 60–61°; UV (nm):  $\lambda_{\text{max}}^{\text{EtOH}}$  a 231 ( $\epsilon = 6800$ ), 292.5 ( $\epsilon = 15800$ );  $\lambda_{\text{max}}^{\text{EtOH--AlCl}_3\text{--HCl}}$  252.5 ( $\epsilon = 18400$ ), 283.5 ( $\epsilon = 21500$ ); IR: 3600

(OH), 1680 ( $\text{C=O}$ ), 1600, 1500, (aromatic), 1280, 1235, 1130, 960, 840, 810  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (Table 1); MS,  $m/z$  (%): 250 ( $\text{M}^+$ , 11), 182 ( $\text{M}^+ - \text{C}_5\text{H}_8$ , 18), 167 (182–Me, 58), 164 (11), 138 (28), 135 (14), 110 (56), 109 (48), 97 (86), 96 (100), 81 (81), 77 (9) 68 (77), 55 (77), 43 (20).

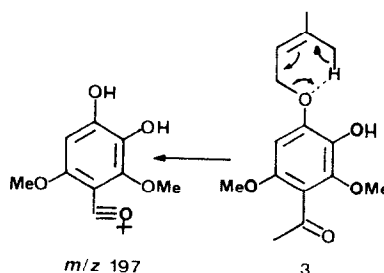
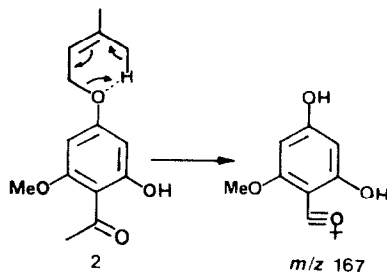
Acetylation of **2** (40 mg) yielded 41 mg of **2a**, mp 59°; IR: 1755, 1250 (acetate), 1670 ( $\text{C=O}$ ), 1600, 1500 (aromatic), 1190, 1020, 870, 810  $\text{cm}^{-1}$ ;  $\text{M}^+ m/z$  308.

**1 - Acetyl - 3 - hydroxy - 2,6 - dimethyl - 4 - isopentenylphloroglucinol (3).** Viscous oil; UV (nm);  $\lambda_{\text{max}}^{\text{EtOH}}$  231 ( $\epsilon = 10100$ ), 282 ( $\epsilon = 7900$ ); IR: 3600 (OH), 1680 ( $\text{C=O}$ ), 1630 ( $\text{C=C}$ ), 1600, 1500 (aromatic), 1290, 1180, 1050, 850, 810  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (Table 1); MS,  $m/z$  (%) 280 ( $\text{M}^+$ , 18), 212 ( $\text{M}^+ - \text{C}_5\text{H}_8$ , 58), 197 (212–Me, 100), 179 (19), 167 (52), 135 (16), 69 (20).

Acetylation of **3** (20 mg) yielded 21 mg of **3a**, viscous oil; IR: 1760, 1260 (acetate), 1690 ( $\text{C=O}$ ), 1600, 1500 (aromatic), 1200, 1180, 1150, 1100, 1000, 880, 840  $\text{cm}^{-1}$ ;  $\text{M}^+ m/z$  338.

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\*The material was identified by Prof. B. Casaseca Mena, from the Botany Department of Salamanca University, where a specimen is held (Herbarium no. 8669).