The NMR spectra assignments, the MS fragmentation patterns and CD-data are in full agreement with a melampolide skeleton as shown for **1b**. On the basis of the similarity of the NMR parameters, longipilin (**1b**) should exhibit the same configurational and conformational relationships as enhydrin (**1a**), the structure of which has been established by X-ray diffraction [5].

EXPERIMENTAL

Melampodium longipilum (Hartman-Funk No. 4151; Mexico: Puebla: roadside 1 mile S of Ascuncion de Chila) leaves and stems (800 g) were extracted in 3 l. $CHCl_3$. After the standard workup [6], 8.9 g crude syrup were obtained which yielded upon titration with *iso*-PrOH 2.0 g enhydrin. The remaining syrup was chromatographed over 250 g Si gel, using $CHCl_3$–*n*-propyl acetate (6:4) as eluant. Longipilin (40 mg) crystallized readily from fractions 35–50 when treated with *iso*-PrOH–petrol mp 170–173°; λ_{max} (MeOH) 213 nm (ε, 2.1×10^4); CD (c 4.93×10^{-5}, MeOH): $[\theta]_{216} = -5.38 \times 10^4$, $[\theta]_{247} = 7.1 \times 10^3$; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400 (*br*.OH), 1770 (γ-lactone), 1710 (ester). The low resolution MS exhibited significant peaks at *m/e* (rel. int): 406 (2.4, M^+), 388 (1.7, $M - H_2O$), 375 (0.5, $M - OCH_3$), 323 (2.5, $M - C_5H_7O$), 306 (5.1, $M - C_5H_8O_2$), 291 (6.8, $M - C_5H_8O_2 - CH_3$), 83 (100, C_5H_7O). ^{13}C NMR ($CDCl_3$) 168.32, 167.32, 166.54 ($>C=O$); 145.31, 140.21 ($-CH=$); 133.92, 133.33 ($>C=$); 122.50 ($=CH_2$); 76.28, 72.24, 70.95, 62.80 (HCO); 59.18 ($>CO$); 52.40 (OCH_3); 46.07 ($>CH$); 35.44, 24.71 ($>CH_2$); 20.51, 17.72, 15.92 ($-CH_3$). (Calc. for $C_{21}H_{26}O_8$: MW, 406.1628. Found: MW (MS), 406.1628).

Longipilin acetate (**1c**) (30 mg) was prepared from 40 mg **1b** in 1 ml Py and 1 ml Ac_2O under standard conditions: oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770 (γ-lactone) 1735 and 1245 (acetate) and 1710 (ester)

Acknowledgements—This work was supported by Grant Number 1-R-01-CA19800-02, awarded by the National Cancer Institute, DHEW, and by a grant from the National Science Foundation (DEB-76-20585). We thank Dr. R. Hartman and V. Funk for plant collections and Professor F. Bohlmann for making available spectral facilities at the Technical University Berlin.

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Phytochemistry, 1978, Vol 17, pp 2132–2133 © Pergamon Press Ltd Printed in England 0031-9422/78/1201-2132 \$02.00/0

13-HYDROXYBALLONIGRINOLIDE, A NEW DITERPENOID FROM *BALLOTA LANATA*

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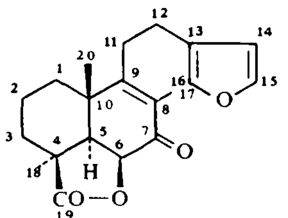
(*Received* 14 *June* 1978)

Key Word Index—*Ballota lanata*, Labiatae; diterpenoid, ballonigrin.

We have described the isolation of a number of new bicyclic diterpenoids from *Ballota* (Labiatae) species including *B. nigra* [1, 2], *B. rupestris* [3] and *B. acetobulosa* [4]. In continuation of this work we have examined *B. lanata* which is used as a herbal medicine, Wolfstrappkraut. Chromatography of the acetone extract afforded ballonigrin (**1**) previously obtained from *B. nigra* [1, 2] and *B. rupestris* [3], together with a new diterpenoid, $C_{20}H_{26}O_6$. The IR and UV spectra showed that the oxygen functions were disposed as a hydroxyl, two γ-lactones and an $\alpha\beta$-unsaturated ketone implying a similarity to ballonigrin. However the spectra lacked absorption associated with the furan ring. The ^1H and ^{13}C NMR spectra (Table 1) led to the structure **2** for the diterpenoid, 13-hydroxyballonigrinolide. The ^1H NMR spectrum contained two tertiary C Me resonances and one olefinic C-Me resonance whilst spin decoupling of two ^1H doublets (δ 4.95 and 2.18, $J = 8$ Hz) established their vicinal relationship as H(6) and H(5), respectively. The spectrum also contained an AB quartet, δ 4.36 and 4.57, associated with a $-\overset{|}{\underset{|}{C}}-CH_2-O-C=O$ grouping together with a two proton singlet, δ 2.94, which was assigned to a $-\overset{|}{\underset{|}{C}}-CH_2-C=O$ grouping. The ^{13}C NMR spectrum showed marked similarities to that of ballonigrin [1, 2] and rupestralic acid (**3**) [5]. In particular the SFORD showed that the additional hydroxyl group was tertiary in character and was associated with the side chain. The ^{13}C NMR spectrum may be interpreted in terms of structure **2**.

The MS of 13-hydroxyballongrinolide showed substantial ions at *m/e* 237 and 219 associated with the fragment **4** and its dehydration product. Two other major ions at *m/e* 233 (**5**) and 109 (**6**) are associated with the bicyclic ring systen and provide strong evidence for the location of the functional groups.

The isolation of this compound with a $\Delta^{8,9}$-double



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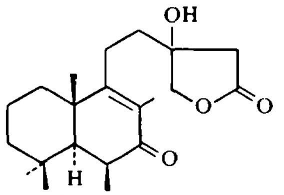

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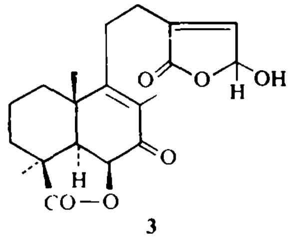

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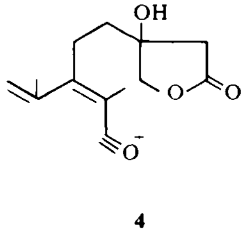

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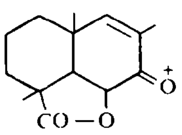

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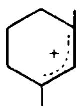

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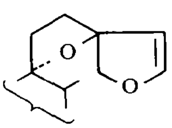

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bond and a 13-hydroxyl group is of interest in view of the occurrence of 'prefuran' labdane diterpenoids possessing the 9,13-ether linkage (e.g. 7) in other Labiates. Whereas marrubiin with a 9-hydroxyl group represents one form of cleavage of this ether, the 13-hydroxyl group might represent an alternative arising as a consequence of the 7-ketone. The ^{13}C NMR spectrum of rupestralic acid contained a doublet signal at δ 98.5 ppm, showing that it exists predominantly in the lactol form (3).

Table 1. ^{13}C NMR Signals of compounds **2** and **3** in d_5-pyridine; ppm from TMS

Carbon	**2**	**3**
1	30.2*t*	30.1*t*
2	18.1*t*	18.1*t*
3	28.1*t*	28.1*t*
4	42.1*s*	42.3*s*
5	49.3*d*	49.4*d*
6	76.1*d*	76.1*d*
7	193.6*s*	193.8*s*
8	131.1*s*	131.7*s*
9	167.1*s*	165.6*s*
10	37.0*s*	36.9*s*
11	24.3*t*	24.7*t*
12	†37.5*t*	27.3*t*
13	76.4*s*	136.0*s*
14	†42.5*t*	146.5*d*
15	180.2*s*	98.5*d*
16	79.1*t*	172.1*s*
17	*24.5*q*	*24.7*q*
18	*27.9*q*	*27.8*q*
19	180.9*s*	180.7*s*
20	12.1*q*	12.1*q*

*† These assignments may be interchanged.

EXPERIMENTAL

General details have been described previously [1, 2].

Extraction of Ballota lanata. Plant material was obtained from Messrs. R. Kottas-Heldenberg, Vienna, Austria. Dry leaves and twigs (1 kg) were extracted with Me_2CO (2 l.) at room temp. for 4 days. The solvent was evapd, the residue taken up in EtOAc, washed with H_2O, dried and the solvent evapd. The residual gum was chromatographed on Si gel (Merck deactivated with 15% H_2O). Elution with EtOAc–petrol (3:7) gave ballonigrin (30 mg) identified by its NMR spectrum. Elution with MeOH–EtOAc (5:95) gave *13-hydroxyballonigrinolide* (35 mg) which crystallized from Me_2CO as prisms, mp 227°, $[\alpha]_D$ + 15° (*c* 0.25 in MeOH) (Found: 362.173, $C_{20}H_{26}O_6$ requires: 362.173), IR ν_{max} cm^{-1}: 3500, 1755 (br) 1670, 1603, UV_{max} 260 nm ε 7500, NMR (Py): δ 1.06 (3H, *s*), 1.25 (3H, *s*), 1.91 (3H, *s*), 2.18 (1H, *d*, *J* = 8 Hz), 2.94 (2H, *s*) 4.36 and 4.57 (2H, AB *q*, *J* = 10 Hz), 4.95 (1H, *d*, *J* = 8 Hz). MS (rel. int.): 362 (7), 344 (2), 316 (1), 237 (46), 233 (30), 219 (10), 109 (40), 44 (100).

Acknowledgements—We thank the National Research Council (CNR), Roma and N.A.T.O. for financial support.

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