**Neo-clerodane diterpenoids from Teucrium polium subsp. vincentinum (rouy) D. Wood**

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**A R T I C L E  I N F O**

**Keywords:**
- Teucrium polium
- Lamiaceae
- Neo-Clerodane diterpenes

**A B S T R A C T**

Four neo-clerodane diterpenoids, the new polivincins A – C and the known teulamifin B, were isolated by the phytochemical investigation of the acetone extract prepared from the aerial parts of Teucrium polium subsp. vincentinum, (Lamiaceae). The structure and stereochemistry of the compounds were established by IR, HRMS and different (Al-Khalil, 1995) NMR and 2D-NMR techniques.

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**1. Introduction**

The genus *Teucrium* (Lamiaceae) has been thoroughly studied as a rich source of neo-clerodane diterpenoids with a great variety of biological activity. *T. polium*, a species belonging to the genus *Teucrium*, is a medicinal plant used in traditional folk medicine to treat many diseases such as abdominal pain, indigestion and diabetes (Al-Khalil, 1995; Said et al., 2002; Ljubuncic et al., 2006). The taxonomy studying of the section *Polum* of the genus determined 125 taxa and many variances (Navarro and El, 2000). Bruno and co-workers drew attention to the distribution of neo-clerodanes in the subspecies of the species *T. polium* (Bruno et al., 2003). They suggested that *T. capitatum* is taxonomically close to *T. polium* subsp. *polium* based on the presence of captitain and aupolin in both species. The authors emphasized the fact that the diterpenoids, isolated by them from authentic *T. polium* subsp. *polium*, are distinctly different from those occurring in all the taxa in- 

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**2. Results and discussion**

The bitter fraction obtained from the acetone extract of the plants was separated to three subfractions (I-III). For compound 1, named polivinic A (received after TLC chromatography of I) was assigned the molecular formula C\(_{24}\)H\(_{30}\)O\(_8\) based on the pseudo-molecular positive ion peak, in its HR-ESIMS, at m/z 469.1844 [M + Na]\(^+\), (calcd. for C\(_{24}\)H\(_{30}\)O\(_8\)Na: 469.1838).

The IR spectrum displayed absorptions for furan ring (1508, 875 cm\(^{-1}\)), \(\gamma\)-lactone and ester carbonyl groups (1743 cm\(^{-1}\), broad band). The \(^{13}\)C NMR spectrum displayed the presence of twenty-four carbons, and a DEPT experiment identified three methyls, seven methylenes, seven methines (three for olefinic double bonds) and seven unprotonated carbon atoms, three of them are for carbonyl groups at \(\delta_C\) 171.0 and 172.0 (acetates) and 177.6 (\(\gamma\)-lactone) (Table 1). The presence of furan ring in the structure of the molecule was corroborated by the signals at \(\delta_H\) 125.0 (C-13), 108.1/\(\delta_H\) 6.39 (dd, CH-14); 144.2/7.44 (t, CH-15) and 139.6/7.45 (m, CH-16) in the \(^{13}\)C and \(^{1}H\) NMR spectra.

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https://doi.org/10.1016/j.phytol.2019.04.013

Received 9 January 2019; Received in revised form 19 March 2019; Accepted 15 April 2019

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Assignments of the olefinic protons to the corresponding carbon atoms were in agreement with the data from HSQC spectrum and observed HMBC correlations from H-14 to C-15 and C-16, from H-15 to C-13 and from H-16 to C-14 and C-15. In the HMBC spectrum were displayed additional correlations from the downshifted at $\delta^H$ 5.40 proton H-12 (connected with carbon at $\delta^C$ 72.2) to carbon C-13 and from the resonated at $\delta^H$ 4.16 (H-11$\alpha$) showed cross peaks with the signal at $\delta^C$ 177.7 (carbonyl C-20) and C-9. The COSY experiment, the olefin proton at $\delta^H$ 7.44 bounded to the carbon at $\delta^C$ 144.2 (C-15), correlated with the methine proton at $\delta^H$ 6.39, which correlated with the carbon at $\delta^C$ 108.1 (C-14) in the HSQC experiment. Another methine proton, resonated at $\delta^C$ 54.4 and connected with the oxygenated carbon C-12 ($\delta^C$ 72.2), correlated to the two doublet of doublets at $\delta^H$ 2.47 (H-11$\alpha$) and 2.33 (H-11$\beta$). We placed the furan moiety at 12$\beta$ position in accordance with the displayed in the NOESY spectrum cross peaks of Me-17 ($\delta^H$ 0.94) with H-14 (H-11$\alpha$) and H-16 (H-11$\beta$), as well as of H-1$\alpha$ (H$\delta$ 2.19) with H-12$\alpha$ (H$\delta$ 5.40).

Table 1

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*CDCl$_3$, $^1$H 600.13 MHz, $^1{\delta} 7.26$; $^1$C 150.9 MHz, $^1{\delta} 77.0$ ppm; $^b$ endo hydrogen with respect to ring B; $^c$ data from HSQC; ov overlapped signal.

Fig. 1. Structures of the isolated and used in the discussion neo-clerodane diterpenoids.
additional NOESY interaction, in turn, with H-2α and with H-7α.

The last oxygenated quaternary carbon atom at δ 86.2 (C-4) was involved in an oxetane ring in the molecule supported by mentioned heterocorrelations to carbon C-4 in the HMBC spectrum from H-18a, H-18b and H-19b.

1H NMR data of 1 are very close to those reported by Malakov et al. for product received after acetylation of montanin D (5), received from T. montanum (Malakov et al., 1978). Quoted data were: δ: 2.10 and 2.05 (each 3H, s)/vs 2.10 and 2.06 in 1; 4.05 (H2-18)/vs 4.06 and 4.10; 5.62 (1H, J = 4.0 Hz)/vs 5.68 (1H, dd, J = 3.7; 2.1 Hz) and an AB type quartet at δ 5.08 and 4.35 (1H each, J = 7.5 Hz, H2-19)/vs 4.77 (1H, d, J = 8.0 Hz, H-19α) and 4.16 (1H d, J = 8.0 Hz, H-19β). The differences in the data were probably due to the resolution ability of the used spectrometers for 1H NMR spectra, operating at 600.130 MHz for 1 and quoted 80, 100 and 220 MHz by Malakov for semi-synthetic product. Also, it is not clear the kind of solvent used by Malakov. He reported using solvents CDCl3 and C2D2N jointly for all measurements without particularization of the conditions for individual compounds. The written above proton data were the only reported by Malakov, as 13C NMR spectrum missed.

The HR-ESIMS of compound 2, obtained from subfraction II, with the trivial name polivincin B, showed a pseudo-molecular positive ion peak at m/z 441.1861 [M + Na]+, which indicated the molecular formula of C23H30O7 (calcd. for C23H30O7Na: 441.1889), while in its IR spectrum were observed absorptions consistent with the presence of a furan ring (3089, 1506, 1083 and 875 cm−1), a γ-lactone (1762 and 1181 cm−1) and acetate (1737 and 1246 cm−1) groups.

The 13C NMR spectrum displayed the presence of twenty-three carbons, and a DEPT experiment identified three methyls, six methylenes, nine methines (three from furan double bonds) and five quaternary carbon atoms, two of which are for carbonyl groups at δ 177.0 (γ-lactone) and 170.0 (acetate) (Table 1). The conjunctural furan moiety in the molecule was confirmed by the signals, in the 1H NMR spectrum of 2, for aromatic protons at δH 7.44 (4H, d, J= 1.5 Hz), 7.43 (4H, d, J= 1.5 Hz) and 6.38 (4H, d, J= 1.5 Hz), observed as triplet at δH 5.33/δ 5.38/δ 5.36, assigned for the H-12 proton, was characteristic signal for neo-clerodane diterpenoids possessing furan ring and γ-lactone (atom numbers C-11 – C-16 and C-20). The γ-lactone included carbon atoms C-9, C-11, C-12 and C-20 (δC 177.0). This connectivity was supported by the 2D NMR data. Olefin methines protons H-14, H-15 and H-16 and the H-12 sp (Ljubuncić et al., 2006) methine proton were attached to corresponding carbons resonated at δC 108.1, 144.1, 139.5 and 71.7 on the ground of HSQC results. The abundance of 1H –13C HMBC correlations from H-14 to C-16 showed HMBC crosspeak to C-4, C-6 (δC 73.2) and C-18 (δC 108.7). The signal for methyl protons at δH 3.25 (3H s, MeOH-181), bound to the carbon at δC 54.4 (CH3), correlated in HMBC spectrum to δC 108.7 (C-18). For the discussed above protons H-1 – 1H COSY correlations between H-19a/H-19b, H-6α/H-7α (δH 4.24, 3.24) and H-6α/H-7β (δH 1.87) were evident. All above data, together with the characteristic signal for the methine proton at δH 2.18 (dd, J= 12.6; 3.2, H-4) disclosed the presence in the structure of an acetal moiety formed by the C-18 carbon with the H-19 hydroxymethyl and a methanol molecule. Methoxy group was attached at C-18 in endo position with respect to the ring B of the decalin ring on the ground on the cross peak in the NOESY experiment between H-18a/H-3α and MeO-181/H-6α. The NOESY interaction of the proton H-10 with H-1, H-2, H-8 and H-11 protons indicated, that all they were cofacial and β oriented.

Acetoxy group, resonated at δH 2.08 (3H s)/170.0 (C) and 21.4 (CH3), was located at 6β position in accordance with small value of coupling constants of the geminal equatorial 6α proton, and also the NOESY interactions between H-6α/7α, H-6α/Me-18 (Al-Khalil, 1995) and H-6α/19α.

Further, the protons in the upfield region of the spectrum were a multiplet for methine at δH 1.78, which was bound to carbon at δC 33.2 (C-8), correlated in the 1H – 1H COSY spectrum with H-7α, H-7β and Me-17; there were seven overlapped protons detected in the 1.38–1.79 ppm range.

Finally, the spectral data of polivincin B were very close to those of teupolin XII (6) isolated by Fiorentino et al. in 2003 (Fiorentino et al., 2011). Observed differences were the downshifted signal in 1H NMR spectrum for the proton H-6α, from δH 4.23 in 6 to δH 5.36 in the spectrum of 2, besides the additional signals in 1H and 13C NMR spectra of 2 for acetoxy group at δH 2.08/δC 170.0 (CO) and 21.4 (CH3).

For the new compound polivincin C (3), isolated from the subfraction III, was established molecular formula C23H30O7 by the negative [M – H]– molecular ion peak, in its HRESIMS, at m/z 377.1599, (calcd. for C23H30O7: 377.1600). The IR spectrum displayed absorptions for hydroxyl (3439 cm−1), acetate (1506, 875 cm−1), γ-lactone and carbonyl (1759 cm−1, broad band) functionalities. The 13C NMR spectrum displayed the presence of twenty carbons, and a DEPT experiment identified one methyl, seven methylenes, six methines and six unprotonated carbon atoms, as two of them are for carbonyl groups at δC 211.0 (ketone) and 177.9 (γ-lactone). The signals at δC 125.0 (C-13), δC 108.2/δC 63.9 br s (C-14), δC 144.1/δC 74.3 dd (H-15) and δC 139.6/δC 7.45 br s (CH-16) in the 1H and 13C NMR spectra indicated the presence of furan ring in the structure of the molecule (Table 1). Attachments of the furan protons to the corresponding carbons were in agreement with HSQC spectrum and observed HMBC correlations from H-14 to C-16, from H-15 to C-16 and from H-16 to C-16 and C-14. In the HMBC spectrum were displayed additional correlations to carbon C-13 from H-10 proton at δC 6.38 (C-12) and from the resonated at δC 108.2 (C-14) in the HSQC experiment. Further, the 1H – 1H COSY spectrum displayed additional correlations to carbon C-11 from the downshifted at δH 5.38 proton H-12 and from the resonated at δH 2.32 proton H-11β, which showed cross peak in the HSQC spectrum, with carbon at δC 41.7. Two protons, H-11β (δH 2.32) and H-8 (δH 2.07) showed cross peak with the signal at δC 177.9 (carbonyl C-20). In the COSY experiment, the furan proton at δH 7.43, which was bound to the carbon at δC 144.1 (C-15), correlated with the methine proton at δH 6.39, which correlated with the carbon at δC 108.2 (C-14) in the HSQC experiment. Another methine proton, resonated at δH 5.38 and connected with the oxygenated carbon C-12 (δC 72.2), correlated to the two doublet of doubletts at δH 2.47 (H-11α) and 2.32 (H-11β). We placed the furan moiety at 12β position in accordance with the displayed in the NOESY spectrum cross peaks of Me-17 (δH 0.94) with H-14 and H-16, as well as between the protons H-11α/H-12α, H-11α/H-1α (δH 2.13) and H-12α/H-1α. The last proton (H-1a) showed NOESY interaction with signals at δH 4.04 (H-19a) and 4.74 (H-19b), which indicated its α-orientation.

The rest four signals of oxygenated carbons, two unprotonated and two methylenes, were assigned in the decalin core for carbons C-4 (δC 88.2, C-7 (δC 211.0, CO), C-18 (δC 66.6, CH2) and C-19 (δC 71.8, CH3). Assignments were in consistence with 2D spectra. In HMBC spectrum were observed cross peaks from the doublets at δH 3.37 and
4.14, which are bounded with carbon resonated at δC 66.6 (C-18) as it was seen in HSQC experiment, in turn to δH 88.2 (C-4), 47.6 (C-5) and to 30.1 (C-3), C-4, C-5. The doublets at δH 4.04 and 4.74, which showed in HSQC direct bound with carbon resonated at δC 71.8 (C-19), had HMBC correlations, in turn to C-4, C-5 and C-9 (δH 69.6).

The signal for ketone functional group at δC 211.0 was unambiguously assigned for C-7 on the ground on observed HMBC correlations from the singlet for two protons at δH 2.63 (CH₂-6) to δC 211.0 (C-7), 301 (C-3), 69.6 (C-9) and from the doublet of doublets at δH 2.17 (H-10) to δC 53.7 (C-6) and to 211.0 (C-7). Also, the usual multiplet for H-8, in diterpenoids with unsubstituted carbon C-7, was reduced into quartet at δH 2.07. This simplified signal (H-8) displayed interaction, in the 1H–1HCOSY spectrum, with the doublet for three protons at δH 0.94 (Me-17), and HMBC cross peak to the carbonyl atom at δδ 177.9 (C-20). On the other hand, Me-17 protons heterocorrelated to δδ 32.1 (C-8) and 53.7 (C-6).

The interaction between protons H-18a and H-19a, observed in the NOESY experiments, confirmed the α-orientation of the H-18 hydroxymethylene group and the β-orientation of the tertiary hydroxyl group at C-4, respectively. Other NOESY interactions, H-3α (δH 1.58)/H-1α, H-3α/H-2α (δH 2.15), 10β/1β (δH 1.80) and 10β/2β (δH 1.72), were observed.

The last fraction III provided second compound identical in all respects (IR, HRESIMS, 1H NMR, 13C NMR and 2D NMR experiments) with teuvin B (4), previously isolated by Malakov in 1988 (Malakov et al., 1988). From the acetone extract of Tecucrium polium subsp. vincentinum four furococlodean diterpenoids, the new polivincins A–C and previously known teuvin B, were isolated and structural elucidated by extensive spectroscopic investigation. The absolute configuration of compounds 1-3 was not ascertained. However, on biogenetic grounds, it may be supposed that 1–3 belong to the trans neo-clerodane series like the other diterpenoids isolated from Tecucrium polium species (Bruno et al., 2003; Malakov et al., 1978; Fiorentino et al., 2011). The presence of capitatin and auropolin were not detected in our plant material and the four isolated by us compounds were different from all diterpenoids reported previously by Malakov as constituents of the plant Tecucrium polium. Our suggestion, that Malakov and coauthors had studied Tecucrium polium subsp. capitatum, was corroborated.

3. Experimental

3.1. Structural data

1H NMR spectra were recorded on Bruker Avance II + spectrometers, operating at 600.130 MHz. 13C NMR spectra were recorded at 150.903 MHz spectrometer. TMS was used as internal standard and CDCl₃ as solvent. Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hertz. The IR spectra were registered in KBr pellet on a Vertex 70 spectrometer from 4000 cm⁻¹ to 400 cm⁻¹ at resolution 4 cm⁻¹ with 25 scans. The mass spectra were measured on Hewlett Packard 6890 GC System Plus/5973 MSD. The melting points were determined by a SMP-10 digital melting point apparatus (Fig. 1).

3.2. Plant material

The stems of Tecucrium polium subsp. vincentinum L. were collected in July 2018 from sand dunes of seaside resort Atleman in Kiten, Bulgaria, and voucher specimens (n. 7212) were deposited in the Herbarium of the Higher Institute of Agriculture at Plovdiv, Bulgaria.

3.3. Extraction and isolation

Dried and finely powdered aerial parts of Tecucrium polium subsp. vincentinum (Rouy) D. Wood (0.850 kg) were extracted with Me₂CO (4 × 3 L) at room temperature for a week. After filtration, the solvent was evaporated to dryness under reduced pressure and low temperature (< 40°C) yielding a gum (15.7 g), which was dissolved in aq. Me₂CO (40% H₂O, v/v, 100 mL). This solution was cooled to 4°C for 24 h and filtered. The filtrate was extracted with CHCl₃ (3 x 100 mL) and the organic layer was dried (Na₂SO₄) and evaporated in vacuum to afford a residue (2.4 g, bitter fraction). This residue was subjected to CC (55 g silica gel Merck n. 7734, deactivated with 10% H₂O, w/w). Pure petroleum ether (101), followed by a gradient of CH₂Cl₂ – CH₂OH mixtures (10:10 to 9:80:2) were used as eluting solvents. Initially, three diterpene fractions I - III were obtained. Preparative TLC of the fractions (n-hexane- EtOAc, 1:4 was used as eluent) afforded pure compounds as follows, 12.5 mg of polivincin A (1) from fraction I, 9.2 mg of polivincin B (2) from fraction II, 8.0 mg of polivincin C (3) and 11.3 mg of teuvin B (4) from fraction III.

Polivincin A (1). Colorless resin. TLC: Rf 0.75 (EtOAc). IR νmax (KBr): 3447, 2929, 1743, 1637, 1508, 1383, 1246, 1106, 1046, 982, 875, 758, 667 cm⁻¹.

H and 13C NMR: see Table 1. Positive ESIMS (70 eV, direct inlet) m/z (rel. int. in %): 469 [M + Na]⁺ (96.2), 425 (37.2), 381 (38.1), 353 (26.7), 304 (13.8). HRESIMS m/z 469.1844 [M + Na]⁺, (calcd. for C₂₄H₂₉O₈Na: 469.1838).

Polivincin B (2). Amorphous solid. MP: 97–99°C, TLC: Rf 0.72 (EtOAc). IR νmax (KBr): 2931, 1762, 1737, 1655, 1506, 1458, 1383, 1325, 1246, 1212, 1181, 1157, 1083, 1062, 1024, 988, 955, 929, 875, 853, 800, 779, 730, 708, 647, 602 cm⁻¹.

H and 13C NMR: see Table 1. Positive ESIMS (70 eV, direct inlet) m/z (rel. int. in %): 441 [M + Na]⁺ (97.1), 393 (53.9), 358 (6.6), 304 (29.7), 127 (4.0). HRESIMS m/z 441.1861 [M + Na]⁺, (calcd. for C₂₃H₂₈O₇Na: 441.1889).

Polivincin C (3). Colorless oil. TLC: Rf 0.69 (EtOAc). IR νmax (KBr): 3439, 2928, 1759, 1506, 1459, 1383, 1321, 1159, 1056, 1023, 930, 875, 797, 731, 669, 647, 601 cm⁻¹.

H and 13C NMR: see Table 1. Negative ESIMS (70 eV, direct inlet) m/z (rel. int. in %): 377 [M – H]⁻ (95.1), 287 (13.4), 255 (9.1), 183 (6.7), 137 (3.2). HRESIMS m/z 377.1599 [M – H]⁻ (calcd. for C₂₃H₂₇O₇: 377.1600).

3.4. Supplementary data

Tables of complete spectral data, IR spectra, HRESIMS spectra and the 1H NMR, 13C NMR and 2D NMR spectra (with enlarged detailed sections for multiplets and cross peaks) are included in a ‘Supplementary Data’ section.

Declarations of interest

none.

Acknowledgments

We thanks to Bulgarian Ministry of Education and Sciences for the funds Grant DKOF7R0P02/20 and EC FP7 REGPOT Project Bio-Support.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.phytol.2019.04.013.

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