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MONTANIN A AND B, NEW FURANOID DITERPENES OF NOR-CLERODANE TYPE FROM TEUCRIUM MONTANUM L.

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Furanoid diterpenes of the clerodane and nor-clerodane type are common in Teucrium species (Labiatae)[1]. During the course of studies on the chemical constituents of the bitter fraction of Bulgarian T. montanum L. several new compounds of this type were isolated. We now report the structure and stereochemistry of two new nor-clerodane diterpenoids designated as montanin A and montanin B.

Montanin A (1) crystallizes as colorless needles with m.p. 126-7°, $[\alpha]_D$ + 11.5°($CHCl_3$) and molecular formula $C_{19}H_{20}O_4$ (Found, C% 73.48, H% 6.93; Calcd, C% 73.06, H% 6.45; M^+, m/e 312). The IR spectrum of 1 contains an intense band for a γ-lactone at 1760 cm^{-1}. The absorption at 3130, 1600, 1505 and 873 cm^{-1} is due to a furan ring (UV spectrum λ_{max} 217 nm, ε 10800; positive Ehrlich test).

The examination of the ^{1}H-NMR spectrum of 1 shows the α and β protons of the furan ring at δ 7.36 (2H,m) and 6.32 (1H,m). The singlet at 6.98 (1H) is assigned to the C-18 proton. The triplet at 5.38 (1H, J=8 Hz) is due to C-12 proton while the doublet at 1.08 (3H, J=7 Hz) is assigned to the secondary methyl group at C-8.

The structure and stereochemistry of 1 was proved by correlation with teucvin, a nor-clerodane diterpenoid isolated from T. viscidum var. Miquelianum[2]. When 1 was kept five days in $CHCl_3$ autooxidation occurred[3] to give teucvin. The comparison was made with an authentic sample of teucvin[4] by means of IR, ^{1}H-NMR and mass spectra. The autooxidation of 1 proceeds with high stereoselectivity since the yield of teucvin is about 70%.

Montanin B (2), a colourless crystalline compound, m.p. 164-5°, $[\alpha]_D$ + 79° (CH_3OH), $C_{19}H_{24}O_5$ (Found, C% 68.97, H% 7.33; Calcd, C% 68.65, H% 7.28; M^+-H_2O, 314). IR spectrum: 3475 and 3360 cm^{-1}(OH), 3130, 1600, 1505 and 875 cm^{-1}(furan ring), 1760 cm^{-1}(γ-lactone). ^{1}H-NMR spectrum: 7.36 (2H,m, α-furan protons), 6.30 (1H,m, β-furan proton), 5.28 (1H,t, J=8 Hz, C-12 proton), 4.86 (1H, t, J=3 Hz, C-6 proton), 3.86 and 4.20 (each 1H, AB q., J=12 Hz , C-18 proton), 0.90 (3H, d, J=7 Hz, C-17 methyl group).

The presence of two hydroxyl groups was proved by acetylation. When 2 is treated with acetic anhydride in pyridine, 3 is obtained as a colourless resin.

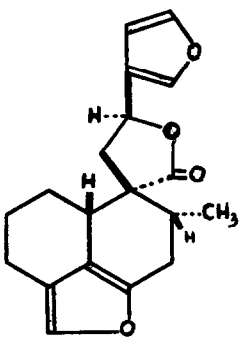
IR spectrum: 1735 and 1720 cm^{-1}(acetyl groups). ^{1}H-NMR spectrum: δ 1.96 and 2.05 (each 3H, two acetyl groups). Mass spectrum: m/e 356 (M^+- CH_3COOH).

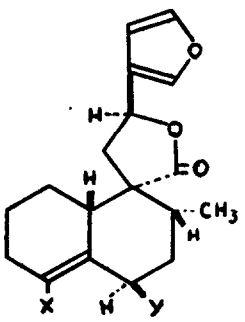
The oxidation of 2 by MnO_2 led to 4, a colourless crystalline compound, m.p. 196-8°. Mass spectrum: m/e 330 (M^+). IR spectrum: 1750 cm^{-1} (γ-lactone) and 1670 cm^{-1}(conjugated aldehyde group). ^{1}H-NMR spectrum: δ 10.36 (1H, aldehyde proton). Treating 4 with P_2O_5 in CH_2Cl_2 solution for 5 min. at room temperature or heating it for 2 - 3 min. near the melting point gave 1. The identification was made by IR, ^{1}H-NMR and mass spectra.

The above-mentioned experiments showed that one of the hydroxyl groups is primary and located at C-18. The second is at C-6 and is secondary one. A double bond should be at C-4 - C-5. The configuration of 2 is the same as 1. The resonance signal of C-6 proton give us the reason to assume an equatorial position for it while the hydroxyl group is axial.

A biogenetic relationship can be suggested between 2, 1 and teucvin. They are connected in one possible biogenetic pathway for derivation of furan and γ-lactone rings in terpenoid compounds[5]. Teucvin was shown to be present in the bitter fraction of T. montanum L. by TLC.

1.





2. X=CH_2OH; Y=OH
3. X=CH_2OAC; Y=OAc
4. X=CHO; Y=OH

References and Note

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4. We thank Professor Eiichi Fujita for the sample of teucvin.
5. F. Sorm, Pure and Applied Chemistry, 21, 281 (1970).