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ABIETANE DITERPENOIDS FROM THE ROOTS OF *SALVIA CRYPTANTHA*

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Key Work Index—*Salvia cryptantha*; Labiatae; diterpenoids; horminone; 7-acetylhorminone; 2β-hydroxyroyleanone; cryptanol (11,12,14-trihydroxyabietae-6,8,11,13-tetraen).

Abstract—In addition to the known compounds horminone and 7-acetylhorminone, two new abietane diterpenoids, 2β-hydroxyroyleanone and cryptanol, were isolated from the roots of *Salvia cryptantha*.

INTRODUCTION

The aerial parts of *Salvia* species contain several triterpenoid compounds [1–6]. However, only two species, *S. triloba* [7] and *S. tomentosa* [8], have given diterpenoids. As a continuation of our investigations, we have examined the roots of *Salvia cryptantha* Montbret and Auches ex. Bentham for diterpenoids. The possible pharmacological activities of *S. cryptantha* will be the subject of another study.

RESULTS AND DISCUSSION

We isolated four diterpenoids from the roots of *S. cryptantha*, two of which are new compounds. The known diterpenoids horminone (7β-hydroxyroyleanone) (1) and 7-acetylhorminone (7β-acetoxyroyleanone) (2) were previously isolated from *S. lanata* [9]. The structures of the known compounds were established by comparing their spectral data to literature values.

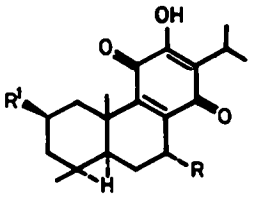
Cryptanol (3) has the composition $C_{20}H_{28}O_3$ on the basis of mass spectrometry ($[M]^+$ *m/z* 316, 44%). Its IR spectrum showed bands at 3350 cm^{-1} for a hydroxyl group, aromatic bands at 1600, 1550, 1535 cm^{-1} and conjugation at 1635 cm^{-1}; the absence of the bands at 1665 and 1645 cm^{-1} indicated an aromatic rather than an *ortho*- or *para*-quinone ring system. Its UV spectrum (λ_{max} 332 and 274 nm) indicated conjugation of an aromatic ring to a double bond rather than conjugation between a *para*-quinoid system and a double bond as in dehydroroyleanone [10]. Its ^1H NMR spectrum showed three methyl signals as singlets at δ0.87 (C-4α), 0.91 (C-4β) and 1.27 (C-10), and two methyl doublets for an isopropyl group at δ1.0 and 1.05 (J = 7 Hz for each, $-HC\langle^{CH_3}_{CH_3}$); the isopropyl methine proton was at δ3.14 (septet, J = 7 Hz). All these signals are common for methyl groups in the abietan skeleton [10–12]. The other protons were as follows: a double-doublet at δ6.45 (J = 3 and 9 Hz, H-6) and 6.79 (J = 3 and 9 Hz, H-7) forming the AB part of an ABX system indicated a double bond in the molecule, the X part being at δ2.13 (t, J = 3 Hz, H-5). There are three possible positions for the double bond: C-1, C-2 or C-6. Since there is conjugation between the double bond and the aromatic ring system as shown by its UV spectrum (332 nm), the only possibe position for the double bond is at C-6. This was confirmed by COSY experiments. The absence of any signals between δ3.14 and 6.45 indicated that the hydroxyl groups were in the aromatic ring rather than in rings A and B. The signals at δ7.3, 7.24 (under the $CHCl_3$ peak) and at δ7.2 indicated three phenolic hydroxyl groups. All these data showed the structure of cryptanol as given in 3.

The mass peak of 2β-hydroxyroyleanone (4) indicated the molecular formula $C_{20}H_{28}O_4$ ($[M]^+$ *m/z* 332, 14%). Its IR spectrum showed a hydroxyl band at 3420 cm^{-1} and *para*-quinone bands at 1665, 1640 and 1610 cm^{-1}. In addition, the UV spectrum (λ, λ_{max} 399, 272 nm) indicated the presence of a *para*-quinone group. The ^1H NMR spectrum of 4 showed the methyl signals as singlets at δ0.88 (C-4α), 0.9 (C-4β) and 1.27 (C-10), and two methyl doublets at δ1.25 (J = 7 Hz, for each $-HC\langle^{CH_3}_{CH_3}$); the isopropyl methyine proton was at δ3.14 (septet, J = 7 Hz). A H_1 triple doublet at δ4.2 (J = 1.1, 2.5 and 4.5 Hz) indicated the presence of a secondary alcohol group having two methylene groups in the structure; the coupling constants established the equatorial position of the proton at C-2. After comparing the chemical shifts and splitting pattern to those of 6α, 6β, 7α, 7β, 2α and 3β-hydroxyroyleanones [10, 12, 13] the structure of 4 is established as 2β-hydroxyroyleanone.

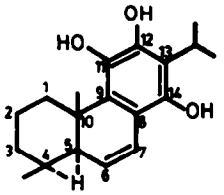
EXPERIMENTAL

Roots of *Salvia cryptantha*, collected from Afyon (western Turkey) in July 1982, were identified by Dr. E. Tuzlaci (University of Marmara, Istanbul). A voucher specimen (ISTE 48915) has been deposited at the Herbarium of the Faculty of Pharmacy, University of Istanbul.

Extraction and isolation of the compounds. Air-dried and powdered roots (370 g) were extracted with petrol, Me_2CO and EtOH, respectively at room temp. The solvents were removed *in*



1 R=OH R¹=H
2 R=OAc R¹=H
4 R=H R¹=OH



3

vacuo. The petrol concentrate (2 g) when separated on a silica gel column (2 × 50 cm) yielded diterpenoids, which were further purified and/or separated by prep. TLC. Elution was started with petrol; a gradient of EtOAc was added up to 100%. The 5–20% EtOAc eluate yielded, in order of elution, cryptanol (20 mg), horminone (15 mg), 7-acetylhorminone (12 mg) and 2β-hydroxyroyleanone (10 mg). Me_2CO and EtOH extracts contained almost the same compounds together with triterpenoids and flavonoids.

Cryptanol (3). Mp 138–142°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3350, 2970, 2920, 2840, 1635, 1600, 1550, 1535, 1455, 1435, 1405, 1385, 1375, 1330, 1270, 1250, 1155, 1100, 960, 900, 800, 770, 755, 735, 720; UV λ_{max}^{MeOH} nm: 332 (log ε 2.9), 274 (log ε 4.2); ^{1}H NMR (FT-NT, 300 MHz, $CDCl_3$): see text; MS (probe, 70 eV, Varian MAT 311) *m/z* (rel. int.): 316 $[M]^+$ (44), 301 $[M-15]^+$ (7.5), 279 (8.8), 271 (2.3), 258 (2.7), 245 (9.7), 232 (11.6), 231 (15.5).

2β-Hydroxyroyleanone (4). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3420, 2970, 2925, 2860, 1665, 1640, 1610, 1460, 1430, 1395, 1375, 1330, 1250, 1170, 1150, 1130, 1060, 1025, 960; UV λ_{max}^{MeOH} nm: 399 (log ε 2.8), 272 (log ε 4.2); ^{1}H NMR (FT-NT, 300 MHz, $CDCl_3$) given in the text; MS (probe, 70 eV, Varian MAT 311) *m/z* (rel. int.): 332 $[M]^+$ (14), 314[M-18]$^+$ (18.1), 299 $[M-18-15]^+$ (3.5), 245 (7.4), 231 (9.6).

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