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TERPENOIDS AND FLAVONOIDS FROM *SALVIA CYANESCENS*

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Key Word Index—*Salvia cyanescens*; Lamiaceae; sesquiterpenes; diterpenes; triterpenes; steroids; flavonoids.

Abstract—The following compounds have been identified in the aerial parts of *Salvia cyanescens*: a new diterpenoid 12-isopentenyl-3-oxosalvipisone, two sesquiterpenes caryophyllene oxide, spathulenol, five diterpenes manoyl oxide, 11β-hydroxymanoyl oxide, ferruginol, aethiopinone and salvipisone, three triterpenes α-amyrin, α-amyrin 3-acetate and lupeol 3-acetate as well as sitosterol and four flavonoids salvigenin, 6-hydroxyapigenin-7,4′-dimethyl ether, 6-hydroxykaempferol-3,6-dimethyl ether and kaempferol-3,7-dimethyl ether.

INTRODUCTION

As a part of our investigations of Turkish *Salvia* species we have studied the aerial parts of *S. cyanescens* Boiss *et* Ball. In addition to a new diterpenoid 12-isopentenyl-3-oxo-salvipisone we have isolated two sesquiterpenes caryophyllene oxide [1], spathulenol [2], five diterpenes manoyl oxide [3], 11β-hydroxymanoyl oxide [4], ferruginol [5], aethiopinone [6], salvipisone [7], three triterpenes α-amyrin, α-amyrin 3-acetate and lupeol 3-acetate together with sitosterol and four flavonoids salvigenin, 6-hydroxy-apigenin-7,4′-dimethyl ether, 6-hydroxy-kaempferol-3,6-dimethyl ether, kaempferol-3,7-dimethyl ether. The structures of the known compounds were determined by comparing their spectral data to those of literature values and by TLC comparison with authentic samples. The structure of the new compound was established by spectral data.

RESULTS AND DISCUSSION

The HREI mass spectrum of the new compound (**1**) gave the molecular formula $C_{25}H_{30}O_4$ (*m/z* 394.2136, calc 394.2144). The ^{1}H NMR spectrum of **1** showed typical signals of salvipisone at δ 7.96 (1H, *d*, $J = 8$ Hz, H-7), 7.50 (1H, *d*, $J = 8$ Hz, H-6), 4.75 (2H, *br s*, CH_2-18), 3.37 (1H, *sept.* $J = 7$ Hz, H-15), 3.16 (2H, *m*, CH_2-1), 2.43 (3H, *s*, Me-20), 1.78 (3H, *s*, Me-19), 1.28 (6H, *d*, $J = 7$ Hz, Me-16 and Me-17), and additional signals for the isopentenyl moiety at δ 5.30 (1H, *br t*, $J = 6.5$ Hz, H-2′), 4.50 (2H, *br d*, $J = 6.5$ Hz, H_2-1′), 1.80 (3H, *br s*), 1.72 (3H, *br s*) (Me-4′ and Me-5′). The relationships between the protons of C-1 and C-2, as well as between H-6 and H-7, between H-1′ and H-2′ were deduced by spin decoupling experiments. The signal at δ 3.16 (2H, *m*) was typical for the C-1 protons of salvipisone which was also observed in the ^{1}H NMR spectrum of 3-oxosalvipisone [8]. Since the C-1 protons were not present in the ^{1}H NMR spectrum of 1-oxosalvipisone [9], the location of the oxo group can not be considered at this position. If the oxo group was placed at C-2, two sets of isolated methylene doublet signals should be observed clearly, therefore the only plausible place for the oxo group was C-3. The ^{13}C NMR spectrum of **1** showed the *p*-quinoid carbonyl signals at δ 184.5 and 183.2. The ketone at C-3 was indicated by the signal at δ 201.7. The IR and ^{1}H NMR spectrum did not show the presence of a hydroxyl group, the acetylation of **1** was unsuccessful indicating that the fourth oxygen in the molecule should be an ether function which followed from the resonance at δ 65.8 *s* in the ^{13}C NMR spectrum. Mass spectral fragment ions at *m/z* 325 [M-C_5H_9]$^+$ and 309 [M-C_5H_9O]$^+$ indicated the presence of an isopentenyl moiety in the molecule. The spectral data showed that compound **1** was 12-isopentenyl-3-oxosalvipisone.

EXPERIMENTAL

Plant material. The aerial parts of *S. cyanescens* were collected from central Turkey (Konya, Ermenek)

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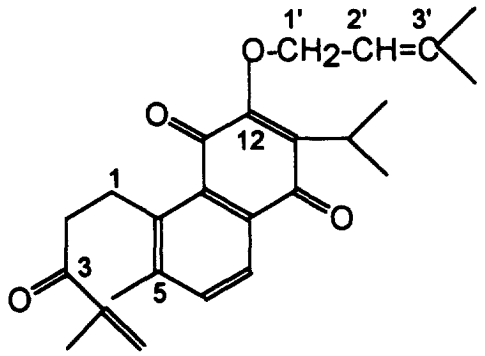

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at an elevation 1650 m in late June 1995. The plant was identified by Dr M. Vural (Ankara), a voucher specimen is deposited in the Herbarium of the Faculty of Pharmacy, University of Ankara AEF 19485.

Extraction and isolation. Powdered plant material (1.8 kg) was extracted with Me_2CO in a Soxhlet to yield 35 g of a residue. The Me_2CO extract was sepd by flash chromatography using solvent mixts hexane–CH_2Cl_2, CH_2Cl_2–Me_2CO and MeOH. Combined frs were further sepd on smaller flash chromatography columns and some frs were sepd on a chromatotron and purified by prep. TLC when necessary. The compounds were isolated in the following order, caryophyllene oxide (20 mg), spathulenol (15 mg), **1** (18 mg), ferruginol (12 mg), aethiopinone (10 mg), salvipisone (10 mg), manoyl oxide (20 mg), lupeyl 3-acetate (20 mg), 11-hydroxymanoyl oxide (15 mg), α-amyrin 3-acetate (16 mg), salvigenin (17 mg), 6-hydroxyapigenin-7,4′-dimethyl ether (5 mg), α-amyrin (12 mg), sitosterol (25 mg), 6-hydroxykaempferol-3,6-dimethyl ether (8 mg), kaempferol-3,7-dimethyl ether (6 mg).

12-*Isopentenyl-3-oxosalvipisone* (**1**). UV λ_{max}^{MeOH} nm (log ε): 445 (3.5), 350 (3.2), 285 (3.4), 270 (3.4), 210 (4.2). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3050, 2950, 2860, 1710, 1670, 1670, 1645, 1595, 1560, 1460, 1380, 1250, 1150. ^1H NMR ($CDCl_3$) given in the text. ^{13}C NMR ($CDCl_3$): C-1 38.1 *t*, C-2 30.2 *t*, C-3 201.7 *s*, C-4 145.5 *s*, C-5 133.4 *s*, C-6 136.3 *d*, C-7 125.4 *d*, C-8 131.5 *s*, C-9 126.4 *s*, C-10 145.5 *s*, C-11 184.5 *s*, C-12 153.2 *s*, C-13 126.4 *s*, C-14 183.2 *s*, C-15 25.7 *d*, C-16 19.8 *q*, C-17 20.2 *q*, C-18 110.2 *t*, C-19 22.4 *q*, C-20 22.4 *q*, C-1′ 65.8 *t*, C-2′ 123.7 *d*, C-3′ 142.9 *s*, C-4′ 24.5 *q*, C-5′ 19.2 *q*. HREIMS *m/z* (rel. int.): 394.2136 $[M]^+$ (4), 325 $[M-69]^+$ (25), 309 $[M-85]^+$ (40), 244 $[M-C_6H_8O-C_4H_6]^+$ (100), 229 (16), 185 (20), 141 (30), 94 (24), 83 (20), 69 (78).

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