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Constituents of *Salvia Verticillata*

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Three new and fourteen known compounds were isolated from the roots of *Salvia verticillata* L. Spectral methods were used for the structure determination besides TLC comparisons with authentic samples for the known compounds.

Key words: *Salvia verticillata*; Lamiaceae; diterpenoids; long chain ester; aromatic ester; steroidal ester.

Introduction

In a previous study of *Salvia verticillata* L. ¹esculetin, luteolin 7-0-glucoside, 6-hydroxyluteolin 5-0-glucoside, cirsimaritin, ursolic, oleanolic, crataegolic, vergaic and betulinic acids, β -sitosterol and sitosterol 3 β -D-glucoside were obtained. In this study, three new compounds, 1-hydroxy-3,5,7-trien-nonanoic acid isobutyl ester (**1**), 4-acetyl-4'-palmityl-1,1'-oxybiphenyl (**2**) and 3 β -p-pentyl-benzoic acid 7-oxositoseryl ester (**3**) and fourteen known compounds were isolated from the new collection of the same plant. The known compounds were identified as diterpenoids manool² (**4**), microstegiol³ (**5**), 2,3-dehydrosalvipisone⁴ (**6**), salvipisone⁵ (**7**), condissiol⁶ (**8**), salvinolonyl 12-Me ether⁷ (**9**) and ferruginol⁸ (**10**), and alcohol, nonacosanol-1⁹ (**11**) (Figure 1), five triterpenoids, α -amyrin¹⁰ (**12**), β -amyrin¹⁰ (**13**), α -amyrin-28-al¹¹ (**14**), ursolic acid¹⁰ (**15**), acetyl oleanolic acid¹⁰ (**16**) and β -sitosterol¹² (**17**) (Figure 2). The structures of the known compounds were decided by comparison of their spectral data of those of literature values (Tables 1-3) and by TLC comparison with authentic samples. The structures of the new compounds were established by UV, IR, ¹H NMR, spin-decoupling and mass spectral data.

Table 1 H NMR DATA of 4,5,6,7,8,9 and 10

H	4	5	6	7	8	9	10
1a		2.78		3.13	2.77		
1b		3.60	3.02		4.08	3.27	2.17
2a		1.47	5.60	1.61	1.68		
2b		1.76			1.82		
3a		1.12	6.82	2.24	1.33		
3b		2.39			2.24		
6		7.06	7.58	7.50	7.12	6.45	
7		6.89	7.97	7.95	7.02		
11							6.64
14	5.91	6.96			7.08	7.72	6.84
15a	5.21	3.02	3.37	3.37	3.00	3.22	3.11
15b	5.05						
16	1.26	1.16	1.28	1.30	1.21	1.25	1.22
17a	4.80	1.21	1.28	1.30	1.13	1.27	1.24
17b	4.47						
18a	0.87	0.79	4.81	4.74	2.48	1.25	0.96
18b			4.81		2.25		
19a	0.78	0.81	1.84	1.79	4.92	1.34	0.94
19b					4.97		
20	0.67	2.32	2.42	2.43	2.30	1.65	1.19
OH		4.51	7.64	7.77	4.40	6.29	
OMe						3.82	

Table 2. C NMR DATA of 5,7,8 and 9

C	5	7	8	9
1	26.82	27.1	25.79	40.5
2	23.50	30.0	30.02	18.7
3	43.11	38.5	32.38	34.2
4	38.16	145.5	152.26	38.2
5	137.15	143.0	137.89	175.4
6	130.20	136.3	130.24	123.5
7	127.01	125.5	127.96	185.4
8	129.20	133.5	125.79	127.4
9	139.25	126.5	139.11	136.7
10	142.25	144.8	144.8	42.2
11	84.45	183.4	80.09	145.8
12	206.02	153.2	209.15	148.2
13	141.50	123.8	142.37	139.7
14	140.19	184.5	140.72	115.8
15	27.09	24.6	26.79	26.8

16	21.10	19.9	21.66	23.6
17	22.08	19.9	20.16	23.6
18	21.68	110.3	54.27	24.8
19	27.99	22.4	117.72	29.3
20	21.35	20.2	20.01	33.2
OMe				61.9

Table 3. H NMR DATA of 12,14,15 and 17

H	12	14	15	17
3	3.24	3.1	3.2	3.52
6				5.37
12	5.18	5.3	5.24	
18				0.7
19				1.0
21				0.8
23	0.87	0.85	0.73	
24	0.79	0.75	0.78	
25	0.85	0.87	0.90	
26	1.04	1.02	1.05	0.92
27	1.06	1.05	1.24	0.92
28	0.96	9.22		
29	1.00	1.00	0.97	0.85
30	1.02	1.05	0.97	

Experimental

General

UV (Varian Techtron 635, in MeOH), IR (Permin Elmer 983, in CHCl₃), ¹H(200 MHz) and ¹³C(50.31 MHz) NMR (Bruker AC 200L, in CDCl₃), HREIMS (VG ZabSpec).

Plant Material

The roots of *Salvia verticillata* L. were collected from Çorum (Sungurlu) (Central Turkey) in July, 1995. The plant was identified by Dr. Neriman Özhatay (Isanbul), a voucher specimen is deposited in the Herbarium of the Faculty of Pharmacy, University of Istanbul, ISTE 68379.

Extraction and Isolation of the Compounds

Air dried and powdered plant material (552 g) was extracted with distilled acetone in a Soxhlet, evaporated under a vacuum, wherein 7.2 g crude extract was obtained, it was then fractioned in a Si gel column (4x70 cm)eluting with PE, a gradient of EtOAc and EtOH were added up to 100%. The compounds were isolated by using a Chromatotron and by preparative TLC. The ¹H NMR data of the diterpenoids **4-10** are given in Table 1, the ¹³C NMR data of compounds **5-9** in Table 2 ad the ¹H NMR data of triterpenoids **12, 14,15** and **17** in Table 3.

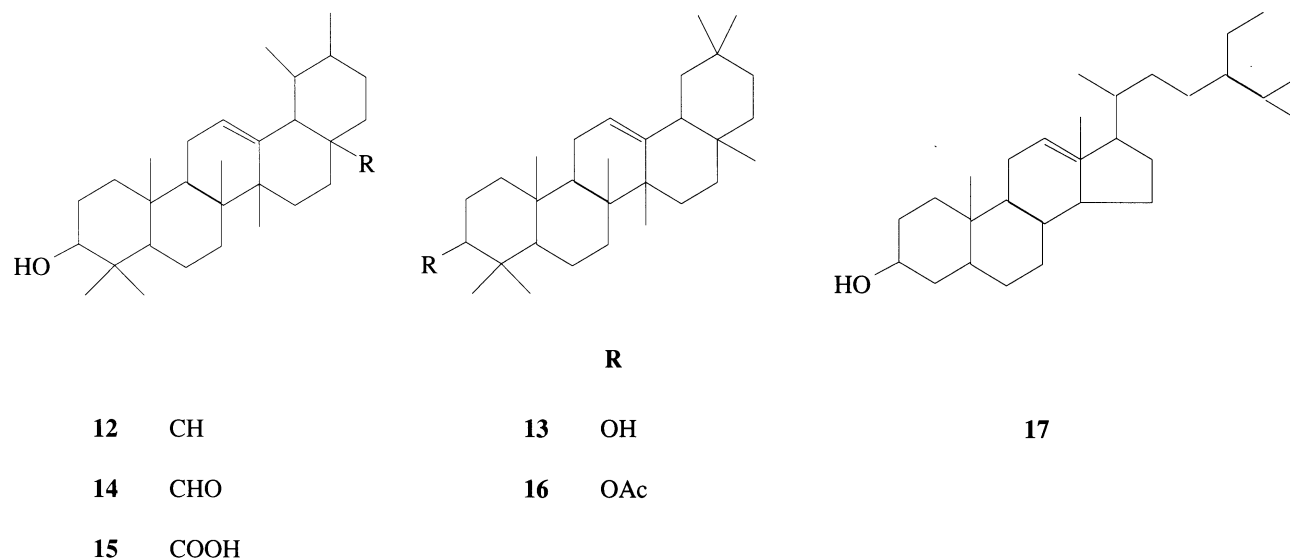


Figure 2.

4-Acetyl-4'-palmityl-1,1'-oxybiphenyl (2)

Amorphous compound. UV λ_{\max} (MeOH) nm (log ϵ): 314 sh, 276 (3.0), 241 (4.1). IR ν_{\max} (CHCl₃)cm⁻¹: 3050, 2918, 2850, 1733, 1605, 1576, 1540, 1464, 1377, 1275, 1175. ¹H NMR δ (CDCl₃): 7.98(4H,d,J=7.5 Hz, H-2 and H-6, H-2' and H-6), 7.48 (4H, d, J=7.5 Hz, H-3 and H-5, H-3' and H-5'), 3.28 (2H,t,J=6,5 Hz, H-1''), 2.28 (3H, s, OAc), 1.6[28H,s, (CH₂)₁₄], 0.78 (3H,t,J=7.0 Hz, Me-16'').HREIMS *m/z* (rel.int): 452.3286 [M]⁺ (6) C₃₀H₄₄O₃, 438 [M-Me+1]⁺ (9), 301 [M-C₈H₇O₃]⁺ (6), 225 [M-C₁₄H₁₁O₃]⁺ (5), 203 (100), 190 (46), 175 (29), 133 (41), 121 (26), 109(30), 95 (43), 81 (37), 69 (50).

3- β -p-Pentyl-benzoic acid 7-oxo-sitosteryl ester (3)

Amorphous compound. UV λ_{\max} (MeOH) nm (log ϵ): 311 sh, 283 (2.7), 245(4.3). IR ν_{\max} (CHCl₃) cm⁻¹: 3050, 2960, 2920, 2880, 1730, 1680, 1620, 1520, 1460, 1380, 1230, 1190, 1115, 860, 830. ¹H NMR δ (CDCl₃): 7.08 (2H, d, J=8.5 Hz, H-3'and H-5'), 6.78 (2H, d, J=8.5 Hz, H-2'and H-6'), 5.72 (1H, br s, H-6), 4.22 (1H, t, J=7.0 Hz, H-3), 2.85 (2H, t, J=7.0 Hz, H-1''), 2.32 (2H, m, H-2''), 2.01 (4H, m, H-3'' and H-4''), 1.0 (3H,t,J=7.0 Hz, Me-5''), 1.17 (3H, s, Me-19), 0.7 (3H, s, Me-18), 0.81 (3H, d, J=7.0 Hz, Me-21), 0.83 (6H, d, J=7.0 Hz, Me-26 and Me-27), 0.88 (3H, t, J=6.0 Hz, Me-29). HREIMS *m/z* (rel.int): 602.4678 [M]⁺ (15) C₁₄H₂₆O₃, 573 [M-C₂H₅]⁺ (9), 428 [M-C₁₂H₁₄O]⁺ (4), 368 (87), 339 (24), 327 (14), 313 (52), 285 (23), 264 (34), 248 (51), 236 (64), 203 (24), 190 (18), 164 (26), 151 (34), 135 (19), 120 (100), 109 (26), 98 (33), 84 (53), 72 (11).

Nonacosanol-1(11)

Amorphous compound. UV λ_{\max} (MeOH) nm (log ϵ): 214 (3.5). IR ν_{\max} (CHCl₃) cm⁻¹: 3300, 2930, 2850, 1720, 1460, 1380, 1219, 1120, 1065, 760. ¹H NMR δ (CDCl₃): 3.65 (2H,t,J=6.5 Hz, H-1), 1.3 [54H, s, (CH₂)₂₇], 0.87 (3H, s, Me-29), 0.8 (1H,s,1-OH). HREIMS *m/z* (rel.int.): 424.4280 [M]⁺ (8) C₂₉H₆₀O, 413 (8), 364 (7), 336 (9), 308 (8), 280 (13), 218 (30), 189 (13), 153 (21), 139 (32), 125 (56), 111 (77), 97 (100), 83 (97), 69 (8), 57 (75).

Results and Discussion

1-Hydroxy-3,5,7-trien-nonanoic acid isobutyl ester (1) had a molecular formula C₁₃H₂₀O₃, as indicated by its HR mass spectrum (*m/z* 224.1410, calc. 224.1412). The UV spectrum showed conjugation at 276 nm

indicating a successive three unsaturated carbons in a sequence. The IR spectrum indicated hydroxyl (3440 cm^{-1}), aliphatic (2950, 2920, 2880 cm^{-1}) and ester (1723, 1280 cm^{-1}) groups. In the ^1H NMR spectrum, isobutyl group was observed a δ 0.98 (6H, d, $J=7.0$ Hz, Me-3' and Me-4'), 2.04 (1H, m, H-2') and 4.1 (2H, d, $J=6.5$ Hz, H-1'). Spin-decoupling experiments showed the relations between H-2', H-3', H-4' as well as with H-1'. The sequence from C-1-C-4 and from C-5-C-8 were also established by spin-decoupling experiments, when the signal at δ 1.7 (1H, pentet, $J=7.0$ Hz, H-2b) irradiated the triplet at δ 4.3 (2H,t, $J=6.5$ Hz, H-1) collapsed to a singlet and the pentet at δ 1.45 (1H, $J=7.0$ Hz, H-2a) turned to a triplet. The signals at δ 7.52 (1H, m, H-3), 7.54 (2H, m, H-5 and H-4), 7.71 (2H, m, H-6 and H-7) and 7.72 (1H, d, $J=10$ Hz, H-8) revealed the conjugated triene group. The mass degradation pattern also verified the given structure of compound **1**.

The molecular formula $\text{C}_{30}\text{H}_{44}\text{O}_3$ of 4-acetyl-4'-palmityl-1,1'-oxybiphenyl (**2**) derived from its HREI mass spectrum (m/z 452.3286, calc. 452.3290). Its UV spectrum showed a conjugated aromatic system at 314(sh), 276 and 241. The IR spectrum indicated the presence of aliphatic group (2918, 2850 cm^{-1}), ester (1733, 1275 cm^{-1}), ether (1175 cm^{-1}) and aromatic (1605, 1576 and 1540 cm^{-1}) groups. The ^1H NMR spectrum of **2** showed the structure quite clearly. The acetyl group that was observed at δ 2.28 (3H, s, OAc) must be placed to para position of the aromatic ring due to signals being present at δ 7.98 (4H, d, $J=7.5$ Hz, H-2, H-6 and H-2', H-6') and 7.48 (4H, d, $J=7.5$ Hz, H-3, H-5 and H-3', H-5'). Other signals is the ^1H NMR spectrum correlated the presence of a long chain hydrocarbon group, the methylene signal at δ 3.28 (2H,t, $J=6.5$ Hz) showed CH_2-1'' , the rest of this group were observed at δ 1.6 (28H, s, $(\text{CH}_2)_{14}$) and 0.78 (3H,t, $J=7.0$ Hz, Me-16"). The presence of this hydrocarbon moiety in compound **2** was also observed from the mass degradation. All spectral data verified the structure of **2**.

The HR mass spectrum of **3** exhibited molecular formula $\text{C}_{41}\text{H}_{62}\text{O}_3$ (m/z 602.4678, calc. 602.4698). The IR spectrum of **3** showed absorbances for aromatic (3053, 1620, 1520, 1460 cm^{-1}), aliphatic (2960, 2920, 2880 cm^{-1}), ester carbonyl (1730 cm^{-1}) and enone (1680 cm^{-1}) groups. Its UV spectrum showed conjugation with maxima at 311(sh), 283 and 245nm. The ^1H NMR signals were observed at δ 0.7 (3H, s, Me-18), 1.17 (3H,s,Me-19), 0.81(3H,d, $J=7.0$ Hz, Me-21), 0.83 (6H, d, $J=7.0$ Hz, Me-26 and Me-27), 0.88 (3H,t, $J=6.0$ Hz, Me-29), 4.22 (1H,t, $J=7.0$ Hz, H-3) and 5.72 (1H,br s, H-6). Since vinylic proton (H-6) was observed at δ 5.72 as a broad singlet an oxo group should be placed at C-7. Based on the above given data compound **3** was decided to have a steroidal skeleton with an additional side chain, also as understood from is MS degraditon. In the ^1H NMR spectrum the signals of the side chain were observed at δ 7.08 (2H, d, $J=8.5$ Hz, H-3' and H-5'), 6.78 (2H, d, $J=8.5$ Hz, H-2' and H-6') (aromatic protons), 2.85 (2H,t, $J=7.0$ Hz, H-1"), 2.32 (2H, m, H-2"), 2.01 (4H,m,H-3" and H-4"), .0 (3H, t, $J=7.0$ Hz, Me-5") indicating the pentyl group. The Spectral data indicated that compound (**3**) was 3β -p-pentyl-benzoic acid 7-oxo-sitosteryl ester.

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