

**ANTHRAQUINONE, NAPHTHALENE,
AND NAPHTHOQUINONE COMPONENTS
OF *Asphodeline lutea***

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The genus *Asphodeline* belongs to the family Asphodelaceae, subfamily Asphodeloideae. The 1,8-dihydroxy-anthraquinones based on a chrysophanol unit are characteristic compounds of this subfamily. Anthraquinones, flavonoids, oxepines, and sesquiterpene lactones have been reported to occur in the genus *Asphodeline* [1–4].

Asphodeline lutea is a perennial plant growing in the Mediterranean region. The only report found on this plant species reveals the presence of 1,8-dihydroxyanthraquinones, flavonoids, and a chlorogenic acid [5]. Data on the biological activity and the medicinal use of *A. lutea* are not available. However, the edible use of its roots, shoots, and flowers has been reported [6]. The ancient Greeks roasted the roots like potatoes and ate them with salt and oil or mashed them with figs. The raw fresh flowers are very decorative and a tasty addition to salad, while the young shoots are eaten cooked.

The roots of *A. lutea* were collected in June 2005 near the town of Pernik, Bulgaria. The dried roots (0.70 kg) of *A. lutea* were extracted with methanol (3 times $\times$ 24 h $\times$ 2.7 L) at room temperature, then concentrated in vacuum to give a crude methanol extract (22.0 g). Solvent-solvent partition of this extract using petroleum ether, chloroform, and ethylacetate afforded the corresponding petroleum ether (4.3 g), chloroform (5.2 g), and ethylacetate (0.5 g) extracts and an aqueous residue (15.2 g).

The petroleum ether extract was subjected to liquid vacuum chromatography (LVC) on silica gel using PE, PE-CHCl₃ (3:1 $\rightarrow$ 1:3), CHCl₃, CHCl₃-EtOAc (1:1), and EtOAc to give fractions F1-F6. Silica gel CC and repeated pTLC of F6 afforded compounds **1** (2 mg), **2** (6 mg), **3** (7 mg), **4** (3 mg), and **5** (1 mg).

LVC of the chloroform extract with PE-CHCl₃ (20:1 $\rightarrow$ 1:1) and CHCl₃ gave fractions F1-F4. From F4 after silica gel CC and pTLC separation components **6** (4 mg), **7** (2 mg), **5** (5 mg), and **8** (6 mg) were isolated.

The chemical structures of the isolated compounds were determined by a combination of spectral methods (UV, IR, 1D and 2D NMR, and MS) and comparison with literature data as chrysophanol (**1**) [7], 1,5,8-trihydroxy-3-methylantraquinone (**2**) [8], 2-acetyl-1,8-dimethoxy-3-methylnaphthalene (**3**) [9, 10], 1-hydroxy-8-methoxy-3-methylantraquinone (**4**) [11], asphodeline (**5**) [12], 2-acetyl-1-hydroxy-8-methoxy-3-methylnaphthalene (**6**) [9, 10], 2-acetyl-8-methoxy-3-methylnaphthoquinone (**7**) [13], and 1,1',8,8',10-pentahydroxy-3,3'-dimethyl-10,7'-bianthracene-9,9',10'-trione (**8**) [14]. Of them only chrysophanol (**1**) and asphodeline (**5**) have been reported to occur in *A. lutea* [5]. The anthraquinones **2** and **4** and the naphthalene compounds **3** and **6** are new for the genus *Asphodeline*. The naphthoquinone **7** is a known synthetic compound [13]. However, this is the first report on its natural occurrence and on the presence of naphthoquinones in *Asphodeline* species.

A full assignment of all protons and carbons in the molecule of **3** was undertaken by detailed 1D and 2D NMR measurements because of the discrepancy between the assignments of C signals in previous reports [9, 10]. Our data are presented in Table 1. The ¹³C NMR data of **7** have been reported by Piggot and Wege without any assignment [13]. Our results from the complete assignment of all protons and carbons achieved by 1D and 2D NMR experiments are presented in Table 1.

2-Acetyl-1,8-dimethoxy-3-methylnaphthalene (3). UV (EtOH, $\lambda_{\max}$, nm): 225, 299, 313 sh, 329; IR (KBr, $\nu_{\max}$, cm⁻¹): 2924, 2839, 1700, 1623, 1568, 1460; EI-MS (m/z , I_{rel} , %): 244 (M⁺, 70.9), 229 (100), 214 (8.1), 201 (1.5), 186 (25.8), 158 (4.8), 128 (19.3), 127 (9.7), 115 (20.9), 43 (5.6). For ¹H and ¹³C NMR data, see Table 1.

TABLE 1. ^1H and ^{13}C NMR Data for **3**, **6**, and **7** (CDCl_3 , δ , ppm, J/Hz)

C atom	3		6		7	
	δ_{H}	δ_{C}	δ_{H}	δ_{C}	δ_{H}	δ_{C}
1		153.0		152.4		182.8
2		134.6		124.7		147.2
3		132.1		134.2		140.0
4	7.36 (q, J = 1.0)	125.1	7.10 (q, J = 1.0)	119.8		185.4
5	7.32 (dd, J = 7.8, 1.3)	120.3	7.31 ^a	121.1	7.76 (dd, J = 7.2, 1.1)	118.0
6	7.39 (t, J = 7.3)	127.1	7.32 ^a	127.0	7.72 (t, J = 8.0)	135.3
7	6.83 (dd, J = 7.8, 1.3)	105.4	6.75 (dd, J = 6.2, 2.2)	104.0	7.31 (dd, J = 8.0, 1.1)	119.5
8		156.0		156.5		159.7
9		118.0		113.2		119.0
10		137.2		136.6		133.8
11		206.2		205.4		202.0
12	2.60	32.6	2.62 s	32.3	2.50 s	31.9
13	2.35 (d, J = 1.0)	19.0	2.37 (d, J = 1.0)	20.0	2.07 s	12.6
OMe-1	3.82	64.0				
OMe-8	4.02	56.0	4.06 s	56.2	4.03 s	56.5

^aOverlapping signals.

2-Acetyl-1-hydroxy-8-methoxy-3-methylnaphthalene (6). UV (EtOH, λ_{max} , nm): 225, 260, 299, 313 sh, 336; IR (KBr, ν_{max} , cm^{-1}): 3347, 2924, 2850, 1683, 1631, 1581, 1470; EI-MS (m/z , I_{rel} , %): 230 (M^+ , 60.7), 215 (100), 200 (49.0), 187 (2.0), 172 (4.0), 144 (4.0), 128 (8.0), 127 (8.0), 115 (17.6), 43 (2.0). For ^1H and ^{13}C NMR data, see Table 1.

2-Acetyl-8-methoxy-3-methylnaphthoquinone (7). UV (EtOH, λ_{max} , nm): 248, 397; IR (KBr, ν_{max} , cm^{-1}): 2923, 2851, 1713, 1654, 1642, 1581, 1472, 1276, 1264; EI-MS (m/z , I_{rel} , %): 244 (M^+ , 100), 229 (74.2), 201 (56.0), 186 (14.3), 173 (15.9), 158 (6.0), 145 (6.7), 128 (6.7), 115 (21.2), 43 (10.6). For ^1H and ^{13}C NMR data, see Table 1.

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