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# ABIETANE DITERPENOIDS FROM THE ROOT OF *SALVIA PHLOMOIDES*

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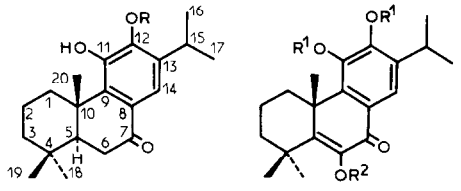
**Key Word Index**—*Salvia phlomoides*; Labiatae; diterpenoids; new abietane derivatives; demethylcryptojaponol; 14-deoxycoleon U; salviphlomone.

**Abstract**—From the root of *Salvia phlomoides* three new abietane diterpenoids, demethylcryptojaponol, 14-deoxycoleon U and salviphlomone, have been isolated, besides the previously known diterpenes 8,13-abietadiene, 8,11,13-abietatriene, royleanone, 7α-acetoxyroyleanone, taxodione, taxodone, cryptojaponol and sugiol. The structures of demethylcryptojaponol (11,12-dihydroxy-8,11,13-abietatrien-7-one), 14-deoxycoleon U (6,11,12-trihydroxy-5,8,11,13-abietatetraen-7-one) and salviphlomone (6α,7β-dihydroxy-8,13-abietadiene-11,12-dione) were established by chemical and spectroscopic means.

## INTRODUCTION

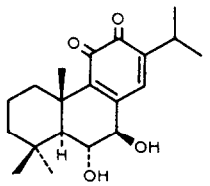
In a continuation of our studies on the diterpenoid compounds from *Salvia* spp. [1, 2], we have now investigated the root of *S. phlomoides*, a species from the aerial part of which several new triterpenoids have been previously isolated [3, 4]. From the root of this plant 11 diterpenic compounds have been isolated, eight of which are the previously known 8,13-abietadiene [5, 6], 8,11,13-abietatriene [7–9], royleanone (12-hydroxy-8,12-abietadiene-11,14-dione) [10, 11], 7α-acetoxyroyleanone (7α-acetoxy-12-hydroxy-8,12-abietadiene-11, 14-dione) [10], taxodione [11-hydroxy-7,9(11),13-abietatriene-6,12-dione] [11], taxodone [6α,11-dihydroxy-7,9(11),13-abietatrien-12-one] [11], cryptojaponol (**2**, 11-hydroxy-12-methoxy-8,11,13-abietatrien-7-one) [12–14] and sugiol (12-hydroxy-8,11,13-abietatrien-7-one) [11, 13–15], and the other three are new substances, whose structures are established as 11,12-dihydroxy-8,11,13-abietatrien-7-one (**1**, demethylcryptojaponol), 6,11,12-trihydroxy-5,8,11,13-abietatetraen-7-one (**3**, 14-deoxy-coleon U) and 6α,7β-dihydroxy-8,13-abietadiene-11,12-dione (**6**, salviphlomone).



**1** R = H
**2** R = Me



**3** $R^1 = R^2 = H$
**4** $R^1 = Ac$, $R^2 = H$
**5** $R^1 = R^2 = Ac$



**6**

## RESULTS AND DISCUSSION

The first of the new diterpenoids (demethylcryptojaponol, **1**), $C_{20}H_{28}O_3$, had an IR spectrum which showed phenolic (3590, 3380 broad, $cm^{-1}$) and aryl-ketone (3020, 3010, 1655, 1635, 1570 $cm^{-1}$) absorptions. The presence of an *o*-diphenol moiety conjugated with a ketone function in compound **1** was revealed by its UV spectra obtained after addition of base, aluminium chloride and boric acid (Table 1), which showed characteristic band shifts of this chromophore [16].

However, it was the $^1H$ NMR spectrum of demethylcryptojaponol that provided the most information and established an abietane structure such as **1** for this new diterpenoid. Effectively, this spectrum (Table 2) showed signals of an isopropyl group attached to an aromatic ring, and of three methyl groups attached to fully substituted $sp^3$ carbon atoms. A one-proton doublet of triplets signal at $\delta$ 3.81 was assigned to the C-1β equatorial proton ($J_{1\beta,1\alpha} = 12$ Hz, $J_{1\beta,2\alpha} = J_{1\beta,2\beta} = 3$ Hz), which appears at lower field because of the existence of an oxygenated function on C-11 [17, 18]. The C-14 aromatic proton showed a singlet at $\delta$ 8.08, strongly deshielded by the C-7 ketone grouping, as has been shown in cryptojaponol (**2**) and sugiol [11–15]. Finally, an ABX system at $\delta$ 1.85 (1H, *dd*, $J_{5\alpha,6\beta} = 11$ Hz, $J_{5\alpha,6\alpha} = 6$ Hz), 2.67 (1H, *dd*, $J_{6\alpha,6\beta} = 15$ Hz) and 2.70 (1H, *dd*) was assigned to the C-5 methyne and the C-6 methylene groups. Final proof that demethylcryptojaponol has the structure and absolute configuration depicted in formula **1** was obtained by

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Table 1. UV spectra of compounds **1**, **3** and **6** [$\lambda_{max}$ nm (log $\varepsilon$)]

| | EtOH | | + NaOMe | | + $AlCl_3$ | | + $AlCl_3$–HCl | | + NaOAc–$H_3BO_3$ | |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | 216.5 | (4.10) | 218.5 | (4.29) | 218 | (4.22) | 217 | (4.22) | 217 | (4.22) |
| | 235 | (3.96) | 259 | (4.00) | 257 | (4.18) | 235 | (4.15) | 252 | (4.16) |
| | 290 | (3.90) | 364 | (4.21) | 280 sh | (3.64) | 290 | (4.02) | 315 | (3.88) |
| | 364 sh | (3.36) | | | 318 sh | (3.85) | 362 sh | (3.23) | 349 | (3.94) |
| | | | | | 357 | (4.02) | | | | |
| | | | | | 420 sh | (3.65) | | | | |
| **3** | 215 | (4.10) | 221 | (4.21) | 224 | (4.22) | 221 | (4.19) | 219 | (4.18) |
| | 251.5 | (3.99) | 270 | (4.16) | 270 | (4.12) | 256 | (4.04) | 266 | (4.22) |
| | 288 | (3.91) | 295 | (3.76) | 280 | (4.20) | 314 | (4.00) | 296 | (3.85) |
| | 343 | (3.95) | 412 | (4.09) | 329 | (4.00) | 409 | (4.08) | 340 sh | (3.70) |
| | | | | | 380 | (3.70) | | | 390 | (3.94) |
| | | | | | 464 | (4.09) | | | | |
| **6** | 217 | (3.99) | 225 | (4.18) | † | | † | | † | |
| | 256 sh | (3.52) | 257 | (4.02) | | | | | | |
| | 422 | (3.48) | 364 | (4.12) | | | | | | |
| | 582 | (1.90) | * | | | | | | | |

*Decomposition; addition of hydrochloric acid does not regenerate the spectrum in ethanol.
†No variation was observed.

Table 2. $^1$H NMR data of compounds **1**, **3** and **6** (90 MHz, pyridine-$d_5$, TMS as internal standard)*

| | **1** | **3** | **6** |
|---|---|---|---|
| H-1$\beta$ | 3.81 *dt*<br>$J_{1\beta,1\alpha}$ = 12 Hz<br>$J_{1\beta,2\alpha} = J_{1\beta,2\beta}$ = 3 Hz | ≅ 3.50§ | 2.76 *dt*<br>$J_{1\beta,1\alpha}$ = 12.6 Hz<br>$J_{1\beta,2\alpha} = J_{1\beta,2\beta}$ = 3 Hz |
| H-5 | 1.85 *dd*<br>$J_{5\alpha,6\beta}$ = 11 Hz<br>$J_{5\alpha,6\alpha}$ = 6 Hz | — | 1.53 *d*<br>$J_{5\alpha,6\beta}$ = 11.1 Hz |
| H-6$\alpha$ | 2.70 *dd*<br>$J_{6\alpha,6\beta}$ = 15 Hz | — | — |
| H-6$\beta$ | 2.67 *dd* | — | 4.35 *dd*<br>$J_{6\beta,7\alpha}$ = 7.8 Hz |
| H-7$\alpha$ | — | — | 4.58 *br d*<br>$J_{7\alpha,14}$ < 1 Hz |
| H-14 | 8.08 *s* | 8.12 *s* | 7.40 *br s*<br>$W_{1/2}$ = 3 Hz |
| H-15 | 3.59 *septet*<br>$J_{15,16} = J_{15,17}$ = 7.5 Hz | 3.53 *septet*<br>$J_{15,16} = J_{15,17}$ = 7.2 Hz | 2.90 *br septet*<br>$J_{15,16} = J_{15,17}$ = 6.9 Hz<br>$J_{15,14}$ < 1 Hz |
| Me-16† | 1.28 *d* | 1.28 *d* | 1.04 *d* |
| Me-17† | 1.27 *d* | 1.28 *d* | 1.03 *d* |
| Me-18‡ | 0.86 *s* | 1.59 *s* | 1.23 *s* |
| Me-19‡ | 0.91 *s* | 1.63 *s* | 1.37 *s* |
| Me-20 | 1.55 *s* | 1.89 *s* | 1.50 *s* |

*Spectral parameters were obtained by first order approximation.
†,‡Assignments bearing the same sign may be reversed.
§Overlapped with the H-15 signal.

treatment with ethereal diazomethane, which yielded a compound identical in all respects (mp, mmp, $[\alpha]_D$, IR, UV, $^1$H NMR and mass spectra) with natural cryptojaponol (**2**) [12–14], a diterpenoid whose structure is firmly established by partial syntheses [9, 19]. Demethylcryptojaponol (**1**) has been previously synthesized, but it was transformed without characterization into cryptojaponol [9, 19].

Another of the new diterpenoids, 14-deoxycoleon U (**3**), had a molecular formula $C_{20}H_{26}O_4$, and its IR spectrum showed phenolic (3530, 3390, 3240–2500 broad, $cm^{-1}$) and additionally conjugated aryl-ketone (3030, 1630, 1585, 1555 $cm^{-1}$) absorptions. The UV spectra of compound **3**, obtained in neutral medium and after addition of alkali, aluminium chloride, aluminium chloride plus hydrochloric acid, and boric acid (Table 1), showed that

the molecule of this diterpenoid possessed *o*-diphenol and diosphenol groupings, because the observed band shifts in different media are characteristic of these chromophores [16]. The $^1$H NMR spectrum of 14-deoxycoleon U (Table 2) was almost identical with the spectrum of coleon U (6, 11, 12, 14-tetrahydroxy-5, 8, 11, 13-abietatetraen-7-one) [18], the only difference was the presence in the spectrum of compound **3** of a one-proton singlet signal at $\delta$ 8.12, which must be assigned to the C-14 aromatic proton [11–15]. Thus, structure **3** was established for this new diterpenoid and this structure is in agreement with its $^{13}$C NMR spectrum (Table 3). Effectively, the C-1–C-7, C-10, and C-18–C-20 carbon atom resonances of compound **3** were almost identical with those reported for coleon U [18], whereas their C-8, C-9 and C-11–C-17 carbon atom resonances were the same as the ones observed in carnosolone (20,6$\beta$-epoxy-6$\alpha$,11,12-trihydroxy-8,11,13-abietatrien-7-one) [20]. Finally, a normal abietane absolute configuration was established for 14-deoxycoleon U (**3**), because the variation of the optical rotations of this compound and its di- and triacetyl derivatives (**4** and **5**, respectively, see Experimental) is similar to that observed for coleon U and its acetates, and the normal abietane absolute configuration of these last compounds is well-known [18].

Table 3. $^{13}$C NMR chemical shifts (in $\delta$-values from TMS) of compound **3***

| | | | |
|---|---|---|---|
| C-1 | 30.4 *t*† | C-11 | 139.9 *s* |
| C-2 | 18.2 *t* | C-12 | 149.7 *s* |
| C-3 | 37.0 *t* | C-13 | 135.4 *s* |
| C-4 | 36.6 *s* | C-14 | 116.4 *d* |
| C-5 | 143.8 *s*‡ | C-15 | 27.6 *d* |
| C-6 | 143.9 *s*‡ | C-16 | 22.8 *q*§ |
| C-7 | 180.5 *s* | C-17 | 23.0 *q*§ |
| C-8 | 121.3 *s* | C-18 | 28.1 *q*‖ |
| C-9 | 142.3 *s*‡ | C-19 | 27.6 *q*‖ |
| C-10 | 41.3 *s* | C-20 | 28.4 *q*‖ |

*At 20.15 MHz, in pyridine-$d_5$ solution.

†SFORD multiplicity.

‡, §, ‖Assignments bearing the same sign may be interchanged.

The last diterpenoid was named salviphlomone. It possesses the structure depicted in **6**, which is in complete agreement with the following results. Salviphlomone (**6**) had a molecular formula $C_{20}H_{28}O_4$, and its IR spectrum showed hydroxyl (3570, 3460 cm$^{-1}$) and *o*-benzoquinone (1677, 1660, 1605, 1580 cm$^{-1}$) absorptions [21]. The presence in salviphlomone of an *o*-benzoquinone moiety was also confirmed by its UV spectrum (Table 1) which was identical to that of 3,5-di-*t*-butyl-1,2-benzoquinone [21], and by the fact that in its mass spectrum there were two ions at *m/z* 330 $[M-2]^+$ and 334 $[M+2]^+$, which are only typical of *o*-quinonoid compounds [21]. The $^1$H NMR spectrum of salviphlomone (**6**) showed signals of an isopropyl group and three methyl groups identical with those found in the other diterpenoids (Table 2). A one-proton doublet of triplets signal at $\delta$ 2.76 was assigned to the C-1$\beta$ equatorial proton [17, 18] and three signals at $\delta$ 1.53 (*d*), 4.35 (*dd*) and 4.58 (*br d*) were attributed to the C-5–C-7 protons, respectively. The coupling values of these protons ($J_{5,6}$ = 11.1 Hz, $J_{6,7}$ = 7.8 Hz) are only compatible with a 5$\alpha$-H, 6$\beta$-H, 7$\alpha$-H arrangement in abietanes with an aromatic or pseudoaromatic C ring [22]. Finally, the C-14 quinonoid proton of salviphlomone (**6**) appeared in its $^1$H NMR spectrum at $\delta$ 7.40 as a broad singlet ($W_{1/2}$ = 3 Hz) and, on irradiation at this field, the lines of the signals at $\delta$ 4.58 (H-7$\alpha$) and 2.90 (H-15) were clearly sharpened. Thus, this quinonoid proton must be allylic to both C-7 and C-15 protons, the *o*-quinone group of salviphlomone must be at the C-11 and C-12 positions of an abietane skeleton and, in consequence, only structure **6** is likely for this new diterpenoid.

The absolute configuration of salviphlomone was not ascertained. However, compound **6** is believed to belong to the normal series like the other diterpenoids co-occurring in the same species.

Two of the previously known diterpenoids now isolated from the root of *Salvia phlomoides*, taxodione and taxodone, possess tumor-inhibitory activity against the Walker 256 intramuscular carcinosarcoma in rats [11], and this is the second report of their occurrence in plants, although the 14-methoxy or hydroxy derivatives of taxodione have been previously isolated from Labiatae species [23, 24]. From a chemotaxonomic point of view it is important to note that only two (royleanone and 7$\alpha$-acetoxyroyleanone) of the 11 diterpenoids isolated from *Salvia phlomoides* have been previously found in plants belonging to the Labiatae family.

## EXPERIMENTAL

Mps are uncorr. For general details on methods see refs. [1–4]. Assignments of $^{13}$C NMR chemical shifts were made with the aid of off-resonance and noise-decoupled $^{13}$C NMR spectra. Plant materials were collected in April 1982, near Zaorejas (Guadalajara, Spain), and voucher specimens were deposited in the Herbarium of the Faculty of Pharmacy (Madrid 'Complutense' University).

*Extraction and isolation of the diterpenoids.* Dried and finely powdered *S. phlomoides* Asso. roots (370 g) were extracted with $Me_2CO$ (2.5 l.) at room temp. for 1 week. After filtration, the solvent was evaporated yielding a red gum (17 g) which was subjected to dry CC over Si gel (400 g, Merck No. 7734, deactivated with 10% $H_2O$). Elution with *n*-hexane and *n*-hexane–EtOAc mixtures yielded the following compounds in order of elution: 8,13-abietadiene (6 mg) [5, 6], 8,11,13-abietatriene (53 mg) [7–9], *royleanone* (60 mg) [10, 11], *taxodione* (1.7 g) [11], 7$\alpha$-acetoxyroyleanone (210 mg) [10], cryptojaponol (**2**, 26 mg) [12–14], taxodone (75 mg) [11], sugiol (48 mg) [11, 13–15], demethylcryptojaponol (**1**, 460 mg), 14-deoxycoleon U (**3**, 280 mg) and salviphlomone (**6**, 145 mg). The previously known diterpenoids were identified by their physical (mp, $[\alpha]_D$) and spectroscopic (IR, UV, $^1$H NMR, MS) data and, in some cases, by comparison with authentic samples.

*Demethylcryptojaponol* (**1**). Mp 184–187° (from EtOAc–*n*-hexane, pale yellow plates); $[\alpha]_D^{26}$ + 31.2° ($CHCl_3$; *c* 0.635); IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3590, 3380 br, 3020, 3010, 2970, 2940, 2880, 2860, 1655, 1635, 1570, 1465, 1330, 1250, 1205, 1145, 1110, 995, 895, 890, 790, 780; UV: see Table 1; $^1$H NMR: see Table 2; EIMS (direct inlet) 75 eV *m/z* (rel. int.): 316 $[M]^+$ (100), 301 (79), 260 (49), 247 (37), 233 (67), 231 (73), 219 (79), 205 (40), 203 (23), 189 (22), 179 (27), 128 (22), 115 (29), 105 (16), 91 (30), 83 (23), 77 (29), 69 (51), 55 (47). (Found: C, 75.52; H, 8.94. $C_{20}H_{28}O_3$ requires: C, 75.91; H, 8.92%.)

*Cryptojaponol* (**2**) *from demethylcryptojaponol* (**1**). Ethereal

Table 4. Optical rotations of $[\alpha]^{24}$ compounds **3**–**5** (solvent $CHCl_3$)

| Compound | 589 (D) nm | 578 nm | 546 nm | 436 nm | 365 nm | *c* |
|---|---|---|---|---|---|---|
| **3** | +26.8° | +25.8° | +20.9° | −120.3° | — | 0.620 |
| **4** | +32.1° | +31.5° | +28.1° | −92.6° | — | 0.471 |
| **5** | +79.5° | +83.3° | +93.4° | +140.1° | −111.6° | 0.516 |

$CH_2N_2$ treatment of **1** (80 mg) for 3 hr at 5° yielded 78 mg of a compound identical (mp, mmp, $[\alpha]_D$, TLC, IR, UV, $^1H$ NMR and MS) in all respects with natural cryptojaponol (**2**) [9, 12–14, 19].

*14-Deoxycoleon U* (**3**). Mp 205–207° (EtOAc–*n*-hexane, yellow prisms); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3530, 3390, 3240–2500 br, 3030, 3000, 2970, 2940, 2880, 1630, 1585, 1555, 1470, 1415, 1380, 1345, 1300, 1275, 1190, 1140, 1065, 1000, 915, 880, 805, 790; UV: see Table 1; $^1H$ NMR: see Table 2; $^{13}C$ NMR: see Table 3; EIMS (direct inlet) 75 eV *m/z* (rel. int.): 330 $[M]^+$ (47), 315 (12), 302 (4), 287 (15), 274 (12), 269 (5), 261 (68), 260 (100), 248 (16), 247 (13), 245 (18), 233 (13), 231 (13), 219 (11), 217 (10), 203 (6), 128 (7), 115 (7), 91 (6), 83 (7), 77 (5), 69 (5), 55 (7). (Found: C, 73.02; H, 8.00. $C_{20}H_{26}O_4$ requires: C, 72.70; H, 7.93%.)

*11,12-Diacetyl-14-deoxycoleon U* (**4**) *and 6,11,12-triacetyl-14-deoxycoleon U* (**5**) *from compound* **3**. $Ac_2O$–pyridine treatment of **3** (135 mg) for 24 hr at room temp. yielded a mixture of compounds **4** and **5**, which was subjected to CC (Si gel, *n*-hexane–EtOAc, 2:1, as eluent) to yield the diacetate **4** (68 mg, less polar component) and the triacetyl derivative **5** (61 mg).

*Compound* **4**. An amorphous solid, mp 80–85°; IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3390, 2980, 2950, 2890, 1780, 1645, 1635, 1610, 1565, 1445, 1375, 1325, 1200, 1180, 1140, 1025, 930, 860, 810, 800, 760; UV $\lambda_{max}^{EtOH}$ nm (log ε): 217 (4.24), 265 (4.02), 315 (4.05); $^1H$ NMR (90 MHz, $CDCl_3$): δ 8.11 (1H, *s*, H-14), 7.03 (1H, *s*, disappears after $D_2O$ exchange, –OH), 2.95 (1H, *septet*, *J* = 7 Hz, H-15), 2.33 and 2.30 (3H each, *s*, two –OAc), 1.25 and 1.21 (3H each, *d*, *J* = 7 Hz, 3H-16 and 3H-17), C–Me singlets at 1.59 (3H), 1.47 (3H) and 1.43 (3H); EIMS (direct inlet) 75 eV *m/z* (rel. int.): 414 $[M]^+$ (18), 372 (17), 344 (8), 330 (15), 303 (25), 261 (30), 260 (32), 245 (12), 232 (10), 217 (10), 128 (10), 115 (10), 91 (8), 83 (14), 77 (12), 69 (20), 55 (18), 43 (100). (Found: C, 69.14; H, 7.37. $C_{24}H_{30}O_6$ requires: C, 69.54; H, 7.30%.)

*Compound* **5**. Mp 154–156° ($Et_2O$–*n*-hexane); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3040, 3020, 2995, 2950, 2890, 1775, 1670, 1630, 1615, 1565, 1470, 1430, 1395, 1370, 1340, 1265, 1210, 1170, 1110, 1060, 1025, 1000, 925, 895, 865, 815, 797, 760, 696; UV $\lambda_{max}^{EtOH}$ nm (log ε): 220 (4.03), 263 (4.10), 279 (4.08); $^1H$ NMR (90 MHz, $CDCl_3$): δ 8.09 (1H, *s*, H-14), 2.93 (1H, *septet*, *J* = 6.5 Hz, H-15), 2.35 (6H, *s*, two –OAc), 2.30 (3H, *s*, one –OAc), 1.23 and 1.20 (3H each, *d*, *J* = 6.5 Hz, 3H-16 and 3H-17), C–Me singlets at 1.63 (3H) and 1.38 (6H); EIMS (direct inlet) 75 eV *m/z* (rel. int.): 456 $[M]^+$ (15), 414 (20), 372 (18), 345 (7), 344 (6), 330 (12), 303 (26), 261 (21), 260 (20), 231 (5), 128 (5), 115 (5), 105 (5), 91 (6), 83 (7), 77 (5), 69 (8), 55 (7), 43 (100). (Found: C, 68.66; H, 7.17. $C_{26}H_{32}O_7$ requires: C, 68.40; H, 7.07%.)

*Optical rotations of compounds* **3**–**5**. See Table 4.

*Salviphlomone* (**6**). Mp 163–165° (EtOAc–*n*-hexane, deep red needles); $[\alpha]_D^{25}$ −330.4°, $[\alpha]_{578}$ +69.6°, $[\alpha]_{546}$ +1217.4° (MeOH; *c* 0.232); IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3570, 3460, 3020, 2970, 2930, 2870, 1675, 1653, 1580, 1465, 1395, 1258, 1120, 1090, 1020, 1010, 990, 920, 890, 760; $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3590, 3400, 1677, 1660, 1605, 1580; UV: see Table 1; $^1H$ NMR: see Table 2; EIMS (direct inlet) 75 eV *m/z* (rel. int.): 334 $[M+2]^+$ (18), 332 $[M]^+$ (37), 330 $[M-2]^+$ (8), 317 (14), 314 (8), 303 (68), 299 (13), 286 (50), 271 (39), 247 (50), 231 (37), 219 (42), 215 (34), 203 (32), 179 (39), 161 (26), 145 (26), 129 (24), 128 (29), 121 (24), 115 (39), 109 (32), 105 (34), 91 (66), 77 (63), 69 (81), 55 (100); 10 eV *m/z* (rel. int.): 332 $[M]^+$ (100), 317 (19), 316 (22), 314 (18), 303 (72), 286 (12), 247 (12), 146 (17), 109 (10). (Found: C, 72.60; H, 8.58. $C_{20}H_{28}O_4$ requires: C, 72.26; H, 8.49%.)

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