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TWO NEW DITERPENOID ACETATES FROM *SIDERITIS SERRATA**

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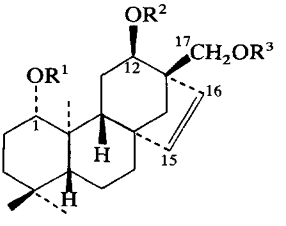
Key Word Index—*Sideritis serrata*; Labiatae; jativatriol derivatives; *ent*-1β,12α-diacetoxy-17-hydroxy-beyer-15-ene; *ent*-1β,17-diacetoxy-12α-hydroxy-beyer-15-ene; 12-acetyl jativatriol.

In a previous communication [1] we reported some *ent*-beyer-15-ene, *ent*-atis-13-ene and *ent*-8,5-*friedo*pimar-5-ene derivatives as the major diterpenic constituents of *Sideritis serrata*. A new study of the extract of this plant has now allowed the isolation of three minor diterpenoid acetates, one of which is the known 12-acetyl jativatriol (**1**, *ent*-12α-acetoxy-1β,17-dihydroxy-beyer-15-ene) previously found in the species *S. reverchonii* [2].



	R^1	R^2	R^3
1	H	Ac	H
2	H	H	H
3	Ac	Ac	Ac
4	Ac	H	Ac
5	Ac	Ac	H

The other new diterpenoids now isolated are two isomeric compounds $C_{24}H_{36}O_5$. On alkaline hydrolysis both substances yielded the known diterpenoid jativatriol (**2**) [3] and Ac$_2$O–pyridine treatment gave the same triacetyl derivative, identified with triacetyl jativatriol (**3**) [3].

The first one of these jativatriol diacetates (**4**) had the C-1 and C-17 hydroxyl functions esterified (^{1}H NMR spectrum: H-1 at δ 4.51, H-12 at 3.77 and 2H-17 as an AB system centred at 4.04). The other one is the 1,12-diacetyl derivative **5** (H-1 at 4.52, H-12 at 5.03 and 2H-17 as an AB system centred at 3.25). Jativatriol triacetate (**3**) had resonances at 4.53, 4.97 and 3.94, respectively [3].

The new compounds are thus 1,17-diacetyl jativatriol (**4**, *ent*-1β,17-diacetoxy-12α-hydroxy-beyer-15-ene) and 1,12-diacetyl jativatriol (**5**, *ent*-1β,12α-diacetoxy-17-hydroxy-beyer-15-ene).

From a biogenetic point of view it is very important to note that although *S. serrata* possesses eight different diterpenic alcohols, only acetyl derivatives of jativatriol (**2**) are present in detectable amounts.

EXPERIMENTAL

Mps were determined in a Kofler apparatus and are uncorr. ^{1}H NMR spectra were measured at 90 MHz in CDCl$_3$ soln with TMS as int. standard. Plant materials were collected in June 1978 near Tobarra (Albacete) and voucher specimens were deposited in the Herbarium of the Faculty of Pharmacy (Madrid 'Complutense' University).

Isolation of the diterpenoids. The extraction of the aerial parts of *S. serrata* Lag. (4 kg) was carried out as previously described [1]. The crude diterpenic fraction (77 g) was chromatographed on a Si gel (Merck, 7734, deactivated with 15% H$_2$O) column (1 kg). Elution with *n*-hexane and *n*-hexane–EtOAc mixtures gave, in order of elution, a mixture of compounds **4** and **5** (800 mg), tobarrol [1] (2.3 g), serradiol [1] (1.8 g), lagascol [1] (2.7 g), benuol [1] (2.2 g), 12-acetyl jativatriol [2] (**1**, 650 mg), lagascatriol [4] (12.3 g), conchitriol [3] (10.8 g), jativatriol [3] (**2**, 14.2 g) and sideritol [5] (8.1 g). The previously known diterpenoids were identified by their physical (mp, $[\alpha]_D$) and spectroscopic (IR, ^{1}H NMR, MS) data and by comparison with authentic samples. The mixture of compounds **4** and **5** (which has been previously obtained by partial acetylation of 1-acetyl jativatriol [6]) was easily separated on a Si gel plus 8% AgNO$_3$ dry column eluted with *n*-hexane–EtOAc (1 : 1).

The less polar component was 1,17-jativatriol diacetate (**4**, 300 mg), a syrup, $n_D^{16°}$ 1.5158, $[\alpha]_D^{25}$ +32.6° (*c* 1.08, CHCl$_3$). IR ν_{max}^{NaCl} cm^{-1}: 3480, 3060, 1720, 1250, 770, 760. ^{1}H NMR: δ 5.77 (2H, AB system, $J = 6$ Hz, H-15 and H-16), 4.51 (1H, *q*, $J_{aa'} = 9$, $J_{ae'} = 6$ Hz, H-1), 4.04 (2H, AB system, $J = 11$ Hz, 2H-17), 3.77 (1H, *m*, $W_{1/2} = 7$Hz, H-12), 2.06 and 1.98 (3H each, *s*, two –OAc) and C-Me singlets at 0.88 (3H), 0.86 (3H) and 0.83 (3H). MS (70 eV, direct inlet) *m/e* (rel. int.): 404 (M$^+$, 2), 386 (4), 344 (10), 326 (7), 314 (4), 302 (100), 287 (14), 284 (78), 269 (30), 256 (17), 242 (24), 227 (37), 215 (8), 213 (8), 161 (34), 104 (95), 103 (99), 92 (99), 91 (70). $C_{24}H_{36}O_5$ MW 404.

The most polar component was 1,12-jativatriol diacetate (**5**, 370 mg), mp 146–148° (acetone–*n*-hexane), $[\alpha]_D^{25}$ +9.7° (*c* 1.48, CHCl$_3$). IR ν_{max}^{KBr} cm^{-1}: 3470, 3060, 2960, 2920, 2880, 2850, 1725, 1705, 1435, 1370, 1260, 1050, 1030, 990, 765, 760. ^{1}H NMR: δ 5.89 (2H, *s*, H-15 and H-16), 5.03 (1H, *m*, $W_{1/2} = 7$ Hz, H-12), 4.52 (1H, *q*, $J_{aa'} = 9$ Hz, $J_{ae'} = 6$ Hz, H-1), 3.25 (2H, AB system, $J = 12$ Hz, 2H-17), 2.07 and 1.97 (3H each, *s*, two –OAc) and C-Me singlets at 0.87 (3H), 0.85 (3H) and 0.83 (3H). MS (70 eV, direct inlet) *m/e* (rel. int.): 404 (M$^+$, 3), 386 (4), 344 (22), 326 (17), 314 (17), 302 (60),

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* Part 41 in the series "Diterpenoids from *Sideritis*". For Part 40 see García-Alvarez, M. C., Martín-Panizo, F. and Rodríguez, B. (1979) *An. Quím.* **75**, 752.

287 (12), 284 (100), 269 (37), 266 (30), 256 (32), 228 (35), 227 (42), 215 (15), 213 (17), 104 (45), 103 (7), 92 (65), 91 (77). (Found: C, 71.12; H, 8.96. $C_{24}H_{36}O_5$ requires: C, 71.25; H, 8.97%).

Alkaline hydrolysis of **4** *and* **5** *to yield jativatriol* (**2**). A soln of compound **5** (50 mg) in N ethanolic KOH (10 ml) was refluxed for 2 hr. The soln was then extracted with $CHCl_3$ and the $CHCl_3$ extract was dried, filtered and concd *in vacuo* to leave a residue (32 mg) of pure **2**, mp 214–215° (Me_2CO–*n*-hexane), $[\alpha]_D^{25}+38.9°$ (*c* 0.23, EtOH) (lit. [3]: mp 214–215°, $[\alpha]_D+39.5°$); IR and MS spectra superimposable with the spectra of authentic jativatriol. Treatment of compound **4** (100 mg) in the same conditions also yielded jativatriol (**2**).

Acetylation of **4** *and* **5** *to yield jativatriol triacetate* (**3**.) Treatment of compounds **4** (80 mg) and **5** (100 mg) with Ac_2O–Py in the usual manner gave the same compound **3**, mp 123–124.5° (aq. EtOH), $[\alpha]_D^{25}-41.8°$ (*c* 2.18, $CHCl_3$) (jativatriol triacetate [3]: mp 124–124.5°, $[\alpha]_D-41.1°$); IR, ^1H NMR and MS spectra identical in all respect with authentic jativatriol triacetate.

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