ing solvents. For analytical and preparative GLC, Shimadzu GC-4AP was used with OV-1 as the stationary phase at 180°. NMR spectra were obtained using TMS as the internal standard. IR spectra were obtained in liquid film.

Triacetic acid lactone. A soln of dehydroacetic acid (20 g) in 90% H_2SO_4 (100 g) was heated in an oil bath at 140° for 1 min, the reaction mixture was poured on crushed ice immediately Resulting crystals were filtered and recrystallized from diluted ethanol. MP 187° Yield 6·9 g.

4-*Methylpentanoyl chloride.* 4-Methylpentanoic acid (23·2 g) was added dropwise into $SOCl_2$ (28·6 g) under refluxing during the course of 30 min and the reaction mixture was refluxed for 1 hr. It was distilled directly and the fraction of bp 119–131° was collected. Yield 17·4 g.

2-*Methylbutyryl chloride.* DL-2-Methylbutyric acid (16·7 g) was treated by the same way as above bp 106–119°C. Yield 14·8 g

3 - (4 - *Methylpentanoyl* -)3,4 - *dihydro* - 6 - *methyl* - 1,2 - *pyran* - 2,4 - *dione.* Triacetic acid lactone (3·1 g) was added to 4-methylpentanoyl chloride (9·7 g) previously mixed with 0·5 ml of H_2SO_4 and cooled with ice H_2O below 10°. The mixture was gradually heated and kept at 85–90° for 30 min. After generation of HCl gas ceased the reaction mixture was poured onto crushed ice The resulting oil was extracted with *n*-hexane, washed with H_2O, dried and evaporated. The oil obtained was purified by means of column chromatography using Kieselgel-G and then alumina. Yield 0·65 g

3 - (2 - *Methylbutyryl* -)3,4 - *dihydro* - 6 - *methyl* - 1,2 - *pyran* - 2,4 - *dione* DL 2-Methylbutyryl chloride was treated in the same way as above. Yield 0·2 g.

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A NEW DITERPENOID ACETATE FROM *SIDERITIS REVERCHONII*[*]

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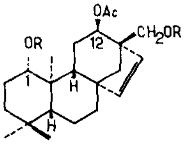
Key Word Index—*Sideritis reverchonii*; Labiatae; *ent* - 15 - beyerene, *ent* - 16*S* - atis - 13 - ene and *ent* - 8,5 - *friedo*pimar - 5 - ene derivatives.

Plant. Sideritis reverchonii Wk. *Source.* Reduced areas in the S. of the Iberian Peninsula (Cerro de San Antón, near Málaga). *Previous work.* None. *Present work.* From the aerial parts of the species quoted above have been isolated eight diterpenoids previously described: *ent* - 8, 5 - *friedo*pimar - 5 - ene - 15*S*,16 - diol (lagascol) [1], *ent* - 8,5 - *friedo*pimar - 5 - ene - 11β,15*S*,16 - triol (lagascatriol)[2], *ent* - 15 - beyerene - 12α,17 - diol (tobarrol)[1], *ent* - 15 - beyerene - 7α,17 - diol (benuol)[1], *ent* - 15 - beyerene - 1β,12α,17 - triol (jativatriol)[3], *ent* - 15 - beyerene - 7α,12α,17 - triol (conchitriol)[3], *ent* - 16*R* - atis - 13 - ene - 16,17 - diol (serradiol)[1] and *ent* - 16*R* - atis - 13 - ene - 1β,16,17 - triol (sideritol)[4], plus a new compound **1** ($C_{22}H_{34}O_4$), which when subjected to the action of Ac_2O in pyridine solution affords **2**, identical (physical and spectroscopic data) with the triacetate of jativatriol. The NMR spectrum of **1** shows a narrow multiplet at δ 5·18 assigned to the equatorial proton geminal to the C-12 acetoxyl function[3].



1 R = H
2 R = Ac

The new diterpenoid (**1**) is thus 12-acetyl jativatriol (*ent* - 12α - acetoxy - 15 - beyerene - 1β,17 - diol).

EXPERIMENTAL

For general details on extraction and separation of diterpenes from *Sideritis*, see part 17[1] of this series; for most experimental details, see part 13[3]. The previously described compounds have been characterized by their physical and spectrospcopic (IR and NMR) data and by

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[*] Part 26 in the series' Studies on diterpenes from *Sideritis* genus'. For part 25 see von Carstenn-Lichterfelde, C , Rodríguez, B and Valverde, S. (1975) *Experientia* **31**, 757.

comparison with authentic samples. 12-*Acetyl jativatriol* (**1**) Mp 206–208° (Et_2O–*n*-hexane); $[\alpha]_{\mathrm{D}}^{20^\circ}$ −17·3° (EtOH; *c* 0·23). IR (KBr) ν_{max} cm^{-1} 3440, 3380 (–OH); 3055, 770 (olefin), 1710, 1260 (–OAc). NMR (60 MHz, $CDCl_3$) δ 5·95 (2H, AB *q*, *J* 6 Hz, C-15 and C-16 vinylic protons), 5·18 (1H, *m*, $W_{1/2}$ 8 Hz, C-12 equatorial proton), 3·28 (1H, *m*, $W_{1/2}$ 18 Hz, C-1 axial proton), 3·15 (2H, AB *q*, *J* 12 Hz, C-17 methylene), 2·11 (3H, *s*, –OAc), C–Me singlets at 0·88, 0·83 and 0·76 MS (70 eV) *m/e* (rel int.)· 344 M^+-18 (8), 302 M^+-60 (100, base peak), 284 (36), 269 (20), 267 (18), 242 (22), 161 (20), 106 (90), 92 (96) (Found· C, 72·61, H, 9·67 $C_{22}H_{34}O_4$ requires C, 72·89, H, 9·45%)

Acetylation of **1** Treatment of compound **1** (50 mg) with Ac_2O–Py 24 hr at room temp. gave **2** (51 mg) mp 124–125° (aq EtOH), $[\alpha]_{\mathrm{D}}^{25^\circ}$ −41·3° ($CHCl_3$; *c* 0·61). IR (KBr) ν_{max} cm^{-1} 3080, 3070, 770 (olefin), 1735, 1250 (–OAc) NMR δ 5·86 (2H, AB *q*, *J* 6 Hz, C-15 and C-16 vinylic protons), 4·97 (1H, *m*, $W_{1/2}$ 7 Hz, equatorial C-12), 4·53 (1H, *m*, $W_{1/2}$ 18 Hz, axial C-1), 3·94 (2H, AB *q*, *J* 12 Hz, C-17), 1·99 (3H, *s*, –OAc), 2·03 (6H, *s*, two –OAc), C–Me singlets accumulated at 0·86 (9H) (Found C, 69·79; H, 8·61 Calc. for $C_{26}H_{38}O_6$: C, 69·93, H, 8·58%) Compound **2** was identical in all respects with jativatriol triacetate[3]

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(-)-(*TRANS*-4′-HYDROXYCINNAMOYL)LUPININE, A NEW ALKALOID IN *LUPINUS* SEEDLINGS

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Key Word Index—*Lupinus luteus*, Leguminosae, alkaloid, lupinine, 4-hydroxycinnamic acid ester, (-)-(*trans*-4′-hydroxycinnamoyl)lupinine

In connection with our studies on the lupin alkaloids[1, 2], variations in alkaloid content at various stages of seedling growth of *Lupinus luteus* were examined and a new alkaloid was observed in varying concentration at different times in young seedlings. The present report describes its isolation and characterization as a *trans*-4-hydroxycinnamic acid ester of (-)-lupinine, i.e. (-)-(*trans*-4′-hydroxycinnamoyl)-lupinine (**1**).

No detectable amount of **1** was found in the mature and immature seeds, and in the later stages of the plant's growth. However, its concentration increased rapidly during the first 4–8 day's growth of seedlings; during further growth, the concentration fell gradually to a very low level

The structure of **1** was determined by spectrometric (IR, MS and NMR) data and by direct comparison with a synthetic sample, prepared as described in the Experimental. Both the natural and synthetic samples showed the presence of a