Further elution of the Si gel column with *n*-hexane–$CHCl_3$ (9:1 and 8:2) gave lupeol acetate (**2**, 57 mg) and lupeol (**1**, 42 mg) which were identical (IR, MS [3], ^{1}H NMR and TLC) with authentic samples. Alkaline hydrolysis of **2** yielded **1**.

Elution with *n*-hexane–$CHCl_3$ (7:3) yielded 20 mg of a sterol mixture which was investigated directly by GC (SE-32 on Chromosorb W, 80–200 mesh, 250°, N_2 at 75 ml/min) and GC/MS (SE-30). By comparison with authentic samples the following sterols were identified in a 5:1:1 ratio: sitosterol (MS *m/z*: 414 $[M]^+$, 399, 396, 381, 314, 303, 273, 255, 213); stigmasterol (MS *m/z*: 412 $[M]^+$, 297, 394, 374, 369, 351, 300, 271, 255, 213); campesterol (MS *m/z*: 400 $[M]^+$, 385, 382, 367, 315, 289, 273, 255, 231, 213).

Alkaline hydrolysis of **3**. Compound **3** (15 mg) was boiled with 2 ml 5% KOH in MeOH in 20 ml C_6H_6 for 24 hr. The soln was evaporated to dryness and the residue, after addition of H_2O, extracted (× 6) with $CHCl_3$ to remove the triterpene. The triterpene component was characterized by its MS, ^{1}H NMR and TLC data, in comparison with an authentic sample, as lupeol (**1**). The alkaline soln was acidified with HCl and extracted (× 6) with EtOAc to remove the fatty acids. The soln was evaporated to dryness and esterified with CH_2N_2 in C_6H_6. The methyl esters were investigated by GC (glass column 2.1 m × 4 mm, 1% SE 30, Celite 80–100 mesh, 230°, N_2 at 80 ml/min) and GC/MS (as described for the sterol mixture).

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CONSTITUENTS OF THE ESSENTIAL OIL OF *LAVANDULA LATIFOLIA*

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Key Word Index—*Lavandula latifolia*; Labiatae; essential oil; terpenes; δ-terpineol.

Abstract—Thirty components were identified in *Lavandula latifolia* essential oil (spike oil). One of the compounds, espliegol (δ-terpineol), is a new natural product.

INTRODUCTION

Lavandula latifolia is widely distributed throughout the Mediterranean region but is found mainly in Spain. This plant gives an essential oil, called spike oil, its principal application being in the perfumery industry. Although there are some reports on the analysis of this essential oil [1–3] we now describe the isolation and structural determination of a new natural compound, δ-terpineol [*p*-ment-1(7)-en-8-ol] and another three monoterpenoids, seven sesquiterpenoids and a coumarin derivative previously undescribed in *L. latifolia*. All these compounds are minor components of the essential oil. The sesquiterpene concentration and the minor components are responsible for the smell of the spike oil [3].

RESULTS AND DISCUSSION

The essential oil from the plant was obtained by steam distillation. Fractionation of the oil was carried out by distillation at reduced pressure. The fraction containing the monoterpene hydrocarbons and the main components, 1,8-cineole (33.6%), linalool (26.3%) and camphor (5.3%), was analysed by GC and the identifications were confirmed by comparison with authentic samples. In the distillation residue the hydrocarbons were separated from the oxygen-containing fraction by CC and the components identified by IR, ^{1}H NMR and mass spectrometry. The results of the essential oil analysis are given in Table 1.

The monoterpene hydrocarbons constitute 7% of the oil of which α-pinene (4.2%) is the most abundant. The sesquiterpene hydrocarbons represent 7.3% and the oxygenated monoterpenoids constitute the bulk of the oil (75.2%). Coumarin is present in high concentration (9%).

Among the oxygenated compounds, an oily fragrant substance, with an odour different from that of α-terpineol, was isolated. The IR spectrum showed absorption of a tertiary hydroxyl (3400, 1100 cm^{-1}) and unsaturation (3060, 1645, 895, $C=CH_2$). The ^{1}H NMR spectrum showed signals at δ 1.12 (6H, *s*, Me_2–C–OH), 1.2–2.4 (10H, *m*) and 4.67 (2H, *s*, $C=CH_2$). In the mass spectrum there were fragments at *m/z* (rel. int.) 139 $[M-Me]^+$ (3),

Table 1. Constituents of the essential oil of *Lavandula latifolia*

GC peak No.	Compound	Total oil (%)	GC peak No.	Compound	Total oil (%)
1	α-Pinene	4.21	16	α-Terpineol	1.71
2	Camphene	0.23	17	Borneol	4.89
3	β-Pinene	0.84	18	β-Bisabolene	0.40
4	Sabinene	0.86	19	γ-Cadinene	0.80*
5	β-Myrcene	0.15	20	Myrthenol	0.23*
6	1,8-Cineole	33.65	21	*trans*-α-Bisabolene	1.90*
7	*p*-Cymene	0.91	22	Geraniol	0.20
8	Linaloyl oxide	0.53	23	*cis*- and *trans*-Calamanenes	0.29*
9	α-Gurjunene	0.47*	24	Cymenol	0.37
10	Camphor	5.31	25	Carveol	0.35
11	Linalool	26.34	26	β-Farnesene	0.03*
12	Caryophyllene	1.39	27	Caryophyllene oxide	1.04
13	δ-Cadinene	0.98*	28	Cuminyl alcohol	0.23*
14	*trans*-Pinocarveol	0.37*	29	Herniarin	1.07*
15	δ-Terpineol	1.02*	30	Coumarin	9.04

*Components not previously reported.

136 $[M-H_2O]^+$ (6), 121 (5), 107 (5), 93 (24), 91 (21), 81 (41), 67 (40), 59 (100), 55 (36), 53 (42), 43 (87), 41 (67) and 39 (44). These spectral data matched those published [4] for synthetic δ-terpineol [5, 6].

Recently, Blute *et al.* [4] obtained δ-terpineol in high yields from β-pinene and mercury (II) salts in a step reaction. We have also synthesized δ-terpineol by this method; the GC and spectral data of the synthetic product matched those of the substance isolated from *L. latifolia* as a new natural product. A compound tentatively identified as δ-terpineol on the basis of its mass spectrum has also been reported in Spanish origanum essential oil [7].

EXPERIMENTAL

^{1}H NMR spectra were recorded at 60 MHz using TMS as int. standard. The MS were taken at 70 eV with the ion source at 180°. GC analysis was on 2 m × 4 mm stainless steel columns packed with 20% Apiezon-L and 20% Carbowax 20 M; temp. programmed from 80° to 200°, isothermal 8 min, at 4°/min; N_2 30 ml/min. Quantitation of the components was performed with an integrator. Analytical TLC was performed on Si gel G, prep TLC was on Si gel PF_2^{34-336} and CC was on Si gel 60.

Methodology. The plant material was collected in Sept. near Corrales del Vino (Zamora, W. Spain) and identified by Professor B. Casaseca Mena, Botany Department, Salamanca University. Steam distillation of 5 kg of plant material for 8 hr yielded 30 g (0.6%) of essential oil. The oil was distilled at 8 mm Hg to give a distilled fraction bp 40–65° (40.8%) and a distillation residue (58.9%). In the first fraction, α-pinene, camphene, β-pinene, sabinene, β-myrcene, 1,3-cineole, *p*-cymene, linalool and camphor were identified by GC. The distillation residue was fractionated by CC on Si gel. The hexane eluate, was a hydrocarbon mixture which, on $AgNO_3$–Si gel chromatography, gave sesquiterpene hydrocarbons (Table 1). The Et_2O eluate containing oxygenated compounds was chromatographed on Si gel to give two fractions, eluted with 8:2 and 7:3 hexane–Et_2O. The less polar fraction, was rechromatographed on 20% $AgNO_3$–Si gel and the following substances were isolated (elution order): borneol, *p*-cymenol, mirthenol, coumarin, *trans*-pinocarveol and epoxilinalool. The more polar fraction, chromatographed in the same way, gave cuminyl alcohol, α-terpineol, δ-terpineol, geraniol and herniarin. The spectroscopic properties were directly compared with the lit. data of authentic samples.

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