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LUPEOL LONG-CHAIN FATTY ACID ESTERS AND OTHER TRITERPENOID CONSTITUENTS FROM *PLUMERIA OBTUSIFOLIA**

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Key Word Index—*Plumeria obtusifolia*; Apocynaceae; lupeol fatty acid esters; lupeol; lupeol acetate; phytosterols.

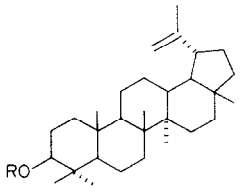
Abstract—From the bark of *Plumeria obtusifolia* was isolated a series of lupeol fatty esters with the carbon numbers 16, 18, 20 and 21–28 in the fatty acid part. Furthermore, lupeol, lupeol acetate, sitosterol, stigmasterol and campesterol were also identified.

INTRODUCTION

Recently, we described the plant growth inhibiting properties of plumieride, a compound isolated from the methanolic extract of the bark of *Plumeria obtusifolia* (Apocynaceae) [1]. We now wish to report the isolation and identification of the triterpene and sterol constituents of the same plant.

RESULTS AND DISCUSSION

The residue of a chloroform extract of dried powdered bark was separated by repeated CC on Si gel with *n*-hexane–$CHCl_3$ gradient elution and TLC-monitoring. In addition to lupeol (**1**), lupeol acetate (**2**) and a sterol mixture, a fraction was isolated which contained a series of saturated lupeol fatty acid esters (**3**). The ^1H NMR spectrum of **3** showed, besides the typical chemical shifts



1 R = H
2 R = Ac
3 R = $-CO-(CH_2)_n-Me$
n = 14, 16, 18, 19, 20, 21 22, 23, 24, 25 or 26

for lupeol, a pattern of signals which were assigned to long-chain fatty acid esters (δ 0.87, *t*, one terminal methyl of Me–CH_2–; 1.24, *br*, large (–CH_2–)$_n$; 2.27, *t*, –CH_2–CO–O–). The 3α-hydrogen signal (*dd*) of the lupeol part was shifted downfield to δ 4.45 (lupeol, δ3.12). Alkaline hydrolysis of **3** yielded lupeol (**1**) and a complex long-chain fatty acid mixture which was esterified with diazomethane and investigated by GC and GC/MS. Eleven fatty acids with the carbon numbers 16, 18, 20 and 21–28 were identified (Table 1). Lupeol behenate was the main component. Lupeol esters with acid components from C_1 to C_{20} have been reported in *Pistacia lentiscus* [2, 3].

Table 1. GC analysis of the fatty acids (as methyl esters) derived from **3**

Fatty acid	%
16:0	9.7
18:0	6.4
20:0	5.1
21:0	1.0
22:0	31.0
23:0	2.5
24:0	21.9
25:0	2.9
26:0	15.7
27:0	1.0
28:0	2.7

Sitosterol, stigmasterol and campesterol were identified in a 5:1:1 ratio by GC and GC/MS analysis of the sterol fraction of *P. obtusifolia*.

EXPERIMENTAL

Plumeria obtusifolia L., collected near Hanoi, was identified by Dr. N. V. Phu, Institute of Biology, University of Hanoi, and a voucher specimen is kept there.

Extraction and separation. Air-dried powdered bark (500 g) of *P. obtusifolia* was extracted with $CHCl_3$ in a Soxhlet. The $CHCl_3$ extract was concd and 1.1 g of the residue (total 50 g) was separated by repeated CC on Si gel with gradient elution and TLC-monitoring (Si gel, petrol–$CHCl_3$, 9:1). Elution with *n*-hexane gave 50 mg of amorphous ester mixture (**3**).

*Part 7 in the series "Natural Products from Vietnamese Plants". For Part 6 see Adam, G., Lischewski, M., Phiet, H. V., Preiss, A., Schmidt, J. and Sung, T. V. (1982) *Phytochemistry* **21**, 1385.

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),