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# TRITERPENES FROM THE GALLS OF *PISTACIA PALESTINA*[*]

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**Key Word Index**—*Pistacia palestina*; galls; triterpene composition.

## INTRODUCTION

In previous papers [1, 2] we have reported the chemical study of the resinous exudates of three kinds of galls which are produced by different insects of the *Pemphigus* species on the young leaves of *Pistacia terebinthus*, a plant belonging to Anacardiaceae which is widespread in the south of Italy. Comparison of the results obtained showed significant differences of chemical composition, thus suggesting that the altered metabolism of the galls compared with the uninfected tissues of the plant might be ascribed to the insect independently of the plant itself. We have now examined the galls which are produced by one of the above mentioned insects, *Pemphigus cornicularius* (*Baizongia pistaciae*), on the leaves of *Pistacia palestina* in order to compare their chemical composition with that of the galls produced by the same insect on *P. terebinthus*.

## RESULTS

Unlike the galls which are produced by *Pemphigus cornicularius* on *Pistacia terebinthus*, the galls under study, which were collected in autumn, were smooth greenish-yellow spheres, 2–3 cm in diameter, not visibly resinous. After removal of all foreign materials, such as leaves and insects, the galls were minced and extracted with $Et_2O$. Evaporation of the solvent afforded a very viscous yellow oil (*ca* 5% of the starting galls) which was separated by conventional methods into an acid fraction (32%)[†] and a neutral fraction (68%), respectively.

Chromatography of the acid fraction on HCl-washed Si gel gave only poor results so that the enriched fractions thus obtained were treated with excess ethereal diazomethane, and the acidic components isolated and characterized as the corresponding methyl esters which are listed in Table 1. Structures of the nine methyl esters were assigned on spectroscopic grounds and by comparison with authentic samples.

The neutral part of the ethereal extract was first roughly chromatographed on neutral alumina in order to remove most of the hydrocarbons and fats (*ca* 20%) and then fractionated by repeated chromatography on alumina and/or Si gel to afford ten neutral triterpenes which are listed in Table 2.

20α-Eupha-7,24-diene-3β-ol was not previously known and was assigned structure **1e**, on the basis of its spectroscopic characteristics (see Experimental). This assignment was then confirmed by comparison of **1e** with a semi-synthetic authentic sample prepared from methyl masticadienonate (**1a**). Dioxolanation [14] of **1a** followed by LAH reduction of the resulting **1g** yielded the compound **1h** (mp 190–2°; $[\alpha]_D$ −63°). Subsequent tosylation [15] of the primary hydroxyl group of **1h** and reduction [16] of the resulting tosylate then afforded compound **1i** (mp 169–171°; $[\alpha]_D$ −41°) which after acid hydrolysis and $NaBH_4$ reduction of the parent C-3 ketone, led to **1e** which was found identical in every respect to the natural sample.

## DISCUSSION

A direct comparison between the chemical composition of the galls of *P. palestina* and of the galls produced by the same insect on *P. terebinthus* appears difficult and probably meaningless. In fact possibly due to climatic factors, the oxidation levels of the various triterpenes in the galls of the two species examined are quite different. By contrast, several similarities are evident in considering the distribution of the various skeletons instead of the amounts of the individual substances. It seems that $\Delta^7$ euphene compounds are more abundant in the acid fraction, whereas the $\Delta^8$ euphenes predominate in the neutral fraction. Oleanane and dammarane compounds

Table 1. Methyl esters of the acidic triterpenes obtained from *Pistacia palestina* galls*

| Methyl esters | | mp | $[\alpha]_D$ | % Amount | Ref. |
|---|---|---|---|---|---|
| Masticadienonate | (**1a**) | 125–126 | −73 | 9.6 | 3 |
| Isomasticadienonate | (**2a**) | 110–111 | +35 | 6.0 | 4 |
| Oleanonate | (**3a**) | 181–182 | +76 | 2.8 | 5 |
| Masticadienolate | (**1b**) | 121–123 | −44 | 2.0 | 1 |
| 3-*O*-Acetyl-3-epimasticadienolate | (**1c**) | 129–130 | −26 | 1.0 | 6 |
| Oleanolate | (**3b**) | 195–197 | +82 | 0.7 | 5 |
| 3-*O*-Acetyl-3-epiisomasticadienolate | (**2b**) | 86–87 | −2 | 0.6 | 6 |
| 3-Epiisomasticadienolate | (**2c**) | 140–141 | −16 | 0.5 | 1 |
| 3-Epimasticadienolate | (**1d**) | 100–101 | −45 | 0.4 | 1 |

*Fatty acids and minor components: 8.2%.

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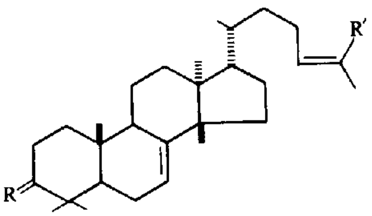
[*] Part 7 in the series "Anacardiaceae". For Part 6 see ref. [6].

[†] All the percentages are referred to the ethereal extract.

Table 2. Neutral triterpenes obtained from *Pistacia palestina* galls*

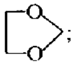
| Compounds | | mp | $[\alpha]_D$ | % Amount | Ref. |
|---|---|---|---|---|---|
| Tirucallol | **(2d)** | 132–135 | +5 | 13.6 | 7 |
| Dipterocarpol | **(4a)** | 135–136 | +67 | 9.5 | 8 |
| Oleanonic aldehyde | **(3c)** | 138 139 | +88 | 6.5 | 2 |
| 20α-Eupha-7,24-diene-3β-ol | **(1e)** | Oily | +3 | 4.8 | — |
| Erythrodiol | **(3d)** | 231 235 | +79 | 3.1 | 9 |
| Dammarenediol | **(4b)** | 142–144 | +27 | 2.7 | 10 |
| Masticadienediol | **(1f)** | 186–187 | −50 | 2.0 | 11 |
| Isomasticadienediol | **(2e)** | 152–154 | −7 | 1.9 | 2 |
| β-Amyrenone | **(3e)** | 176–178 | +107 | 1.7 | 12 |
| Tirucallone | **(2f)** | Oily | +16 | 1.6 | 13 |

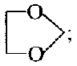
*Hydrocarbons, fats and minor components: 19.8%.

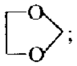


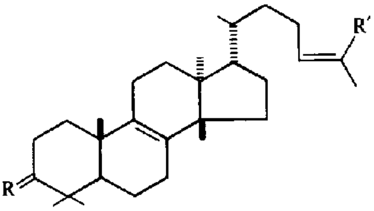
**1a** R = O; R' = $CO_2Me$
**1b** R = H; βOH; R' = $CO_2Me$
**1c** R = H; αOAc; R' = $CO_2Me$
**1d** R = H; αOH; R' = $CO_2Me$
**1e** R = H, βOH; R' = Me

**1f** R = H, βOH; R' = $CH_2OH$

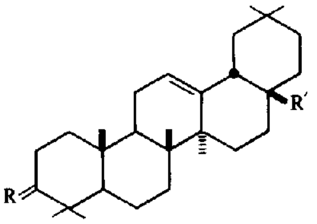
**1g** R =

; R' = $CO_2Me$

**1h** R =

; R' = $CH_2OH$

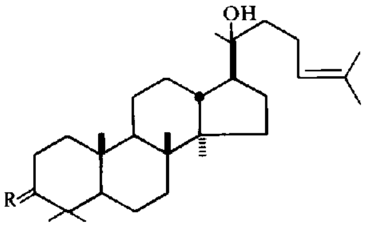
**1i** R =

; R' = Me



**2a** R = O; R' = $CO_2Me$
**2b** R = H; αOAc; R' = $CO_2Me$
**2c** R = H; αOH; R' = $CO_2Me$
**2d** R = H, βOH; R' = $CH_3$
**2e** R = H, βOH; R' = $CH_2OH$
**2f** R = O; R' = Me



**3a** R = O; R' = $CO_2Me$
**3b** R = H, βOH; R' = $CO_2Me$
**3c** R = O; R' = CHO
**3d** R = H, βOH; R' = $CH_2OH$
**3e** R = O, R' = Me



**4a** R = O
**4b** R = H, βOH

have similar distributions in both the species examined. Finally, the distribution patterns of C-3 oxygenated acidic and neutral euphane triterpenes in both the galls are quite similar.

The rather close similarity of the chemical compositions of two galls which are produced by the same insect on different plants represents an interesting result which, in our opinion, supports the hypothesis of a chemical stimulus in the gall formation. We now have further work in progress to see if both the plants under investigation show also analogous differences between the chemical composition of the galls and of the uninfected tissues.

## EXPERIMENTAL

General experimental and procedures of extraction of the galls and separation of acid and neutral fractions have already been described [13]. The galls were collected in the Mt. Meiron area (Galilea), Israel.

*20α-Eupha-7,24-diene-3β-ol.* (**1e**). A group of fractions from the general chromatography (1.2 g; petrol–$Et_2O$, 19:1; 0.41), mainly consisting of tirucallol (**2d**), were collected and recrystallized several times from MeOH. Chromatography of the mother liquors on 3% $AgNO_3$/Si gel (petrol–$Et_2O$, 19:1) afforded more tirucallol besides a small amount (150 mg) of crude **1e**, which after further purification was an oil $[\alpha]_D + 3°$ ($c = 0.8$). (Found: C, 84.61; H, 11.94. $C_{30}H_{50}O$ requires: C, 84.44; H, 11.81%); MW 426 (MS); IR $\nu_{max}$ $cm^{-1}$: 3400; $^1H$ NMR: δ5.20 (*br m*, 2H). A pure sample of **1e** was compared and found identical with a semi-synthetic sample specially prepared (see above) from methyl masticadienonate (**1a**).

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# TRITERPENE QUINONE-METHIDES FROM *SCHAEFFERIA CUNEIFOLIA* ROOTS*

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**Key Word Index**—*Schaefferia cuneifolia*; Celastraceae; sitosterol; epifriedelanol; pristimerin; tingenone; germination inhibitors; dulcitol.

**Abstract**—The two quinone-methides, pristimerin and tingenone, have been isolated from the roots of *Schaefferia cuneifolia*. Both compounds strongly inhibit the germination of lentil seeds.

The Celastraceae is a relatively small, widely distributed family, several species of which are used in folk medicine [1]. From *Maytenus* sp. and *Tripterygium wilfordii*, highly active tumor inhibitory alkaloids have been isolated [2, 3]. There are 33 Mexican native species from this family and 8 of them are used for medicinal purposes [4]. In particular, the reddish roots of *Schaefferia cuneifolia* A. Gray (capul), are used as a remedy for venereal diseases. We have found that the root extracts from this plant contain sitosterol, epifriedelanol, pristimerin **1** and tingenone **2**. On a bioassay of **1** and **2** with corn and lentil seeds, both triterpene quinone-methides exhibited strong inhibitory activity toward the germination of lentil seeds [5].

## EXPERIMENTAL

The mps are uncorr. The elemental analyses were obtained in Alfred Bernhardt Laboratories, Engelskirchen, Germany. For TLC and column chromatography, Si gel (Merck) was used. Air-dried roots (950 g) of *Schaefferia cuneifolia* (collected at Grutas de García, N.L., in June 1975, a voucher specimen XAD 7489, is deposited in the Herbarium, ITESM), were ground

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* Part 33 in the series "Mexican Medicinal Plants". For Part 32 see (1978) *Rev. Latinoam. Quim.* **9**, 33.