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TRITERPENE COMPONENTS OF GALLS ON THE LEAVES OF *PISTACIA TEREBINTHUS*, PRODUCED BY *PEMPHIGUS SEMILUNARIUS**†

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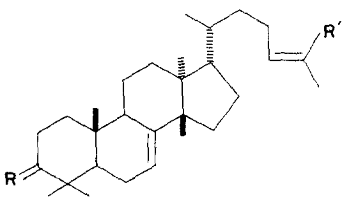
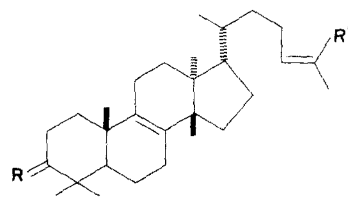
Key Word Index—*Pistacia terebinthus*; Anacardiaceae; galls; triterpenes.

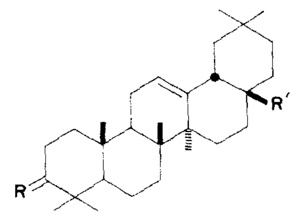
In previous papers,[1,2] we reported a study of the resinous exudate of the galls produced on the leaves of *Pistacia terebinthus* by the insect *Pemphigus cornicularius*.[3] *P. terebinthus* is known to produce different galls, depending on the *Pemphigus* species[4] and we have now extended our study to another gall which is produced on the young leaves of *P. terebinthus* by *Pemphigus semilunarius*.[4]



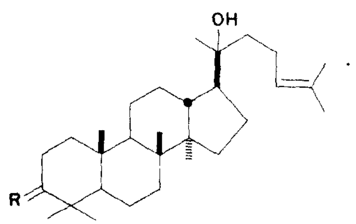
(1a) R = O; R' = COOH
(1b) R = H, βOH; R' = COOH
(1c) R = H, αOH; R' = COOH
(1d) R = H, βOH; R' = COOMe
(1e) R = H, αOH; R' = COOMe



(2a) R = O; R' = Me
(2b) R = O; R' = CH_2OH
(2c) R = H, βOH; R' = Me
(2d) R = H, βOH; R' = CH_2OH



(3a) R = O; R' = CHO
(3b) R = H, βOH; R' = CHO
(3c) R = H, βOH; R' = CH_2OH



(4a) R = O
(4b) R = H, βOH

These galls, unlike those produced by *P. cornicularius* on the same plant, look like small greenish-yellow flat beans with thin red veins, very similar to the galls produced by *Aploneura lentisci* on *P. lentiscus*,[5] and are not visibly resinous. A quantity of galls were

* Part IV in the series "Anacardiaceae".

† References 1, 2 and 5 are respectively considered as Parts I, II and III.

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collected at the beginning of summer and, after removal of leaves, insects and other foreign materials, were continuously extracted with cold ether for several hours. In this way, a clear yellow oil (4% of the starting material) was obtained. Its subsequent fractionation by conventional methods afforded a semicrystalline acidic fraction (60%)‡ and an oily neutral fraction (35%). Chromatography of the acidic fraction on silica gel (HCl washed; eluent hexane–Et_2O) gave masticadienonic acid (**1a**) and a mixture of both epimeric masticadienolic acids (**1b**) and (**1c**), which were isolated as the corresponding methyl esters (**1d**) and (**1e**), through treatment of the mixture with ethereal diazomethane followed by PLC of the crude esters. Physical constants and percentages of the compounds (**1a**), (**1d**) and (**1e**) are reported in Table 1, in which the compounds obtained, from the neutral part of the extract are also listed.* Furthermore, more than 50% of the neutral extract consisted of mixtures of hydrocarbons, fats and waxes which have not been investigated.

TABLE 1

Compounds		m.p.	$[\alpha]_D$	% Amount	Ref.
Masticadienonic acid	(**1a**)	181–183°	−71°	18·0	6
Methyl masticadienolate	(**1d**)	122–123°	−44°	3·1	1
Methyl 3-epimasticadienolate	(**1e**)	100–101°	−47°	3·7	1
Tirucallone	(**2a**)	Oily	+16°(*)	2·1	—
26-Hydroxy-tirucallone	(**2b**)	Oily	+14°	0·6	2
Tirucallol	(**2c**)	132–135°	+	3·3	7
Isomasticadienediol	(**2d**)	152–154°	− 7°	3·1	2
Oleanonic aldehyde	(**3a**)	138–140°	+89°	2·8	2
Oleanolic aldehyde	(**3b**)	169–172°	+71°	3·2	8
Erithrodiol	(**3c**)	231–235°	+79°	2·7	8
Dipterocarpol	(**4a**)	135–136°	+67°	0·7	9
Dammarenediol	(**4b**)	142–144°	+27°	0·4	10

* Whose LAH reduction product was identical with an authentic sample of tirucallol (**2c**).

Examination of Table 1 enables some conclusions to be made about the distribution pattern of triterpenes in the gall we have studied. First of all, the co-occurrence of both epimeric 3-hydroxy acids together with the corresponding 3-keto acid seems to be characteristic of Anacardiaceae galls.[1,5] Such a co-occurrence suggests the action of an oxidoreductase system, although it is rather peculiar that the neutral 3-hydroxy compounds although existing together with their 3-keto analogs, have only the usual equatorial configuration. This must mean that the acid oxidoreductase either does not act towards neutral compounds or acts with a stereospecificity which is lost with the acids. Finally, it is noteworthy that in the neutral fraction, the Δ^8 euphane compounds are present with no traces of the corresponding Δ^7 isomers which, on the contrary, are the only euphane compounds of the acidic fraction. Furthermore, no traces of oleanane compounds were detected in the acidic fraction, although the aldehydes (**3a**, **3b**) and the diol (**3c**) are found in the neutral constituents.

Acknowledgements—The authors gratefully acknowledge financial support by Italian National Research Council (CNR).

‡ All the percentages are referred to the ethereal extract.
* For general experimental details, see Ref. 2 and 5.

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