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TRITERPENES OF GALLS OF *PISTACIA TEREBINTHUS*: GALLS PRODUCED BY *PEMPHIGUS UTRICULARIUS**

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

INTRODUCTION

Following our chemical study of the galls of plants belonging to the *Pistacia* genus [1], we have now examined the ethereal extract obtained from the galls produced by the insect *Pemphigus utricularius* [2] on the young leaves of *P. terebinthus*. The latter is a widespread plant in Southern Italy and it is known [2] to produce galls which morphologically differ, according to the *Pemphigus* species.

RESULTS AND DISCUSSION

The galls, collected at the beginning of the summer, were smooth, yellow-reddish, small spheres, 1–2 cm in diameter and, unlike the galls produced by *P. cornicularius*, they were not visibly resinous. All foreign materials, such as leaves and insects, were removed from the galls which were then minced and extracted with Et_2O to yield a yellow waxy residue (about 3·3% of the starting material). Separation of the extract by conventional methods afforded an acid fraction (40%)† and a neutral fraction. The acid fraction was not directly separable into its components and, therefore, was first treated with excess ethereal diazomethane and the resulting crude mixture of methyl esters was subjected to chromatography on silica gel. The subsequent chromatographic fractionations and purifications then gave the methyl esters which are listed in Table 1. All the structures were assigned on spectroscopic grounds and by comparison with authentic samples. Methyl dihydroisomasticadienonate (**2b**) and dihydromasticadienediol (**1d**) (Table 2) have not previously been isolated from natural sources and were known only as synthetic products [4]. Methyl 3-epidihydroisomasticadienolate was not known and the structure **2c** was

Table 1. The acidic triterpene methyl esters obtained from *Pistacia terebinthus* galls

Methyl esters		mp	$[\alpha]_D$	% Amount	Ref.
Isomasticadienonate	(**4c**)	110–111°	+35°	12·7	3
Masticadienonate	(**3c**)	124–125°	−72°	8·5	4
Oleanonate	(**5c**)	181–182°	+76°	8·3	5
3-Epiisomasticadienolate	(**4a**)	140–141°	−16°	1·4	6
3-Epimasticadienolate	(**3a**)	100–101°	−47°	1·1	6
Isomasticadienolate	(**4b**)	142–143°	−11°	1·0	6
3-Epioleanolate	(**5a**)	198–200°	+43°	0·9	7
Dihydroisomasticadienonate	(**2b**)	75–77°	+26°	0·7	—
Dihydro-3-epiisomasticadienolate	(**2c**)	80–86°	−22°	0·7	—
Masticadienolate	(**3b**)	122–123°	−44°	0·6	6
Oleanolate	(**5b**)	195–197°	+82°	0·6	5
Dihydromasticadienonate	(**1b**)	90–91°	−76°	0·5	8
Dihydro-3-epimasticadienolate	(**1c**)	Oily	—	0·4	8
Dihydroisomasticadienolate	(**2a**)	Oily	—	0·2	(*)
Dihydromasticadienolate	(**1a**)	117–118°	−43°	0·2	8

* Identified as the corresponding acid [4] mp 210–212°, $[\alpha]_D$ −6°.

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* Part V in the series 'Anacardiaceae'. For Part IV see Ref. 1.

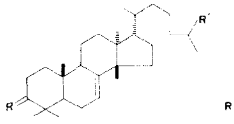
† All the percentages are referred to the ethereal extract.

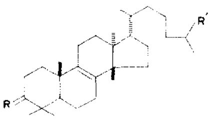
Table 2. The neutral triterpenes obtained from *Pistacia terebinthus* galls

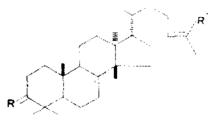
Compounds		mp	$[\alpha]_D$	% Amount	Ref.
Tirucallol	(**4f**)	132–135°	+5	10·8	9
β-Amyrin	(**5f**)	198–199	+88°	2·7	11
Oleanonic aldehyde	(**5e**)	138–140°	+89°	2·5	10
Masticadienediol	(**3d**)	186–187°	−50°	1·6	8
Isomasticadienediol	(**4d**)	152–154°	−7°	1·4	10
Erithrodiol	(**5h**)	231–235°	+79°	1·1	12
Oleanolic aldehyde	(**5d**)	169–172°	+71°	0·8	12
Dihydromasticadienediol	(**1d**)	165–166°	−55°	0·8	···
26-Hydroxy-tirucallone	(**4c**)	Oily	+14°	0·8	10
Dammarenediol	(**6a**)	142–144°	+27°	0·6	13
Dipterocarpol	(**6b**)	135–136°	+67°	0·6	14
Tirucallone	(**4g**)	Oily	+16°	0·6	1
β-Amyrone	(**5g**)	176–178°	+107°	0·3	11
28-Hydroxy-β-amyrone	(**5i**)	189–192°	+85°	0·3	10

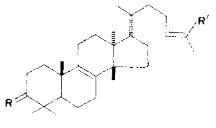
confirmed by Jones oxidation of **2c** into the corresponding ketoester (**2b**) which was identical with an authentic sample.

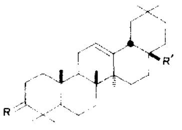
The neutral part of the starting ethereal extract was directly chromatographed on alumina to produce three main fractions: a less polar one consisting of hydrocarbons and fats (NMR, GLC), a second fraction consisting mainly of triterpenes and, finally, the most polar fraction consisting of polyhydroxy-compounds which have not yet been examined. The intermediate polarity fraction, after rechromatography on silica gel and further purification of the various fractions, afforded the triterpenes which are listed in Table 2.

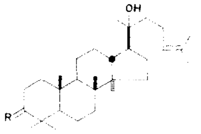

(1a) R = H, βOH; R′ = COOMe
(1b) R = O ; R′ = COOMe
(1c) R = H, αOH; R′ = COOMe
(1d) R = H, βOH; R′ = CH₂OH


(2a) R = H, βOH; R′ = COOMe
(2b) R = O ; R′ = COOMe
(2c) R = H, αOH; R′ = COOMe


(3a) R = H, αOH; R′ = COOMe
(3b) R = H, βOH; R′ = COOMe
(3c) R = O ; R′ = COOMe
(3d) R = H, βOH; R′ = CH₂OH


(4a) R = H, αOH; R′ = COOMe
(4b) R = H, βOH; R′ = COOMe
(4c) R = O ; R′ = COOMe
(4d) R = H, βOH; R′ = CH₂OH
(4e) R = O ; R′ = CH₂OH
(4f) R = H, βOH; R′ = Me
(4g) R = O ; R′ = Me


(5a) R = H, αOH; R′ = COOMe
(5b) R = H, βOH; R′ = COOMe
(5c) R = O ; R′ = COOMe
(5d) R = H, βOH; R′ = CHO
(5e) R = O ; R′ = CHO
(5f) R = H, βOH; R′ = Me
(5g) R = O ; R′ = Me
(5h) R = H, βOH; R′ = CH₂OH
(5i) R = O ; R′ = CH₂OH


(6a) R = H, βOH
(6b) R = O

The results of this study, together with those obtained in the examination of the galls produced on the same plant by *P. cornicularius* and *P. semilunarius* respectively, clearly show that the metabolism of the plant is alterated in the galls, according to the insect species producing them.

Once again, the simultaneous presence was noted in the acid fraction of both the C-3 epimeric hydroxy acids in addition to the corresponding 3-keto acids. By contrast only 3β-hydroxy compounds were found in the neutral fraction. The presence of 3α-hydroxy acids cannot be accounted for simply by the action of a non-stereospecific oxidoreductase system since, in all the galls examined, the amount of 3α-hydroxy acids was found to be even higher than that of the corresponding C-3 epimers.

EXPERIMENTAL

Mps are uncorr. Rotations were taken for $CHCl_3$ solns at room temp. Si gel (0·05–0·2 mm, Merck) or alumina (Woelm, neutral, grade III) was used for column chromatography.

General procedures for the extraction of the galls and for the separation of acid and neutral fractions have been described [1].

Separation of the acid components. The acid extract (12g) was dissolved in Et_2O and treated with excess ethereal CH_2N_2 in an ice bath for 5 hr (absence of IR carboxyl group absorption). Chromatography of the crude esters on Si gel (400g; eluent C_6H_6–Et_2O, 9:1 14 l.) then gave a fraction (1·3g) consisting of fatty acid methyl esters besides fractions whose further purification led to the substances listed in Table 1.

Methyl 3-epidihydroisomasticadienolate (**2c**). A crude mixture (350mg) of **2c** and **1c**, eluted after 10 l of C_6H_6–Et_2O (9:1) was separated by PLC (Si gel impregnated with $AgNO_3$; eluent C_6H_6–Et_2O, 9:1; 2 runs). The crude **2c** (200mg) was crystallized from hexane to give needles mp 80–86°, $[\alpha]_D$ −22° (*c* 1·5); (Found: C, 78·70; H, 11·13. $C_{31}H_{52}O_3$ requires: C, 78·76; H, 11·09%); IR $\nu_{max}(CCl_4)$: 3545, 1710 cm^{-1}; NMR ($CDCl_3$): δ 3·42 (1H, br $W_{\frac{1}{2}}$ 6Hz, =CH–OH), 3·65 (3H, *s* –COOMe). Pure **2c** treated with Jones reagent, gave **2b** mp 73–6°, identical with authentic material.

Separation of the neutral compounds. The neutral extract (18g) was absorbed on alumina (600g). Elution with C_6H_6 gave 3 fractions: A (5·0g), B (8·1g) and C (4·1g). Rechromatography of fraction B on Si gel (250g; eluent petrol–Et_2O 9:1, 7 l) then gave the compounds listed in Table 2.

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