acetylation and chromic acid/pyridium oxidation of the hydroxyl groups. The spectral data, the mps and the optical rotations of all compounds are in good agreement with those reported in the literature [1].

Acknowledgements—We thank Dr. O. Hilliard, Dept. of Botany, University of Natal, for her help in the identification of the plant material and the 'Deutsche Forschungsgemeinschaft' for supporting this work.

LITERATURE

1. Herz, W. and Sharma, R. P. (1976) *J. Org. Chem.* **41**, 1021.
2. Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) *Naturally Occurring Acetylenes.* Academic Press, London.

Phytochemistry, 1978, Vol 17, pp 815–817 Pergamon Press. Printed in England

TRITERPENES FROM THE BLED RESIN OF *PISTACIA VERA*[*]

ROMUALDO CAPUTO†, LORENZO MANGONI†, PIETRO MONACO†, GIOVANNI PALUMBO†, YAGHOUB AYNEHCHI‡
and MOUSA BAGHERI‡

†Institute of Organic and Biological Chemistry of the University Via Mezzocannone 16, Napoli 80134, Italy; ‡ School of Pharmacy, University of Tehran, Iran

(*Received* 24 *October* 1977)

Key Word Index—*Pistacia vera*; galls, triterpene composition.

INTRODUCTION

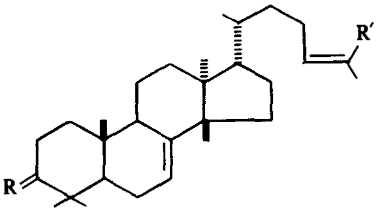
In connection with previous work concerning the chemical study of the galls of plants belonging to the *Pistacia* genus, we have now examined the chemical composition of the oleoresin exuded from the trunk of *P. vera*. Comparative chemical studies of galls and of uninfected tissues of the gall forming plant have not been carried out up to now. To our knowledge, such a comparison has only been reported for *Quercus robur* galls by *Cynips mayri* and this study showed the metabolism in the gall tissues to be greatly altered and leading to triterpenes with different skeletons as well as to increased amounts of highly oxidized substances [2].

RESULTS

The crude oleoresin, collected during Summer, was treated with cold Et_2O to remove polymers and other foreign materials. The light yellow viscous oil thus obtained was subsequently fractionated by conventional methods to give a semicrystalline acid fraction (40%) and an oily neutral fraction (60%).†

The acid fraction, submitted to repeated chromatography on HCl washed Si gel, afforded seven triterpene acids identified as the corresponding methyl esters which are listed in Table 1. All the structures were assigned on spectroscopic grounds and by comparison with authentic samples.

The unknown acetoxy esters (**1b**) and (**2b**) were converted into the corresponding hydroxy methyl esters [5] by alkaline hydrolysis followed by esterification with ethereal diazomethane.



(**1a**) R = O ; R' = CO_2Me
(**1b**) R = H, αOAc; R' = CO_2Me
(**1c**) R = H, βOH ; R' = CO_2Me
(**1d**) R = H, αOH ; R' = CO_2Me
(**1e**) R = H, βOH ; R' = CH_2OH
(**1f**) R = O ; R' = CHO

Table 1. The acidic triterpene methyl esters obtained from *Pistacia vera* resin*

Methyl esters		mp	$[\alpha]_D$	%Amount	Ref.
Masticadienonate	(**1a**)	125–126	−73	8.7	3
3-*O*-Acetyl-3-epimasticadienolate	(**1b**)	129–130	−26	3.5	—
Isomasticadienonate	(**2a**)	110–111	+36	3.4	4
Masticadienolate	(**1c**)	121–123	−43	2.0	5
3-*O*-Acetyl-3-epiisomasticadienolate	(**2b**)	86–87	−2	1.8	—
3-Epimasticadienolate	(**1d**)	100–101	−45	1.1	5
24,25-Dihydromasticadienonate	(**3a**)	91–93	−76	0.9	6
24,25-Dihydro-3-epimasticadienolate	(**3b**)	Oily	—	0.8	†
Oleanonate	(**4a**)	180–182	+76	0.5	7

* Fatty acids and minor components: 12.8%.
† Characterized as the corresponding acid [6] mp 96–97°, $[\alpha]_D$ −47°.

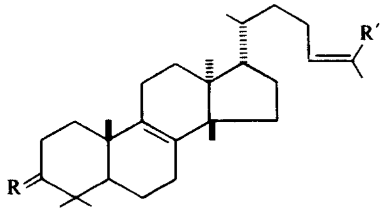
---

[*] Part 6 in the series 'Anacardiaceae'. For Part 5 see ref. [1].
† All the percentages are referred to the ethereal extract.

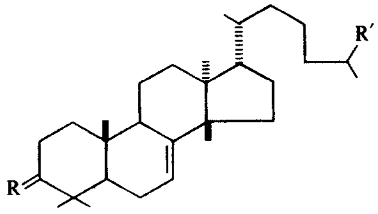
The neutral part of the resin was directly fractionated by chromatography on neutral alumina. Rechromatography and purification of the enriched fractions thus obtained led to the isolation of eleven neutral triterpenes which are listed in Table 2. The α,β-unsaturated ketoaldehyde (**1f**) was a very labile substance which could not be obtained sufficiently pure to determine any of its physical constants. Therefore, structure (**1f**) was assigned on the basis of the main spectroscopic features of the crude product (see experimental) and by conversion into masticadienediol (**1e**).

DISCUSSION

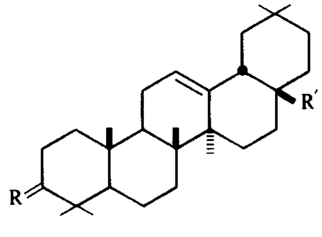
At the moment a direct comparison between chemical constitutions of the resin of *P. vera* and the galls produced by the same plant has not been achieved mainly owing to the difficulty encountered in obtaining galls from the same area. However, the distribution of triterpenes in the resin we have now examined seems to show the same main features already evidenced in the study of Anacardiaceae galls. The occurrence of both the C-3 epimeric hydroxy acids and of only C-3 β-equatorial neutral hydroxy compounds is in fact quite general [1] in the galls we have studied. In this view, the isolation from the resin of the acetyl derivatives (**1b**) and (**2b**) could now suggest a selective acetylation of the α-axial C-3 hydroxy acids which should preserve these in subsequent oxidation processes rather than the action of a non-stereospecific oxido reductase [13]. However, the occurrence of a simple hydrolysis of the less hindered β-equatorial C-3 acetoxy group, perhaps in the fractionation process, cannot be excluded although we could not detect any trace of β-equatorial acetates in the crude oleoresin.



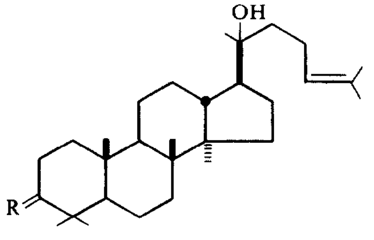
(**2a**) R = O ; R′ = CO_2Me
(**2b**) R = H, αOAc; R′ = CO_2Me
(**2c**) R = H, βOH ; R′ = Me
(**2d**) R = O ; R′ = CH_2OH
(**2e**) R = H, βOH ; R′ = CH_2OH
(**2f**) R = O ; R′ = Me



(**3a**) R = O ; R′ = CO_2Me
(**3b**) R = H, αOH; R′ = CO_2Me



(**4a**) R = O ; R′ = CO_2Me
(**4b**) R = O ; R′ = Me
(**4c**) R = O ; R′ = CHO
(**4d**) R = H, βOH; R′ = CHO



(**5a**) R = O
(**5b**) R = H, βOH

EXPERIMENTAL

General experimental and procedures of extraction and separation of acid and neutral fractions have been described [13]. The fresh oleoresin was collected from various plants in Damghan, 350 km east of Tehran, Iran. Identification of the plant was by Professor Sadegh Mobayen of Tehran University.

Acetoxy methyl esters (**2b**) *and* (**1b**). A fraction from the general chromatography (2200 mg; petrol–Et_2O, 19:1; 3 l.) mainly consisting of a mixture of (**2b**) and (**1b**) was adsorbed on 3% $AgNO_3$/Si gel (65 g). Elution with petrol–C_6H_6 (7:3; 0.7 l.) gave the crude **2b** (750 mg) which after crystallization from MeOH

Table 2. The neutral triterpenes obtained from *Pistacia vera* resin*

Compounds		mp	$[\alpha]_D$	%Amount	Ref.
Tirucallol	(**2c**)	132–133	+5	12.9	8
Dipterocarpol	(**5a**)	134–137	+67	6.5	9
Dammarenediol	(**5b**)	142–144	+27	5.0	10
26-Hydroxy-tirucallone	(**2d**)	Oily	+15	2.5	11
β-Amirone	(**4b**)	176–177	+107	2.5	12
Isomasticadienediol	(**2c**)	152–153	−8	2.4	11
Oleanonic aldehyde	(**4c**)	138–139	+89	2.3	11
Masticadienediol	(**1e**)	186–188	−52	1.8	6
Tirucallone	(**2f**)	Oily	+16	1.6	13
Oleanolic aldehyde	(**4d**)	169–170	+72	1.3	14
Masticadienonic aldehyde	(**1f**)	—	—	0.7	—

* Hydrocarbons and minor components: 13.6%.

had mp 86–87°, $[\alpha]_D$ −2° (*c* = 1); (Found: C, 76.96; H, 10.06. $C_{32}H_{52}O_4$ requires: C, 76.75; H, 10.47%); IR ν_{max} cm^{-1}: 1720, 1710, 1250; PMR: δ 5.98 (*t*, 1H), 4.45 (*m*, 1H), 3.70, 2.10, 1.88 (three 3H, *ss*). Pure **2b**, by hydrolysis with 10% hydromethanolic KOH and esterification with excess ethereal CH_2N_2, was quantitatively converted into methyl 3-epiisomasticadienolate mp and mmp 140–141°, $[\alpha]_D$ −16°, identical with an authentic specimen [5]. Further elution with petrol–C_6H_6 (1:1; 0.8 l.) gave the crude **1b** (1400 mg) which after crystallization from MeOH had mp 129–130°, $[\alpha]_D$ −26° (*c* = 0.9); (Found: C, 76.12; H, 10.96. $C_{32}H_{52}O_4$ requires: C, 76.75; H, 10.47%); IR ν_{max} cm^{-1}: 1720, 1710, 1250; PMR: δ 5.88 (*t*, 1H), 5.20 (*m*, 1H), 4.45 (*m*, 1H), 3.70, 2.10, 1.88 (three 3H *ss*). Pure **1b**, under the conditions reported above for **2b**, afforded quantitatively methyl 3-epimasticadienolate (**1d**) mp and mmp 100–101°, $[\alpha]_D$ −44°, identical with the natural **1d**.

Masticadienonic aldehyde (**1f**). Evapn of the mother liquors (280 mg) of crystallization of oleanonic aldehyde afforded a semicrystalline solid which was recrystallized from MeOH to give crude **1f**. Further purification of **1f** was not possible since the substance was very prone to undergo visible alterations. IR ν_{max} cm^{-1}: 1675; PMR: δ 9.45 (*s*, 1H, —CHO), 6.50 (*m*, 1H, C-24 vinyl H), 5.20 (*m*, 1H, C-7 vinyl H), 1.75 (*s*, 3H, Me on double bond). LAH reduction of crude **1f** (100 mg) led to a crystalline product which after two crystallizations gave pure masticadienediol (**1e**) mp and mmp 186–187°, $[\alpha]_D$ −50°, identical with an authentic specimen.

Acknowledgements—The authors gratefully acknowledge financial support by the Italian National Research Council (RC, LM, PM and GP) and by Research Council of University of Tehran (YA and MB). The skilful technical assistance of Mr. A. Cantilena is also acknowledged.

REFERENCES

1. Caputo, R., Mangoni, L., Monaco, P. and Palumbo, G. (1975) *Phytochemistry* **14**, 809.
2. Monaco, P., Caputo, R., Palumbo, G. and Mangoni, L. (1973) *Phytochemistry* **12**, 946.
3. Barton, D. H. R. and Seoane, E. (1956) *J. Chem. Soc.* 4150.
4. Seoane, E. (1956) *J. Chem. Soc.* 4158.
5. Caputo, R. and Mangoni, L. (1970) *Gazz. Chim. Ital.* **100**, 317.
6. Monaco, P., Caputo, R., Palumbo, G. and Mangoni, L. (1973) *Phytochemistry* **12**, 2534.
7. Cheung, H. T. and Feng, M. C. (1968) *J. Chem. Soc.* 4150.
8. Arigoni, D., Jeger, O. and Ruzicka, R. (1955) *Helv. Chim. Acta* **38**, 222.
9. Crabbe, P., Ourisson, G. and Takahashi, T. (1958) *Tetrahedron* **3**, 279.
10. Mills, J. S. (1956) *J. Chem. Soc.* 2196.
11. Monaco, P., Caputo, R., Palumbo, G. and Mangoni, L. (1973) *Phytochemistry* **12**, 939.
12. Simonsen, G. and Ross, L. (1951) *The Terpenes* Vol. 4. Cambridge University Press, London.
13. Monaco, P., Caputo, R., Palumbo, G. and Mangoni, L. (1974) *Phytochemistry* **13**, 1992.
14. Shamma, M. and Rosenstock, P. D. (1959) *J. Org. Chem.* **24**, 726.

Phytochemistry, 1978, Vol 17, pp. 817–818 Pergamon Press. Printed in England

ON THE OCCURRENCE OF FILICAN-3-ONE IN *STRYCHNOS DOLICHOTHYRSA*

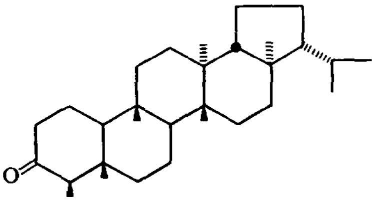
ROBERT VERPOORTE

Department of Pharmacognosy, Gorlaeus Laboratories, State University Leiden, P.O. Box 9502, Leiden, The Netherlands

(*Received* 4 *November* 1977)

Key Word Index—*Strychnos*; Loganiaceae; filican-3-one; triterpene.

Plant material of *Strychnos dolichothyrsa* Gilg ex Onochie et Hepper (Loganiaceae) was collected by Dr A. J. M. Leeuwenberg and Prof. F. Sandberg in the vicinity of Kribi, Cameroun (collection number Lg 7870) [1, 2]. A voucher specimen is kept in the herbarium at Wageningen, The Netherlands. The stem bark of this species was investigated for its muscle relaxant alkaloids [3, 4]. Prior to the alkaloid extraction the ground stem bark was extracted with hexane. Upon evaporation of the hexane, a crystalline compound was formed. The isolated compound proved to be a saturated pentacyclic triterpene, filican-3-one (**1**) (D: A. Friedo-B′: A′-neogammaceran-3-one), its structure and its stereochemistry having been established by X-ray crystallography [5]. Filican-3-one has been described previously in connection with the structure elucidation of triterpenes with the filicane skeleton [6, 7]. However, to our knowledge its natural occurrence has not been reported before.



Filican-3-one (1)

Filican-3-one (recrystallized ×2 ether) mp 248–249° (some sublimation was observed). $[\alpha]_D^{25°}$ −25.4, no depression of the mmp with an authentic sample of filican-3-one (kindly provided by Prof. A. Marsili, Pisa, Italy). High resolution mass spectrometry (direct inlet, 240°, 70 eV) *m/e* M^+ ($C_{30}H_{50}O$) 426 (32), 411 (36), 383 (4) M^+-isopropyl, 341 (44) $C_{24}H_{37}O^+$, 274 (18) $C_{19}H_{30}O^+$, 273 (20) $C_{20}H_{33}^+$ and $C_{19}H_{29}O^+$ (1:3), 259 (20) $C_{18}H_{27}O^+$, 257 (20) $C_{18}H_{25}O^+$, 234 (56) $C_{16}H_{26}O^+$ and $C_{17}H_{19}^+$ (1:10), 233 (32) $C_{16}H_{25}O^+$ and $C_{17}H_{29}^+$ (1:1), 231 (16) $C_{16}H_{23}O,^+$ 219 (20) $C_{15}H_{23}O,^+$ 206 (36)