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TRITERPENES FROM THE GALLS OF *PISTACIA LENTISCUS*

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

In pursuing our chemical study of the galls produced by plants of the genus *Pistacia*,[1,2] we examined the galls of *P. lentiscus*. The galls, produced by *Aploneura lentisci* on the young leaves of the plant, were collected in various areas of Central and Southern Italy at the end of summer. They looked like flat small beans, 2–3 cm long, of a green colour with thin red veins and, unlike *P. terebinthus* galls, were not visibly resinous.

Ether extraction of the minced galls gave a waxy extract in a 2·6% yield, which was separated into an acid fraction (41%) and a neutral fraction (55%). The separation of the acid components was then performed in several steps: chromatography separated a mixture of triterpene acids from a larger fraction, mainly fatty acids, whose composition has not yet been investigated. The triterpene fraction, after treatment with diazomethane and further chromatographic separations, gave the 9 esters listed in Table 1.

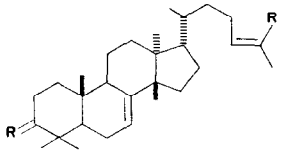
TABLE 1

Methyl esters		m.p.	$[\alpha]_D$	Ref.
Masticadienonate	(Ia)	124–125°	−72°	3
Dihydromasticadienonate	(IIa)	90–91°	−76°	—
Oleanonate	(IIIa)	181–182°	+76°	4
Masticadienolate	(Ib)	122–123°	−144°	1
Dihydromasticadienolate	(IIb)	117–118°	−43°	—
Oleanolate	(IIIb)	195–197°	+82°	4
3-Epimasticadienolate	(Ic)	100–101°	−47°	1
Dihydro-3-epimasticadienolate	(IIc)	oily*	—	—
3-Epioleanolate	(IIIc)	198–200°	+43°	5

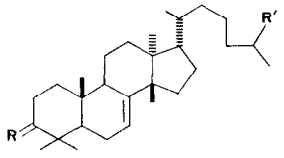
* Characterized as the corresponding acid m.p. 96–97°, $[\alpha]_D$ −47°.

[1] CAPUTO, R. and MANGONI, L. (1970) *Gazz. Chim. Ital.* **100**, 317.
[2] MONACO, P., CAPUTO, R., PALUMBO, G. and MANGONI, L. (1973) *Phytochemistry* **12**, 939.
[3] BARTON, D. H. R. and SEONANE, E. (1956) *J. Chem. Soc.* 4150.
[4] CHEUNG, H. T. and FENG, M. C. (1968) *J. Chem. Soc.* 1047.
[5] HUNECK, S. (1963) *Tetrahedron* **19**, 479.

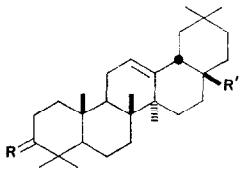
All structures were assigned on the basis of spectroscopic properties and known substances were all compared with authentic samples either directly or through their derivatives. The esters (IIa), (IIb) and (IIc) had never been found in nature before. The first showed a NMR spectrum very similar to that of the methyl masticadienonate (Ia): the absence of the vinylic proton at 5·88 δ and the chemical shift of the carbomethoxyl group at 3·65 δ suggested the structure (IIa). In fact this ester was found to be identical to the catalytic hydrogenation[3] product of (Ia). Esters (IIb) and (IIc) had very similar NMR spectra: the only difference was in the shape of the band of the proton geminal with the hydroxyl group, thus suggesting[6] that they were epimers. Accordingly, chromic oxidation of both (IIb) and (IIc) led to the same ketoester (IIa), identical with authentic material.



(Ia) R = O; R′ = COOMe
(Ib) R = H, βOH; R′ = COOMe
(Ic) R = H, αOH; R′ = COOMe
(Id) R = H, βOH; R′ = CH_2OH



(IIa) R = O; R′ = COOMe
(IIb) R = H, βOH; R′ = COOMe
(IIc) R = H, αOH; R′ = COOMe



(IIIa) R = O; R′ = COOMe
(IIIb) R = H, βOH; R′ = COOMe
(IIIc) R = H, αOH; R′ = COOMe
(IIId) R = O; R′ = Me
(IIIe) R = H βOH; R′ = Me
(IIIf) R = O; R′ = CHO
(IIIg) R = H, βOH; R′ = CHO
(IIIh) R = O; R′ = CH_2OH
(IIIi) R = H, βOH; R′ = CH_2OH

We next examined the small terpene fraction in the neutral part: chromatography afforded a large less polar fraction consisting of hydrocarbons and fats. The triterpene fraction, however, still contained fats and it was subjected to alkaline hydrolysis. Chromatography of nonsaponifiable material then gave the eight neutral triterpenes listed in Table 2.

TABLE 2

Compounds		m.p.	$[\alpha]_D$	Ref.
β-Amyrone	(IIId)	176–178°	+107°	7
β-Amyrin	(IIIe)	198–199°	+88°	7
Oleanonic aldehyde	(IIIf)	138–140°	+89°	2
Oleanolic aldehyde	(IIIg)	169–172°	+71°	8
28-Hydroxy-β-amyrone	(IIIh)	189–192°	+85°	2
Dammarenediol	—	142–144°	+27°	9
Erithrodiol	(IIIi)	231–235°	+79°	8
Masticadienediol	(Id)	186–187°	−50°	—

At present, it is not possible to relate the substances found in the galls to those in the plant, though the resin of *P. lentiscus*, also known as gum mastic,[10] has already been shown

[6] BHACCA, N. S. and WILLIAMS, D. M. (1964) *Applications of NMR Spectroscopy in Organic Chemistry*, Holden Day, San Francisco.
[7] SIMONSEN, G. and ROSS, L. (1951) *The Terpenes*, Vol. 4, University Press, Cambridge.
[8] SHAMMA, M. and ROSENSTOCK, P. D. (1959) *J. Org. Chem.* **24**, 726.
[9] MILLS, J. S. (1956) *J. Chem. Soc.* 2196.
[10] TABACIK-WLOTZKA, CH. and PISTRE, P. (1967) *Phytochemistry* **6**, 597.

to contain masticadienonic, isomasticadienonic and oleanonic acids and tirucallol.[3,11] This is because the resin producing varieties of *P. lentiscus* grow in the Middle East,[10] while the plants we have examined do not produce any resin.

On the other hand, there is an interesting analogy between this resin and that of the galls of *P. terebinthus*, since both contain triterpenes having equatorial and axial hydroxyl groups at C_3. As far as we know, the co-occurrence of pairs of epimers at C_3 is rather rare; furthermore, the finding in the galls of the corresponding 3-keto-acids suggests that the epimeric hydroxy-acids may be interconvertible. However, it is rather strange that the neutral triterpenes found only have the usual equatorial configuration at C_3.

EXPERIMENTAL

M.ps are uncorrected. NMR spectra were recorded with TMS as an internal standard. Rotations were taken for $CHCl_3$ solns at r.t. TLC and PLC were performed on silica-gel F_{254}(Merck). Silica-gel 0·05–0·20 mm (Merck) or alumina (Woelm, neutral) was used for column chromatography. General procedures for the extraction of the galls and for the separation of acid and neutral fractions have been already described.[1]

Separation of the acid components. The acid extract (10 g) was adsorbed on silica-gel (300 g; HCl washed). Elution with light petrol.–Et_2O (9:1) gave a little polar fraction (6 g); further elution with light petrol.–Et_2O (7:3) afforded a second fraction (1·85 g); elution with Et_2O–MeOH (19:1) finally gave a more polar fraction (2·05 g). The fraction of intermediate polarity was then treated with excess CH_2N_2 and the crude product chromatographed on silica-gel (185 g). Elution with light petrol.–Et_2O (4:1) gave an unhydroxylated fraction (1·2 g), whereas the elution with light petrol.–Et_2O (3:2) afforded a hydroxy-lated fraction (0·6 g). The semicrystalline unhydroxylated fraction was then rechromatographed on silica-gel treated with $AgNO_3$ (36 g), eluted with light petrol.–Et_2O (19:1) and gave 3 ketoesters: (a) methyl masticadienonate (Ia) (0·6 g) m.p. 124–125° (from MeOH), $[\alpha]_D$ −72° (*c* 1) identical with an authentic sample; (b) methyl oleanonate (IIIa) (0·45 g) m.p. 181–182° (from MeOH), $[\alpha]_D$ +76° (*c* 0·9) identical with an authentic sample; (c) methyl dihydromasticadienonate (IIa) (0·01 g) m.p. 90–91° (from MeOH) $[\alpha]_D$ −76° (*c* 0·9), MW 470 (MS). (Found: C, 79·5; H, 10·7. $C_{31}H_{50}O_3$ requires: C, 79·1; H, 10·7%); δ 5·25 (1H, *m*, vinylic proton), 3·65 (3H, *s*,–COOMe). The ester (IIa) was found to be identical with the catalytic hydrogenation (PtO_2–AcOH) product of (Ia). The hydroxylated fraction showed on TLC two spots having respectively R_f 0·5 and 0·4 (eluent C_6H_6–Et_2O, 9:1, twice). By PLC, it was separated in two fractions, both then rechromatographed on silica-gel treated with $AgNO_3$ (eluent C_6H_6–Et_2O, 9:1). Elution of the higher R_f fraction afforded a crystalline hydroxy ester (150 mg) and a mixture of 2 further hydroxy esters: the former was methyl 3-epimasticadienolate (Ic), m.p. 100–101°, $[\alpha]_D$ −47° (*c* 1) identical with an authentic sample; the latter, by crystallization from MeOH, afforded the pure methyl 3-epioleanolate (IIIc) (70 mg) m.p. 198–200° (from MeOH), $[\alpha]_D$ +56° (*c* 1·5) then transformed, by CrO_3 oxidation, into the ketoester (IIIa). Chromatography (silica-gel; hexane–Et_2O, 7:3) of the mother liquors of crystallization of (IIIc) then led to the isolation of the oily methyl 3-epidihydromasticadienolate (IIc) (40 mg) [ν_{max} 3550, 1710 cm^{-1}; δ 5·25 (1H, *m*, vinylic proton), 3·65 (3 H, *s*, –COOMe), 3·42 (1H, *br* $W_{1/2}$ 6Hz, =CHOH)]. Alkaline hydrolysis (KOH–MeOH 10%) of (IIc) gave the corresponding crystalline acid m.p. 96–97° (from hexane), $[\alpha]_D$ −47° (*c* 0·8), MW 458 (MS). (Found: C, 78·50; H, 10·80. $C_{30}H_{50}O_3$ requires: C, 78·55, H, 10·85%.) The CrO_3 oxidation product of (IIc) was identical with the ketoester (IIa). The fraction with R_f 0·4, when chromatographed on silica-gel treated with $AgNO_3$ in the same conditions as above, also gave a mixture of two hydroxy-esters beside the pure methyl masticadienolate (Ib) (200 mg) m.p. 122–123°, $[\alpha]_D$ −44° (*c* 1) which was identical with an authentic sample. The mixture, by fractionated crystallization from MeOH, then gave the pure methyl oleanolate (IIIb) (100 mg) m.p. 195–197°, $[\alpha]_D$ +82° (*c* 1) compared with an authentic sample, beside the methyl dihydromasticadienolate (IIb) (50 mg), m.p. 117–118° (from MeOH), $[\alpha]_D$ −43° (*c* 1); MW 472 (MS); (Found: C, 78·70; H, 10·81. $C_{31}H_{52}O_3$ requires: C, 78·75; H, 11·1%); ν_{max} 3550, 1710 cm^{-1}; δ 5·25 (1H, *m*, vinylic proton), 3·65 (3H, *s*, –COOMe), 3·23 (unresolved *dd*, =CHOH). The pure (IIb) was found to be identical with the catalytic hydrogenation product of (Ib).

Separation of the neutral compounds. The neutral extract (15 g) was adsorbed on alumina (450 g; grade III). Benzene eluted a less polar fraction (12 g) consisting of hydrocarbons and fats. C_6H_6–Et_2O (8:2) gave a mixture of triterpenes together with fats. Alkaline hydrolysis (KOH–MeOH, 10%) of this mixture then gave a non-saponifiable residue (1 g) which was adsorbed on silica-gel (30 g). Light petrol. eluted the crystalline β-amyrone (IIId) (70 mg) m.p. 176–178° (from MeOH), $[\alpha]_D$ +107° (*c* 1·1), compared with an authentic sample; light petrol.–Et_2O (9:1) then gave a mixture of two substances whose fractional crystallization by MeOH afforded β-amyrin (IIIe) (150 mg) m.p. 198–199°, $[\alpha]_D$ +88° (*c* 1) compared with an authentic sample, beside oleanonic aldehyde (IIIf) (70 mg) m.p. 138–140°, $[\alpha]_D$ +89° (*c* 1) whose $LiAlH_4$ reduction

[11] SEOANE, E. (1956) *J. Chem. Soc.* 4158.

product was identical with an authentic sample of erithrodiol (IIIi). Light petrol.–Et_2O (17:3) gave oleanolic aldehyde (III g) (170 mg) m.p. 169–172°, $[\alpha]_D$ +71° (*c* 1) whose $LiAlH_4$ reduction yielded erithrodiol (IIIi). Light petrol.–Et_2O (8:2) eluted 28-hydroxy-β-amyrone (IIIh) (60 mg) m.p. 189–192°, $[\alpha]_D$ +85° (*c* 0·9) which was compared with an authentic sample. Elution with light petrol.–Et_2O (7:3) gave a mixture of two diols. The mixture, by acetylation (Ac_2O-pyridine at r.t. over night), gave a crude producte whose chromatography afforded both oily a mono- and di-acetate. Alkaline hydrolysis (KOH–MeOH, 10%) of the former led to dammarenediol (150 mg) m.p. 142–144°, $[\alpha]_D$ +27° (*c* 1) compared with an authentic sample; the hydrolysis of the latter gave erithrodiol (IIIi) (120 mg) m.p. 231–235°, $[\alpha]_D$ +27° (*c* 1·2). Finally, elution with light petrol.–Et_2O (6:4) gave masticadienediol (Id) (110 mg) m.p. 186–187° (from C_6H_6), $[\alpha]_D$ −50° (*c* 1·4) found identical with the $LiAlH_4$ reduction product of (Ia).

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ISOLEMENT DE LA DEHYDRO-14 ISOEBURNAMINE DE *MELODINUS CELASTROIDES**

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Key Word Index—*Melodinus celastroides*; Apocynaceae; indole alkaloids; Δ^{14}-eburnamine.

Melodinus celastroides H. Baillon (Apocynacées–Plumérioïdées) est un arbrisseau rameux, lianescent, croissant dans les régions littorales de la Nouvelle-Calédonie. L'espèce étudiée ici provient d'une zone humide adjacente à une mangrove; un spécimen de référence est conservé à l'Herbier du Museum de Paris, sous le numéro Sévenet 287 *S*. Aucune étude chimique n'a été publiée jusqu'ici sur cette espèce.

Les alcaloïdes sont extraits de manière classique: les tiges feuillées pulvérisées sont épuisées par Et_2O après alcalinisation par NH_3. Le rendement est de 0,58 g % en alcaloïdes totaux.

La chromatographie sur silice (élution par le mélange C_6H_6–Et_2O 80–20) permet de séparer successivement la (−)-tabersonine[1] I et un alcaloïde nouveau (0,07 % des alcaloïdes totaux), amorphe, donnant une belle coloration jaune au réactif cérique.[9] Le poids moléculaire (294), déterminé par SM est compatible avec la formule brute: $C_{19}H_{22}ON_2$. Le

* Partie XXVII dans la série "Plantes de Nouvelle Caledonie". Pour Partie XXVI voir RABARON, A., PLAT, M. et POTIER, P. (1973) *Phytochemistry*, á paraitre.

[1] JANOT, M.-M., POURRAT, H. et LE MEN, J. (1954) *Bull. Soc. Chim. Fr.* 705.