Phytochemistry, 1974 Vol 13 pp 1551 to 1552 Pergamon Press Printed in England

TRITERPENES IN HUSKS OF *OLEA EUROPAEA*

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(*Received* 14 *October* 1973)

Key Word Index—*Olea europaea*, Oleaceae, triterpenes, biological hydroxylation, oleanolic acid, maslinic acid

Abstract—Oleanolic acid was found to be the major triterpene acid of fresh olive husks After storage of the husks or after incubation under humid conditions maslinic acid was formed with a corresponding reduction in the amount of oleanolic acid

IN CONNECTION with our work on the oleanane triterpenes of galls produced by plants of the genus *Pistacia*,[1] we needed a quantity of maslinic acid (2α-hydroxyoleanolic acid). This compound has been reported, by Caglioti *et al*.,[2] to be the main triterpene component of olive husks, but extraction of several batches of fresh husks enabled us to isolate only oleanolic acid, thus confirming the earlier work of Parisi and DeVito [3] However the examination of samples of husks of different ages led to the isolation of widely variable amounts of maslinic acid accompanying oleanolic acid.

We have also demonstrated that maslinic acid, is produced, during the ageing of olive husks, possibly through microbial α-hydroxylation of oleanolic acid. A batch of fresh husks was divided into two after expression of the oil. The first was immediately extracted with organic solvents and the second incubated at 37° under high humidity for 4 months and then extracted in the same way The triterpenoid acids from both samples were purified by column chromatography and recovered as the corresponding methyl ester derivatives. The fresh sample yielded 5·9% methyl oleanolate (fresh weight basis) whereas the incubated sample gave methyl maslinate 2·7% and methyl oleanolate 2·9%.* As far as we know biological systems leading to 2α,3β *trans*-diequatorial diols, by hydroxylation of the C-2 position of 3β-hydroxy triterpenes, are not common. Furthermore, since the synthesis of triterpene 2α,3β-diols is difficult the development of an enzymatic process based on this system may be of interest.

EXPERIMENTAL

General extraction procedure Either fresh or old husks were continuously extracted with light petrol, (b p 40–70°) for 6 hr to remove fats and waxes, and then with Et_2O for a further 8 hr Evaporation of the Et_2O gave a waxy black–green residue which was directly adsorbed onto a large column of silica-gel (HCl washed) Prolonged elution with C_6H_6 gave a major fraction consisting of fats, further elution with C_6H_6–Et_2O (4 1) then afforded a second fraction containing the triterpene acids Ethereal CH_2N_2 treatment of the latter, followed by chromatography on silica-gel, afforded the triterpene methyl esters methyl oleanolate (eluent C_6H_6–Et_2O 4 1)

* Yields are calculated on the weight of the fresh husks

[1] MONACO, P., CAPUTO, R., PALUMBO, G and MANGONI, L (1973) *Phytochemistry* **12**, 2534
[2] CAGLIOTI, L., CAINELLI, G AND MINUTILLI, F (1961) *Gazz Chim Ital* **91**, 1387
[3] PARISI, E and DEVITO, G (1931) *Ann Chim* **21**, 323

m.p. 195–197° (from MeOH), $[\alpha]_D$ + 82° (c = 1 in $CHCl_3$), and, when present, methyl maslinate (eluent: C_6H_6–Et_2O 3:2) m.p. 229–232° (from MeOH), $[\alpha]_D$ + 65° (c = 1·1 in $CHCl_3$).

Extraction of fresh husks. Fresh husks (350 g) were extracted within 24 hr of pressing the olives. Only methyl oleanolate was obtained in 5·9% yield.

Extraction of aged husks. Fresh material (350 g) was kept at room temp. for 4 months. Methyl oleanolate was obtained in 4·6% yield together with methyl maslinate in 1·2% yield.

Extraction of incubated husks. Fresh material (350 g) was kept in a thermostat at 37° at 80% humidity for 4 months. Extraction then afforded methyl oleanolate in 2·9% yield and methyl maslinate in 2·7% yield.