

## TRITERPENOIDS AND STEROLS FROM SEEDS OF *PHYTOLACCA ESCULENTA*

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**Key Word Index**—*Phytolacca esculenta*, *P. acinosa*, Phytolaccaceae, triterpene, sterol, 3-acetylmyricadiol, acetylaleuritic acid,  $\alpha$ -spinasterol, stigmast-7-en-3 $\beta$ -ol

**Abstract**—Chromatographic separation of the chloroform-soluble part of the methanol extract from *Phytolacca esculenta* seeds resulted in the isolation of acetylaleuritic acid, 3-acetylmyricadiol,  $\alpha$ -spinasterol and stigmast-7-en-3 $\beta$ -ol

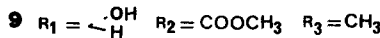
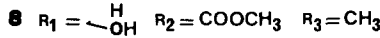
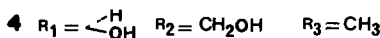
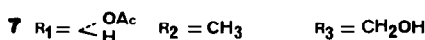
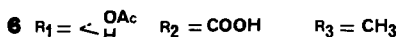
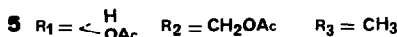
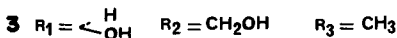
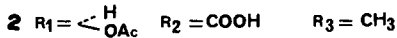
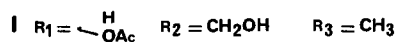
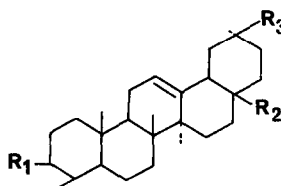
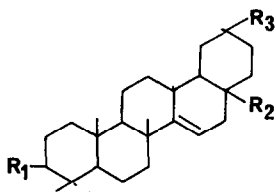
In the course of studies of the genus *Phytolacca* (Phytolaccaceae) [1–3], we have now isolated a new triterpenoid, 3-acetylmyricadiol (1) together with the known acetylaleuritic acid (2),  $\alpha$ -spinasterol and stigmast-7-en-3 $\beta$ -ol from the seeds of *P. esculenta*.

Column chromatography of the chloroform-soluble fraction of the methanol extract from the seeds and crystallization gave needles of 1, C<sub>32</sub>H<sub>52</sub>O<sub>3</sub>, mp 257–258°, [ $\alpha$ ]<sub>D</sub><sup>22</sup> +20°, (c 0.15, CHCl<sub>3</sub>), which gave positive Lieberman–Burchard and tetranitromethane tests and showed in its IR spectrum hydroxyl peaks at 3520 and 3470 cm<sup>-1</sup>, acetoxy peaks at 1710 and 1242 cm<sup>-1</sup> and trisubstituted double bond peak at 810 cm<sup>-1</sup>. The <sup>1</sup>H NMR spectrum of 1 revealed seven tertiary methyl signals between  $\delta$  0.87 and  $\delta$  1.06, an acetoxy signal at 2.02, two double doublets centred at 4.43 (1H, *J* = 6.5 and 9 Hz) due to a proton on a carbon atom bearing a

secondary acetoxy group and at 5.48 (1H, *J* = 4 and 8 Hz) due to a proton of a trisubstituted double bond, and a well-defined AB quartet at 3.10 and 3.24 (1H each, *J* = 11 Hz), indicating the presence of a primary hydroxyl group. Thus this compound (1) must be a dihydroxy triterpene with a trisubstituted double bond, which does not belong to the  $\beta$ -amyrin series.

The mass spectrum of 1 showed the molecular ion peak at *m/z* 484 (2.5%) and the fragment ion peaks at *m/z* 344 (RDA fragment, 4.9%), 329 (RDA – Me, 3.4%), 284 (RDA – HAc, 3.9%), 269 (RDA – Me – HAc, 16.3%), 220 (rings D/E, 17.2%), 189 (rings D/E – CH<sub>2</sub>OH, 100%), indicating that 1 is a  $\Delta^{14}$ -taraxerene derivative [4]. The most abundant fragment appearing at *m/z* 189 is indicative of the attachment of the primary alcohol group at C-17 [4].

Alkaline hydrolysis (NaOH) of 1 yielded myricadiol (3)



but acidic hydrolysis (HCl) gave an isomerized product, erythrodiol (4). Therefore compound 1 was identified as 3-acetylmyricadiol. Finally, compound 1 proved to be identical by direct comparisons (co-TLC, mmp, IR and  $^1\text{H}$  NMR) with an authentic sample of 3-acetylmyricadiol prepared from myricadiol diacetate (5) by partial hydrolysis ( $\text{K}_2\text{CO}_3$ ). This is the first report of its occurrence in nature to the best of our knowledge.

Very recently, Razdan *et al* [5] reported the isolation of 3 $\alpha$ -acetoxytaraxer-14-en-28-oic acid (6) and taraxer-14-ene-3 $\alpha$ ,30 $\beta$ -diol 3-acetate (7) from the berries of *P. acinosa*. However, their samples (6 and 7) were identical with ours of acetylaleuritic acid (2) (as methylester) and 3-acetylmyricadiol (1), respectively, by direct comparisons (co-TLC, mmp, MS and  $^1\text{H}$  NMR). The  $\beta$ -configuration of the C-3 acetoxy group of 2 and 6 was confirmed by the comparison of acid treatment products of both methyl esters of 2 and 6 with an authentic sample of methyl oleanolate (8), which is quite different from methyl epioleanolate (9) in its TLC behaviour [6] and  $^1\text{H}$  NMR spectrum [7]. This finding is positive in denying the presence of these *epi*-form compounds (6 and 7) in *P. acinosa*.

#### EXPERIMENTAL

**Plant material** Seeds of *P. esculenta* were collected near Seoul in October 1983. A voucher specimen (Chl No. 764) has been deposited in the herbarium of the Institute.

**Isolation of the compounds** The seeds (1.6 kg) were extracted

with MeOH and concd to a dark residue, which was partitioned between  $\text{CHCl}_3$  and  $\text{H}_2\text{O}$ . The  $\text{CHCl}_3$  extract (12 g) was then subjected to silica gel CC, using hexane– $\text{Me}_2\text{CO}$  (gradient), to yield acetylaleuritic acid (2), mp 303–304°, 3-acetylmyricadiol (1), mp 257–258° and a mixture of  $\alpha$ -spinasterol and stigmat-7-en-3 $\beta$ -ol. Compound 2 was identified by direct comparison (co-TLC, mmp, IR, MS and  $^1\text{H}$  NMR) with an authentic sample of acetylaleuritic acid isolated from the berries of *P. americana* [8].

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