

MASLINIC LACTONE FROM THE HEARTWOOD OF
TERMINALIA ALATA

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Terminalia alata Heyne ex Roth (Combretaceae) is a large deciduous tree found in the forests throughout India. Its bark is used traditionally as a cardiac stimulant (1). In our earlier paper (2), we reported the isolation of β -sitosterol, oleanolic acid, maslinic acid, arjunolic acid, and two unidentified minor triterpenoids from the heartwood of *T. alata*. We now report the isolation and identification of these two minor compounds, TA-2 and TA-5.

Compound TA-2, mp 285-90°, $C_{30}H_{48}O_4$ (M^+ 472.355), was recognized as a triterpenoid lactone from its ir spectrum (1750 cm^{-1}). It formed an amorphous diacetate whose $^1\text{H-nmr}$ spectrum showed the presence of two protons on carbons carrying the acetoxy groups in diaxial orientation [δ 4.66 (d, $J=10$ Hz), 5.5 (sextet)]. The acetoxy groups are, therefore, diequatorially oriented. From the ir, $^1\text{H-nmr}$, and ms data, we inferred that this minor triterpenoid TA-2 could be $2\alpha,3\beta$ -dihydroxyolean-28,13-lactone (maslinic lactone). The identity was further confirmed by direct comparison of the diacetate with maslinic lactone diacetate prepared according to the method of Barton and Holness (3). This is the first report of the occurrence of maslinic lactone in nature.

The second minor compound, TA-5, was identified as terminolic acid ($2\alpha,3\beta,6\beta,23$ -tetrahydroxyolean-12-ene-8-oic acid) (4) from the ir, $^1\text{H-nmr}$, and ms of its methyl ester and methyl ester triacetate.

EXPERIMENTAL

PLANT MATERIAL.—The heartwood of *T. alata* was obtained from the Forest Research Institute, Bangalore, India.

EXTRACTION AND ISOLATION OF THE TRITERPENOID.—The powdered heartwood of *T. alata* (750 g) was extracted successively with hexane, ether, and acetone. The residue from the hexane extract on chromatography (silica gel, 100-200 mesh) gave β -sitosterol (50 mg) and oleanolic acid (TA-1) (250 mg). The ether extract gave a solid (12 g) containing three major and two minor compounds (tlc, chloroform-methanol 92:8, silica gel G). The mixture was chromatographed over silica gel (400 g) eluting the column with chloroform and chloroform containing 2% methanol. The compounds obtained from the fractions were oleanolic acid (TA-1) (2.55 g), TA-2 (25 mg) purified by tlc (silica gel G, chloroform-methanol 98:2), maslinic acid (TA-3) (0.85 g), arjunolic acid (TA-4) (7.6 g), and a mixture of TA-4 and TA-5 (0.15 g).

The mixture of TA-4 and TA-5 was methylated with diazomethane and separated by chromatography over neutral alumina to obtain methyl arjunolate (105 mg) and TA-5 methyl ester (methyl terminolae) (30 mg), colorless needles from methanol mp 162-65° [Lit. (4) mp 164-65°], ir 3360 (hydroxyl), 1730 (ester); ms m/z (rel. int.): 518 (M^+ , 4.2), 500 ($M^+ - H_2O$, 2.6), 485 ($M^+ - H_2O - Me$, 1.6), 482 (6), 262 (retro Diels-Alder fragment 58.85), 248 (28.9), 203 (263-COOCH₃, 100), 189 (27.6), 175 (6.65), 133 (19.6), 121 (6.6), 119 (13.7), 109 (9.9), 95 (9.78), and 69 (13.3).

Anal. calcd. for $C_{31}H_{50}O_5$: C, 71.81; H, 9.65%. Found: C, 71.55; H, 9.85%.

It gave an amorphous triacetate (acetic anhydride-pyridine), ir 3400 (hydroxyl), 1740, 1730 cm^{-1} (ester); $^1\text{H-nmr}$ (270 MHz, CDCl_3): δ 0.908, 0.935, 1.017, 1.085, 1.254, 1.277 (singlets 3H each, 6 C-methyls), 1.990, 2.037, 2.069 (singlets, 3H each, 3 \times OAc), 3.650 (s, 3H, COOCH₃), 3.716, 3.945 (dd, $J=11.7$ Hz, $-CH_2OAc$), 4.349 (bs, $W_{1/2}=7$ Hz, 6 β H), 5.012 (d, $J=10$ Hz, 3 β H), 5.214 (ddd, $J=11, 10.4$ Hz, 2 β H), 5.300 (m, 12H).

TA-2 (maslinic lactone) crystallized from methanol as colorless needles, mp 285-90°; ir (chloroform) 3450 (hydroxyl), 1750 cm^{-1} (lactone); $^1\text{H-nmr}$ (270 MHz, CDCl_3): 0.79, 0.91, 0.93, 1.02, 1.31 (singlets, 7 C-methyls), 3.65 (bm, 2H, 2 \times CHOH), ms m/z (rel. int.): 472.355 (M^+ , 9.6), 454 (16.7), 439 (1.7), 436 (5.4), 421 (2.9), 411 (5), 372 (2.3), 235 (30),

223 (8.3), 205 (50), 203 (35), 189 (55), 177 (90.3), 175 (47), 163 (23), 161 (26.7), 149 (27), 145 (18.3), 137 (25), 135 (42), 133 (44), 121 (72), 119 (75), 109 (50), 107 (73.5), 95 (76.7), 93 (56.5), 81 (68.3), 59 (93.3), and 44 (100).

Anal. calcd for $C_{30}H_{48}O_4$: C, 76.28; H, 10.17%. Found: C, 76.55; H, 10.45%.

TA-2 diacetate (acetic anhydride-pyridine) gave: ir (chloroform): 1755 (-lactone), 1735 cm^{-1} (ester); 1H -nmr: (270 MHz, $CDCl_3$): δ 0.808, 0.817, 0.833, 0.859, 0.904, 1.182, 1.247 (singlets, 3H each, 7 C-methyls), 1.942, 2.000 (s, $2 \times OAc$), 4.660 (d, $J=10$ Hz, $3\alpha H$), 5.050 (ddd, 1H, $2\beta H$). The diacetate was found to be identical with maslinic lactone diacetate prepared from maslinic acid by reaction with $HBr-HOAc$ (ir, co-tlc, 1H -nmr).

The acetone extract afforded a solid (21.5 g) that was found by tlc to be mainly arjunolic acid with a contamination of terminolic acid.

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