dissolved in Et_2O, dried and the Et_2O was removed to leave a crude solid which on CC over 50 g silica gel (60–120 mesh) furnished glut-5(10)-en-1-one, $C_{30}H_{48}O$ (3), mp 312°, $[\alpha]_D + 30°$ ($CHCl_3$). It did not respond to a Zimmermann test; its UV, IR, ^1H NMR and MS data were similar to those in the lit. [3].

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3-ACETYLMASLINIC ACID FROM THE ROOT BARK OF *TERMINALIA ALATA*[*]

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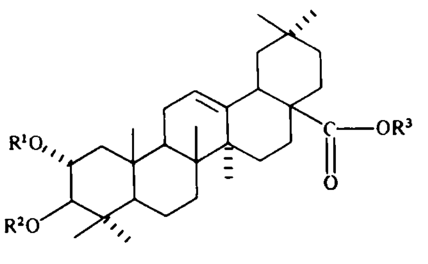
Key Word Index—*Terminalia alata*; Combretaceae; triterpenoids; 3-acetylmaslinic acid.

Abstract—A new triterpene acid, 3-acetylmaslinic acid, has been isolated from the root bark of *Terminalia alata* together with oleanolic acid, arjunic acid, arjunolic acid and arjunetin.

The isolation of triterpenoids from the heartwood of *Terminalia alata* Heyne *ex* Roth (syn. *T. tomentosa* W. & A.) was reported recently [1, 2]. Continuing our studies on the chemical constituents of the genus *Terminalia*, we report here the isolation of a new triterpene acid, identified as 3-acetylmaslinic acid, from the root bark of *T. alata* together with the known compounds oleanolic acid, arjunic acid, arjunolic acid and arjunetin.

Extraction of the ground root bark with $CHCl_3$ and EtOAc afforded a mixture of triterpenoids. Separation by repeated column chromatography and preparative TLC over silica gel led to the isolation of the above known triterpene acids and the new acid TARB-2. The compound TARB-2, mp 192–195°, $[\alpha]_D + 32°$, analysed for $C_{32}H_{50}O_5$ and gave a positive Liebermann–Burchard test and yellow colour with tetranitromethane. Its IR spectrum showed the presence of hydroxyl (3500 cm^{-1}), ester carbonyl (1740 cm^{-1}) and carboxyl (1690 cm^{-1}) groups. The ^1H NMR spectrum showed the resonances for seven tertiary methyls, one acetate and olefinic groups. In addition, it showed the presence of CHOH with a signal at δ3.29 (*m*) and a CHOAc signal at 4.68 (*d*, $J = 12$ Hz). The large coupling constant indicated a diaxial relation; therefore the hydroxyl and acetoxyl groups are in diequatorial orientation. Acetylation with acetic anhydride and pyridine gave diacetylmaslinic acid (**1b**), which on treatment with diazomethane afforded diacetylmethyl



1 $R^1 = R^2 = R^3 = H$
1a $R^1 = R^3 = H$; $R^2 = Ac$
1b $R^1 = R^2 = Ac$; $R^3 = H$
1c $R^1 = R^2 = Ac$; $R^3 = Me$

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maslinate (**1c**). Alkaline hydrolysis of TARB-2 gave maslinic acid (**1**) [2]. The above data lead to the identification of TARB-2 as 3-acetylmaslinic acid (**1a**).

Although the occurrence of acetyloleanolic acid in plants is very common, this is the first report of the isolation of 3-acetylmaslinic acid (**1a**) from a plant and, to our knowledge, it has also not been prepared from maslinic acid. The isolation of maslinic acid [1, 2], as well as its acetate, from *T. alata* is of biogenetic significance in providing the missing link for a dihydroxytriterpene amongst a mixture of mono- to tetrahydroxytriterpenoids found in the plant. The methanol extract gave a crude material which afforded a small amount of ellagic acid.

EXPERIMENTAL

Mps are uncorr. IR spectra were measured on KBr discs and ^{1}H NMR spectra were recorded in $CDCl_3$ soln using TMS as internal standard. The root bark of *T. alata* was obtained from CIMAP Experimental Station, Hebbale, Coorg District, Karnataka State, India and a voucher specimen has been deposited at CIMAP, Bangalore.

Extraction and isolation. Dried ground root bark (650 g) of *T. alata* was first defatted with hexane and extracted with $CHCl_3$, EtOAc and MeOH successively. The $CHCl_3$ extract gave a material (2.0 g) which was separated into hexane (0.22 g) and Et_2O (1.1g) soluble fractions. The hexane-soluble fraction on repeated crystallization from MeOH gave oleanolic acid (TARB-1; 80 mg), mp 310–311° [2]. The Et_2O-soluble fraction was found by TLC (silica gel; $CHCl_3$–MeOH, 98 : 2) to consist of one major and three minor compounds. CC over silica gel (100–200 mesh), eluting with $CHCl_3$ and a $CHCl_3$–MeOH mixture of increasing polarity, gave a further amount of oleanolic acid (20 mg), a mixture of oleanolic acid and TARB-2 (60 mg), arjunic acid (TARB-3; 625 mg), mp 334–335°, [3] and arjunolic acid (TARB-4; 50 mg), mp 330–332° [2]. The EtOAc extract gave a mixture (10 g) which was subjected to repeated CC and prep. TLC over silica gel: oleanolic acid (50 mg), TARB-2 (40 mg), arjunic acid (500 mg), arjunolic acid (60 mg) and arjunetin (TARB-5, 65 mg), mp 238–240° [4].

Compound TARB-2 (3-acetylmaslinic acid, **1a**) mp 192–195° (from $CHCl_3$–MeOH), $[\alpha]_D$ + 32° (*c* 0.5; $CHCl_3$). IR ν_{max} cm^{-1}: 3500 (OH), 1740 (OAc), 1695 (COOH), 1460, 1265, 830 (–C=CH). ^{1}H NMR: δ0.70, 0.81, 0.85, 0.95, 1.05, 1.07 (6 × *s*, 7 Me), 2.02 (*s*, OAc), 3.29 (*m*, 1H, H-2), 3.62 (*br s*, OH), 4.62 (*d*, 1H, *J* = 12 Hz, H-3). Found: C, 74.76; H, 9.75. Calc. for $C_{32}H_{50}O_5$: C, 74.71; H, 9.72%. Acetate (Ac_2O–pyridine), mp 232–234° (MeOH), identical to diacetylmaslinic acid (**1b**) (mmp, IR, ^{1}H NMR, co-TLC). Methyl ester diacetate mp 176–178° (CH_2N_2–Et_2O), identical to diacetylmethyl maslinate (**1c**) [1] (mmp, IR, ^{1}H NMR, co-TLC). Hydrolysis of TARB-2 (15 mg) with 6% KOH in MeOH (10 ml) for 6 hr under reflux afforded after the usual work-up maslinic acid (**1**), mp 268–270° [2].

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