Phytochemistry, 1980, Vol. 19, pp. 2482–2483. © Pergamon Press Ltd. Printed in England. 0031-9422/80/1101-2482 $02.00/0

TRITERPENE ACIDS FROM *MYRIANTHUS ARBOREUS*

CHUKWUNONYE M. OJINNAKA,* JOSEPH I. OKOGUN† and DOMINIC A. OKORIE

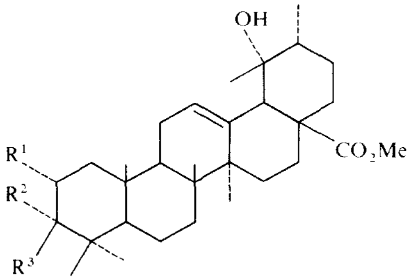
Department of Chemistry, University of Ibadan, Ibadan, Nigeria

(*Received* 11 *January* 1980)

Key Word Index—*Myrianthus arboreus*; Urticaceae; triterpenoids; tormentic acid; euscaphic acid; 3-acetyltormentic acid; 2-acetyl tormentic acid; methyl 19α-hydroxyurs-12-en-28-oate.

Myrianthus arboreus P. Beauv, Urticaceae [1], is a small tropical African tree, without latex, readily recognized by its large compound leaves [2]. The young leaves of *Myrianthus* along with those of *Alcohornea cordifolia* (Euphorbiaceae) are macerated in water and the extract drunk at intervals for the cure of dysentery; a similar decoction forms a wash for urethral discharges [3]. The study of the root extracts of *M. arboreus* was initiated in an attempt to isolate any biologically active components that could justify its use in herbal medicine and as a component of ordeal mixtures (Okogun Omovuon, personal communication). Early work on *M. arboreus* reported the isolation of peptide alkaloids from the leaves [4]. We now report the isolation from the root wood of *M. arboreus*, of tormentic acid, euscaphic acid and two new triterpene acids viz. 2-acetyl tormentic acid and 3-acetyl tormentic acid as their respective methyl esters **1** [5], **2** [6] **3** and **4** as well as the correlation of methyl tormentate and euscaphate by their respective conversions to methyl 19α-hydroxyurs-12-en-28-oate (**6**).

Column chromatography, on deactivated alumina, of the methyl esters of the crude acid mixture obtained from the methylated spirit extract of the root wood of *M. arboreus* gave crystalline compounds W, X, Y and Z together with a more polar mixture.



1 R^1 = R^3 = —OH, R^2 = —H
2 R^1 = R^2 = —OH, R^3 = —H
3 R^1 = —OAc, R^2 = —H, R^3 = —OH
4 R^1 = —OH, R^2 = —H, R^3 = —OAc
5 R^1 = R^3 = —OAc, R^2 = —H
6 R^1 = R^2 = R^3 = —H

Both compounds W and X had the molecular formula $C_{31}H_{50}O_5$ and were respectively identified through their IR, ^{1}H NMR spectra and MS [5–8] as methyl tormentate (**1**), mp 156–158° (lit. [5] mp 156°) and methyl euscaphate (**2**) mp 130–132° (lit. [6] mp 125–130°).

Compounds Y, mp 134–135° and Z, mp 123–125°, were similar in many respects. In the MS each had its M$^+$ at *m/e* 544 and each had diagnostic fragment ions at *m/e* 278, 260 and 179 which were also observed in the spectra of methyl tormentate (**2**) and methyl euscaphate (**4**). In the ^{1}H NMR spectrum of Y there were single proton absorptions at δ 3.18 (*d*, $J = 10$ Hz) and 4.83 (*m*, $W_{1/2} = 20$ Hz) while in the spectrum of Z corresponding absorptions were at 3.8 (*m*, $W_{1/2} = 20$ Hz) and 4.50 (*d*, $J = 10$ Hz). In the ^{1}H NMR spectrum of methyl dihydroalphitolate-2-acetate the absorption at δ 3.1 (1 H, *d*, $J = 10$ Hz) was assigned [9] to the C-3αH. On the basis of these facts Y was assigned the structure methyl tormentate-2-acetate **3**, while Z was methyl tormentate-3-acetate (**4**). These assignments were supported by the fact that on acetylation both Y and Z yielded methyl tormentate diacetate, mp and mmp 161–162°, from either ethanol or methanol (lit. [5] mp 162°). Methyl tormentate and methyl euscaphate were interrelated as follows: each compound was partially oxidized to an α-hydroxyketone which was then acetylated. The α-acetoxyketone was then reduced using the modified Wolff–Kishner (Huang-Minlon) method [10].

The product was treated with diazomethane and purified by column chromatography to give colourless crystals from Et$_2$O–petrol, mmp 148–150°. The products from methyl tormentate and euscaphate were identical and the mp was undepressed on mixing them. The compound analysed for $C_{31}H_{50}O_3$ and had ν_{max} cm^{-1} 3560 (—OH), 1720 (–COOMe) and 1640. The ^{1}H NMR spectrum and MS were consistent with the structure methyl 19α-hydroxyurs-12-en-28-oate (**7**). This result is, as far as we are aware, the first correlation of tormentic and euscaphic acids. The formation of **7** from this series of reactions could be explained on the basis of the fact that the Δ^2-compound first formed [11] from the ring A α-acetoxyketone became reduced by diimide [12] to the final product (**7**, in the acidic form) during the Huang-Minlon reduction.

---

* Present address: Chemical Sciences, University of Port Harcourt, Port Harcourt, Nigeria.

† To whom correspondence should be sent.

EXPERIMENTAL

^{1}H NMR spectra were recorded in $CHCl_3$-*d*, using TMS as internal standard, MS data were obtained operating at 70 eV. Deactivated alumina refers to Spence-activated alumina treated with 5% its weight by vol. of 10% dil HOAc.

Extraction of Myrianthus arboreus. The plant which is semi-cultivated in parts of Nigeria for its edible leaves was collected at Odeda along the Ibadan–Ile-Ife road. The powdered root wood (22.5 kg) was successively extracted with petrol (bp 60–80°), $CHCl_3$ and methylated spirit. The concentrates of the extracts gave solids (70 g from $CHCl_3$ and 60 g from methylated spirit).

Isolation of the triterpene acids. The solid from the methylated spirit extract (11 g) which proved to be a mixture of K^+ and Na^+ salts of carboxylic acids was redissolved in aq. MeOH, filtered and the filtrate acidified (2 M HCl). The colourless ppt. of the acids (6 g) was isolated by extraction with $CHCl_3$ and treated in MeOH with ethereal CH_2N_2 to yield on removal of solvent a hard gum (6 g). The gum was chromatographed on a column of deactivated alumina (200 g) using Et_2O–petrol mixtures as the eluting solvents. The compounds are described in this section in the order in which they were eluted from the alumina column and in some cases the impure compound from the alumina column was further purified by chromatography on Si gel (Merck, 0.05–0.2 mm). Compound Y, methyl tormentate-2-acetate (**3**) gave crystals (0.2 g) from Et_2O–petrol, mp 134–135°, IR ν_{max}^{KBr} cm^{-1}: 3480 (—OH), 1730 (—OCOMe), 1720 (—COOMe), 1630 (—C=CH—); ^{1}H NMR: δ 0.9–1.26 (7 × 3 H, *s*, methyls), 2.06 (3 H, *s*, —OCOMe), 2.60 (1 H, *s*, C-18 H), 3.18 (1 H, *d*, *J* = 10 Hz, C-3 H), 3.59 (3 H, *s*, COOMe), 4.83 (1 H, *m*, $W_{1/2}$ = 20 Hz, C-2 H), 5.33 (1 H, *m*, C-12 H); MS *m/e* 544 (M^+), 526, 484, 466, 278, 265, 260, 219, 218, 201, and 179. Compound Z, methyl tormentate-3-acetate (**4**) gave crystals (0.3 g) from Et_2O–petrol, mp 123–125°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3497 (—OH), 1720 (—COOMe), 1639 (double bond), 1235; ^{1}H NMR: δ 0.9–1.26 (7 × 3 H, *s*, methyls), 2.08 (3 H, *s*, —OAc), 2.6 (1 H, *s*, C-18 H), 3.58 (3 H, *s*, —COOMe), 3.8 (1 H, *m*, C-2 H), 4.50 (1 H, *d*, *J* = 10 Hz, C-3 H), 5.33 (1 H, *m*, C-12 H); MS *m/e*: 544 (M^+), 526, 484, 466, 278, 265, 260, 219, 218, 201, and 179. Each of the monoacetates **3** and **4** on acetylation in pyridine gave methyl tormentate diacetate (**5**) mp 178° (petrol), 162° (EtOH or MeOH) (lit. [5], mp 162°). (Found: C, 71.69; H, 9.40. Calc. for $C_{35}H_{54}O_7$: C, 71.64; H, 9.28%). IR, ^{1}H NMR spectra and MS were in agreement with the expected structure of the compound. Compound X, methyl euscaphate (**2**), gave crystals (0.5 g), mp 130–132° (Et_2O–petrol) (lit. [7], mp 125–130°); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3509 (—OH), 1724 (—COOMe), 1613 (double bond); ^{1}H NMR δ 0.68–1.28 (7 × 3 H, *s*, methyls), 2.62 (1 H, *s*, C-18 H), 3.44 (1 H, *d*, *J* = 3 Hz, C-3 H), 3.62 (3 H, *s*, —COOMe), 4.00 (1 H, *m*, $W_{1/2}$ = 20 Hz, C-2 H), 5.38 (1 H, *m*, C-12 H); MS *m/e* 502 (M^+), 484, 442, 370, 278, 260, 219, 201 and 179. (Found: C, 73.78; H, 10.22. calc. for $C_{31}H_{50}O_5$: C, 74.06; H, 10.03%). Compound W, methyl tormentate (**1**) gave crystals (0.6 g) from Et_2O–*n*-hexane, mp 156–158° (after drying at 100° *in vacuo*) (lit. [5], mp 156°); IR ν_{max}^{Nujol} cm^{-1}: 3597, 3436 (—OH), 1724 (—COOMe), 1658 (double bond); ^{1}H NMR: δ 0.70–1.26 (7 × 3 H, *s*, methyls), 2.60 (1 H, *s*, C-18 H) 3.08 (1 H, *d* on adding D_2O, *J* = 10 Hz, C-3 H), 3.61 (3 H, *s*, —COOMe), 3.78 (1 H, $W_{1/2}$ = 17 Hz), 5.40 (1 H, *m*, C-12 H), MS *m/e*: 502 (M^+), 484, 443, 442, 370, 278, 260, 219, 201, 179 and 146 (lit. [5]). (Found: C, 74.07; H, 10.16. Calc. for $C_{31}H_{50}O_5$: C, 74.06; H, 10.03%). On acetylation this compound gave the same diacetate (**5**) as the one resulting from monoacetates **3** and **4**, mp and mmp 162°. Et_2O–MeOH (9:1) eluted from the deactivated alumina column a highly polar solid mixture (1.1 g).

Methyl 19α-hydroxyurs-12-ene-28-oate (**6**). Methyl tormentate (1.86 g) in Me_2CO (150 cm^3) was cooled to −13° and treated dropwise and with stirring with Jones reagent (1.10 ml). MeOH (25 ml) was added to the reaction mixture and the reaction mixture stirred with H_2O (200 ml). The amorphous solid product (1.14 g) was isolated by extraction with Et_2O. IR ν_{max}^{KBr} cm^{-1}: 3450, 1720, 1710, 1645 cm^{-1}; ^{1}H NMR: δ 0.72 (3 H, *s*), 0.87 (3 H, *s*), 1.00 (3 H, *s*), 1.23 (9 H, *s*), 1.33 (3 H, *s*), 2.6 (1 H, *s*), 3.62 (3 H, *s*), 3.90 (1 H, *m*), 5.36 (1 H, *m*). The hydroxyketone was acetylated in pyridine to give the corresponding acetate as an amorphous solid (1 g). IR ν_{max}^{KBr} cm^{-1}: 3610, 1745, 1720, 1710, 1645, 1250; ^{1}H NMR: δ 0.70 (3 H, *s*), 0.88 (3 H, *s*), 0.93 (6 H, *s*), 1.12 (3 H, *s*), 1.23 (3 H, *s*), 1.33 (3 H, *s*), 2.17 (3 H, *s*), 2.60 (1 H, *s*), 3.59 (3 H, *s*), 4.93 (1 H, *s*), 5.33 (1 H, *m*). The acetylation product (0.9 g) in diethylene glycol (30 ml) was reduced with hydrazine hydrate (98–100%, 13 ml) and KOH (6 g) using the Huang-Minlon procedure [10]. The crude acid product (0.4 g) gave with ethereal diazomethane the methyl ester (0.3 g) which on chromatography on Si gel gave **6** (0.2 g), mp 148–150° from Et_2O-petrol. IR ν_{max}^{KBr} cm^{-1}: 3560, 1720, 1640; ^{1}H NMR: δ 0.7 (3 H, *s*), 0.83 (3 H, *s*), 0.87 (3 H, *s*), 0.93 (3 H, *s*), 0.98 (3 H, *s*), 1.22 (3 H, *s*), 1.27 (3 H, *s*), 2.58 (1 H, *s*), 3.60 (3 H, *s*), 5.36 (1 H, *m*); MS *m/e*: 470 (M^+) 452, 410, 338, 260, 219, 201, 191, 179 and 146. (Found: C, 79.06; H, 10.46. $C_{31}H_{50}O_3$ requires: C, 79.10; H, 10.71%). Methyl euscaphate was converted by a similar procedure [13] to an identical compound, mp and mmp 148–150°.

Acknowledgements—C.M.O. is grateful to the University of Ibadan, Nigeria for the award of a scholarship. We thank Dr. Robert-Wolff (Institut de Chimie Strasbourg, Laboratoire de Chimie Organique) and Mr. P. I. Mowete (UI) for microanalysis of samples and Mr. G. Adesida, Dr. (Mrs.) J. Lowe and the Forest Research Institute, Ibadan for the collection and identification of plant species.

REFERENCES

1. Willis, J. C. (1966) *A Dictionary of the Flowering Plants and Ferns*, 7th edn., pp. 748–750. Cambridge University Press, Cambridge.
2. Keay, R. W. J., Onochie, C. F. A. and Stanfield, D. P. (1964) *Niger. Dep. For. Mes. Tech. Note: Niger. Trees* **2,** 164.
3. Dalziel, J. M. (1937) *The Useful Plants of West Tropical Africa*, p. 285. Crown Agents, London.
4. Marchand, J., Monseur, X. and Pais, M. (1968) *Ann. Pharm. Fr.* **26,** 771.
5. Potier, P., Das, B. C., Bui, A., Janot, M. and Pournat, A. H. (1966) *Bull. Soc. Chim.* 2458.
6. Takahashi, K., Kawaguchi, S., Nishimura, K., Kubota, K., Tanabe, Y. and Takani, M. (1974) *Chem. Pharm. Bull.* **22,** 650.
7. Budzikiewicz, J., Wilson, J. M. and Djerassi, C., (1963) *J. Am. Chem. Soc.* **85,** 3688.
8. Djerassi, C., Budzikiewicz, H. and Wilson, J. M. (1962) *Tetrahedron Letters* 263.
9. Cheung, H. T. and Feng, M. C. (1968) *J. Chem. Soc. C* 1047.
10. Huang-Minlon, (1949) *J. Am. Chem. Soc.* **71,** 3301.
11. Szmant, H. H. (1968) *Angew. Chem. Int. Ed. Eng.* **7,** 120.
12. Furst, A., Berlo, R. C. and Hooton, S. (1965) *Chem. Rev.* **65,** 51.
13. Ojinnaka, C. M. (1977) Ph.D. Thesis, Ibadan.