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A PENTACYCLIC TRITERPENE DIACID FROM *MYRIANTHUS ARBOREUS*

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Key Word Index—*Myrianthus arboreus*; Cecropiaceae; bark; euscaphic acid; tormentic acid; myrianthinic acid; arboreic acid; myriaboric acid.

Abstract—In addition to myrianthinic acid, arboreic acid, and the known tormentic and euscaphic acids, a new ursane derivative, myriaboric acid, has been isolated from the polar material of the stembark of *Myrianthus arboreus*, and its structure elucidated by spectroscopic methods.

INTRODUCTION

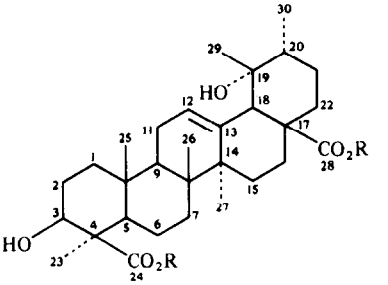
Myrianthus arboreus P. Beauv. [1] is a small tropical African tree, which grows from Guinea to Uganda, through Angola and Tanzania. Previous works on *M. arboreus* described the isolation of peptide alkaloids [2], and of many triterpene acids [3–5]. Recently, we obtained two novel pentacyclic triterpenoids, myrianthinic acid [6] and arboreic acid [7] from the polar extract of the plant, both as their methyl esters. We now report, from the same source, the structural elucidation of a new pentacyclic diacid, myriaboric acid, as its dimethyl ester derivative (**1**).

RESULTS AND DISCUSSION

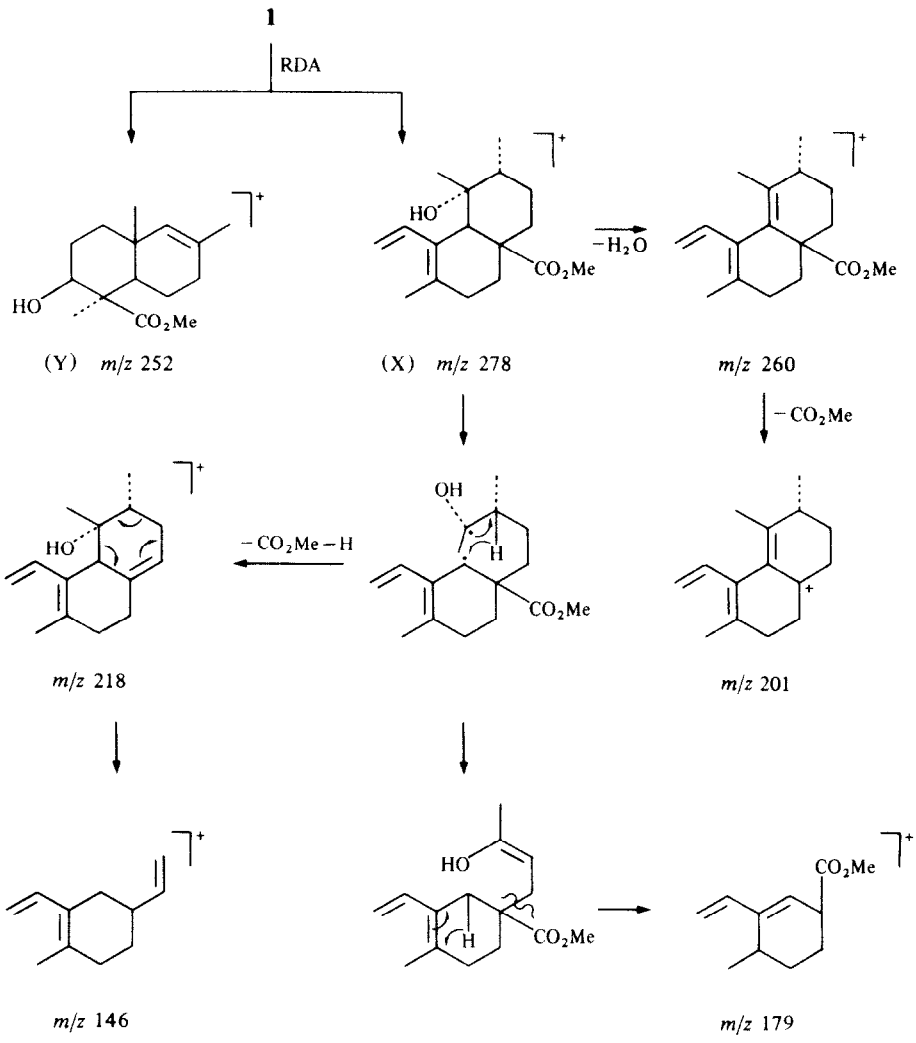
The methylated ethyl acetate extract of pulverized bark gave the methyl ester of myriaboric acid (**1**), which crystallized from hexane as colourless needles, mp 258–260°. A positive response to Liebermann–Buchard, TCA [8] and TNM tests showed compound **1** to be an unsaturated pentacyclic triterpene. Its molecular formula was established as $C_{32}H_{50}O_6$ (M^+ at *m/z* 530). The IR spectrum of **1** exhibited main absorptions at ν_{max} 3510 and 3460 (sharp, OH), 1725, 1710 (−OAc), 1630 (trisubstituted double bond), 1050, 1000 (secondary OH) and 930 (tertiary OH) cm^{-1} [8]. The 200 MHz ^1H NMR spectrum of **1** in $CDCl_3$ showed two carbomethoxyl signals at δ3.60 and 3.76, a vinylic proton at δ5.34, four tertiary methyl groups at δ0.71 (3H, Me-26), 0.89 (3H, Me-29), 1.13 (3H, Me-25), 1.22 (3H, Me-27), 1.30 (3H, Me-23) and a secondary methyl group at δ0.94 (3H, *d*, J = 6.9 Hz, Me-30) [9].

Since the two carbomethoxyl groups accounted for four of the six oxygens present in **1**, the remaining oxygens should exist as hydroxyl functions if an ursane skeleton is assumed for the compound.

The mass spectrum of **1** indicated that by a retro-Diels–Alder fragmentation of ring C, two main fragments [X, *m/z* 278 and Y, *m/z* 252 (Scheme)] were produced, which were quite diagnostic. The presence in **1** of four tertiary methyl groups, one secondary methyl group, two carbomethoxyl groups and the chemical shift of H-18 [9] in conjunction with the mass spectral fragmentation [10] confirmed that the compound was an urs-12-ene derivative, carrying a hydroxyl and a carbomethoxyl both in ring A/B and in ring D/E. The fragment obtained from the retro-Diels–Alder rupture of ring C at *m/z* 278, and subsequent fragmentations from the latter ion suggested the same ring D/E substitution as in methyltormentate **4** [11]. Moreover, the multiplicity of the hydrogen atom H-18 was in accord with the presence of a substituent on C-19. The above proton resonance which appeared as a singlet at δ2.59, agreed with the existence of a 19α-hydroxyl group. Also, the presence of the hydroxyl was corroborated by a downfield effect on Me-29, which shifted from δ0.80 to 0.93, as it does in methyl urs-12-en 28-Oate [4]. The hydroxyl in ring A/B was assigned to the 3β-position, on biogenetic grounds and because of the presence of a 3α proton at δ3.20, as a multiplet on its ^1H NMR spectrum [9]. The carbomethoxyl in ring A/B had to be located at C-23, C-24, C-25, or C-26. Two main arguments led us to locate the carbomethoxyl at C-24: from Bory and co-workers [12], when a di or a triterpene carries an equatorial carbomethoxyl function, a very intense IR absorption band is observed at ν_{max} 1245 ± 5 cm^{-1}. But when the carbomethoxyl is axially oriented, three characteristic bands are observed at ν_{max} 1155 ± 4, 1190 ± 5 and 1230 ± 5 cm^{-1}. In the IR spectrum of **1**, three intense absorption bands were observed at ν_{max} 1159, 1185 and 1235 cm^{-1}. This result is in good agreement with the axial orientation of the two carbomethoxyl



1 R = Me
2 R = H

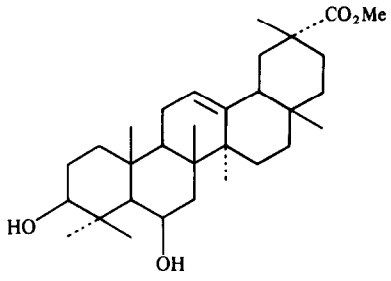


groups in the molecule, and consequently, the ester in ring A/B is also axially oriented. The second argument in favour of the location of the above carbomethoxyl at C-24 is the downfield effect on the C-23 methyl group which appeared at δ1.30 in compound **1**, compared to its position at δ0.96 in methyl urs-12-en 28-Oate [9, 13, 14]. Accordingly, the carbomethoxyl was finally located at C-24.

The ^{13}C NMR spectrum strongly supported structure **1**. Close inspection of the spectrum led us to rule out most of the known triterpene skeletons and to retain that of an ursane derivative [15]. The signals were attributed by means of single frequence off-resonance decoupling techniques [16,17] and application of known chemical shift rules involving different substitution shifts, and steric effects [17], as well as by comparison with ^{14}C NMR spectral data of known ursane derivatives [15, 18]. More specifically, comparison of the ^{13}C NMR spectrum of compound **1** with that of α-amyrin (**7**) was especially helpful (Table 1). The C-18 carbon resonated at δ53.7 in compound **1** and δ58.9 in **7**, this difference of up to 4 ppm resulted in an upfield effect due to the C-28 carbomethoxyl group in coupound **1** [19]. Similarly, C-22 resonated at δ37.4 in **1** and δ41.5 in **7**, for the same reason. An analogous effect was observed for C-3 which appeared at δ73.2 in **1** and 78.8 in α-amyrin, because of the presence of C-24 carbomethoxyl group. The carbonyl of the two carbomethoxyls resonated at δ177.0 and 178.2 for C-24 and C-28 respectively. These values agreed with those observed in the same positions in other derivatives

Table 1. ^{13}C NMR data for compounds **1** and **7** [15]

C	1	7	C	1	7
1	41.3	38.7	17	48.5	33.7
2	27.5	27.2	18	53.7	58.9
3	73.2	78.8	19	77.6	39.6
4	48.1	38.7	20	41.1	39.6
5	53.1	55.2	21	25.7	31.2
6	20.9	18.3	22	37.4	41.5
7	33.3	32.9	23	25.5	28.1
8	41.3	40.0	24	177.0	15.6
9	47.1	47.7	25	15.7	15.6
10	41.5	36.9	26	17.3	16.8
11	25.1	17.4	27	26.1	23.3
12	129.1	124.3	28	178.2	28.1
13	138.6	139.3	29	27.4	23.3
14	41.3	42.0	30	16.1	21.3
15	28.6	28.7	24CO_2Me	52.1	
16	25.5	26.6	28CO_2Me	51.5	



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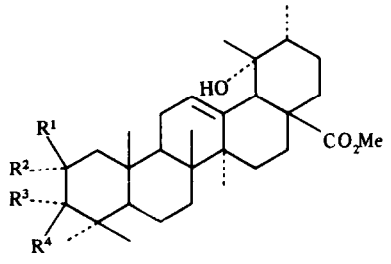
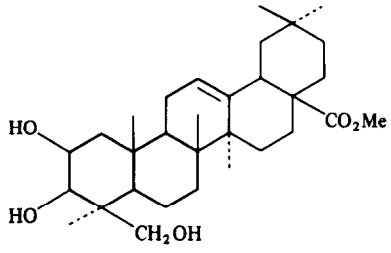


4 $R^2 = R^4 = OH$; $R^1 = R^3 = H$
5 $R^2 = R^3 = OH$; $R^1 = R^4 = H$



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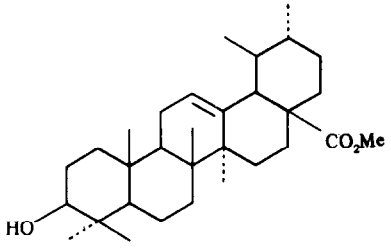

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[18]. On the other hand, the carbons α to these carbomethoxyls were subjected to a downfield effect. In fact, C-4 and C-17 appeared at δ48.1 and 48.5 respectively in **1** and δ38.7 and 33.7 respectively in compound **7**. These chemical shifts agree with the proposed structure. In view of the above evidence, myriaboric acid methyl ester was assigned structure **1** and accordingly, myriaboric acid is 3β,19α-dihydroxyurs-12-en, 24,28-dioic acid (**2**), which to our knowledge, has not yet been reported in the literature.

During the course of this investigation, myrianthinic acid, arboreic acid, both recently reported [6,7] and the known tormentic and euscaphic acids were also isolated, all as their methyl esters **3**,**6**,**4**, and **5** respectively.

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