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ARBOREIC ACID: A PENTACYCLIC TRITERPENOID FROM *MYRIANTHUS ARBOREUS*

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Key Word Index—*Myrianthus arboreus*; Cecropiaceae; bark; pentacyclic triterpenoids; arboreic acid.

Abstract—A new oleanane derivative, arboreic acid, has been isolated from the ethyl acetate extract of the defatted barks of *Myrianthus arboreus*, and characterized by spectroscopic methods.

INTRODUCTION

Myrianthus arboreus Beauv is a small tropical African tree [1], which grows from Guinea to Angola, and from Soudan to Tanzania through Ouganda. The plant is widely used in traditional African medicine [2]. Previous work on this species reported the isolation from the leaves of peptide alkaloids [3], and from the root wood of tormentic acid, 2-acetyltormentic acid, 3-acetyltormentic acid, euscaphic acid [4, 5], and myrianthic acid [6], all as their methyl esters. In our last paper [7], we reported the isolation of a new triterpenic acid, myrianthinic acid, from the stem bark of the plant material. We now describe the structure of a novel triterpenic constituent, arboreic acid (2), as its methyl ester (1).

RESULTS AND DISCUSSION

In continuation of the investigation undertaken on the polar material of *M. arboreus* [7], we isolated, from the methylated ethyl acetate extract of pulverized bark, the methyl ester of arboreic acid (1), $C_{31}H_{50}O_5$ as colourless needles, mp 239–240° (methanol). The IR spectrum exhibited main absorptions at ν_{max} 1705 (–COOMe), 1625 (trisubstituted double bond) and 3400 (broad) cm^{-1} indicative of chelated hydroxyl groups. Furthermore, arboreic acid methyl ester (1) furnished, upon acetylation with acetic anhydride–pyridine, the triacetate (3), $C_{37}H_{56}O_8$, the IR spectrum of which showed no residual hydroxyl group absorption.*

The ^1H NMR spectrum of 1 in $CDCl_3$ was characteristic of a pentacyclic triterpene of the β-amyrin group, with a 12(13) double bond. Five methyl group singlets were visible at δ0.71(6H), 0.88(3H), 0.91(3H), 0.96(3H) and 1.13(3H). The respective positions of these methyl groups were indicative of the presence of a 28-carbomethoxyl function [5]. Also, a one-proton doublet was observed at δ3.50 (J = 4.5 Hz, H-3), a one-proton multiplet at δ3.57 (H-2), and a three-proton singlet at δ3.54 (28-carbomethoxyl). The coupling constant between H-2 and H-3(4.5 Hz) is in agreement with the assigned stereochemistry of two of the hydroxyl groups at 2β, 3β [8, 9]. The one-proton multiplet at δ5.22 was ascribed to H-12. The third hydroxyl function had to be primary, because of the presence of a two-proton AB quartet, and was located either at C-23 or at C-24. In fact, from the work of Polonsky *et al.* [10], when a primary alcohol is located at C-23, the 23-methylene protons appear upfield at δ3.65, but when it is located at C-24, the corresponding methylene group resonates downfield at δ3.75–4.15, because of the influence of the 3β-hydroxyl group. In our case, the methylene protons appeared downfield as a quartet-like multiplet at δ3.95–4.02, which is in good agreement with the location of the primary alcohol at C-24. The above evidence suggests structure (1) for arboreic acid methyl ester.

The mass spectrum of 1 had $[M]^+$ at m/z 502, with prominent peaks at m/z 484, 466, 448, 262, 240, 203, 202 and 189. The fragments at m/z 484, 466, and 448, obtained from the molecular ion by the loss of one, two and three water molecules respectively, were characteristic of the presence of the three hydroxyl functions. The peak at m/z 262 (248 + 14) obtained from a retro Diels–Alder cleavage, confirmed that the compound is a pentacyclic triterpene of the β-amyrin group, with a 12(−13) double bond [11, 12]. The latter ion further showed that the carbomethoxyl group was either at C-14, C-17 or at C-20. However, the ready loss of 59 a.m.u. from 4 to give 6 (m/z 203, base peak) was consistent with its location at C-17 [13].

The peak at m/z 240, which also resulted from a retro Diels–Alder cleavage, but with the retention of the positive charge on the rings A and B, confirmed the presence of the three hydroxyl functions on these rings. Finally, the fragment at m/z 189 could be formed by the fragmentation of 4 (m/z 262), probably involving the loss of C-17 along with CO_2Me group, with a double hydrogen transfer, to afford the conjugated allylic cation 7 [13].

In view of the above evidence, arboreic acid methyl ester was therefore assigned structure (1) and consequently, arboreic acid is 2β,3β, 24-trihydroxy-olean-12-en-28-oic acid (2), which to our knowledge, has not yet been described in the literature.

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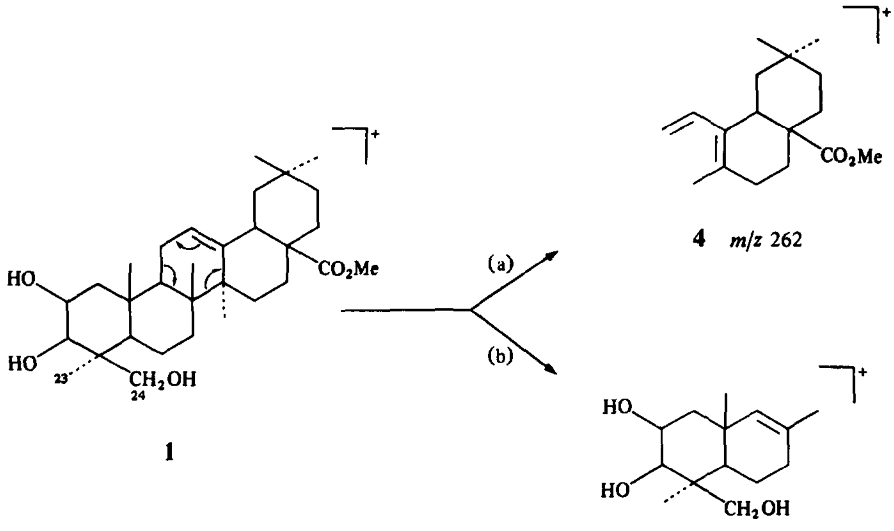
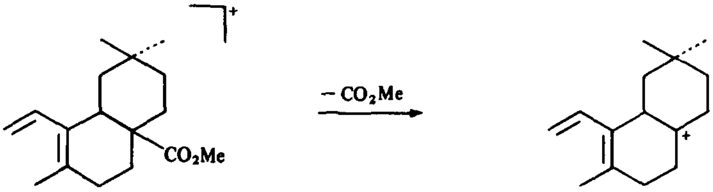
* Because a very small amount of arboreic acid methylester was available, only the IR spectrum of the triacetate derivative was obtained, and we were unable to carry out any other chemical transformations.



1

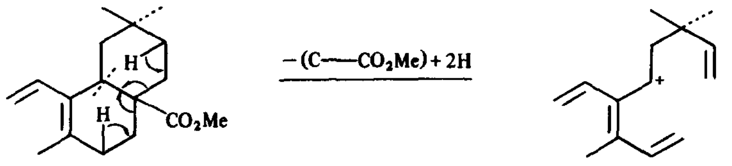
4 *m/z* 262

5 *m/z* 240



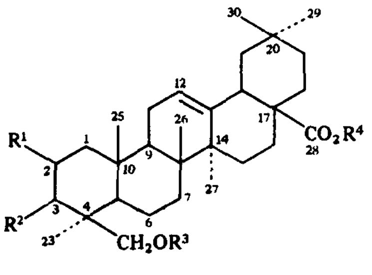
4 *m/z* 262

6 *m/z* 203



4 *m/z* 262

7 *m/z* 189



1 $R^1 = R^2 = OH$, $R^3 = H$, $R^4 = Me$

2 $R^1 = R^2 = OH$, $R^3 = R^4 = H$

3 $R^1 = R^2 = OAc$, $R^3 = Ac$, $R^4 = Me$

During the course of this investigation, tormentic acid and euscaphic acid were also obtained, as their methyl esters. Full details of the isolation and spectral identification of the known compounds are available on request to the authors.

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TRITERPENE FATTY ACID ESTERS AND FLAVONOIDS FROM *INULA BRITANNICA*

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Key Word Index—*Inula britannica*; Compositae; triterpene fatty acid esters; 3β,16β-dihydroxylupeol 3-palmitate; 3β,16β-dihydroxylupeol 3-myristate; flavonoids; quercetin 3-sulphate; 6-hydroxykaemperol 3-sulphate.

Abstract—Two new triterpene fatty acid esters, 3β,16β-dihydroxylupeol 3-palmitate and 3β,16β-dihydroxylupeol 3-myristate, and a new kaempferol derivative, 6-hydroxykaempferol 3-sulphate were isolated from the aerial parts of *Inula britannica*. Furthermore, *epi*-friedelinol, β-amyrin palmitate, olean 13(18)-en 3-acetate, sitosteryl 3-glucoside and quercetin 3-sulphate were also identified.

INTRODUCTION

Inula britanica is a widespread plant growing in the western part of Turkey. In earlier articles, sesquiterpene lactones, thymol derivatives and flavonoids [1–3] were reported from this plant. Our reinvestigation of *I. britanica* afforded two new triterpene fatty acid esters, 3β,16β-dihydroxylupeol 3-palmitate **1** and 3-myristate **1a** besides the known compounds epi-friedelinol **2** [4], β-amyrin palmitate **3** [5], olean 13(18)-en 3-acetate **4** [6] and sitosteryl 3-glucoside.

From an ethanolic extract of the aerial parts, in addition to the known flavonoids quercetin 3-glucoside, 6-methoxyquercetin 7-glucoside, quercetin 7-glucoside, 6-methoxyluteolin 7-glucoside and quercetin 3-sulphate [7], a new kaempferol derivative 6-hydroxykaempferol 3-sulphate **5** was also isolated.

RESULTS AND DISCUSSION

The residue from a petrol–ether extract of the dried plant material was separated by CC on silica gel and triterpenes were obtained. The first fractions gave olean 13(18)-en 3-acetate **4**, *epi*-friedelinol **2** and β-amyrin palmitate **3**.

Compound **4** was found to be olean 13(18)-en 3-acetate **4** by comparing its ^{1}H NMR and mass spectrum to that of an authentic sample.

Compound **2** was identified as *epi*-friedelinol by