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BARTOGENIC ACID, A NEW TRITERPENE ACID FROM *BARRINGTONIA SPECIOSA*

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Key Word Index—*Barringtonia speciosa*; Lecythadaceae; bartogenic acid; new triterpene.

Abstract—A new triterpene acid, bartogenic acid, was isolated from the fruits of *Barringtonia speciosa*. Its structure was established as 2α,3β,19α-trihydroxyolean-12-ene-24,28-dioic acid from chemical and spectroscopic data and confirmed by its conversion into methyl sericiate.

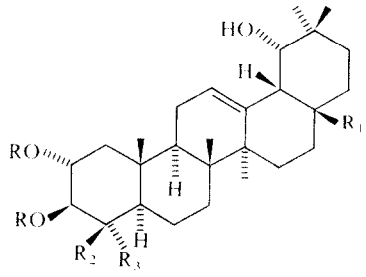
Several novel triterpenes have been isolated from *Barringtonia acutangula* [1] and other species. We report the structure and stereochemistry of a new triterpene dicarboxylic acid, bartogenic acid (**1**), isolated from the chloroform extract of the fruits of *Barringtonia speciosa* Forst, a drug traditionally used [2] in the indigenous medicine.

Bartogenic acid (**1**), $C_{30}H_{46}O_7$ (M^+ at *m/e* 518), mp 318° gave a dimethylester (**2**), mp 275–278° and a dimethylester diacetate (**3**) mp 196°. Further acetylation of **3**, with Ac_2O–$HClO_4$ afforded an amorphous triacetate free from hydroxyl absorption in its IR spectrum. The ^1H NMR spectrum of **3** showed signals at δ 0.69 (*s*, 3H), 0.8 (*s*, 3H), 0.99 (*s*, 6H), 1.28 (*s*, 6H) due to the six tertiary methyl groups, 1.99 (*s*, 3H, $-OCOC\underline{H}_3$), 2.01 (*s*, 3H, $OCOC\underline{H}_3$), 3.3 (*d*, J = 5.06 Hz, 1H, C<u>H</u>OH), 3.63 (*s*, 3H, $COOC\underline{H}_3$), 3.71 (*s*, 3H, COOC<u>H</u>), 4.85 (*d*, J = 10 Hz, 1H, C<u>H</u>OAc), 5.43 (*t*, 1H, J = 2.25 Hz) and 5.72 (*m*, 1H, C<u>H</u>OAc). The mass spectrum of **3** exhibited our intense peak at *m/e* 278 due to the retro Diels–Alder fragmentation of ring C characteristic of the Δ^{12}-oleananes [3], indicating the disposition of the two acetates and a carboxymethyl group in rings A and B and that of the other carboxymethyl group and the hydroxyl group in rings D and E.

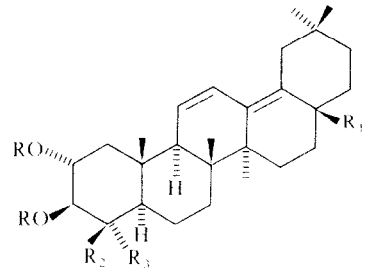
Oxidation of **3** with CrO_3 afforded a βγ-unsaturated ketone (**4**), UV λ_{max} 292 nm (ε, 90), IR ν_{max} 1730, 1720 cm^{-1} which was isomerized [4] to the stable α,β-unsaturated ketone (**5**), UV λ_{max} 253 nm (ε, 7100), IR ν_{max} 1730, 1720, 1690 cm^{-1}, thus establishing the relationship between the double bond and the hindered hydroxyl group. Dehydration of **3** with $POCl_3$–pyridine afforded a diene (**6**) which was isomerized, under acidic conditions, to the more stable transoid diene (**7**) having the typical UV absorption spectrum, λ_{max} 244, 252, 261 nm (ε, 19 950, 25 120, 16 600) characteristic of the 11,13(18)-diene system [5] thus confirming the position of the hydroxyl group as 19α-axial.

The fact that dimethylbartogenate (**2**) rapidly consumed 1 mol of periodic acid and afforded a diosphenol on oxidation with CrO_3–pyridine, coupled with the ^1H NMR spectral data of **3** indicated the presence of a 2α,3β-dihydroxy system in the molecule. Further, the 2β-proton of diacetyldimethylbartogenate (**3**) appeared considerably deshielded at δ 5.72, and this is attributed to the presence of a 24α-axial carboxymethyl group. Hence bartogenic acid is represented as 2α,3β,19α-trihydroxyolean-12-en-24,28-dioic acid (**1**) in analogy with other triterpenes [4, 6–8]. This was confirmed as follows. Reduction of **3** with (70% solution of sodium bis 2-methoxyethoxy aluminium hydride) Vitride reagent afforded a monoester (**8**), $C_{31}H_{50}O_6$ (M^+ at *m/e* 518), mp 165° which gave a triacetate (**9**), mp 175°. The mass spectrum of **9** showed an intense peak at *m/e* 278 due to retro Diels–Alder fragmentation suggesting the presence of the carboxymethyl group and the hydroxyl group in rings D and E. Hence the other carboxymethyl group of **3** was selectively reduced. This compound (**8**) was identified as methylsericiate [9] by comparison with an authentic specimen (IR; ^1H NMR; ^{13}C NMR and ORD). A notable observation was the appearance of the two protons of 24-CH_2OAc as a singlet at δ 4.18 in the ^1H NMR spectrum of **9**, unlike triacetylmethyl arjunolate (**11**) where the protons of 23-CH_2OAc normally appear as a quartet at 3.65 (J = 11 Hz). This difference in the chemical shift and their patterns can be readily used to distinguish between the axial and equatorial CH_2OAc groups at C-4 in triterpenes.

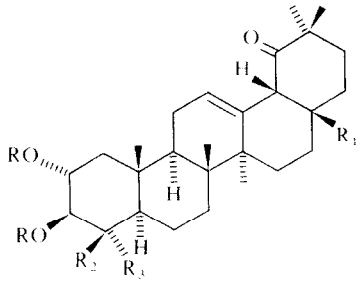
Dehydration of **9** with $POCl_3$–pyridine, followed by isomerization afforded a diene (**12**) which was different (^1H NMR, ORD) from the diene (**13**) obtained by the SeO_2 oxidation of **11**. Oxidation of **9** with CrO_3–pyridine, afforded a βγ-unsaturated ketone (**14**) which was reduced using modified Wolf–Kishner reduction [10] and the resulting compound was isomeric but different from methylarjunolate (**10**) (^1H NMR, ORD, CD). Reduction of **3** with $LiAlH_4$, followed by acetylation gave **15** which was dehydrated and isomerized to the diene (**16**). This compound (**16**) was not identical with the diene (**17**) obtained from tetraacetyl barringtogenol (**18**), its spectral data indicating that they are isomers at C-4. These reactions, together with the conversion of diacetyldimethylbartogenate (**3**) to methylsericiate (**8**) clearly establish the structure and stereochemistry of bartogenic



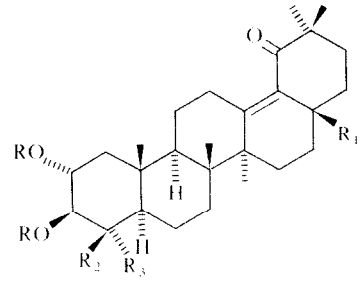
1 R = H; R_1 = R_2 = COOH; R_3 = Me
2 R = H; R_1 = R_2 = COOMe; R_3 = Me
3 R = Ac; R_1 = R_2 = COOMe; R_3 = Me
8 R = H; R_1 = COOMe; R_2 = CH_2OH; R_3 = Me
9 R = Ac; R_1 = COOMe; R_2 = CH_2OAc; R_3 = Me
15 R = Ac; R_1 = R_2 = CH_2OAc; R_3 = Me



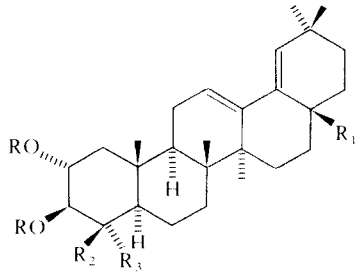
7 R = Ac; R_1 = R_2 = COOMe; R_3 = Me
12 R = Ac; R_1 = COOMe; R_2 = CH_2OAc; R_3 = Me
13 R = Ac; R_1 = COOMe; R_3 = CH_2OAc; R_2 = Me
16 R = Ac; R_1 = R_2 = CH_2OAc; R_3 = Me
17 R = Ac; R_1 = R_3 = CH_2OAc; R_2 = Me



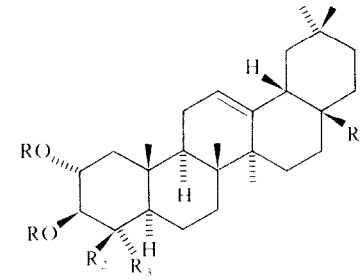
4 R = Ac; R_1 = R_2 = COOMe; R_3 = Me
14 R = Ac; R_1 = COOMe; R_2 = CH_2OAc; R_3 = Me



5 R = Ac; R_1 = R_2 = COOMe; R_3 = Me



6 R = Ac; R_1 = R_2 = COOMe; R_3 = Me



10 R = H; R_1 = COOMe; R_2 = Me; R_3 = CH_2OH
11 R = Ac; R_1 = COOMe; R_2 = Me; R_3 = CH_2OAc
18 R = Ac; R_1 = R_3 = CH_2OAc; R_2 = Me

acid as 2α,3β,19α-trihydroxyolean-12-en-24,28-dioic acid (**1**).

All the new compounds gave satisfactory analytical and spectral data.

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