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ANHYDROBARTOGENIC ACID AND 19-EPIBARTOGENIC ACID, TWO TRITERPENES FROM *BARRINGTONIA SPECIOSA*

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Key Word Index—*Barringtonia speciosa*; Barringtoniaceae; triterpenoid acids; anhydrobartogenic acid; 19-epibartogenic acid.

Abstract—Two new triterpene dicarboxylic acids, isolated from the fruits of *Barringtonia speciosa*, have been identified as anhydrobartogenic acid and 19-epibartogenic acid by spectral and chemical evidence.

INTRODUCTION

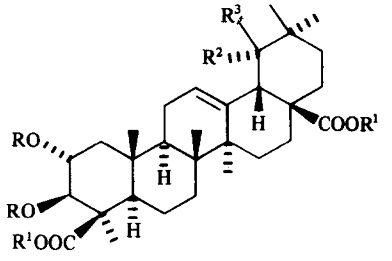
Recently, we reported [1] the isolation of a new triterpene, bartogenic acid, from *Barringtonia speciosa* Forst and established its structure as 2α,3β,19α-trihydroxyolean-12-en-24,28-dioic acid (**1**). In continuation of our studies on the minor constituents from the fruits of *B. speciosa*, we have isolated two new triterpene dicarboxylic acids, isolated as their dimethyl esters, BS-1 and BS-3, and the present paper describes their structures.

RESULTS AND DISCUSSION

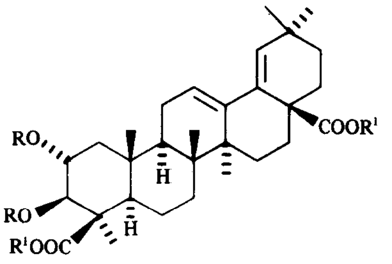
Compound BS-1, mp 270–272°, $C_{32}H_{48}O_6$ ($[M]^+$ at *m/z* 528); UV λ_{max} 242 nm (ε 7900); IR ν_{max} 3500 (hydroxyl) and 1725 (ester) cm^{-1}; ^1H NMR ($CDCl_3$): δ0.78, 0.85, 0.86, 0.95, 0.97, 1.25 (*s*, 3H each, 6 × Me), 3.61, 3.69 (*s*, 2 × COOMe), 2.92 (*br d*, *J* = 10 Hz), 4.07 (*m*, 1 H), 5.40 (*s*, 1H) and 5.48 (*m*, 1H). From the UV data, BS-1 was considered to be a heteroannular diene. Acetylation with acetic anhydride–pyridine afforded a diacetate (**9**), $C_{36}H_{52}O_8$, mp 140–142°, $[\alpha]_D + 80°$ ($CHCl_3$), λ_{max} 242 nm (ε 7900). The ^1H NMR spectrum indicated the presence of two acetoxyls (δ1.98 and 2.08) and the protons geminal to the acetoxyls appeared at δ4.84 (*d*, *J* = 10 Hz) and 5.70 (*m*) in *trans*-diaxial orientation as in diacetyl dimethyl bartogenate (**2**) [1, 2]. Thus the two acetoxyls in BS-1 diacetate (**9**) are *trans*-diequatorial. The low-field signal for 2β-H (δ5.70) indicated that it is in the carbonyl zone of a carboxymethyl group. The carboxymethyl group is β-axial at C-4 as in diacetyl dimethyl bartogenate (**2**). The presence of a 12,18-diene system is inferred from its ^1H NMR spectral data since the vinyl protons appeared at δ5.40 and 5.48. If the 11,13(18)-diene system were present in the molecule, the signals for the olefinic protons would have appeared as an ABX pattern, the 12-H being deshielded very much downfield (δ6.5). Furthermore, the signal for 19-H appeared as a singlet at δ5.40. Isomerization of BS-1 diacetate with methanol–hydrochloric acid afforded the stable transoid diene (**10**) [1, 2], having the typical UV absorption spectrum [λ_{max} 244, 252, 261 nm (ε 19 959, 25 120, 16 600)] characteristic of the 11,13(18)-diene system [3], which was identified by comparison with an authentic specimen obtained from diacetyl dimethyl bartogenate. This conclusively proves that BS-1 has a 12,18-diene system and is therefore assigned the structure dimethyl-2α,3β-dihydroxyolean-12,18-diene-24,28-oate (**8**). Corroborative evidence for the presence of a Δ^{18}-double bond was obtained from the mass spectrum of BS-1 which showed an ion at *m/z* 260 for the fragment **11** due to retro-Diels–Alder fission [4].

Compound BS-3, $C_{32}H_{50}O_7$, mp 252–254°, $[\alpha]_D$ + 100° ($CHCl_3$); UV λ_{max} 205 nm; IR ν_{max} 3500, 1725, 1700 cm^{-1}; ^1H NMR ($CDCl_3$): δ0.77, 0.82, 0.90, 1.06, 1.16, 1.25 (*s*, 3H each, 6 × Me), 2.59 (*d*, 1H, *J* = 11 Hz), 3.36 (*d*, *J* = 11 Hz), 3.49 (*d*, 1H, *J* = 10 Hz), 3.63 (*s*, 3H, COOMe), 3.68 (*s*, 3H, COOMe), 4.0 (*m*, 1H), 5.45 (*m*, 1H) is assigned structure **4** on the basis of the following evidence.

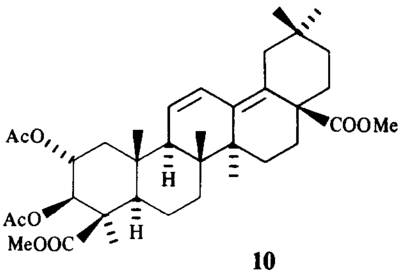
BS-3 formed a diacetate (**5**), $C_{36}H_{54}O_9$, ($[M]^+$ at *m/z* 630), mp 138–140°, whose IR spectrum showed the presence of a free hydroxyl (3540 cm^{-1}). On treatment with perchloric acid–acetic anhydride, it formed an amorphous triacetate. The ^1H NMR spectrum of BS-3 diacetate showed the presence of hydrogens geminal to the acetoxyls in a *trans*-diaxial system (δ4.85, *d*, *J* = 10 Hz; 5.69, *m*). The presence of a carboxymethyl group at C-4 in the axial position caused a downfield shift of the 2β-H, as in the case of BS-1 diacetate. A high-field signal observed for one of the methyl groups indicated the presence of a methoxy carbonyl group at C-17. The presence of a methoxy carbonyl in ring A at C-4 caused the C-23 methyl to resonate at low field (δ1.25). The positions of the acetoxyls and carboxymethyls in BS-3 diacetate having been established, the position of the hindered hydroxyl group remained to be settled. The mass spectrum of BS-3 and its diacetate showed an intense peak at *m/z* 278 due to retro-Diels–Alder fragmentation [4], suggesting that the hindered hydroxyl group is present in ring D or E. Oxidation of BS-3 diacetate with CrO_3–pyridine produced a ketone (**6**), mp 236–238°, which was found to be identical to the ketone obtained [1, 2] from oxidation of diacetyl dimethyl bartogenate (**2**). Thus in BS-3 diacetate the hydroxyl group is present at C-19, and has β-configuration. This is supported by the ^1H NMR spectral data; the 19α-H appeared as a broad doublet at δ3.36 (*J* = 11 Hz) and the 18β-H as a doublet at 2.59 (*J* = 11 Hz). Thus 18β-H and 19α-H are *trans*-



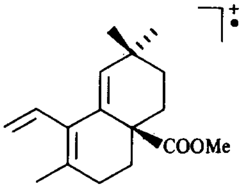
1 R = R^1 = R^3 = H; R^2 = OH
2 R = Ac; R^1 = Me; R^2 = OH; R^3 = OH
3 R = R^1 = R^2 = H; R^3 = OH
4 R = H; R^1 = Me; R^2 = H; R^3 = OH
5 R = Ac; R^1 = Me; R^2 = H; R^3 = OH
6 R = Ac; R^1 = Me; R^{2}R^3 = O



7 R = R^1 = H
8 R = H; R^1 = Me
9 R = Ac; R^1 = Me



10



m/z 260

11

diaxial to each other and therefore the hydroxyl has the β-configuration. Thus the structure of BS-3 is confirmed as dimethyl 2α,3β,19β-trihydroxyolean-12-en-24,28-dioate (**4**).

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