Bondenolide, a New Diterpenoid from the Seeds of *Caesalpinia bonduc*

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A new diterpenoid named as bodenolide (1) was isolated from the ethyl acetate soluble part of the methanolic extract of *Caesalpinia bonduc* (seeds). In addition to 1, four known triterpenoids: α-amyrin [12-ursen-3β-ol], β-amyrin [12-oleanen-3β-ol], (+)-20(29)-en-3β-ol, (+)-20(29)-en-3β-yl acetate and two known sterols: β-sitosterol [24(R)-stigmast-5-en-3β-ol] and β-sitosterol α-D-galactoside [3-O-β-D-galactopyranosyl-stigmasta-5-en] were also isolated from the same source.

**Introduction**

The seeds of *Caesalpinia bonduc* belonging to the family Caesalpiniaceae were used as a folk medicine to treat asthma and chronic fever. They were found to be very potent as an antiperiodic, antipyretic and utilized as febrifuge, antispasmodic, antirheumatic and mild purgative [1,2]. The chemical literature survey revealed the presence of diterpenoids such as α-caesalpin and β-caesalpin [3,4], δ-caesalpin [4,5], γ-caesalpin [3,6], ε-caesalpin [7] and caesalpin F [8]. Our phytochemical investigations have led to the isolation of a new diterpenoid named as bodenolide (1) together with some known triterpenoids and two known sterols.

**Results and Discussion**

The compound 1 was obtained from the ethyl acetate soluble fraction of the methanolic extract of *Caesalpinia bonduc* (seeds). The molecular formula was determined by high resolution mass spectrum (HRMS) as C_{25}H_{34}O_{10} inferring nine degrees of unsaturation. The electron impact mass spectrum (EIMS) showed the molecular ion peak at m/z 494 which was further confirmed by field desorption mass spectrum (FDMS). The IR spectrum of 1 showed the hydroxyl absorption at 3400, the double bond absorption at 1649 and the α,β-unsaturated lactone at 1750 cm⁻¹. The two acetalate carbonyls and ketonic function show their absorption at 1735 and 1720 cm⁻¹, respectively. The α,β-unsaturation was also confirmed by UV spectrum which showed the absorption band at 217 nm [9].

The 1H NMR spectrum of 1 showed the presence of seven methyl singlets at δ 1.10, 1.26, 1.38, 1.50, 2.00, 2.06 and 3.26. The two downfield methyl singlets at δ 2.00 and 2.06 were due to the two acetoxy methyls in the molecule. The most downfield methyl singlet in the 1H NMR spectrum at δ 3.26 was due to the methoxyl group. The remaining four methyls signals at δ 1.10, 1.26, 1.38 and 1.50 were due to the methyls 19, 18, 20 and 17, respectively. The three methine signals appeared at δ 5.40, 5.53 and 5.98. The signal at δ 5.98 arising as singlet was due to the olefinic proton adjacent to the lactone carbonyl carbon atoms. The other two methine signals at δ 5.40 and 5.53 were assigned to the carbons (C-1 and C-2) at which the two acetoxy groups are attached. They appeared as a doublet (δ 5.40) having coupling constants J = 9.5 Hz and a triplet at δ 5.53 with coupling constants 10.0 and 9.5 Hz, corresponding to the C-1 and C-2, respectively. The coupling constants for H-1 and H-2 signals show their axial positions at C-1 and C-2. The diaxial position of these protons must be in the form of α at C-1 and β at C-2. On the basis of these arguments the orientation of acetoxyieties C-1 and C-2 at the ring A molecule could easily be assigned as equatorial and α at C-1 and equatorial and β at C-2. The stereochemistry of the substituents at C-8, C-9 and C-13 could not be determined. The coupling constant

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between H-1 and H-2 is 9.50 Hz and hence, the conformation of vicinal acetoxy groups at C-1 and C-2 is suggested to be anti.

The carbon spectrum of compound 1 showed the twenty five signals. The dept experiment displays the presence of seven methyls, four methylenes, three methines and eleven quaternary carbon atoms in the molecule. The seven methyls, at 15.05, 199.81, 21.01, 21.09, 25.75, 33.98 and 51.56. The signals at 199.81 and 21.09 were assigned to the acetoxy methyls whereas the most downfield signal at 51.56 was diagnostic for the methoxy group. The remaining four methyl singlets were due to the C-17, C-18, C-19 and C-20. The three methine signals appeared at δ 71.98, 74.69 and 115.9. The signals at δ 71.98 and 74.69 were due to the C-1 and C-2. The third downfield methine signal displayed its resonance in the 13C NMR spectrum at δ 115.9 assigned to C-15. The down-field shift of this methine supports the presence of sp² (olefinic) carbon next to the carbonyl function. This olefinic signal appeared as a singlet at δ 5.98 in the proton NMR. The broad-band spectrum of 1 also showed the eleven quaternary carbon atoms. Among them the five downfield quaternary carbons appeared at δ 169.3, 169.4, 170.4, 173.0 and 211.0. Signals at δ 169.3, 169.4, 170.4 and 211.0 were indicated the presence of four carbonyl functions in the molecule. The carbon signal at δ 170.4 was due to the lactone carbonyl in the pentacyclic enolide ring D whereas the other at δ 211.0 was due to the C-11 ketonic function. The remaining signals at 169.3 and 169.4 were due to the acetoxy carbonyls. Another quaternary carbon signal at δ 173.0 was attested for the olefinic quaternary carbon (C-14). The other signals in the broad band spectrum of 1 were due to the methine carbons in the molecule which were correlated with protons by hetero-Cosy technique and mentioned in the experimental section.

On the basis of above spectral data and the additional informations from hetero-Cosy technique the structure of bonendoide assigned as 1. This compound has not been isolated so far from any natural source. The similar type of compounds have been isolated from the same source having rearranged enolide ring (2, 3) [9] with a methoxyl group and reverse stereochemistry of acetoxy groups at C-1 and C-2 in ring A. It has already been described by T. Kinoshita et al. [9] that how the furan-fused tetracyclic diterpenoids which are the most common dieterpenoids in the genus Caesalpinia convert into the α,β-butenolide-fused tetracyclic diterpenoids. The known constituents were identified by direct comparison with their published data [10–21].

Experimental

The 1H and 13C NMR spectra were recorded in CDCl₃ at 500 and 125 MHz, respectively, on Bruker AM-500.

Collection, extraction and isolation

The seeds of Caesalpinia bonduc were collected from Karachi in the period of November–December. The fresh seeds (6.5 kg) were ground in a homogenizer and soaked in MeOH for two weeks. After concentration under reduced pressure, the crude extract (95 g) was partitioned between EtOAc and H₂O. The EtOAc extract was condensed by removing the solvent under reduced pressure and the material thus obtained (39.7 g), was subjected to column chromatography using solvent systems hexane; hexane:CHCl₃; CHCl₃: MeOH and finally pure methanol, as a mobile phase.

The fraction eluted with hexane; CHCl₃ (3:7) was further purified by flash chromatography using hexane: EtOAc (2:8). As a result of this, a solid material was obtained. Final purification was

![Chemical Structure](image-url)
achieved by washing the solid material with Me₂CO and the Me₂CO insoluble white waxy residue was crystallized from a mixture of CHCl₃ and MeOH yielded a colourless needle like crystalline uv active pure compound 1 (13.2 mg).

**Bondenolide** (1): [α]D − 0.21° (c = 0.10, CHCl₃); m.p. 230−234 °C; IR νmax; 3400, 1735, 1750, 1720, 1649 cm⁻¹; UV λmax 217 nm; EIMS m/z 494 [M]+, 463 (M−OMe)+, 435 (M−OAc)+, 376 (M−(OAc)₂)+, 476 (M−H₂O)+; HRMS m/z 494.531 found 494.537 (calcld for C₂₅H₃₄O₁₀).

**1H NMR** (500 MHz, CDCl₃): δ 5.40 (1H, d, J = 9.5 Hz, H-1), 5.53 (1H, br.t, J = 10.0, 9.5 Hz, H-2), 2.31 (2H, dd, J 10.0, 7.1 Hz, H-3), 2.73 (2H, m, H-6), 2.72 (2H, m, H-7), 2.42 (2H, br.s, H-12), 5.98 (1H, s, H-15), 1.50 (3H, s, H-17), 1.26 (3H, s, H-18), 1.10 (3H, s, H-19), 1.38 (3H, s, H-20), 3.26 (3H, s, OMe), 2.00 (3H, s, OAc) and 2.06 (3H, s, OAc); ¹³C NMR (125 MHz, CDCl₃): δ 37.25 (C-1), 74.69 (C-2), 71.98 (C-3), 38.95 (C-4), 82.40 (C-5), 34.99 (C-6), 35.14 (C-7), 50.63 (C-8), 74.87 (C-9), 54.86 (C-10), 211.0 (C-11), 38.69 (C-12), 105.0 (C-13), 173.0 (C-14), 115.9 (C-15), 170.4 (C-16), 21.01 (C-17), 25.75 (C-18), 33.98 (C-19), 15.05 (C-20), 21.09 (COCH₃), 169.3 (COCH₃), 169.4 (COCH₃) and 51.56 (OCH₃).

The known compounds were compared with their reported data [10−21] in the literature.

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