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COMPONENTS OF THE GALLS ON THE LEAVES OF *PONGAMIA GLABRA*: STRUCTURES OF PONGAGALLONE-A AND PONGAGALLONE-B

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Key Word Index—*Pongamia glabra*; Leguminosae; pongagallone-A; pongagallone-B; β-diketones.

Abstract—The chemical examination of the galls present on the infected leaves of the plant *Pongamia glabra* has yielded, in addition to a number of known compounds, two new prenylated β-diketones, pongagallone-A and pongagallone-B. Evidence for their structures is presented.

INTRODUCTION

Pongamia glabra Vent. (Leguminosae) is a medium-sized tree popularly known as Karanja growing practically throughout India. The use of various parts of this tree as a folklore medicine has been recorded [1] and the chemical examination of the various parts of the plant has been reported [2]. More recent investigations [3–7] have shown the presence of several furano- and chromenoflavanones, flavones and chalcones. The leaves of this plant are known to be infected by the mite *Eryophyes cheriani* Massee resulting in the growth of galls [8] and the present investigation reports the isolation and complete characterization of two new β-diketones which occur in these galls.

RESULTS AND DISCUSSION

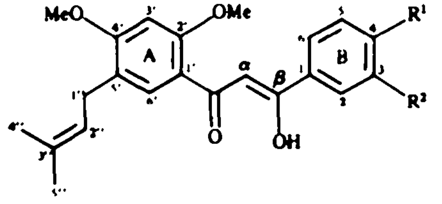
The galls growing on the tender and matured leaves of *Pongamia glabra*, growing both in the university campus and in a residential area in Madurai, were used in the present work. The benzene extract of the defatted galls, after careful column chromatography on a silica gel column (see Experimental), afforded two coloured compounds, pongagallone-A (**1**), and pongagallone-B (**2**), in addition to several other known compounds. The structural evidence for these new β-diketones is presented herein.

Pongagallone-A (**1**), mp 126–127°, crystallized from methanol as orange needles analysing for $C_{22}H_{24}O_4$. It gave a greenish-brown ferric colour with alcoholic ferric chloride, but did not yield any derivative characteristic of phenolic groups. Its UV spectrum had bands at 205, 215 (inf) and 345 nm, practically identical to representative synthetic β-diketones and did not show any shift with the standard flavonoid shift reagents [9]. The IR spectrum revealed a sharp carbonyl band at 1625 cm^{-1} with no hydroxyl band around 3500 cm^{-1}. Its ^1H NMR spectrum ($CDCl_3$) had absorptions at δ1.65 and 1.75 (methyl on a double bond), a methylene doublet centred at 3.29 (J = 7 Hz) and a single proton triplet at 5.20 (J = 7 Hz) suggesting the presence of a C-prenyl group (confirmed further by double irradiation experiments). Two sharp three-proton singlets at δ3.88 and 3.91 revealed the presence of two methoxyls. Two sharp singlets at δ7.78 and 7.81 (one proton each) were attributed to a proton *ortho* to the carbonyl of the A ring and the α-proton of the diketone structure. The absence of an *ortho*-coupled doublet in this region of this spectrum and the presence of a sharp one-proton singlet at δ5.96 (-3′ H) compelled the allocation of the C-prenyl group at position C-5′ as in **1**. The multiplets centred around δ7.35 and 7.55 integrating for five protons were assigned to the protons of ring B. The enolic hydroxylic proton [10] exhibited a signal at δ15.95 and the complete structure of pongagallone-A was thus deduced as **1**. The enolic structure assigned was in agreement with the ^1H NMR spectrum which showed no absorption in the region δ3.5–3.8 where the methylene group of the diketone moiety is expected to absorb [11-13].

The mass spectrum of pongagallone-A exhibited its $[M]^+$ ion peak at m/z 352 and the peaks at m/z 233, 205 and 193 in addition to several others (see Experimental) lent confirmation to the structure assigned.

Degradation of pongagallone-A with methanolic potassium hydroxide afforded benzoic acid confirming the above structure.

Pongagallone-B crystallized from methanol as orange-red needles, mp 161–162°. It analysed for $C_{23}H_{24}O_6$. It



1 $R^1 = R^2 = H$
2 $R^1, R^2 = —OCH_2O—$

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gave a deep greenish-brown ferric colour but did not form any characteristic derivative of a phenolic hydroxyl. However, it gave a positive Labat test (dioxymethylene group). Its UV spectrum was very similar to that of pongagallone-A having absorptions at 205, 215 (inf) and 360 nm. It did not exhibit shifts with the usual flavonoid reagents [9]. Its IR spectrum had strong absorption at 1625 cm^{-1} (carbonyl), a strong band at 1025 cm^{-1} and a weak band at 910 cm^{-1} (indicative of a dioxymethylene function). The ^{1}H NMR spectrum ($CDCl_3$) revealed many characteristic features of its structure. The C-prenyl group was indicated by the absorptions at δ1.65 and 1.75 (methyl on a double bond), a doublet at δ3.29 ($J = 7$ Hz) and a triplet at 5.20 ($J = 7$ Hz). The relationship of the doublet and the triplet absorptions was proved by double irradiation experiments. The strong three-proton singlet at δ3.88 and 3.93 could be assigned to two methoxyls in the A-ring. The strong three-proton singlet at δ6.00 could be attributed to the combination of the dioxymethylene group and the H-3′ of the A ring. The low field singlet at δ7.80 (two protons) accounts for the protons at position C-6′ and α to the diketone structure (**2**). The multiplets centred at δ6.82 and 7.10 (three protons) accounted for the three B-ring protons in structure **2**. The low field singlet at δ15.90 could be attributed to the enolic hydroxylic proton, thus completing the assignments for structure **2** for pongagallone-B. As in the case of pongagallone-A, the absence of any absorption in the region δ3.5–3.8 was in agreement with the enolic structure assigned to pongagallone-B.

The mass spectrum of pongagallone-B exhibited the [M]$^+$ ion peak at *m/z* 396 and other strong peaks at *m/z* 352, 309, 233, 205 and 193 in addition to several others (see Experimental) supporting structure **2**.

Degradation of pongagallone-B with methanolic potassium hydroxide yielded piperonylic acid thus confirming the structure.

The ^{13}C NMR data supported the structures assigned for pongagallone-A and pongagallone-B. The assignments (see Experimental) were made tentatively with off resonance data and also by comparison with known compounds [10, 13]. The absence of a clear triplet around δ55.0 for the presence of the methylene of the diketone moiety [13], coupled with the presence of a doublet at δ86.5/122.8 for the α-carbon, favoured the enolic structure assigned.

EXPERIMENTAL

Galls growing on infected leaves of *Pongamia glabra* Vent. were collected from the Madurai Kamaraj University area, as well as from a residential locality in Madurai. TLC developed with petrol–C_6H_6 (1:9), pure C_6H_6 or C_6H_6 $CHCl_3$ (3:1), were used for monitoring CC results and for comparison. Petrol used in this work had a boiling range 60–80°.

Extraction and separation of compounds. The air dried, powdered galls (2.5 kg) were extracted successively, with hot petrol, C_6H_6, Me_2CO and EtOH. The C_6H_6 extract was evaporated to dryness and the residue (15 g) was chromatographed on silica gel columns separating 5 g portions each time. The residue, dissolved in Me_2CO, was made into a slurry with silica gel (15 g) and the dried slurry chromatographed (silica gel 100 g). Fractions (100 ml) were collected by eluting the column with pure petrol (fractions 1–5), petrol–C_6H_6 (7:3) (fractions 6 19) and petrol–C_6H_6 (3:2) (fractions 20–160). Fractions with identical behaviour on TLC were combined. Fractions 1–5 left no residue on evaporation but fractions 6 19 were found to yield only traces of mixture of substances and were not examined. Fractions 20–60 were found to yield pongagallone-A and fractions 61–160 were found to yield pongagallone-B.

Pongagallone-A (**1**). Orange needles from MeOH (100 mg), mp 126–127°, greenish-brown colour with alcoholic $FeCl_3$. UV λ_{max}^{EtOH} nm: 205, 215, 345. IR ν_{max}^{KBr} cm^{-1}: 1625, 1405, 1210, 1110, 1060, 985, 780, 770, 735 and 670. ^{1}H NMR (90 MHz, $CDCl_3$): δ1.65 (3H, *s*, $=-CH_3$), 1.75 (3H, *s*, $=-CH_3$), 3.29 (2H, *d*, $J = 7$ Hz, H-1″, merges to a singlet upon irradiation at 5.20), 3.88 (3H, *s*, 2′-OMe), 3.91 (3H, *s*, 4′-OMe), 5.20 (1H, *t*, $J = 7$ Hz, 2″-H, merges into a singlet upon irradiation at 3.29), 5.96 (1H, *s*, 3′-H), 7.35 and 7.55 (5H, *m*, B ring protons), 7.78 (1H, *s*, α-H), 7.81 (1H, *s*, 6′-H) and 15.95 (enolic OH). ^{13}C NMR ($CDCl_3$): δ192.9 (C=O), 164.1 (C-β), 163.4 (C-2′), 161.3 (C-4′), 135.7 (C-1), 131.3 (C-3″), 129.9 (C-4), 128.8 (C-2, C-6), 128.2 (C-3, C-5), 127.9 (C-2″), 126.9 (C-6′), 122.8 (C-α or C-3′), 110.0 (C-5′), 106.5 (C-1′), 86.5 (C-3′ or C-α), 55.8 (OCH_3), 55.5 (OCH_3), 25.8 (C-5″), 21.5 (C-1″) and 17.8 (C-4″). MS *m/z* (rel. int.): 352 [M]$^+$ (97), 337 (42), 309 (100), 297 (47), 275 (13), 247 (15), 233 (81), 205 (46), 193 (86), 135 (30), 131 (27), 121 (27), 109 (27), 103 (36), 91 (22), 77 (48), 69 (27), 57 (36).

Pongagallone-B (**2**). Orange red needles from MeOH (150 mg), mp 161–162°, greenish-brown colour with alcoholic $FeCl_3$. UV λ_{max}^{EtOH} nm: 205, 215, 360. IR ν_{max}^{KBr} cm^{-1}: 1625, 1410, 1310, 1025 and 910. ^{1}H NMR (90 MHz, $CDCl_3$): δ1.65 (3H, *s*, $=CH_3$), 1.75 (3H, *s*, $=CH_3$), 3.29 (2H, *d*, $J = 7$ Hz, H-1″ merging to a singlet upon irradiation at 5.2), 3.88 (3H, *s*, 2′-OMe), 3.93 (3H, *s*, 4′-OMe), 5.20 (1H, *t*, $J = 7$ Hz, H-2″ merging to a singlet upon irradiation at 3.29), 6.00 (3H, *s*, H-3″ and $O-CH_2-O$), 6.82 and 7.10 (3H, *m*, 2,5,6 protons), 7.80 (2H, *s*, α- and H-6′), 15.90 (enolic OH). ^{13}C NMR ($CDCl_3$): δ192.8 (C=O), 164.0 (C–β), 163.2 (C-2′), 161.2 (C-4′), 149.4 (C-3), 148.2 (C-4), 131.3 (C-3″), 130.1 (C-1), 125.9 (C-6′ and C-2″), 124.8 (C-6), 122.8 (C-α or C-3′), 110.0 (C-2), 108.6 (C-5 and C-5′), 106.6 (C-1′), 101.5 ($O-CH_2-O$), 86.4 (C-3′ or C-α), 55.8 (OCH_3), 55.4 (OCH_3), 25.8 (C-5″), 21.4 (C-1″) and 17.7 (C-4″). MS *m/z* (rel. int.): 396 [M]$^+$ (100), 352 (85), 233 (87), 205 (48), 199 (5), 193 (98), 191 (42), 179 (7), 175 (30), 163 (15), 145 (15), 135 (35), 121 (26), 117 (15), 105 (10), 91 (16), 89 (22), 77 (17), 69 (20) and 42 (45).

Degradation of the diketones with methanolic KOH. The diketones (20 mg) were refluxed with methanolic KOH (7% soln; 1 ml) for 8 hr. The solvent was distilled off and the residue treated with H_2O (5 ml) and filtered. The alkaline filtrate was acidified with a few drops of conc. HCl and extracted with Et_2O. The Et_2O extract was extracted with aq. $NaHCO_3$ soln and the bicarbonate soln acidified to liberate the acid. The acid was extracted with Et_2O and identified by TLC after evaporation of Et_2O. Pongagallone-A thus yielded benzoic acid while from pongagallone-B, piperonylic acid could be detected.

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