lative step. In the formation of I, the enol form of α-ketoglutaric acid probably undergoes reaction with singlet oxygen. In the next step, I adds on to the unreacted α-ketoglutaric acid to give adduct II. The formation of this type of adduct has already been reported in the literature.\(^5\) In the last step, II cleaves to two molecules of succinic acid and carbon dioxide (see scheme).

![Chemical structure](image)

Percent yield of the succinic acid has been noted in water, methanol and acetone media using eosin-Y and methylene blue (table 1). It has been found that the yield is maximum in acetone medium and minimum in aqueous medium for both sensitizers. This has been attributed to the greater life time of singlet oxygen in acetone medium (26 µs) and comparatively short life time in water (2 µs). Methanol occupies mid position (10 µs).\(^6\)

Effect of scavengers has also been studied and it has been found that the yield of product decreases highly by their use and thereby confirming the participation of singlet oxygen in the reaction.

<table>
<thead>
<tr>
<th>Media used</th>
<th>Percent yield of succinic acid in presence of eosin-Y</th>
<th>Percent yield of succinic acid in presence of methylene blue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>11</td>
<td>14</td>
</tr>
<tr>
<td>Methanol</td>
<td>13</td>
<td>17</td>
</tr>
<tr>
<td>Acetone</td>
<td>16</td>
<td>20</td>
</tr>
</tbody>
</table>

The authors PG and RD are thankful to CSIR, New Delhi for the award of senior fellowship.

17 July 1984; Revised 11 October 1984


NEW GLYOSIDES FROM THE STEM BARK OF APHANAMIXIS POLYSTACHYA

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The plant *Aphanamixis polystachya* is a medicinal plant employed locally as astringent, spleen, liver, tumors and abdominal diseases and in rheumatism.\(^1\) Our earlier studies on the stem bark of *A. polystachya* disclosed the presence of (24 R)-24-ethylcholesta-5, 22-diene-3-O-rhamnoside, \(\beta\)-sitosterol, stigmasterol and a-galactosyl-3-O-rhamnosyl-xylitol. Further examination led to the isolation and characterization of two new glycosides which are assigned as 1,5-dihydroxy-6, 7, 8-trimethoxy-2-methyl-anthrquinone-3-O-\(\beta\)-D-xylopyranoside (A) and naringenin 7, 4'-dimethyl ether-5-O-\(\alpha\)-L-rhamnopyranoside (B) respectively by physico-chemical data.

**Table 1:** Time of reaction half an hour from the initiation of reaction as shown by tlc.

<table>
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aglycone contains 3\times OH (acetate) and 3\times OMe (Zeisel's) groups respectively. It formed a complex with ethanolic CuSO₄ showing the presence of α-OH in the structure. It gave positive colour reaction with con. H₂SO₄ for 1, 5-dihydroxy system \( \chi_{\text{max}} \approx 1610 \text{ cm}^{-1} \). The aglycone was demethylated (H/P) and the product gave an yellow colour with methanolic magnesium acetate, which is characteristic of 1, 3-dihydroxy system with respect to the Me group at position -2. It did not give red colour complex with alkaline zirconium nitrate solution while its demethylated product gave this test (1, 8-dihydroxy system confirming the presence of 1\times OMe at 8-position. The aglycone was methylated by CH₃N₂ to yield a tetramethyl ether showing the presence of two methoxyl groups at positions 6 and 7. Thus the aglycone was identified as 1, 3, 5-trihydroxy-6, 7, 8-trimethoxy-2-methyl-anthraquinone which was further supported by its IR, PMR, Mass and derivatives. The aglycone gave a positive colour reaction for 1,3-dihydroxy system whereas glycoside did not, indicating the attachment of sugar at position-3 in the natural products. The glycoside on NaIO₄ oxidation consumed 2 mol of periodate with the production of 1 mol of HCO₂H per mol of glycoside showing that the sugar is in pyranose form. Enzymatic hydrolysis of the glycoside yielded the above reported aglycone (m.p., m.m.p. and Co-TLC) and D-xylene (Co-PC and osazone) confirming the \( \beta \)-linkage. Thus the glycoside was assigned as compound-A. The aglycone as well as the glycoside are reported for the first time from natural sources.

Compound-B, an yellow brown amorphous substance, C₂₃H₂₆O₉, m.p. 125–28\( ^\circ \) (d), gave all the positive tests for a flavane glycoside. Acid hydrolysis (7\% H₂SO₄) afforded an aglycone and L-rhamnose (Co-paper chromatography and osazone). The aglycone, m.p. 160–61\( ^\circ \) (d), analysed for C₁₅H₁₅O₅ (M⁺ 300). The physico-chemical studies of the aglycone confirmed its identity as naringenin-7, 4'-dimethyl ether [lit. m.p. 160–62\( ^\circ \) (d), m.m.p. and Co-TLC]. By comparing the UV spectra (AlCl₃) and colour reactions of the aglycone and the glycoside, the rhamnose was found to be present at C-5 position. The periodate oxidation and tokadiastase hydrolysis confirmed α-linked rhamnopyranoside unit. This is the first report of compound-B in nature.

**Plant Material:** Plant material was procured from the United Chemicals and Allied Products, Calcutta.

**Isolation and purification of the constituents:** Air dried powdered stem bark (10 Kg) was exhaustively extracted thrice with rectified spirit under reflux for 30 days. The spirit extract (30 l) was concentrated (500 ml) under reduced pressure and poured into water (1 l). The water insoluble fraction was successively extracted with pet. ether, C₆H₆, CHCl₃, EtOAc and Me₂CO. The EtOAc and Me₂CO extracts yielded compounds-A and B respectively. Both the compounds were purified over silica gel column (MeOH:Me₂CO: 5:5) and crystallized (Me₂CO: Et₂O, A, 1.250 g and B, 1.130 g).

**Compound-A:** TLC: \( R_f \) 0.68 (CHCl₃:MeOH; 7:3), 0.85 (Me₂CO:MeOH; 1:9) and PC, \( R_f \) 0.93 (n BuOH:AcOH:H₂O; 4:1:5). (Found; C, 56.00; H, 4.90; C₂₃H₂₄O₁₂ reqd; C, 56.09; H, 4.87%.) Acid hydrolysis (7\% H₂SO₄, 40 ml) of the glycoside (800 mg) as usual afforded an aglycone and D-xylene (Co-PC and osazone, m.p. 157–58\( ^\circ \), lit. m.p. 159\( ^\circ \)). Aglycone: TLC, \( R_f \) 0.63 (CHCl₃:MeOH; 7:3), 0.54 (C₆H₆:CHCl₃; 9:1), 0.72 (Me₂CO:MeOH; 1:9) and PC, \( R_f \) 0.90 (n-BuOH:AcOH:H₂O; 4:1:5), (Found; C, 56.99; H, 4.43; OMe, 25.39; C₁₅H₁₅O₁₂ reqd; C, 60.00; H, 4.44; OMe, 25.83%; \( \chi_{\text{max}} \) 3400, 2925, 2870, 1175, 1680, 1639, 1610, 1455, 1342, 1275, 1220, 922, 862 and 763 cm⁻¹ ; UV \( \lambda_{\text{max}} \) MeOH 235, 287, 432 (nm); PMR (d₅-DMSO, 90 MHz, TMS, δ), 12.02 (s, OH), 7.62 (s, br, H-4), 4.02 (s, 1-OMe), 3.98 (s, 1-OMe), 3.60 (s, 1-OMe), 2.42 (s, br, CH₃-C-2); MS (m/e) 360 (M⁺), 342 (M⁺ – H₂O), 332 (M⁺ – CO), 331 (M⁺ – CH₃) 304 (332-CO), 303 (331-CO), 276 (304-CO), 275 (330-CO), 248 (276-CO), 247 (275-CO), 219 (248-CHO), 218 (247-CHO), 204 (219-CH₃) and 153(204-C₄H₇); acetate (Ac₂O/py method), m.p. 145–50\( ^\circ \) (Found; C, 59.25; H, 4.02, OAc, 26.46; C₂₃H₂₁O₁₁ reqd; C, 59.25; H, 4.52; OAc, 26.54\%); methyl ether (CH₃N₂), m.p. 185–90\( ^\circ \) (Found; C, 60.36; H, 4.80; OMe, 33.00; C₁₅H₁₅O₁₂ reqd; C, 60.96; H, 4.81; OMe, 33.15\%)

**Compound-B:** TLC, \( R_f \) 0.62 (CHCl₃:MeOH; 7:3), 0.73 (Me₂CO:MeOH; 1:9) and PC, \( R_f \) 0.82 (nBuOH:AcOH:H₂O; 4:1:5), (Found; C, 61.78; H, 5.62; C₂₃H₂₆O₉ reqd; C, 61.88; H, 5.82\%.) Acid hydrolysis (7\% H₂SO₄, 40 ml) of the glycoside (800 mg) as usual afforded an aglycone and L-rhamnose (Co-PC and osazone, m.p. 189–90\( ^\circ \), lit. m.p. 191\( ^\circ \). Aglycone: TLC, \( R_f \) 0.53 (CHCl₃:MeOH; 7:3), 0.68 (Me₂CO:MeOH; 1:9) and PC, \( R_f \) 0.78 (nBuOH:AcOH:H₂O; 4:1:5), (Found; C, 68.00; H, 5.26; OMe, 20.64; C₁₅H₁₅O₁₂ reqd; C, 68.00; H, 5.33; OMe, 20.66\%); \( \chi_{\text{max}} \) 3450, 2865, 1680, 1540, 1470, 1362, 1270, 1170, 1120, 1020 and 1075 cm⁻¹; \( \lambda_{\text{max}} \) 290, 330 (sh) (MeOH) nm + AlCl₃, 315, 330 (sh); + NaOAc 290, 330 (sh) nm; PMR (d₅-DMSO, 90 MHz, TMS, δ), 12.40 (s, OH), 7.20 (d, J = 8.5 Hz, H-2'), H-6'); 6.80 (d, J = 8.5 Hz, 2H, H-3'); 6.5 (d, J = 2.5 Hz, 1H, H-
dence for the presence of almost complete Paleocene succession in Jaisalmer basin, western Rajasthan. The Paleocene sequence comprises of sandstone, Fuller's

24 July 1984; Revised 26 September 1984


RECORD OF MARINE PALEOCENE SEQUENCE NEAR SANU, JAISALMER, WESTERN RAJASTHAN

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The study of planktonic foraminifers from the core samples near Sanu, Jaisalmer has provided the evo-