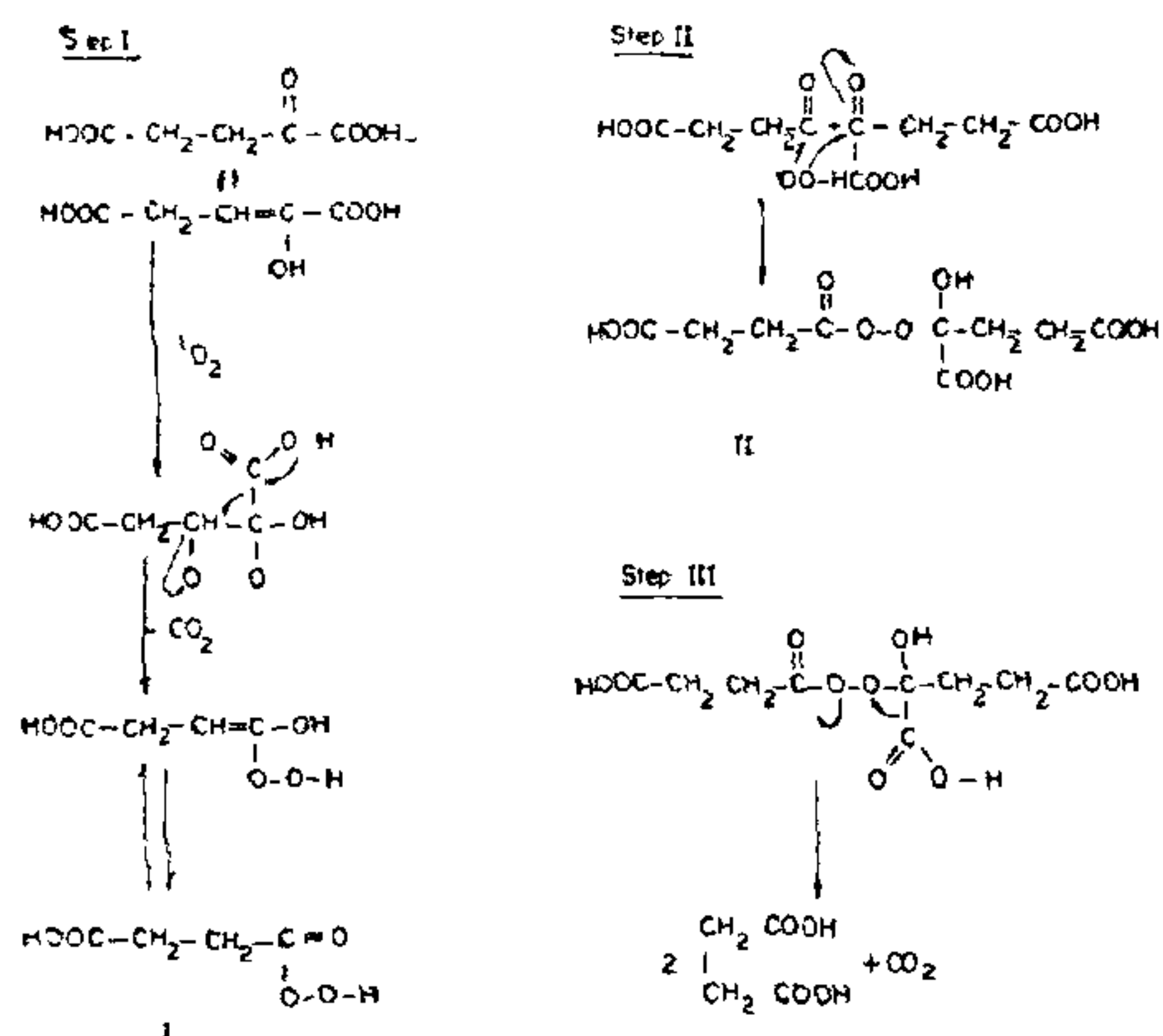


lative step. In the formation of I, the enol form of  $\alpha$ -ketoglutaric acid probably undergoes reaction with singlet oxygen. In the next step, I adds on to the unreacted  $\alpha$ -ketoglutaric acid to give adduct II. The formation of this type of adduct has already been reported in the literature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



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  $\mu\text{s}$ ) and comparatively short life time in water (2  $\mu\text{s}$ ). Methanol occupies mid position (10  $\mu\text{s}$ )<sup>6</sup>.

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

Media used	Percent yield of succinic acid in presence of eosin-Y	Percent yield of succinic acid in presence of methylene blue
Water	11	14
Methanol	13	17
Acetone	16	20

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## NEW GLYCOSIDES FROM THE STEM BARK OF *APHANAMIXIS POLYSTACHYA*

S. K. SRIVASTAVA and V. K. AGNIHOTRI

Department of Chemistry, University of Saugar,  
Sagar 470 003, India.

THE plant *Aphanamixis polystachya* is a medicinal plant employed locally as astringent, spleen, liver, tumors and abdominal diseases and in rheumatism<sup>1,2</sup>. Our earlier studies on the stem bark of *A. polystachya* disclosed the presence of (24R)-24-ethylcholestra-5, 22-diene-3-O-rhamnoside<sup>3</sup>,  $\beta$ -sitosterol, stigmasterol and aglailol-3-O-rhamnosyl-xyloside<sup>4</sup>. 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-anthraquinone-3-O- $\beta$ -D-xylopyranoside (A) and naringenin 7, 4'-dimethyl ether-5-O- $\alpha$ -L-rhamnopyranoside (B) respectively by physico-chemical data.

Compound-A, reddish brown amorphous solid,  $\text{C}_{23}\text{H}_{24}\text{O}_{12}$  m.p. 158–62° gave positive tests for an anthraquinone glycoside. Acid hydrolysis (7%  $\text{H}_2\text{SO}_4$ ) gave an aglycone,  $\text{C}_{18}\text{H}_{16}\text{O}_8$  ( $M^+$  360), m.p. 140–45° and D-xylose (Co-paper chromatography and osazone). The aglycone on Zn dust distillation gave 2-methyl anthracene showing thereby that the compound is related to 2-methyl-anthraquinone. The

aglycone contains 3 × OH (acetate) and 3 × OMe (Zeisel's) groups respectively. It formed a complex with ethanolic CuSO<sub>4</sub> showing the presence of α-OH in the structure<sup>5</sup>. It gave positive colour reaction with con. H<sub>2</sub>SO<sub>4</sub> for 1,5-dihydroxy system<sup>6</sup> ( $\nu_{\max}^{\text{KBr}}$  1610 cm<sup>-1</sup>)<sup>7</sup>. The aglycone was demethylated (HI/P) and the product gave a 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<sup>9</sup> while its demethylated product gave this test (1, 8-dihydroxy system) confirming the presence of 1 × OMe at 8-position. The aglycone was methylated by CH<sub>2</sub>N<sub>2</sub><sup>10</sup> to yield a tetramethyl ether showing the presence of two methoxyl groups at positions 6 and 7<sup>11</sup>. 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 NaIO<sub>4</sub> oxidation<sup>12</sup> consumed 2 mol of periodate with the production of 1 mol of HCO<sub>2</sub>H 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-xylose (Co-PC and osazone) confirming the β-linkage. Thus the glycoside was assigned as compound-A. The aglycone as well as the glycoside are reported for the first time from natural resources.

Compound-B, an yellow brown amorphous substance, C<sub>23</sub>H<sub>26</sub>O<sub>9</sub>, m.p. 125–28° (d), gave all the positive tests for a flavanone glycoside. Acid hydrolysis (7% H<sub>2</sub>SO<sub>4</sub>) afforded an aglycone and L-rhamnose (Co-paper chromatography and osazone). The aglycone, m.p. 160–61° (d), analysed for C<sub>17</sub>H<sub>16</sub>O<sub>5</sub> (M<sup>+</sup> 300). The physico-chemical studies of the aglycone confirmed its identity as naringenin-7, 4'-dimethyl ether [lit. m.p. 160–62° (d), m.m.p. and Co-TLC]<sup>13</sup>. By comparing the UV spectra (AlCl<sub>3</sub>) 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, C<sub>6</sub>H<sub>6</sub>, CHCl<sub>3</sub>, EtOAc and Me<sub>2</sub>CO. The EtOAc and Me<sub>2</sub>CO extracts yielded compounds-A and B respectively. Both the compounds were purified over silica gel column (MeOH:Me<sub>2</sub>CO; 5:5) and crystallized (Me<sub>2</sub>CO:Et<sub>2</sub>O; A, 1.250 g and B, 1.130 g).

**Compound-A:** TLC; R<sub>f</sub> 0.68 (CHCl<sub>3</sub>:MeOH; 7:3), 0.85 (Me<sub>2</sub>CO:MeOH; 1:9) and PC, R<sub>f</sub> 0.93 (n-BuOH:AcOH:H<sub>2</sub>O; 4:1:5), (Found; C, 56.00; H, 4.90; C<sub>23</sub>H<sub>24</sub>O<sub>12</sub> reqd; C, 56.09; H, 4.87%). Acid hydrolysis (7% H<sub>2</sub>SO<sub>4</sub>, 40 ml) of the glycoside (800 mg) as usual afforded an aglycone and D-xylose (Co-PC and osazone, m.p. 157–58°, lit. m.p. 159°); Aglycone: TLC; R<sub>f</sub> 0.63 (CHCl<sub>3</sub>:MeOH; 7:3), 0.54 (C<sub>6</sub>H<sub>6</sub>:CHCl<sub>3</sub>; 9:1), 0.72 (Me<sub>2</sub>CO:MeOH; 1:9) and PC, R<sub>f</sub> 0.90 (n-BuOH:AcOH:H<sub>2</sub>O; 4:1:5), (Found; C, 56.99; H, 4.43; OMe, 25.39; C<sub>18</sub>H<sub>16</sub>O<sub>8</sub> reqd; C, 60.00; H, 4.44; OMe, 25.83%);  $\nu_{\max}^{\text{KBr}}$  3400, 2925, 2870, 1175, 1680, 1639, 1610, 1445, 1342, 1275, 1220, 922, 862 and 763 cm<sup>-1</sup>; UV  $\lambda_{\max}^{\text{MeOH}}$  235, 287, 432 (nm); PMR (d<sub>6</sub>-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, CH<sub>3</sub> C-2); MS (m/e) 360 (M<sup>+</sup>), 342 (M<sup>+</sup> - H<sub>2</sub>O), 332 (M<sup>+</sup> - CO), 331 (M<sup>+</sup> - CHO), 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-CH<sub>3</sub>) and 153 (204-C<sub>4</sub>H<sub>3</sub>); acetate (Ac<sub>2</sub>O/py method), m.p. 145–50° (Found; C, 59.25; H, 4.02; OAc, 26.46; C<sub>24</sub>H<sub>22</sub>O<sub>11</sub> reqd; C, 59.25; H, 4.52; OAc, 26.54%); methyl ether (CH<sub>2</sub>N<sub>2</sub>), m.p. 185–90° (d) (Found; C, 60.36; H, 4.80; OMe, 33.00; C<sub>19</sub>H<sub>18</sub>O<sub>8</sub> reqd; C, 60.96; H, 4.81; OMe, 33.15%).

**Compound-B:** TLC; R<sub>f</sub> 0.62 (CHCl<sub>3</sub>:MeOH; 7:3), 0.73 (Me<sub>2</sub>CO:MeOH; 1:9) and PC, R<sub>f</sub> 0.82 (n-BuOH:AcOH:H<sub>2</sub>O; 4:1:5) (Found; C, 61.78; H, 5.62; C<sub>23</sub>H<sub>26</sub>O<sub>9</sub> reqd; C, 61.88; H, 5.82%). Acid hydrolysis (7% H<sub>2</sub>SO<sub>4</sub>, 40 ml) of the glycoside (800 mg) as usual afforded an aglycone and L-rhamnose (Co-PC and osazone, m.p. 189–90°, lit. m.p. 191°); Aglycone; TLC, R<sub>f</sub> 0.53 (CHCl<sub>3</sub>:MeOH; 7:3), 0.68 (Me<sub>2</sub>CO:MeOH; 1:9) and PC, R<sub>f</sub> 0.78 (n-BuOH:AcOH:H<sub>2</sub>O; 4:1:5); (Found; C, 68.00; H, 5.26; OMe, 20.64; C<sub>17</sub>H<sub>16</sub>O<sub>5</sub> reqd; C, 68.00; H, 5.33; OMe, 20.66%);  $\nu_{\max}^{\text{KBr}}$  3450, 2865, 1680, 1540, 1470, 1362, 1270, 1170, 1120, 1020 and 1075 cm<sup>-1</sup>;  $\lambda_{\max}$  290, 330 (sh) (MeOH) nm; + AlCl<sub>3</sub>, 315, 330 (sh); + NaOAc 290, 330 (sh) nm; PMR (d<sub>6</sub>-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', H-5'), 6.10 (d, J = 2.5 Hz, 1H, H-

8), 6.00 (d,  $J = 2.5$  Hz, 1H, H-6), 5.30 (dd,  $J = 4$  and 12 Hz, 1H, H-2), 4.00 (s, 3H,  $1 \times$  OMe), 3.95 (s, 3H,  $1 \times$  OMe), 2.60 (m, 2H, H-3); MS (m/e); 300 ( $M^+$ ), 299, 285, 282, 133, 134, 107, 192, 193, 166, 181 and 209.

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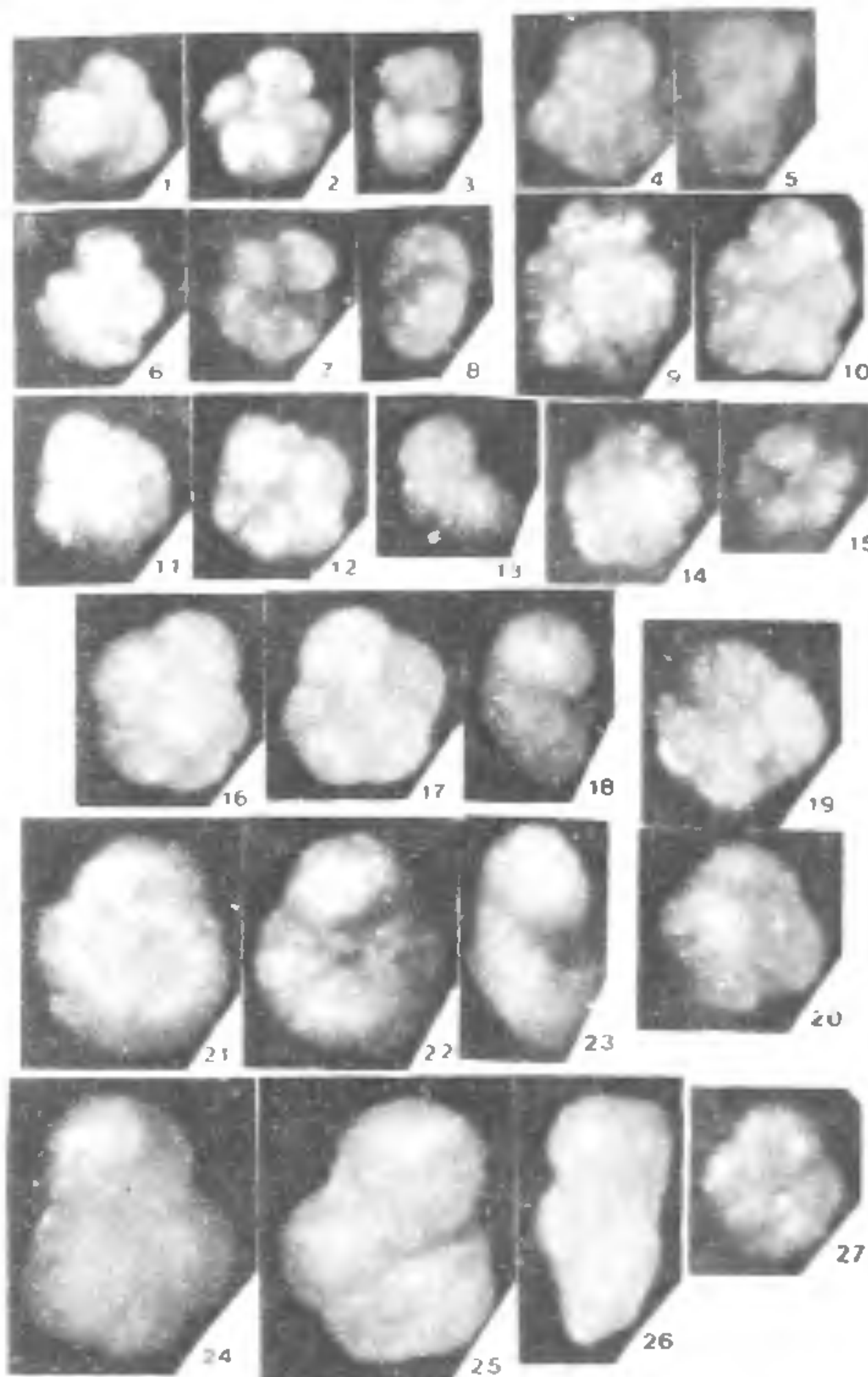
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## RECORD OF MARINE PALEOCENE SEQUENCE NEAR SANU, JAISALMER, WESTERN RAJASTHAN

PRABHA KALIA and DURJOY CHAKRABORTY  
Department of Geology, University of Delhi,  
Delhi 110 007, India.

THE study of planktonic foraminifers from the core samples near Sanu, Jaisalmer has provided the evi-

dence for the presence of almost complete Paleocene succession in Jaisalmer basin, western Rajasthan. The Paleocene sequence comprises of sandstone, Fuller's



Figures 1-27. 1-3. *Subbotina spiralis*. 1. Spiral view 2. Umbilical view 3. Edge view. 4-5. *Subbotina pseudo-bulloides*. 4. Spiral view 5. Edge view. 6-8. *Subbotina praecursoria*. 6. Spiral view 7. Umbilical view 8. Edge view. 9-10. *Morozovella uncinata*. 9. Spiral view 10. Umbilical view. 11-13. *Morozovella pusilla*. 11. Spiral view 12. Umbilical view 13. Edge view. 14-15. *Subbotina edita*. 14. Spiral view 15. Umbilical view. 16-18. *Subbotina inconstans*. 16. Spiral view 17. Umbilical view 18. Edge view. 19-20. *Globigerina daubjergensis*. 19. Umbilical view 20. Spiral view. 21-23. *Morozovella velascoensis*. 21. Spiral view 22. Umbilical view 23. Edge view. 24-26. *Planorotalites pseudomendardii*. 24. Spiral view 25. Umbilical view 26. Edge view. 27. *Morozovella angulata* (Umbilical view) (figures 1-8, 11-27  $\times 114$ , 9, 10  $\times 182$ )