

## GIBBERELLINS FROM MANGROVE PLANTS

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**Key Word Index**—*Sonneratia apetala*; Sonneraliaceae; *Rhizophora mucranata*; Rhizophoraceae; Mangrove plants; Gibberellins A<sub>1</sub>, A<sub>3</sub>, A<sub>4</sub>, A<sub>5</sub>, A<sub>7</sub> and A<sub>9</sub>; comparative biological activity.

**Abstract**—Gibberellins were isolated from three mangrove plants: A<sub>1</sub> and A<sub>3</sub> from *Sonneratia apetala*; A<sub>3</sub>, A<sub>5</sub> and A<sub>9</sub> from *Rhizophora mucranata* and A<sub>3</sub>, A<sub>4</sub> and A<sub>7</sub> from *Bruguiera gymnorhiza*. Biological activity of these gibberellins were examined using three bioassays.

IN CONTINUATION of our investigation on plant growth regulators,<sup>1-5</sup> we now report the isolation of gibberellins from three mangrove plants, *Sonneratia apetala*, *Rhizophora mucranata* and *Bruguiera gymnorhiza* and their characterization and biological activity. The isolation of a new naturally occurring gibberellin from the leaves of *S. apetala* was reported by us.<sup>3,4</sup>

Defatted leaves of *S. apetala* were extracted with methanol. The methanol solution was evaporated to afford an aqueous residue from which the ethyl acetate-soluble acidic extract was obtained. Chromatography of the acidic fraction gave three spots, one of which was identical with tetrahydrogibberellic acid A<sub>3</sub> previously isolated by us.<sup>3,4</sup> Repeated chromatography over silica gel afforded two compounds, m.p. 252–56° (A) and m.p. 228–230° (B) besides tetrahydrogibberellic acid. Compound A had TLC R<sub>f</sub> 0.26 in the lower phase of CCl<sub>4</sub>-HOAc-H<sub>2</sub>O (8:3:5), containing 10% EtOAc. The IR spectrum showed peaks  $\nu_{\max}^{\text{Nujol}}$  3495, 3360, 1760, 1705 and 980 cm<sup>-1</sup>. The MS of its methyl ester showed molecular ion peak at m/e 362. In addition to molecular ion peak there are peaks at m/e 344, 330, 316, 302, 284, 258, 256 and 240 which are in accord with the peaks of GA<sub>1</sub>-methyl ester reported earlier.<sup>6,7</sup> Finally the identity of (A) with GA<sub>1</sub> was established from its m.p., m.m.p., superimposable IR spectrum with authentic GA<sub>1</sub> and co-chromatography with the authentic sample. Compound (B) was homogeneous on TLC and had a yellow fluorescence with bluish tinge in UV light (R<sub>f</sub> 0.15 same solvent as above after spraying with 5% H<sub>2</sub>SO<sub>4</sub> in EtOH followed by heating the plate at 120° for 5 min). The identity of (B) with GA<sub>3</sub> was established by direct comparison of physical properties viz., IR, MS and co-chromatography with authentic GA<sub>3</sub>.

<sup>1</sup> SIRCAR, P. K., DEY, B., SANYAL, T., GANGULY, S. N. and SIRCAR, S. M. (1970) *Phytochemistry* **9**, 735.

<sup>2</sup> SANYAL, T., GANGULY, S. N., SIRCAR, P. K. and SIRCAR, S. M. (1970) *Planta Berl.* **92**, 282.

<sup>3</sup> GANGULY, S. N., SANYAL, T., SIRCAR, P. K. and SIRCAR, S. M. (1970) *Chem. Ind.* 832.

<sup>4</sup> GASKIN, P., MACMILLAN, J., GANGULY, S. N., SANYAL, T., SIRCAR, P. K. and SIRCAR, S. M. (1971) *Chem. Ind.* 424.

<sup>5</sup> GANGULY, S. N., GANGULY, T. and SIRCAR, S. M. (1972) *Phytochemistry* **11**, 3433.

<sup>6</sup> GROVE, J. F., JEFFS, P. W. and MULHOLLAND, T. P. C. (1958) *J. Chem. Soc.* 1236.

<sup>7</sup> MACMILLAN, J., SEATON, J. C. and SUTER, P. J. (1960) *Tetrahedron* **11**, 60.

Chromatography of the acid fraction of the methanolic extract of the defatted leaves of *R. mucranata* gave three compounds, (C)(D) and (E). Compound C, m.p. 206–209° was homogeneous in TLC and gave purple UV-fluorescent spot at  $R_f$  0.77 (solvent) EtOAc–CHCl<sub>3</sub>–HOAc, 15:1:1) after spraying with 5% H<sub>2</sub>SO<sub>4</sub> in EtOH followed by heating at 120° for 5 min. The compound showed IR absorption at 3098, 1755, 1720, 1665 and 890 cm<sup>-1</sup>. The MS of its methyl ester showed a molecular ion peak at  $m/e$  330 and the other peaks were observed at  $m/e$  298, 284, 260, 252, 226, 224 and 208 which are in accord with peaks of GA<sub>6</sub> methyl ester reported earlier.<sup>8</sup> Finally the identity of C with GA<sub>6</sub> was established from its m.p., m.m.p., superimposable IR spectrum with authentic GA<sub>6</sub> and also by co-chromatography with authentic GA<sub>6</sub>. Compound D, m.p. 258–261, homogeneous in TLC ( $R_f$  0.58, same solvent as above), gave a blue UV-fluorescent spot on spraying with ethanol H<sub>2</sub>SO<sub>4</sub> followed by heating the plate at 120°. The IR spectrum of the compound showed peaks  $\nu_{\max}^{\text{Nujol}}$  3435, 2710, 1760, 1730, 1660 and 895 cm<sup>-1</sup>. The MS of its methyl ester showed the molecular ion peak at  $m/e$  344. In addition to the molecular ion peak there are peaks at  $m/e$  312, 298, 284, 282, 266, 240, 238 and 222 similar to the peaks of authentic GA<sub>5</sub> methyl ester.<sup>7</sup> The identity of the compound D with GA<sub>5</sub> was established from its m.p., co-chromatography with authentic GA<sub>5</sub> and superimposable IR spectrum with authentic sample. Compound E, m.p. 228–229 was homogeneous in TLC ( $R_f$  0.38, same solvent as above). The compound was identified as GA<sub>3</sub> on the basis of physical measurements and biological activity.

The fruits of *Bruquiera gymnorhiza* was extracted with methanol. The acidic fraction of the methanolic extract was chromatographed to yield two highly active amorphous

TABLE I. COMPARATIVE POTENCY OF DIFFERENT GIBBERELLINS ISOLATED FROM MANGROVE PLANTS WITH THAT OF GA<sub>3</sub> AS STANDARD

Gibberellins	Lettuce hypocotyl test <sup>9</sup>	Cucumber hypocotyl test <sup>10,11</sup>	Rice second leaf sheath test <sup>12,13</sup>
GA <sub>1</sub>	1/10th of GA <sub>3</sub>	13/10 times more active than GA <sub>3</sub>	3.4th of GA <sub>3</sub>
Tetrahydro-gibberellic acid A <sub>3</sub>	---	Almost inactive	1/10th of GA <sub>3</sub>
GA <sub>4</sub>	4/5th of GA <sub>3</sub>	10 times more active than GA <sub>3</sub>	1/2 of GA <sub>3</sub>
GA <sub>5</sub>	1/10th of GA <sub>3</sub>	1/10th of GA <sub>3</sub>	3/5th of GA <sub>3</sub>
GA <sub>7</sub>	Six times more active than GA <sub>3</sub>	10 times more active than GA <sub>3</sub>	7/10th of GA <sub>3</sub>
GA <sub>9</sub>	3/5th of GA <sub>3</sub>	10 times more active than GA <sub>3</sub>	Almost inactive

<sup>8</sup> BINKS, R., MACMILLAN, J. and PRYCE, R. J. (1969) *Phytochemistry* **8**, 271.

<sup>9</sup> FRANKLAND, B. and WAREING, P. F. (1960) *Nature, Lond.* **185**, 255.

<sup>10</sup> BRIAN, P. W. and HEMMING, H. G. (1961) *Nature, Lond.* **189**, 74.

<sup>11</sup> KATSUMI, M., PHINNEY, B. O. and PURVES, W. P. (1965) *Physiol. Plant.* **18**, 462.

<sup>12</sup> RADLEY, M. (1956) *Nature, Lond.* **178**, 1070.

<sup>13</sup> RADLEY, M. (1958) *Ann. Bot.* **22**, 297.

solids, F and G. Compound G was homogeneous on TLC and had a yellow-green fluorescence with a bluish tinge on spraying with 5%  $H_2SO_4$  in EtOH followed by heating at  $120^\circ$  for 5 min. This was identical with  $GA_3$ . Compound F was not homogeneous in TLC and gave two spots. Due to extreme poor yield of the mixture F, we could not isolate the two components individually. However on the basis of PC and TLC and also by studying their biological activity, the two components in the mixture F were identified as  $GA_4$  and  $GA_7$ .

The results of the biological activity of the isolated compounds are presented in Table 1. Comparative potency of different gibberellins was studied earlier.<sup>14,15</sup> The activity was found similar to that of published data.<sup>14-16</sup>

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<sup>14</sup> BRIAN, P. W., GROVE, J. F. and MULHOLLAND, T. P. C. (1967) *Phytochemistry* **6**, 1475.

<sup>15</sup> BRIAN, P. W., HEMMING, H. G. and LOWE, D. (1964) *Ann. Bot.* **28**, 369.

<sup>16</sup> CROZIER, A., KUO, C. C., DURLEY, R. C. and PHARIS, R. P. (1970) *Can. J. Botany* **48**, 867.