Some Rearrangements of Gibberellins Catalysed by Tetracyanoethylene

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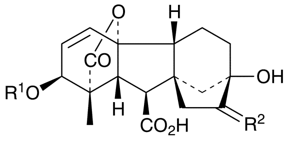
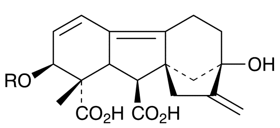
Tetracyanoethylene in methanol has been shown to catalyse the rearrangement of ring A of gibberellic acid to the 3β-methyl ether of gibberellenic acid and to the 19-2α-isolactone whilst the 13-hydroxygibberellin 16,17-epoxides are converted to 8:13-isogibberellins.

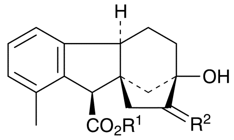
Tetracyanoethylene has recently attracted interest as a mild π-acid catalyst for the methanolysis, cyclization and rearrangement of epoxides.[1–6] The gibberellin plant hormones undergo a number of decomposition and rearrangement reactions in the presence of mineral acid.[7] Under mildly acidic conditions at room temperature, gibberellic acid (**1**) affords gibberellenic acid (**3**) and allogibberic acid (**5**) whilst under more vigorous conditions a Wagner–Meerwein rearrangement of rings C and D takes place, leading to the formation of the 8:13-isogibberellins such as gibberic acid (**7**).[8] This reaction, which is a characteristic of 13-hydroxygibberellins, has also been observed with 13-hydroxy-16,17-epoxides.[11,12]



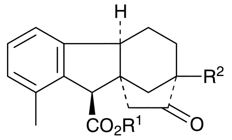
1 R^1 = H, R^2 = CH$_2$
2 R^1 = Ac, R^2 = $\underset{\text{O}}{\triangledown}CH_2$



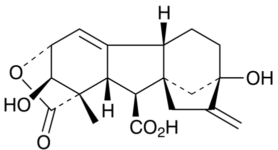
3 R = H
4 R = Me



5 R^1 = H, R^2 = CH$_2$
6 R^1 = Me, R^2 = $\underset{\text{O}}{\triangledown}CH_2$



7 R^1 = H, R^2 = Me
8 R^1 = Me, R^2 = CH$_2$OH



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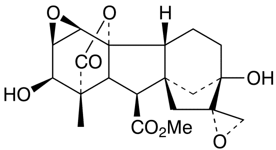

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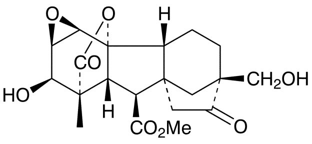

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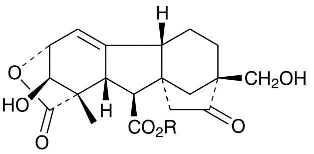

12 R = H
13 R = Me

Treatment of gibberellic acid (**1**) with tetracyanoethylene in methanol at 50 °C gave the 3β-monomethyl ether of gibberellenic acid **4** and the 19-2α-isolactone **9**. Both compounds were identified by the characteristic position and multiplicity of the ^{1}H NMR signals for their ring A protons. The 16α,17-epoxides **2**,**6** and **10** underwent rearrangement under the same conditions to afford the 17-hydroxy-8:13-isogibberellins **12** and **13**, **8**, and **11**, respectively. These were identified primarily by the presence of the primary alcohol resonances in the ^{1}H NMR spectrum and the cyclopentanone signal in the ^{13}C NMR spectrum. Whilst the ring A epoxide of **10** was unchanged, ring A of **2** underwent rearrangement to form the 19-2α-isolactone.

The methyl esters required for this work were prepared by methylation using methyl iodide and caesium fluoride in dimethylformamide.[16] This may be a less hazardous procedure for making gibberellin methyl esters than the conventional procedure using diazomethane.

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Techniques used: IR, ^{1}H and ^{13}C NMR

References: 18

Table 1: ^{13}C NMR data for 8:13-isogibberellins

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