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REARRANGEMENT OF THE 8,15-EPOXIDE OF GIBBERELLIC ACID

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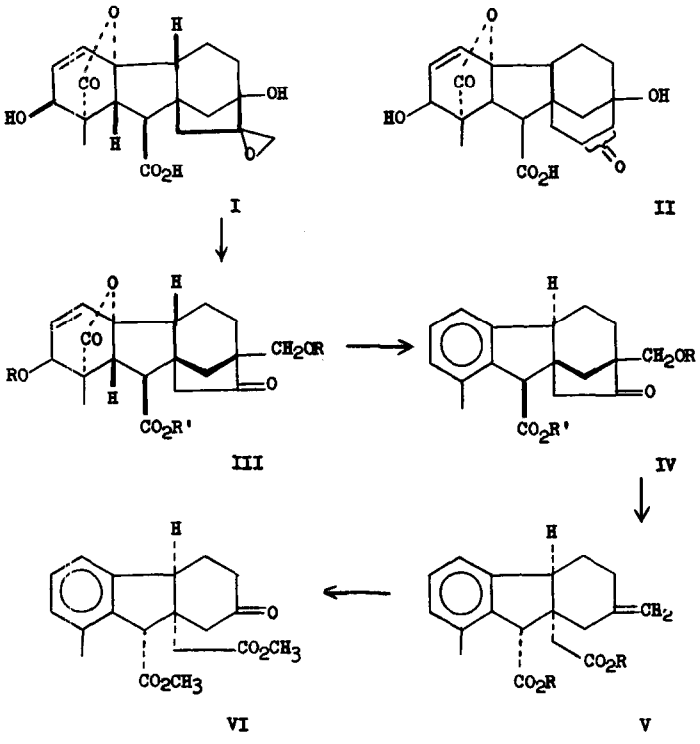
Recently it was reported that the 8,15-epoxide of gibberellic acid I undergoes rearrangement in warm aqueous solution to yield a product of ring-homoannulation, II (1). This reaction course is contrary to the normal rearrangement pathway exemplified by the allo-gibberic ⟶ gibberic acid transformation (2,3).

A reexamination of this rearrangement reveals that the product derived from I has, in fact, the structure to be expected from the established rearrangement sequence, namely, the angular hydroxymethyl system, III, (R = R' = H). The latter structure was characterized by facile conversion of its methyl ester to a diacetate derivative III (R = Ac, R' = CH_3, m.p. 170-2°. Found: C, 62.70; H, 6.03. Calcd. for $C_{24}H_{28}O_9$: C, 62.60; H, 6.13) under conditions whereby the angular 7-OH of gibberellic acid and related systems remains unaffected. The nmr spectrum of III (R = Ac, R' = CH_3) in deuterochloroform displayed two sharp 3-proton signals at 7.96 and 7.88 τ due to the methyls of the two acetoxyl groups and one sharp 2-proton peak at 5.85 τ due to the methylene of the acetoxy methyl moiety.



Confirmation of structure III (R = R' = H) was derived from its conversion with dilute acid to the aromatic analog IV (R = R' = H, m.p. 181-4°. Found: C, 72.10; H, 6.71. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71); the latter in the form of its methyl ester IV (R = H, R' = CH_3, m.p. 153-4°. Found: C, 72.82; H, 7.15. Calcd. for $C_{19}H_{22}O_4$: C, 72.59; H, 7.09); was converted to its tosylate derivative and cleaved with alkali (4) to the methylene diacid V (R = H, m.p. ca. 200°. Found: C, 71.71; H, 6.59. Calcd. for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71). The dimethyl ester V (R = CH_3) was oxidized with OsO_4-HIO_4 to formaldehyde and the known keto diester VI (5)

(m.p. 161-163°, $[\alpha]_{589}$ -77°, negative Cotton effect curve (600 mμ) -285°, (308) -3550° (276) -325° (269) -1025°. Found: C, 69.11; H, 6.91. Calcd. for $C_{19}H_{22}O_5$: C, 69.07; H, 6.71).

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