

STRUCTURE OF RADICLONIC ACID, A NEW PLANT GROWTH-REGULATOR

PRODUCED BY A FUNGUS

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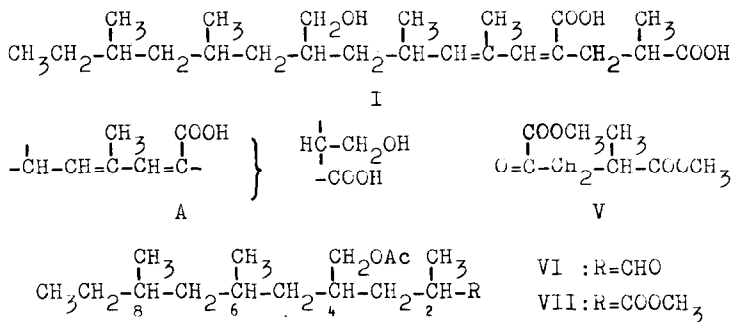
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Radiclonic acid, isolated from the mycelial extracts of an unidentified fungus 489-7 as a root growth-promoter, is a hydroxy-dienoic acid¹. In the present paper, structure I is assigned to radiclonic acid².

Radiclonic acid, C₂₃H₄₀O₅, gave a dimethyl ester(II); UV $\lambda_{\text{max}}^{\text{MeOH}}$: 250 (ϵ 9900), 232(ϵ 9600) nm, IR $\nu_{\text{max}}^{\text{CCl}_4}$: 1735, 1725 cm⁻¹; NMR δ^{CDCl_3} : 6.07(1H, b.s), 5.13(1H, b.d, J=10 Hz), 3.68, 3.63(each 3H, s), 3.47(2H, d, J=5 Hz), 3~2(4H, m), 1.66(3H, d, J=ca. 1 Hz); its acetate(III), NMR δ^{CDCl_3} : 3.93(2H, d, J=5 Hz), 2.04(3H, s)¹. II was hydrogenated on 5% Pd-C in ethanol to yield an α,β -unsaturated ester(IV)³; UV $\lambda_{\text{max}}^{\text{MeOH}}$: 221(ϵ 13000) nm, IR $\nu_{\text{max}}^{\text{CCl}_4}$: 1737, 1723 cm⁻¹; NMR δ^{CDCl_3} : 5.63(1H, d, J=10.5 Hz), MS m/e: 426(M⁺). Data presented so far define the partial structure of a dienoic acid chromophore and functional groups in radiclonic acid(A).

Ozonolysis of III afforded a ketone(V) and an aldehyde(VI) as major products; V, IR $\nu_{\text{C=O}}^{\text{CCl}_4}$: 1734 cm⁻¹; NMR δ^{CCl_4} : 3.83, 3.66(each 3H, s), 3.4~2.5 (3H, m), 1.21(3H, d, J=7 Hz), MS m/e: 188(M⁺), 170, 151, 129, 101, 69, 59, VI, NMR δ^{CDCl_3} : 9.63(1H, d, J=2 Hz), 3.97(2H, d, J=5 Hz), 2.55(1H, m), 2.05 (3H, s). V was identified with 4-methyl-2-oxo-glutaric acid dimethyl ester which was derived from 4-methyl-2-oxy-glutaric acid⁴. Oxidation of VI with Jones reagent, followed by methylation with diazomethane, gave a methyl ester(VII), IR $\nu_{\text{max}}^{\text{CCl}_4}$: 1739 cm⁻¹; MS m/e: 300(M⁺), 257, 240. Extensive spin-decoupling experiments on VII with a NMR shift reagent Eu(DFM)₃ allowed reasonable formulation for the structure of VII. In the



NMR spectra of VII in carbon tetrachloride upon addition of increasing amounts of the shift reagent, signals of seven protons ($\text{C}_2\text{-H} \sim \text{C}_6\text{-H}$), three secondary and one primary methyl group were isolated. Approximate resonance positions for these protons and methyl groups were at δ 10.65 ($\text{C}_2\text{-H}$), 6.0 ($\text{C}_2\text{-CH}_3$), 9.9, 7.15 (each $\text{C}_3\text{-H}$), 8.3 ($\text{C}_4\text{-H}$), 15.15 ($\text{C}_4\text{-CH}_2\text{-O}$), 5.0 (2H, $\text{C}_5\text{-H}$), 4.5 ($\text{C}_6\text{-H}$), 2.4 ($\text{C}_6\text{-CH}_3$), 1.4 ($\text{C}_8\text{-CH}_3$), 1.1 ($\text{C}_9\text{-CH}_3$). Irradiation of the band $\text{C}_6\text{-H}$ decoupled a divided one-proton multiplet at δ 2.9 and a proton at δ ca. 2.1 in the complex band (δ 2.5 \sim 1.5 (ca. 4H)). The only secondary methyl group remaining unassigned in the NMR spectrum must, therefore, be located at C_8 . The presence of a sec-butyl group was supported by the mass spectrum of VII; base peak: m/e 57, characteristic peaks: m/e 227 (15%), 226 (16%), 208 (5%), 207 (3.5%), 170 (9%), 169 (11%). Thus, radiclonic acid is expressed by the structure I because ozonolysis products (V and VI) and dienoic acid system in the partial structure (A) account for all the elements of III.

From a biosynthetic point of view, the structure of radiclonic acid suggests strongly a possibility of acetate-propionate derivation. However, no metabolite derived from propionate units has been found in fungi. We have much interests in biosynthesis of radiclonic acid.

REFERENCES

1. T. Sassa, K. Tomizuka, M. Ikeda and Y. Miura, Agr. Biol. Chem., 37(5)(1973), in press.
2. In addition, dimethyl esters of I-acetate and I-methyl ether were isolated from a mixture of methylated products of the strongly acidic portion of the mycelial extracts.
3. In addition, an 1,4-addition product was obtained as minor product; IR $\nu_{\text{C}=\text{O}}$ CCl_4 : 1736 cm^{-1} , NMR δ^{CDCl_3} : 1.61 (d, $\text{CH}_3\text{-C}=\text{C}$), 4.95 (1H, m).
4. T. Haga and M. Sato, Nippon Kagaku Zasshi, 83, 609 (1962).