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9,10,13-TRIHYDROXYOCTADECANOIC ACID, A NEW FATTY ACID IN THE ROOTS OF KIDNEY BEAN (PHASEOLUS VULGARIS L., "BENI-KINTOKI")

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A new fatty acid was isolated from the roots of kidney bean and identified as 9,10,13-trihydroxyoctadecanoic acid. The hatching stimulating activity to the soybean cyst nematode is also discussed.

The hatching of eggs of the soybean cyst nematode (Heterodera glycines) has recently been found to be stimulated by the root diffusates of several host plants.[1] In connection with the studies[2] on such stimulants, we have examined components of the roots of kidney bean (Phaseolus vulgaris L., "Beni-kintoki") and isolated a new fatty acid (I) in 1.4×10^{-5}% yield from the dried roots, along with a number of acids, phenols,[3] triterpenes and sterols,[4] and abscisic acid-related compounds.[5] The present paper describes the structure and biological activity of the acid.

Aqueous, acidic extracts (42 g) with the relevant biological activity at $10^{-5\sim6}$ g/ml in water, obtained from the dried roots (70 kg) collected in July at Memuro, Hokkaido, were fractionated by chromatography over active charcoal with aqueous acetone and separated oily mixtures (1.7 g), which were active at $10^{-6\sim7}$ g/ml. Futher chromotography over silica gel gave partially solid oil (127 mg) with the same activity, from which acid I (10 mg) could be isolated in, at least chemically, pure state after fractional recrystallizations.

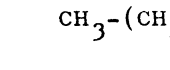
Compound I, $C_{18}H_{36}O_5$, mp 135-137°C; UV (EtOH), no absorption maximum over 220 nm; IR (KBr), ν_{max} 3360, 1710 and 1060 cm^{-1}; was converted into the methyl ester (Ia) (with diazomethane), $C_{19}H_{38}O_5$, mp 117.5-119.5°C; ORD (EtOH), only plain curve, $[\phi]$ -140° (250 nm) and -710° (225); NMR ($CDCl_3$), τ 9.10 (3H, broad t, CH_3), 8.70~8.40 (24H, broad, CH_2), 7.77 (3H, s, OH; disappeared on addition of D_2O), 7.70 (2H, t J = 7 Hz, CH_2COOCH_3), 6.40 (3H, broad, CHOH), and 6.37 (3H, s, $COOCH_3$). Ester Ia and its trimethylsilyl derivative (Ib) (with bis-trimethylsilylacetamide) indicated the following mass spectra, suggesting I to be 9,10,13-trihydroxyoctadecanoic acid[6] Ia, m/e 346 (M^+), 328 ($M^+ - H_2O$), 310 (328 - 18), 292 (310 - 18), 278 (310 - CH_3OH), 187, 159 (M^+ - 187), 155 (187 - 32), 141 (159 - 18), 123 (141 - 18), 83, 81, 67, and 55 (base peak); Ib, m/e 547 ($M^+ - CH_3$), 531 ($M^+ - CH_3O$), 457 [547 - $(CH_3)_3SiOH$], 441 (531 - 90), 389 (M^+ - 173), 303, 299 (M^+ - 173 - 90), 259 (M^+ - 303), 213 (303 - 90), 173, 75, and 73 (base peak). This presumption was confirmed as follows. Oxidation of Ia with potassium

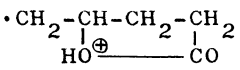
periodate and potassium permanganate followed by treatment with diazomethane afforded two major products, which were fractionated and analyzed by combined gas chromatography-mass spectrometry and identified by comparison with authentic specimens to be dimethyl nonanedioate (II), m/e 185 ($M^+ - CH_3O$), 152 ($M^+ - 2CH_3OH$), 87, 83 and 74 (base peak), and 4-pentyl-4-butanolide (III), m/e 138 ($M^+ - H_2O$), 128 ($M^+ - CO$), 100 (IV), and 85 (V, base peak).[7] Studies on the configurations at C_9, C_{10} and C_{13} are now in progress.

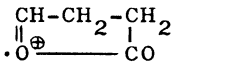
I $CH_3-(CH_2)_4-CH(OH)-CH_2-CH_2-CH(OH)-CH(OH)-(CH_2)_7-COOH$

Ib $CH_3-(CH_2)_4-CH(OT)-CH_2-CH_2-CH(OT)-CH(OT)-(CH_2)_7-COOCH_3$ $T = Si(CH_3)_3$

173 ↔ 389 303 ↔ 259

III 

IV 

V 

The acid I stimulates the hatching of the nematode eggs at 10^{-6} g/ml in water at room temperature. This activity might be caused by contamination of highly active principle(s), because the most active fraction in hatching has been found to be effective at 10^{-12} g/ml.[8] However, in view of the chromatographic procedure, the isolation of I from the active fractions suggests that the principle would possess structure analogous to the acid.

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References and Footnotes

1) M. Tsutsumi and K. Sakurai, Jap. J. appl. Ent. Zool., 10, 129 (1966).
2) Part III of "Constituents from the Kidney Bean." Part II, ref 5.
3) Succinic, suberic, azelaic, sebacic, undecane-1,11-dioic, and dodecane-1,12-dioic acid, benzoic, p-hydroxybenzoic, vanillic, salicylic, and veratric acids, α- and β-furoic acids, maltol and phaseollin and so on.
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5) M. Takasugi, M. Anetai, N. Katsui, and T. Masamune, Chemistry Lett., in press, No. 3 (1973).
6) Cf., J. A. McCloskey, "Topics in Lipid Chemistry," Vol. I, ed. by F. D. Gunstone, Logos Press Limited, London (1969), p. 369.
7) W. H. McFadden, E. A. Day, and M. J. Diamond, Anal. Chem., 37, 89 (1965).
8) T. Masamune et al., unpublished observations.

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