described above for the preparation of 2-acetamido-2-deoxy-D-iditol to yield 2-acetamido-2-deoxy-D-gulitol which after recrystallization from methanol had m.p. 169–170 °C and $[\alpha]_D$ +6.2° (*c*, 0.5 in water) and gave a single spot on paper chromatography (R_{gal} 1.18).

Anal. Calcd. for $C_8H_{17}O_6N$: C, 43.05; H, 7.68; N, 6.27. Found: C, 43.0; H, 7.8; N, 6.2.

The fully acetylated hexitol on gas chromatography gave a single peak having T_G 3.59.

2-Deoxy-D-xylo-hexose

(a) 3,4,5,6-Tetra-O-acetyl-1,2-dideoxy-1-nitro-D-xylo-hexitol

3,4,5,6-Tetraacetoxy-D-*xylo*-1-nitro-1-hexene (10 g) in ethanol (200 ml) was shaken with hydrogen at atmospheric pressure in the presence of palladium black (0.4 g). One mole of hydrogen was absorbed in 20 min. The reaction mixture was filtered and the filtrate was concentrated to a syrup which crystallized. The 3,4,5,6-tetra-*O*-acetyl-1,2-dideoxy-1-nitro-D-*xylo*-hexitol (7.8 g) after recrystallization from ethanol had m.p. 81 °C and $[\alpha]_D$ −5.9° (*c*, 1.5 in chloroform).

Anal. Calcd. for $C_{14}H_{21}O_{10}N$: C, 46.28; H, 5.83; N, 3.86. Found: C, 46.3; H, 6.0; N, 3.8.

(b) 2-Deoxy-D-xylo-hexose

3,4,5,6-Tetra-*O*-acetyl-1,2-dideoxy-1-nitro-D-*xylo*-hexitol (7.5 g) was dissolved in *N* sodium hydroxide (100 ml) and after 1 h at 20 °C the mixture was added dropwise with stirring to a solution of sulfuric acid (12 ml) in water (20 ml). The neutralized ($BaCO_3$) reaction mixture after filtration, was passed down columns of Rexyn 101(H^+) (200 ml) and Duolite A4(OH^-) (25 ml) ion-exchange resins and the eluate and washings were concentrated to a syrup (2.6 g) which was fractionated on a cellulose column (4 × 35 cm), using butan-1-ol half saturated with water as the mobile phase, to yield chromatographically pure 2-deoxy-D-*xylo*-hexose (1.1 g).

The 2-deoxy-D-*xylo*-hexose on paper chromatography had R_{gal} 2.70 and gave the characteristic red color with the periodate – thiobarbiturate spray reagents. It had $[\alpha]_D$ +9.4° (*c*, 0.5 in water) (lit. (14) $[\alpha]_D$ +12 ± 2°).

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.90; H, 7.37. Found: C, 44.0; H, 7.4.

The 2-deoxy-D-*xylo*-hexose (100 mg) on bromine oxidation gave 2-deoxy-D-*xylo*-hexonolactone (90 mg) having $[\alpha]_D$ −56° (*c*, 1.9 in acetone) (lit. (14) $[\alpha]_D$ −57°) which on treatment with phenylhydrazine afforded 2-deoxy-D-*xylo*-hexonic acid phenylhydrazide (38 mg) having m.p. 125–126 °C (lit. (14) m.p. 124–125 °C).

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Formation of a C_{22} dihydroxyketo acid by a yeast

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Saponification of extracellular lipids from the yeast NRRL YB-2501 yielded 8,9,13-trihydroxydocosanoic acid and a new keto dihydroxy acid of melting point 131–132 °C. The keto acid was shown to be 8,9-dihydroxy-13-oxodocosanoic acid by conversion to 5-ketotetradecanoic acid and suberic acid. By means of the method of Ames and Bowman (3), it was established that the vicinal hydroxyls of the new acid have the *erythro* configuration.

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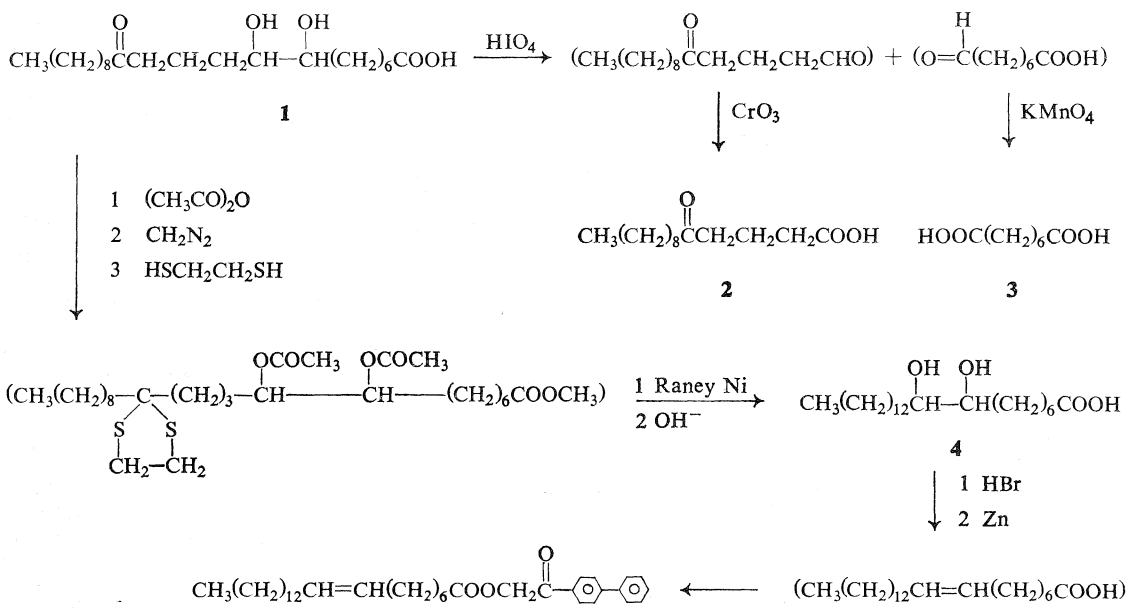
In 1965 we reported (1) that 8,9,13-triacetoxydocosanoic acid is produced by a yeast closely related to *Torulopsis fujisanensis*. More recently, in a review (2) on the extracellular lipids of yeasts, we mentioned that this organism also forms at the same time a smaller amount of

erythro-8,9-dihydroxy-13-oxodocosanoic acid (**1**), presumably in the acylated form; the evidence for the structure of **1** is now presented.

Acid **1** (m.p. 131–132 °C; $[\alpha]_D^{20}$ − 2.8°) was isolated from mother liquors left after the crystallization of 8,9,13-trihydroxydocosanoic acid, obtained by the saponification of the crude lipid excreted by the yeast. The structure and configuration of **1** were established by the following reactions:



Cleavage of **1** with periodic acid gave aldehydes that yielded 5-ketotetradecanoic acid (**2**) and suberic acid (**3**) on oxidation. Configuration of the vicinal hydroxyl groups in **1** was established in the following manner: the diacetyl methyl ester of **1** was converted to 8,9-dihydroxydocosanoic acid (**4**) by way of the thioketal; hydrobromination of **4** according to the method of Ames and Bowman (3), and subsequent debromination yielded a *cis* acid, which indicated an *erythro* configuration of the hydroxyl groups.

In our review (2) we reported the oxidation of 8,9,13-trihydroxydocosanoic acid to acid **1** after protection of the vicinal hydroxyls as an acetonide. A number of unsuccessful attempts to repeat this work, however, have since led us to the conclusion that this oxidation is no value as a structure proof because of very low yields.

Acid **1** is characterized by the following derivatives: methyl ester, m.p. 107–108 °C; *p*-bromophenacyl ester, m.p. 141–142 °C; and the semicarbazone, m.p. 129–130.5 °C.

Experimental

Melting points were determined with a Fisher–Johns apparatus[1] and were not corrected.

Isolation of erythro-8,9-Dihydroxy-13-oxodocosanoic Acid (1)

Crude lipid (48.3 g), obtained from the yeast NRRL YB-2501 by the procedure already described (1), was heated for 1 h at 95 °C with *N*-methylpyrrolidone (300 ml), *t*-butyl alcohol (250 ml), and 180 ml of water containing 43 g KOH. Acidification of the hot solution with 6 *N* HCl (360 ml), gave 34.0 g of crude 8,9,13-trihydroxydocosanoic acid, which on crystallization from acetic acid yielded 25.2 g of almost pure trihydroxy acid, m.p. 157–158 °C. Dilution of the mother liquor with water gave 7.49 g of crude crystalline acid **1** (m.p. 118–123 °C). Three crystallizations from ethyl acetate gave pure acid **1** with a constant melting point of 131–132 °C; yield, 4.83 g; $[\alpha]_D^{20}$ −2.8° (*c*, 10 in dimethyl sulfoxide).

Acid **1** liquefies in a few days on standing in an evacuated sulfuric acid desiccator, presumably due to ring closure between the hydroxyl and keto groups. Similar

[1]Mention of firm names or trade products does not constitute endorsement by the United States Department of Agriculture over other firms or products not mentioned.

behavior was observed when the acid was boiled for a few hours in petroleum ether (b.p. 93–97 °C).

Anal. Calcd. for $C_{22}H_{42}O_5$: C, 68.35; H, 10.95. Found: C, 68.6; H, 11.0.

Methyl 8,9-Dihydroxy-13-oxodocosanate

Acid **1** (100 mg) was treated with excess diazomethane in methanol–ether. The crude ester was crystallized from methanol-saturated petroleum ether (b.p. 65–68 °C), 75 mg, m.p. 107–108 °C.

Anal. Calcd. for $C_{23}H_{44}O_5$: C, 68.96; H, 11.07. Found: C, 69.1; H, 11.2.

p-Bromophenacyl-8,9-dihydroxy-13-oxodocosanate

Acid **1** (38.6 mg) was converted to the phenacyl ester in a mixture of acetone and *N*-methylpyrrolidone, according to the dicyclohexylethylamine (DICE) procedure (4). The crude product (89%, m.p. 125–130 °C) on crystallization from ethanol gave 38 mg of *p*-bromophenacyl ester, m.p. 141–142 °C.

Anal. Calcd. for $C_{30}H_{47}BrO_6$: C, 61.74; H, 8.12. Found: C, 61.8; H, 8.20.

Semicarbazone of Acid 1

Crude semicarbazone (25 mg) from 31.5 mg of acid **1** was crystallized from ethyl acetate, 16 mg, m.p. 129–130.5 °C.

Anal. Calcd. for $C_{23}H_{45}N_3O_5$: C, 62.27; H, 10.22; N, 9.47. Found: C, 62.6; H, 10.3; N, 9.22.

Periodic Acid Cleavage of Acid 1

A mixture of acid **1** (90 mg), periodic acid (106 mg), water (0.06 ml), and acetonitrile (1 ml) was kept in the dark for 1 h at room temperature. Water (0.5 ml) containing 85 mg $NaHCO_3$ was added, and the reaction mixture was extracted with ether. Removal of ether gave 57.5 mg of pale-yellow solid, which was oxidized with 1.55 ml of 0.91 *M* CrO_3 in acetic acid to 5-ketotetradecanoic acid, m.p. 77.5–79 °C (*p*-bromophenacyl ester, m.p. 83–84 °C).

The aqueous fraction yielded suberic acid after $KMnO_4$ treatment, as described in our earlier work (1).

8,9-Dihydroxydocosanoic Acid (4)

Acid **1** (1 g) was converted to the diacetate with acetic anhydride – pyridine (24 h; room temperature), and the crude diacetate was methylated with diazomethane. The methyl ester was dissolved in a mixture of acetic acid (1.25 ml), BF_3 etherate (0.66 ml), and $HSCH_2CH_2SH$ (0.25 ml). After 20 h at room temperature, the reaction mixture was added to 4 *N* NH_4OH (45 ml). An oil (1.33 g), recovered by ether extraction, was heated at 80 °C for 5 h with Raney nickel in ethanol. Filtration and removal of solvent gave 787 mg of product melting at 128–131 °C, which on crystallization from ethyl acetate yielded 592 mg pure acid **4** (m.p. 132–133 °C).

Anal. Calcd. for $C_{22}H_{44}O_4$: C, 70.92; H, 11.90. Found: C, 70.8; H, 11.8.

p-Phenylphenacyl cis-8-Docosenoate

Acid **4** (50 mg) was dissolved in 25% HBr – CH_3COOH (25 ml) containing 0.2 ml of concentrated sulfuric acid. After standing at room temperature for 20 h, the reaction mixture was heated at 95 °C for 3.5 h. Heating was continued for 4 h more after addition of 0.4 ml of 25% HBr – CH_3COOH. The dibromo compound was isolated by petroleum ether extraction and was esterified with diazomethane. The ester was refluxed under nitrogen for 1 h with ethanol (3 ml) and 30-mesh activated zinc (600 mg). The mixture of *cis* and *trans* esters was recovered by petroleum ether extraction and was shown by infrared absorption to be 93% *cis*. Saponification gave 43.8 mg of colorless crystals, which were converted by the DICE method (4) to crude *p*-phenylphenacyl ester (64.1 mg, m.p. 40–60 °C). Recrystallization from alcohol gave an analytical sample (45.1 mg, m.p. 67–68 °C).

Anal. Calcd. for $C_{36}H_{52}O_3$: C, 81.16; H, 9.84. Found: C, 81.0; H, 9.62.

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Monomer and dimer formation in esters of dihydroxyacetone

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The monomer (1-undecanoyloxy-3-hydroxyacetone) and dimer (2,5-diundecanoyloxymethyl-2,5-dihydroxy-1,4-dioxane) of dihydroxyacetone monoundecanoate have been characterized, and the conditions associated with their interconversion have been determined. The respective molecular constitutions have been unequivocally documented with ultraviolet and infrared spectral characteristics.

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In our preceding communication (1), we reported the synthesis of 1-undecanoyloxy-3-hydroxyacetone (**1**), a compound with potential perdurable insect-repellent efficacy. The data available at that time, however, did not permit us to establish unequivocally whether the compound existed as a monomer or dimer (or as a mixture of these two forms). In order to prepare the substantial quantities of **1** required for the evaluation of its repellent properties, we employed a direct