(+)-Tetrahydro-6-heneicosyl-2H-pyran-2-one, a natural product from Heliotropium curassavicum Linn.

P. S. Subramanian¹, S. Mohanraj, P. Kulanthaivel and J. Srinivasan

Department of Organic Chemistry, University of Madras, A. C. College Campus, Madras 600 025 (India), 20 November 1976

Summary. The hitherto unknown lactone of δ -hydroxy hexacosanoic acid, tetrahydro-6-heneicosyl-2H-pyran-2-one has been isolated from hexane extracts of Heliotropium curassavicum Linn,

Heliotropium curassavicum Linn., a glaucous fleshy herb found along the Coromandal coast², is rich in alkaloids³. During the course of our processing this plant for the alkaloids, a neutral material, $C_{26}H_{50}O_2$, m.p. $76\,^{\circ}C$, $[\alpha]_D+25.1\,^{\circ}$ (CHCl³), has been isolated and characterized as the hitherto unknown lactone of δ -hydroxy hexacosanoic acid (I).

Spectroscopic data of I. No UV absorption; IR (KBr) bands at 1718 (C=O), 1460 (CH₂), 1370 (CH₃), 1250 (C-O-C), 718 and 728 cm⁻¹ (CH₂ chain); NMR signals at δ 0.88 (3H, t, -CH₂-CH₃), 1.25 (\sim 42H, s, (CH₂)n),

CH₂–CH₂) and 4.3 (1H, m, –CH–CH₂–CH₂–CH₂); mass spectrum (M+ 394) characteristic of a long chain δ -lactone with the base peak at m/e 99 due to the cleavage adjacent to the lactone oxygen and a series of peaks spaced by 14 mass units revealing the hydrocarbon chain. Chemical reactions of I. Lithium aluminium hydride reduction afforded a diol (II) m.p. 90 °C, [α]_D0° (CHCl₃), ν ^{KBr}_{max} 3250 cm⁻¹ (OH), which exhibited peaks in its mass spectrum at m/e 103 and m/e 325 due to fragmentations

$$\begin{array}{c} \text{OR} \\ \text{CH}_3-(\text{CH}_2)_n \\ \text{O} \\ \text{CH}_3-(\text{CH}_2)_{20}-\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OR} \\ \text{II } n=20 \\ \text{Vii } n=22 \\ \text{Viii } n=10 \\ \end{array}$$

OR
$$CH_3-(CH_2)_{20}-CH-CH_2-CH_2-CH_2-COOCH_3$$

IV R = H
V R = Ac

$$\begin{array}{c} & \text{O} \\ \text{CH}_{3}\text{--}(\text{CH}_{2})_{20}\text{--}\text{C}\text{--}\text{CH}_{2}\text{--}\text{CH}_{2}\text{--}\text{CH}_{2}\text{--}\text{COOCH}_{3} \end{array}$$

VI

on both sides of the secondary OH group. It formed a diacetate (III), m. p. 44°C, $\nu_{\rm max}^{\rm KBr}$ 1740 and 1240 cm⁻¹(OAc), and NMR signals at δ 2.02 (6H, s, OAc), 4.0 (2H, t, CH₂OAc) and 4.8 (1H, m, CHOAc). Methanolysis of I with CH₃OH/H₂SO₄ led to the methyl hydroxyester (IV), m. p. 66°C, [α]_D0° (CHCl₃), $\nu_{\rm max}^{\rm KBr}$ 3350 (OH), 1740, 1200 and 1180 cm⁻¹ (ester), and NMR signals at δ 3.65 (3H, s, COOCH₃) and 4.25 (1H, m, CHOH). The acetate (V), m. p. 54°c, displayed NMR signals at δ 2.05 (3H, s, -OCOCH₃), 3.67 (3H, s, COOCH₃) and 4.85 (1H, m, CHOAc). Oxidation of IV gave the methyl ketoester (VI), m.p. 76°C, $\nu_{\rm max}^{\rm KBr}$ 1750, 1218, 1200 cm⁻¹ (ester), 1730 and 1720 cm⁻¹ (ketone), and NMR signals at δ 3.65 (3H, s, COOCH₃), 2.4

(6H, m, $-CH_2$ – CH_2 – CH_2 – CH_2 – $COOCH_3$), 1.95 (2H, m, O –C– CH_2 – CH_2 – CH_2 – $COOCH_3$), 1.25 (\sim 36H, s, (CH_2)_n), and 0.88 (3H, t, $-CH_2$ – CH_3). Its mass spectrum had fragments (chart) expected ⁵ for methyl 5-oxohexacosanoate thereby proving that **I** is the lactone of δ -hydroxy hexacosanoic acid. Further proof was obtained by reducing the diol(**II**) to the parent hydrocarbon, hexacosane.

As long chain lactones, in common with other components of the plant waxes, occur as homologous series 6 , the mass spectra of I and its degradation products were looked for the presence of such homologs. The presence of only the C_{28} higher homolog (VII), to the extent of 10%, was revealed. The gc-ms of the lactone also revealed only 2 components corresponding to $C_{26}H_{50}O_2$ (92%) and $C_{28}H_{54}O_2$ (8%).

Although the function of the long chain lactones in plant waxes is not known, it is of interest that the pheromone of the queen of the oriental horonet, Vespa orientalis, has been identified? as δ -n-hexadecalactone (VIII).

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