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ENAMINE CONDENSATION ON DERIVATIVES OF ALEURITIC ACID AND SYNTHESIS OF (Z)-9-TRICOSENE (MUSCALURE), ITS (E)-ISOMER, AND (E)-13-HEPTACOSENE

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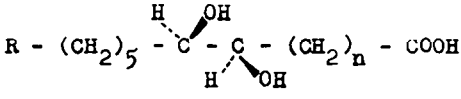
Abstract - Enamine condensation on (9RS,10RS)-9,10,16-triacetoxy hexadecanoyl chloride as well as (7RS,8RS)-7,8-diacetoxy pentadeca-1,15-dioyl chloride using 1-morpholino-1-cyclohexene led to chain elongated products with 22 and 27 carbon atoms respectively. The former was converted into (Z)-9-tricosene and its (E)-isomer while the latter led to a synthesis of (E)-13-heptacosene.

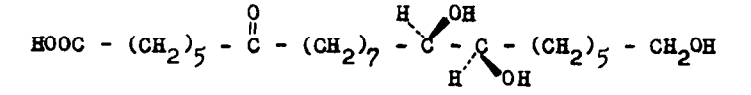
threo-Aleuritic acid, (9RS,10RS)-9,10,16-trihydroxy hexadecanoic acid (1), is a commercial product of India obtainable by an alkaline hydrolysis of lac resin[1]. It has been resolved[2] and several of its simple derivatives[3] reported. One of the key derivatives is the 16-oxo-compound. This aldehyde was earlier obtained from the 16-iodo compound through a dimethyl sulphoxide oxidation[3b]. Further efforts on the direct oxidation of the ω-hydroxyl function of aleuritic acid (as acetonide derivative) with chromium trioxide - pyridine in dichloromethane under controlled conditions were successful, resulting in good yields, and reported in this paper. Another derivative utilized in the present work was threo-7,8-dihydroxypentadeca-1,15-dioic acid (2) obtained from aleuritic acid through a photochemical decarboxylation[4] followed by oxidation to the dioic acid[5].



(1), R = CH_2OH, n = 7
(2), R = COOH, n = 6

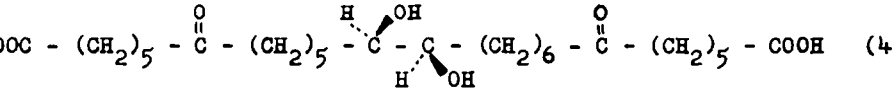
For purpose of chain elongation one of the attractive procedures is through an enamine condensation. This reaction would result in the preservation of configurational purity of the α-glycol function, introduce an oxo group at a well defined position and also maintain the ω-functionalities.

threo-Aleuritic acid was converted into the triacetate by the acetic anhydride - pyridine method followed by the formation of the acid chloride through the oxalyl chloride procedure. Subsequent enamine reaction with 1-morpholino-1-cyclohexene and acid hydrolysis gave a β-diketone giving a ferric reaction (enolic function) and was DNP positive. Further alkaline hydrolysis under controlled conditions yielded crystalline (15RS,16RS)-7-oxo-15,16,22-trihydroxydocosanoic acid (3).

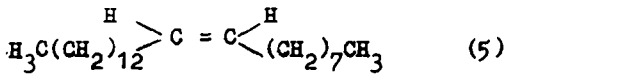


(3)

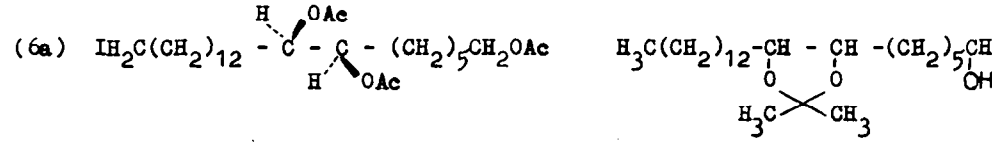
Using (2) and following a similar series of steps, (13RS,14RS)-13,14-dihydroxy-7,21-dioxo-heptacosa-1,27-dioic acid (4) was obtained. While in the former case



six carbons were added at one end in a good yield (85%), in the latter, twelve carbons were added in one step, six carbons at each end (70% yield). Both these compounds were used as intermediates for pheromone syntheses. The keto acid (3) led to the synthesis of muscalure[6] (5).

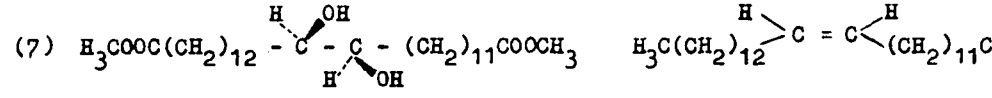


Huang - Minlon reduction of the 7-oxo group of (3) gave (15RS,16RS)-15,16,22-trihydroxydocosanoic acid. This compound has 14-carbon chain at the carboxyl end while in muscalure it has to be 13-carbon chain. Hence the terminal carboxyl was removed by a photochemical decarboxylation with lead tetraacetate and iodine on its triacetate yielding (7RS,8RS)-1,7,8-triacetoxy-21-iodo-heneicosane (6a). Re-



duction with zinc dust in acid medium followed by alkaline hydrolysis gave (7RS,8RS)-1,7,8-trihydroxy heneicosane. At the hydroxyl end of the chain two additional carbons are required in order to have a correct chain length and position of the vicinal glycol function. This was achieved by converting the 7,8-acetonide of the above heneicosane into the aldehyde with chromium trioxide - pyridine reagent. A Grignard reaction on the above aldehyde using ethyl magnesium bromide gave the required chain length (6b). Tosylation of the newly introduced hydroxyl at C-3 followed by a reduction with Zn-NaI and removal of the acetonide function gave threo-9,10-dihydroxytricosane. Olefination by Eastwood procedure[7] using ethyl orthoformate and benzoic acid under pyrolytic conditions gave (E)-9-tricosene. In order to get the (Z)-isomer the configuration of the threo glycol was inverted to that of an erythro glycol by treatment with dry HBr and acetic acid at room temperature followed by alkaline hydrolysis to a trans epoxide and subsequent acetolysis and alkaline hydrolysis to give the erythro glycol, according to an earlier procedure[1]. Stereospecific olefination gave muscalure (5). The identity was confirmed by NMR, IR, and mass spectra.

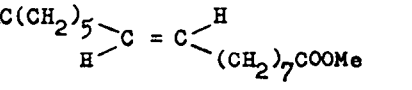
Unlike the case of C_{22} ketone (3) the C_{27} diketone (4) gave a mixture of compounds during a Huang-Minlon reduction or lithium aluminium hydride reduction. It was hence reduced in stages. A borohydride reduction of 7,21-dioxo groups of dimethyl ester followed by tosylation (vicinal glycol as acetonide), reduction with Zn-NaI, and removal of the acetonide group gave dimethyl-13,14-dihydroxy heptacosa-1,27-dioate (7). A lithium aluminium hydride reduction on the acetonide of the

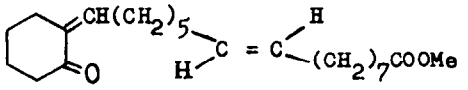


above diester followed by tosylation and reduction with Zn-NaI gave threo-13,14-dihydroxy heptacosane. An attempt to invert configuration at this stage gave mixtures indicating the desirability of starting with the required erythro configuration in the beginning, rather than attempting the inversion on the longer chain. Stereospecific olefination of the threo glycol gave the (E)-isomer of the face fly pheromone (8).

Though the above two syntheses apparently involve a number of steps, most of the stages are of protection and deprotection and the effective stages themselves involve simple laboratory requirements and operations and the yields are very good where it is not quantitative.

An effort was also made to react 16-oxo derivative (9) with 1-morpholino-1-cyclohexene to get (10). The product though obtained in good yield needs an isomerization step to get the endocyclic olefin. In view of the low yield in the second step, the reaction may not be of preparative value.

(9) 



(10)

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were recorded on a Perkin-Elmer infrared 599-B or Shimadzu 435 spectrophotometer, and expressed in wave number (cm^{-1}). All ^1H NMR spectra are expressed in δ scale and recorded in $CDCl_3$ with tetramethylsilane as internal standard on either R-32 (90 MHz) Perkin Elmer or JNM FX (200 MHz) Jeol FT spectrometer.

Formation of (15RS,16RS)-7-oxo-15,16,22-trihydroxy docosanoic acid (3)

(9RS,10RS)-9,10,16-trihydroxy hexadecanoic acid (15 g) was acetylated with pyridine and acetic anhydride (1:1, 30 ml). The completion of the reaction was shown by t.l.c. and n.m.r. spectrum (CH_2OAc, 2H, 4.0; 2 >$CHOAc$, 2H, 4.95; $OCOCH_3$, 9H, 2.0).

The above triacetate was converted into the corresponding acid chloride by refluxing with oxalyl chloride (17 ml) and pyridine (3 ml) in benzene (50 ml) and used in the next step.

A solution of 1-morpholino-1-cyclohexene (20 ml) and anhydrous triethylamine (15 ml) in dry chloroform (40 ml) was taken in a flask equipped with a reflux condenser and a dropping funnel, protected with anhydrous calcium chloride guard tubes. The reaction flask was immersed in water bath at 40° and a solution of threo-9,10,16-triacetoxy hexadecanoyl chloride (22.7 g) in dry chloroform (30 ml) was added to the wellstirred reaction mixture over a period of 1.5 h. which gradually assumed an orange red colour, and a solid precipitated out. It was stirred for additional 3 h. at 35°, 20% hydrochloric acid (10 ml) was added, and the mixture was boiled under reflux for 5 h. with vigorous stirring. After cooling to room temperature, the chloroform layer was separated and washed with water. The washings and aqueous phase were combined, adjusted to a pH of 5-6 with 25% aq. sodium hydroxide and extracted with chloroform, chloroform extract being combined with the original chloroform layer, and the solvent was removed on a steam bath. (9RS,10RS)-9,10,16-triacetoxy-1-oxo-1-(2-oxo-cyclohexyl)-hexadecane was obtained as a gum (21.0 g).

To a solution of methanolic sodium hydroxide (5.0 g in 40 ml of methanol) a warm solution of the above reaction product (11 g) in methanol (20 ml) was added. The mixture was then refluxed for 1 h., diluted with water and acidified when (15RS,16RS)-7-oxo-15,16,22-trihydroxy docosanoic acid (3) precipitated out (DNP positive). It was collected by filtration, washed with water, dried, and recrystallised from ethyl acetate - light petroleum (60-80°) (7.6 g, 85%) m.p. 105°. (Found: C, 65.5; H, 10.5. $C_{22}H_{42}O_6$ requires C, 65.7; H, 10.5%). IR(KBr): 3180-3280, 1690.

Its methyl ester was obtained by reaction with excess ethereal diazomethane containing a little methanol. It was crystallised from ethyl acetate - light petroleum (60-80°), m.p. 67°. (Found: C, 66.0; H, 10.8. $C_{23}H_{44}O_6$ requires C, 66.4; H, 10.6%). IR(KBr): 3200-3300, 1735, 1700. ^1H NMR: 2.35(m, 6H, $-CH_2CO_2Me$ and $-CH_2-CO-CH_2-$), 3.35(br, 2H, -CHOH-CHOH), 3.65(s, $COOCH_3$ overlapping with two proton triplet for CH_2OH).

(15RS,16RS)-15,16,22-Trihydroxydocosanoic acid

Potassium hydroxide (7.0 g) dissolved in ethylene glycol (25 ml) was treated with 7-oxo-15,16,22-trihydroxy docosanoic acid (3) (4 g) and hydrazine hydrate (8 ml, 80%). The temperature of the reaction mixture was raised to 140° and this temperature was maintained for 1 h. Excess of hydrazine hydrate was distilled off and the temperature of the bath was raised to 195°. The reaction mixture was refluxed at this temperature for 6 h. after which it was cooled to 110° and ice cold dilute hydrochloric acid was added slowly when 15,16,22-trihydroxydocosanoic acid separated out as a crystalline solid. It was collected by filtration, washed with water, dried, and recrystallised from ethyl acetate - light petroleum (60-80°) (3.5 g), m.p. 114°, (Found: C, 68.3; H, 11.6, $C_{22}H_{44}O_5$ requires C, 68.0; H, 11.3%). IR(KBr): 3430, 3340, 3240, 1705.

Its methyl ester was obtained by reaction with excess ethereal diazomethane containing a little methanol, m.p. 93°. (Found: C, 69.0; H, 11.8. $C_{23}H_{46}O_5$ requires C, 68.7; H, 11.4%). IR(KBr): 3220-3330, 1740. ^{1}H NMR: 2.25(t, $-CH_2COOCH_3$), 3.3(br, -CHOH-CHOH), 3.55(t, $-CH_2OH$ partially overlapping with the signal for $-COOCH_3$), 3.6(s, $-COOCH_3$).

(7RS,8RS)-1,7,8-Trihydroxy heneicosane

(15RS,16RS)-15,16,22-Trihydroxy docosanoic acid (2.75 g) was acetylated with a mixture of pyridine and acetic anhydride (1:1, 6 ml) to yield a gummy triacetate (t.l.c., i.r. and n.m.r.).

The above triacetoxy derivative (4.16 g) was decarboxylated photochemically[4] using lead tetraacetate (5.5 g) and a saturated solution of iodine in carbon tetrachloride (16 ml). Removal of iodine with thiosulphate followed by removal of solvent gave 1,7,8-triacetoxy-21-iodo-heneicosane (6a) (3.62 g) as a gum. IR(film): 1735, 600. ^{1}H NMR: 2.0(two closely placed singlets, 9H, $-OCOCH_3$), 3.15(t, $-CH_2I$), 4.0(t, $-CH_2OAc$), 4.95(br, -CHOAc-CHOAc).

The iodo acetate on deacetylation gave the corresponding trihydroxy iodo compound m.p. 95°. (Found: C, 53.3; H, 8.7. $C_{21}H_{43}O_3I$ requires C, 53.6; H, 9.1%). IR(KBr) 3200-3340, 600. ^{1}H NMR: 3.05(t, $-CH_2I$), 3.25(br, -CHOH), 3.48(t, CH_2OH).

The above triacetoxy iodo compound (3.6 g) was dissolved in dioxan (5 ml) and zinc dust (18.0 g) was added. To the above reaction mixture concentrated hydrochloric acid was added dropwise with stirring till the whole amount of zinc went into solution. After work up the resulting gum was hydrolysed with 6% aqueous sodium hydroxide in methanolic solution to give (7RS,8RS)-1,7,8-trihydroxyheneicosane (1.5 g) and recrystallised from methanol-water m.p. 83° (Found: C, 73.0; H, 12.4. $C_{21}H_{44}O_3$ requires C, 73.3; H, 12.7%). IR(KBr): 3300. ^{1}H NMR: 0.9(t, $-CH_3$), 3.4(br, -CHOH-CHOH), 3.62(t, $-CH_2OH$).

(7RS,8RS)-7,8-isopropylidenedioxy heneicosanal

(7RS,8RS)-1,7,8-Trihydroxyheneicosane (1.5 g) was converted to its corresponding isopropylidene derivative by stirring with dry acetone and catalytic amount of perchloric acid. It was then oxidised as follows:

A conical flask fitted with a guard tube was charged with pyridine (3.3 ml) and dichloromethane (50 ml). The solution was stirred and cooled in an ice bath to an internal temperature of 5° and chromium trioxide (2.05 g) was added to it in portions. The deep burgundy solution was stirred in the cold for additional 5 min. and then allowed to warm to 20° over a period of 60 min. A solution of (7RS,8RS)-1-hydroxy-7,8-isopropylidenedioxy-heneicosane (1.3 g) in dichloromethane (10 ml) was added to it rapidly when a tarry black deposit separated out. The reaction mixture was stirred for 15 min. and then decanted from the tarry residue. The tarry residue was washed with ether. The combined organic solution was washed with ice cold aqueous sodium hydroxide (5%), aqueous hydrochloric acid (5%), aqueous sodium bicarbonate, saturated brine and finally with water. After drying the organic extract over anhydrous sodium sulphate and distilling the solvent gummy (7RS,8RS)-7,8-isopropylidenedioxy heneicosanal was obtained (1.2 g). IR(film): 2910, 2850, 1740, 1380, 1370. ^{1}H NMR: 0.9(t, $-CH_3$), 2.3(t, $-CH_2CHO$), 3.5(br, -CHO-CHO), 9.62(t, -CHO). It was used without further storage.

(9RS,10RS)-3,9,10-Trihydroxytricosane

Small pieces of clean magnesium ribbon were placed in a 100 ml three necked flask fitted with water condenser, dropping funnel, and a nitrogen gas supply. Above magnesium pieces and a few iodine crystals in dry ether (20 ml) were refluxed with stirring till the colour of iodine disappeared (10 min.). Then ethyl bromide (5 ml) in dry ether (5 ml) was added in lots from a separating funnel. After 10 min. a white precipitate separated out. (7RS,8RS)-7,8-Isopropylidenedioxy heneicosanal (1 g) was dissolved in ether (5 ml) and added dropwise to the ethyl magnesium bromide with stirring and cooling under an atmosphere of nitrogen. After complete addition, the temperature of the reaction mixture was raised to 40° and it was refluxed for 1 h. under an atmosphere of nitrogen. The reaction mixture was diluted with water, acidified with cold dilute hydrochloric acid, extracted into ether and the organic layer was dried over anhydrous sodium sulphate. Solvent was removed and the gum (0.8 g) was chromatographed over silica gel. Elution with 2% ethyl acetate in benzene gave 3-hydroxy-9,10-isopropylidenedioxytricosane(6b)(0.54 g).

Removal of the acetonide group gave 3,9,10-trihydroxy tricosane m.p. 83° (Found: C, 73.8; H, 12.7. $C_{23}H_{48}O_3$ requires C, 74.2; H, 12.9%). IR(KBr): 3260-3300. ^{1}H NMR: 0.9(t, 3H, $-CH_3$), 3.4 [br, 3H, -CHOH and CH(OH)-CH(OH)].

(9RS,10RS)-9,10-dihydroxytricosane

3-Hydroxy-9,10-isopropylidenedioxytricosane (0.54 g) was tosylated using dry pyridine (1.8 ml) and p-toluene sulphonyl chloride (0.675 g) at 0° overnight.

The above tosylate was refluxed with sodium iodide (0.54 g) and zinc dust

(1.8 g) in glyme (7.2 ml) for 1.5 h. After work up, the gummy product was treated with dilute acid for removal of the acetonide group leading to (9RS,10RS)-9,10-dihydroxy tricosane. It crystallised from ethyl acetate - light petroleum (60-80°) (0.32 g) m.p. 65° (Found: C, 77.1; H, 13.0. $C_{23}H_{48}O_2$ requires C, 77.5; H, 13.4%). IR(KBr): 3200-3320. ^{1}H NMR: 0.88(t, 6H, -CH$_3$), 3.42(br, -CHOH-CHOH-).

(9RS,10SR)-9,10-Dihydroxytricosane

A mixture of (9RS,10RS)-9,10-dihydroxytricosane (0.15 g) and HBr-AcOH (48%) (0.5 ml) was kept at room temperature for 15 h. The reaction mixture was diluted with water and extracted into ethyl acetate. The organic extract was washed with aqueous sodium bicarbonate solution followed by water and dried over anhydrous sodium sulphate. After removal of the solvent a gum was obtained which was refluxed with aqueous sodium hydroxide (2N, 1 ml) for 6 h. and acidified. The residue was taken up in ethyl acetate and the organic layer was washed with water and dried over anhydrous sodium sulphate. Removal of the solvent gave (9RS,10RS)-9,10-epoxy-tricosane (0.10 g) as a gum (t.l.c. pure).

Ring opening by refluxing with glacial acetic acid (0.5 ml) for 8 h. followed by alkaline hydrolysis gave (9RS,10SR)-9,10-dihydroxy tricosane (0.09 g). It crystallised from ethyl acetate - light petroleum (60-80°) m.p. 90°(Found: C, 77.3; H, 13.2. $C_{23}H_{48}O_2$ requires C, 77.5; H, 13.4%). IR(KBr): 3200-3300. ^{1}H NMR: 0.88 (t, 6H, -CH$_3$), 3.60(br, -CHOH-CHOH).

(Z)-9-Tricosene (5)

(9RS,10SR)-9,10-Dihydroxy tricosane (20 mg), ethyl orthoformate (0.5 ml) and benzoic acid (2 mg) were mixed and heated in a flask carrying a thermometer. Bath temperature was slowly raised so that ethyl alcohol started slowly distilling (70-80°); it was maintained at this temperature till no more of ethanol distilled. The internal temperature was next slowly raised to 170° when carbon dioxide evolution started. When the evolution of gases practically ceased, the excess ethyl orthoformate was removed under reduced pressure. The residue was taken up in light petroleum (40-60°). The organic extract was washed with aqueous sodium bicarbonate solution, followed by water, and dried over anhydrous sodium sulphate. Removal of the solvent gave (Z)-9-tricosene (5) as an oil (10 mg) (Found: C, 85.3; H, 13.9. $C_{23}H_{46}$ requires C, 85.7; H, 14.3%). IR(film) 3000, 2900, 2800, 1460, 1380, 720. ^{1}H NMR: 0.9(t, 6H, -CH$_3$), 2.04(br, -CH$_2$-CH=CH-CH$_2$-), 5.36(br, -CH=CH-). LR-MS m/z: 322(M^+), 71(base peak).

(E)-9-Tricosene

(9RS,10RS)-9,10-Dihydroxy tricosane (20 mg) was converted to (E)-9-tricosene by a similar procedure (Found: C, 85.4; H, 14.0. $C_{23}H_{46}$ requires C, 85.7; H, 14.3%). IR(film): 3000, 2900, 2830, 1460, 1370, 960. ^{1}H NMR: 0.88(t, 6H, -CH$_3$), 1.94(br, -CH$_2$-CH=CH-CH$_2$-), 5.5(br, 2H, -CH=CH-). LR-MS m/z: 322(M^+), 83(base peak).

Methyl-16-(2-oxo-cyclohexylidene)-(E)-9-hexadecenoate (10)

A mixture of 1-morpholino-1-cyclohexene (1.67 g), methyl-16-oxo-(E)-9-hexadecenoate (9) (2.82 g) and cyclohexane (4 ml) was refluxed for 24 h. using Dean-Stark trap for water separation. The mixture was cooled to 40° and dilute hydrochloric acid (1.2 ml) was added to it slowly and the stirring was continued for 2 h. at room temperature. The reaction mixture was extracted into benzene. The organic extract was washed with water, dried over anhydrous sodium sulphate and concentrated to yield a gum (2.0 g) which was chromatographed over silica gel to obtain pure methyl-16-(2-oxo-cyclohexylidene)-(E)-9-hexadecenoate as a gum(10) (1.5 g). IR(film): 1740, 1685, 970. UV λ_{max}^{MeOH}: 241 nm. ^{1}H NMR: 1.95(br, -CH$_2$-CH=CH-CH$_2$-), 2.25(t, -CH$_2$-CO- and -CH$_2$COOCH$_3$), 3.6(s, -COOCH$_3$), 5.3(br, -CH=CH-), 6.35(t, 1H, -CO-C=CH-).

Methyl-16-(2-oxo-cyclohexyl)-hexadecanoate

Methyl-16-(2-oxo-cyclohexylidene)-(E)-9-hexadecenoate (8) (0.5 g) was hydrogenated in ethyl acetate solution (20 ml) using palladium charcoal (0.075 g) as catalyst. Work up gave a gum which was chromatographed over silica gel to obtain methyl-16-(2-oxo-cyclohexyl)-hexadecanoate (0.3 g) as a solid m.p. 60°. (Found: C, 75.0; H, 11.0. $C_{23}H_{42}O_3$ requires C, 75.4; H, 11.4%). IR(KBr): 1720, 1700. ^{1}H NMR: 2.2(t, -CH$_2$-CO- and -CH$_2$COOMe), 3.55(s, -COOCH$_3$).

(13RS,14RS)-13,14-Dihydroxy-7,21-dioxo heptacosa-1,27-dioic acid (4)

The above keto acid was prepared from (7RS,8RS)-7,8-dihydroxy pentadeca-1,15-dioic acid (2) (6 g) through the formation of diacetate, diacetate diacid chloride, enamine condensation with 1-morpholino-1-cyclohexene followed by alkaline hydrolysis as in the previous case. It crystallized from ethyl acetate - light petroleum (60-80°) (4.6 g) m.p. 100° (Found: C, 64.5; H, 9.1. $C_{27}H_{48}O_8$ requires C, 64.8; H, 9.6%). IR(KBr): 3200-3300, 2700, 1680-1700.

Its methyl ester (diazomethane procedure) crystallised from ethyl acetate - light petroleum m.p. 80°. (Found: C, 65.4; H, 9.3. $C_{29}H_{52}O_8$ requires C, 65.8; H, 9.8%). IR(KBr): 3300, 1735, 1700. ^{1}H NMR: 2.3(br, 12H, $-CH_2-C=O$), 3.3(br, 2H, -CHOH-CHOH-), 3.6(s, 6H, $-COOCH_3$).

Dimethyl(13RS,14RS)-13,14-dihydroxy heptacosa-1,27-dioate (7)

The dimethyl ester of diketo dicarboxylic acid (1.5 g) was reduced with sodium borohydride (1.5 g) in methanol to give dimethyl-7,13,14,21-tetrahydroxy-heptacosa-1,27-dioate (7)(1.4 g). It crystallized from ethyl acetate - light petroleum (60-80°) m.p. 95° (Found: C, 65.0; H, 10.4. $C_{29}H_{56}O_8$ requires C, 65.4; H, 10.5%). IR(KBr): 3260-3320, 1735. ^{1}H NMR: 2.3(t, 4H, $-CH_2-COO-$), 3.4(br, 4H, -CH-OH), 3.65(s, 6H, $-COOCH_3$).

The acetonide derivative of above tetrahydroxy ester was tosylated and reduced with Zn-NaI as described earlier. The acid hydrolysis of the reduced product gave crystalline dimethyl (13RS,14RS)-13,14-dihydroxy heptacosa-1,27-dioate, m.p. 57° (Found: C, 69.2; H, 11.0; $C_{29}H_{56}O_6$ requires C, 69.6; H, 11.2%). IR(KBr): 3200-3300, 1740. ^{1}H NMR: 3.3(br, 2H, -CHOH-CHOH), 3.6(s, 6H, $-COOCH_3$).

(13RS,14RS)-13,14-Dihydroxyheptacosane

The isopropylidene derivative of above diester (560 mg) was reduced with lithium aluminium hydride (1.0 g) in dry ether. Acid hydrolysis of the reduced product gave 1,13,14,27-tetrahydroxyheptacosane m.p. 78° (Found: C, 73.1; H, 12.6. $C_{27}H_{56}O_4$ requires C, 72.9; H, 12.6%). IR(KBr): 3350. ^{1}H NMR: 3.5(t, 6H, $-CH_2OH$ merged with the broad peak of -CHOH-CHOH-).

The acetonide of above tetrol was tosylated, reduced with Zn-NaI, and hydrolysed with acid to give (13RS,14RS)-13,14-dihydroxyheptacosane which crystallised from ethyl acetate - light petroleum (40-60°) m.p. 72° (Found: C, 78.2; H, 13.2. $C_{27}H_{56}O_2$ requires C, 78.6; H, 13.6%). IR(KBr): 3280-3320. ^{1}H NMR: 0.9 (t, 6H, $-CH_2-CH_3$), 3.35(br, 2H, -CHOH-CHOH-).

(E)-13-Heptacosene (8)

(13RS,14RS)-13,14-Dihydroxy heptacosane was converted into (E)-olefin according to Eastwood procedure as described earlier. (E)-13-Heptacosene was obtained as a gum (8). (Found: C, 85.3; H, 13.8. $C_{27}H_{54}$ requires C, 85.7; H, 14.2%). IR(neat): 3000-2900, 2840, 1450, 1370, 960. ^{1}H NMR: 0.88(t, 6H, $-CH_2CH_3$), 1.96(br, 4H, $-CH_2-CH=CH-CH_2$), 5.36(br, 2H, -CH=CH-), LR-MS m/z 378(M^+), 111(base peak).

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