

THE SYNTHESSES OF METHYL ESTERS OF PENTADECANOIC ACIDS WITH DOUBLE BRANCHED CHAIN

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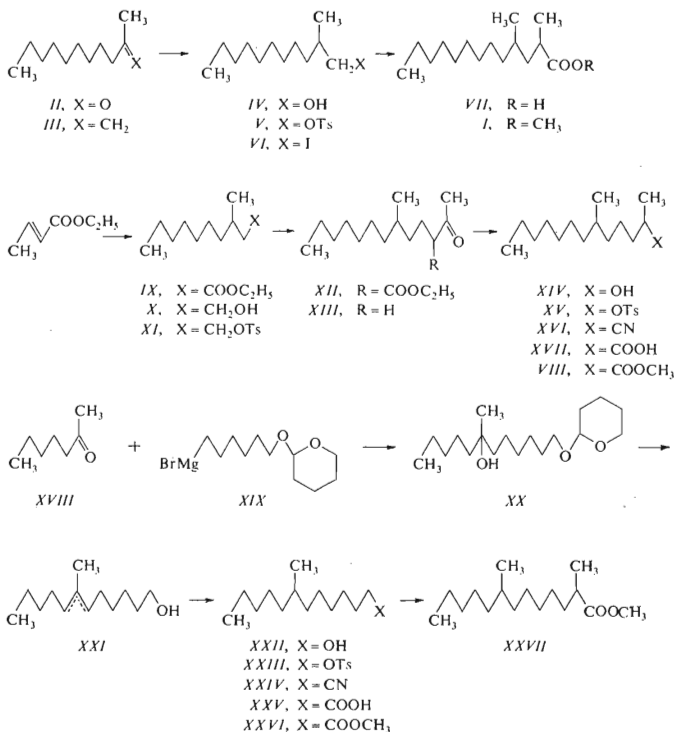
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Methyl 2,4-dimethyltridecanoate, methyl 2,6-dimethyltridecanoate and methyl 2,8-dimethyltridecanoate were prepared in order to identify the components of the lipidic fractions from scotochromogenous bacteria.

The lipidic fractions from scotochromogenous bacteria (*Mycobacterium gordonae* and *M. scrofulaceum*) contain branched acids¹ in addition to a number of fatty acids with a straight chain. The presence of fatty acids with a C₍₂₎-methyl has been demonstrated earlier² in *M. kansasii*. In a GC/MS analysis of a mixture of methyl esters obtained after working up the lipidic fractions from *M. gordonae* and *M. scrofulaceum* we found C₁₅ and C₁₆ fatty acids which contained a second methyl group in addition to the C₍₂₎-methyl. The position of this second methyl group could be determined tentatively by mass spectrometry on the basis of the well known fragmentation pattern of homologous methyl esters of branched C₈—C₁₃ fatty acids³⁻⁷. However, the relative abundances of the ions *m/e* 115, 129, 143, 157, 171, 185 and 199, characteristic of the position of the branching, change to a certain extent with the length of the aliphatic chain. Moreover, the presence of another methyl group in the positions C₍₁₀₎—C₍₁₂₎ cannot be excluded on the basis of a mere analogy. Therefore it was indispensable to synthesize the possible positional isomers and to compare their mass spectra directly with the spectra of the unknown components from natural material. The relative configuration of the methyls has no apparent effect^{6,7} on the mass spectra of aliphatic methyl esters, so that it suffices to prepare mixtures of diastereoisomers. Thus methyl esters of 2,4-, 2,6- and 2,8-dimethyltridecanoic acids were synthesized. These acids were found earlier (as esters) in the wax from the preen glands of the tufted duck⁸.

The synthetic procedures are illustrated in Scheme 1.

The synthesis of methyl 2,4-dimethyltridecanoate (*I*) started from 2-undecanone⁹ (*II*) which was converted to 2-methyl-1-undecene (*III*) (ref.¹¹) on reaction with triphenylmethylphosphorane¹⁰. Hydroboration/oxidation¹² of *III* afforded 2-methyl-1-undecanol (*IV*) (ref.¹³) which gave 1-iodo-2-methylundecane (*VI*) *via* the tosylate *V*. Reaction of *VI* with dilithium salt of propionic acid¹⁴ led to the acid *VII* the esterification of which gave methyl 2,4-dimethyltridecanoate (*I*) in the form of a 1 : 1



SCHEME 1

mixture of the two diastereoisomers. Both diastereoisomers could be resolved by gas chromatography and they gave identical mass spectra.

The synthesis of methyl 2,6-dimethyltridecanoate (*VIII*) is based on the addition of lithium di-*n*-heptyl cuprate to ethyl *trans*-crotonate¹⁵. The ethyl 3-methyldecanoate (*IX*) obtained already contains the future arrangement of the alkyl groups in the position C₍₆₎ of the ester *VIII*. The ester *IX* was reduced to 3-methyl-1-decanol (*X*) the tosylate of which afforded keto ester *XII* on reaction with the sodium salt of ethyl acetoacetate. When hydrolysed and decarboxylated¹⁶ *XII* gave 6-methyl-2-tridecanone (*XIII*) which was further converted to 2,6-dimethyltridecanonitrile (*XVI*) via 6-methyl-2-tridecanol (*XIV*) and tosylate *XV*. Hydrolysis of the nitrile *XVI* gave the acid *XVII* which was esterified to methyl ester *VIII*. The ester *VIII* gave a single peak in gas chromatography, but it is probable that *VIII* is a mixture of both diastereoisomers, which are inseparable under the given conditions.

The synthesis of methyl 2,8-dimethyltridecanoate (*XXVII*) started from 2-heptanone¹⁷ which afforded alcohol *XX* on reaction with Grignard's reagent prepared from 1-bromo-6-hexanol-*O*-tetrahydropyranyl ether¹⁸. The alcohol *XX* was not isolated. The protecting group was removed by acid hydrolysis, during which dehydration also took place under formation of 7-methyldodecen-1-ol (*XXI*) with an undetermined position of the double bond. When hydrogenated, alcohol *XXI* gave 7-methyl-1-dodecanol (*XXII*) which was tosylated to *XXIII* and converted to nitrile *XXIV*. Hydrolysis of the nitrile *XXIV* afforded 8-methyltridecanoic acid (*XXV*). Methyl ester *XXVI* prepared from acid *XXV* was methylated¹⁹ to *XXVII*. Ester *XXVII* is probably a mixture of both diastereoisomers, in spite of giving a single peak in gas chromatography. Methylation of *XXVI* in the position C₍₂₎, takes place reluctantly in comparison with the analogous methylmyristate. In order to achieve an 80% conversion the reaction time had to be prolonged three times.

The mass spectra of esters *I*, *VIII* and *XXVII* contain ions characteristic⁵ of branched chains in the position C₍₂₎, C₍₄₎ or C₍₂₎, C₍₆₎ or C₍₂₎, C₍₈₎, respectively. The relative abundances of these ions differ to a certain extent, however, from the data published for lower homologues⁵. The differences will be discussed elsewhere¹.

EXPERIMENTAL

The mass spectra were measured on a spectrometer JEOL JMS D-100, 75 eV, using the direct inlet technique or in combination with a gas chromatograph (column SE-30, 3% on Chromosorb W). The refractive indices were determined on an Abbé refractometer. The infrared spectra were measured on a Zeiss UR-20 (Jena) spectrophotometer. The course of reactions and the purity of the compounds was checked by thin-layer chromatography on Kieselguhr, Merck, and gas chromatography (SE-30). The "conventional work-up" means that the extract was washed with 5% sodium hydrogen carbonate, dried over sodium sulfate and evaporated on a rotary evaporator. 2-Undecanone⁹, 2-heptanone¹⁷ and 1-bromo-6-hexanol²⁰ were prepared by standard procedures and their physical constants and the spectra were in agreement with the literature data.

2-Methyl-1-undecane (*III*)

A solution of 2-undecanone (2.1 g) in 20 ml of ether was added dropwise at 0°C and under argon to a solution of 14 mmol of triphenylmethylphosphorane in 30 ml of ether. The mixture was stirred at 0°C for 30 min and then refluxed for 2 h. Water (5 ml) and light petroleum (20 ml) were then added to the mixture and the organic phase was worked up in the conventional manner. Distillation of the residue gave 1.64 g (79%) of chromatographically pure *III*, b.p. 87°C/1.6 kPa, n_D^{20} 1.4340, lit.¹³ gives n_D^{20} 1.4323.

2-Methyl-1-undecanol (*IV*)

2-Methyl-1-undecene *III* (1.6 g) was hydroborated by a standard procedure¹². Yield, 1.59 g (90%) of alcohol *IV*, b.p. 125°C/2 kPa, n_D^{20} 1.4396, lit.¹³ gives n_D^{20} 1.4382.

2-Methyl-1-iodoundecane (*VI*)

A mixture of alcohol *IV* (1.52 g), *p*-toluenesulfonyl chloride (1.66 g) and pyridine (5 ml) was allowed to stand at 0°C for 24 h. Chloroform (40 ml) was added and the solution washed with 10% HCl and worked up in the conventional manner. Yield, 2.42 g of an oily tosylate, *V*, which was refluxed with sodium iodide (2.1 g) in acetone (50 ml) for 6 h. A part of the acetone was distilled off *in vacuo*, light petroleum was added to the residue, the separated salts were filtered off under suction and the solvents from the filtrate were evaporated. The residue was distilled *in vacuo*. Yield, 1.89 g (93%) of iodide *VI*, b.p. 108–110°C/13 Pa, n_D^{20} 1.4801. For C₁₂H₂₅I (296.2) calculated: 48.66% C, 8.51% H, 42.84% I; found: 48.39% C, 8.63% H, 43.30% I. Mass spectrum (*m/e*): 296 (M⁺), 169 (M–I)⁺.

2,4-Dimethyltridecanoic Acid (*VII*)

Propionic acid (740 mg) was refluxed with lithium hydride (88 mg) and hexamethylphosphoric triamide (2 ml) in 10 ml of tetrahydrofuran for 2 h. The suspension of lithium propionate was added under argon and at 0°C to a solution of lithium diisopropylamide (prepared from 1.11 g of diisopropylamine and 11 mmol of *n*-butyllithium) in 20 ml of tetrahydrofuran. The mixture was stirred at 0°C for 30 min and at 40°C for 2 h, the iodide *VI* (1.80 g) was then added and the mixture refluxed for 12 h. After acidification to pH 3 the product was extracted with ether and worked up in the conventional manner. Column chromatography on silica gel (elution with light petroleum–ether, 2 : 1) gave 550 mg of acid *VII*, b.p. 150–152°C/13 Pa. For C₁₅H₃₀O₂ (242.4) calculated: 74.32% C, 12.48% H; found: 74.57% C, 12.60% H. IR spectrum (film): 3300 to 2500, 1722, 1475, 1425, 1390, 1300, 1250, 960 cm⁻¹. Mass spectrum (*m/e*): 242 (M⁺), 199, 171, 169, 87, 74, 57 (base peak).

Methyl 2,4-Dimethyltridecanoate (*I*)

A solution of acid *VII* (300 mg) and *p*-toluenesulfonic acid (100 mg) in 20 ml of methanol was refluxed for 15 h. Methanol was distilled off, light petroleum was added to the residue and the mixture worked up in the conventional manner. Distillation gave 285 mg (90%) of ester *I*, b.p. 115°C/13 Pa, n_D^{20} 1.4392. For C₁₆H₃₂O₂ (256.4) calculated: 74.95% C, 12.58% H; found: 75.13% C, 12.43% H. IR spectrum (liquid film): 1146, 1470, 1440, 1386, 1265, 1200, 1175, 1095 cm⁻¹; mass spectrum (*m/e*): 256 (M⁺), 225, 213, 197, 185, 169, 129, 101, 88 (base peak).

Ethyl 3-Methyldecanoate (*IX*)

A 1M- $n\text{-C}_7\text{H}_{15}\text{Li}$ solution (25 ml) in hexane was added to a stirred suspension of cuprous iodide (3.7 g) in ether (30 ml) at -40°C under argon and after 30 min a solution of ethyl *trans*-crotonate (2 g) in 10 ml of ether was added to the mixture. This was then stirred at -20°C for 5 h, poured into 50 ml of 0.1M-HCl and the organic layer separated and worked up as usual. Distillation gave 3 g (83%) of ester *IX*, b.p. $125-130^\circ\text{C}/1.3\text{ kPa}$; n_{D}^{20} 1.4305. For $\text{C}_{13}\text{H}_{26}\text{O}_2$ (214.3) calculated: 72.86% C, 12.23% H; found: 73.01% C, 12.15% H. IR spectrum (liquid film): 1748, 1475, 1380, 1310, 1290, 1250, 1170, 1130, 1040 cm^{-1} ; mass spectrum (*m/e*): 214 (M^+), 171, 169, 157, 143, 115, 88 (base peak).

3-Methyl-1-decanol (*X*)

Ester *IX* (2.8 g) was reduced with lithium aluminum hydride (500 mg) in ether. After the conventional work-up 1.76 g (78%) of alcohol *X* were obtained, n_{D}^{20} 1.4379. For $\text{C}_{11}\text{H}_{24}\text{O}$ (172.3) calculated: 76.68% C, 14.04% H; found: 76.49% C, 14.18% H. IR spectrum (liquid film): 3600, 3350, 1475, 1385, 1065, 1020 cm^{-1} ; mass spectrum (*m/e*): 171 ($\text{M}-\text{H}^+$), 154, 126, 111, 97, 83, 70 (base peak), 31.

Ethyl 2-Acetyl-5-methyldodecanoate (*XII*)

A mixture of alcohol *X* (1.74 g), *p*-toluenesulfonyl chloride (2 g) and pyridine (5 ml) was allowed to stand at 20°C for 72 h. The mixture was poured into water, the product was extracted with chloroform and worked up in the conventional manner. The obtained tosylate *XI* gave a single spot on a thin-layer chromatogram and it was further worked up. Ethyl acetoacetate (1.7 g) in 5 ml of tetrahydrofuran was added to sodium hydride (320 mg), and after 30 min dry sodium iodide (2 g) and a solution of tosylate *XI* in 5 ml of tetrahydrofuran were added to the mixture. This was then refluxed for 24 h, acidified with acetic acid, the solvents were evaporated, and the residue treated with 5% of NaHCO_3 . The product was extracted with ether and worked up in the conventional manner. Column chromatography on silica gel (elution with light petroleum-ether 2 : 1) gave 1020 mg (36%) of keto ester *XII*. For $\text{C}_{17}\text{H}_{32}\text{O}_3$ (284.4) calculated: 71.80% C, 11.34% H; found: 71.56% C, 11.12% H. IR spectrum (liquid film): 1755, 1730, 1475, 1375, 1368, 1250, 1190, 1160 cm^{-1} ; mass spectrum (*m/e*): 284 (M^+), 266, 242, 199, 171, 157, 143, 130 (base peak), 115, 101, 88, 73, 43.

6-Methyl-2-tridecanone (*XIII*)

Keto-ester *XII* (980 mg) was heated in a mixture of water (1 ml) and dimethyl sulfoxide (10 ml) at 165°C for 6 h. After cooling the mixture was poured into water, the product extracted with pentane and worked up in the conventional manner. Distillation at $110^\circ\text{C}/13\text{ Pa}$ (bath temperature) gave 550 mg (75%) of ketone *XIII*, n_{D}^{20} 1.4352. For $\text{C}_{14}\text{H}_{28}\text{O}$ (212.4) calculated: 79.17% C, 13.29% H; found: 79.98% C, 13.25% H. IR spectrum (liquid film): 1732, 1475, 1422, 1385, 1370, 1160 cm^{-1} ; mass spectrum (*m/e*): 212 (M^+), 197, 194, 169, 138, 125, 109, 95, 85, 71, 58 (base peak), 43.

6-Methyl-2-tridecanol (*XIV*)

Ketone *XIII* (500 mg) was reduced with lithium aluminum hydride (100 mg) in ether. After the conventional work-up 470 mg (93%) of alcohol *XIV* were obtained, n_{D}^{20} 1.4401. For $\text{C}_{14}\text{H}_{30}\text{O}$

(214.4) calculated: 78.43% C, 14.10% H; found: 78.66% C, 14.00% H. IR spectrum (liquid film): 3600, 3350, 1470, 1385, 1060, 1035 cm^{-1} . Mass spectrum (m/e): 199 ($\text{M}-\text{CH}_3$)⁺, 196 ($\text{M}-\text{H}_2\text{O}$)⁺, 140, 125, 112, 97, 45 (base peak).

2,6-Dimethyltridecanonitrile (XVI)

Alcohol XIV (430 mg) was tosylated with *p*-toluenesulfonyl chloride (430 mg) in pyridine (at 20°C for 24 h). The mixture was poured into water and the product extracted with chloroform and worked up in the conventional manner. The crude tosylate (a single spot in thin-layer chromatography) was heated with sodium cyanide (1 g) in 5 ml of dimethyl sulfoxide at 100°C for 5 h. The mixture was poured into water, the product extracted with pentane and worked up in the conventional manner. Distillation at 130–140°C/13 Pa (bath temperature) gave 355 mg (79%) of nitrile XVI, n_{D}^{20} 1.4371. For $\text{C}_{15}\text{H}_{29}\text{N}$ (223.4) calculated: 85.22% C, 13.83% H; found: 84.83% C, 13.55% H. IR spectrum (liquid film): 2255, 1480, 1390 cm^{-1} ; mass spectrum (m/e): 223 (M^+), 222, 208, 194, 180, 166, 152, 138, 125 (base peak), 124.

2,6-Dimethyltridecanoic Acid (XVII)

A solution of nitrile XVI (320 mg) and sodium hydroxide (500 mg) in 10 ml of 50% aqueous ethanol was refluxed for 24 h. The mixture was acidified with 5% HCl, the product extracted with chloroform and the extract worked up in the conventional manner. Yield 280 mg (81%) of acid XVII, n_{D}^{20} 1.4362. For $\text{C}_{15}\text{H}_{30}\text{O}_2$ (242.4) calculated: 74.32% C, 12.48% H; found: 74.27% C, 12.55% H. IR spectrum (liquid film): 3300–2500, 1725, 1480, 1430, 1390, 1300, 1250, 950 cm^{-1} ; mass spectrum (m/e): 242 (M^+).

Methyl 2,6-Dimethyltridecanoate (VIII)

A mixture of acid XVII (250 mg), *p*-toluenesulfonic acid (50 mg) and methanol (30 ml) was refluxed for 8 h. Methanol was distilled off under reduced pressure, the residue dissolved in pentane and worked up in the conventional manner. Distillation at 120–125°C/13 Pa (bath temperature) gave 252 mg (95%) of ester VIII, n_{D}^{20} 1.4389. For $\text{C}_{16}\text{H}_{32}\text{O}_2$ (256.4) calculated: 74.95% C, 12.58% H; found: 74.67% C, 12.71% H. IR spectrum (liquid film): 1746, 1470, 1435, 1380, 1205, 1180 cm^{-1} ; mass spectrum (m/e): 256 (M^+), 241, 225, 213, 207, 200, 185, 166, 157, 129, 101, 88 (base peak).

7-Methyldodecen-1-ol (XXI)

1-Bromo-6-hexanol-O-tetrahydropyranyl ether (XIX) (5.1 g) in 20 ml of tetrahydrofuran was added dropwise and under reflux to a suspension of 550 mg of magnesium in 20 ml of tetrahydrofuran. After 3 h refluxing 2-heptanone (XVIII, 1.8 g) was added and the mixture refluxed for another 3 h. Water was added (5 ml), followed by sulfuric acid until the mixture had pH 2 and it was refluxed for 8 h. The product was extracted with benzene and worked up in the conventional manner. After chromatography on a silica gel column (elution with light petroleum–ether 2 : 1) and distillation 2.3 g (61%) of alcohol XXI, b.p. 108–115°C/13 Pa, were obtained, n_{D}^{20} 1.4389. For $\text{C}_{13}\text{H}_{26}\text{O}$ (198.3) calculated: 78.74% C, 13.22% H; found: 78.93% C, 13.10% H. IR spectrum (liquid film): 3600, 3360, 1475, 1390, 1130, 1080, 1060, 1040 cm^{-1} .

7-Methyl-1-dodecanol (XXII)

Alcohol XXI (2.25 g) was hydrogenated on platinum (150 mg) in ethanol. After working up and distillation 2.20 g (92%) of alcohol XXII were obtained, b.p. 110°C/13 Pa, n_D^{20} 1.4381. For $C_{13}H_{28}O$ (200.4) calculated: 77.91% C, 14.08% H; found: 78.22% C, 13.89% H. IR spectrum (liquid film): 3600, 3360, 1475, 1380, 1080, 1060, 1040 cm^{-1} .

8-Methyltridecanonitrile (XXIV)

Alcohol XXII (2 g) was tosylated with *p*-toluenesulfonyl chloride (1.95 g) in pyridine (5 ml) at 20°C for 16 h. The mixture was poured into 20 ml of 5% HCl, the product extracted with chloroform and worked up in the conventional manner. The crude tosylate XXIII (giving a single spot on thin-layer chromatography) was added to a solution of sodium cyanide (1.2 g) in dimethyl sulfoxide and the mixture was heated at 110°C for 3 h. After cooling the mixture was poured into water, the product was extracted with pentane and worked up in the conventional manner. Distillation of the residue gave 1.53 g (73%) of nitrile XXIV, b.p. 108–110°C/40 Pa, n_D^{20} 1.4375. For $C_{14}H_{27}N$ (209.4) calculated: 80.30% C, 13.00% H; found: 80.65% C, 12.82% H. IR spectrum (liquid film): 2255, 1470, 1435, 1385 cm^{-1} ; mass spectrum (*m/e*): 209 (M^+), 208, 194, 180, 166, 152, 138, 111, 110.

8-Methyltridecanoic Acid (XXV)

Nitrile XXIV (1.45 g) was hydrolysed with sodium hydroxide (2 g) in boiling 50% aqueous ethanol for 24 h. Ethanol was distilled off, the residue acidified with 5% HCl, the product extracted with chloroform and worked up in the conventional manner. Column chromatography on silica gel (elution with light petroleum–ether 1 : 1) afforded 1.15 g (73%) of acid XXV, n_D^{20} 1.4336. For $C_{14}H_{28}O_2$ (228.4) calculated: 73.62% C, 12.35% H; found: 73.47% C, 12.39% H. IR spectrum (liquid film): 3300–2500, 1725, 1480, 1430, 1390, 1300, 1250, 950 cm^{-1} ; mass spectrum (*m/e*): 228 (M^+), 185, 157, 143, 129, 87, 73, 60, 57 (base peak).

Methyl 8-Methyltridecanoate (XXVI)

Esterification of acid XXV (1.05 g) by the procedure given for I afforded 940 mg (84%) of ester XXVI, n_D^{20} 1.4369; IR spectrum (liquid film): 1745, 1470, 1435, 1380, 1195, 1180 cm^{-1} ; mass spectrum (*m/e*): 242 (M^+), 211, 199, 183, 171, 157, 143, 139, 129, 87, 74 (base peak).

Methyl 2,8-Dimethyltridecanoate (XXVII)

Ester XXVI (520 mg) in tetrahydrofuran (6 ml) was added at –78°C under argon to a solution of 2.8 mmol of lithium diisopropylamide (prepared from 2.8 mmol of diisopropylamine and 2.9 mmol of *n*-butyllithium) in 10 ml of tetrahydrofuran. The mixture was stirred at –78°C for 2 h, methyl iodide (700 mg) and hexamethylphosphoric triamide (600 mg) in tetrahydrofuran (5 ml) were added and the mixture stirred first at –20°C for 5 h and then at 20°C for another 12 h. After acidification with 5% HCl the product was extracted with light petroleum and then worked up in the conventional manner. Yield, 490 mg of a mixture of 70% of XXVI and 30% of XXVII (according to GC/MS analysis). The methylation of the mixture was repeated twice until the ratio was 20% of XXVI and 80% of XXVII. The mixture was separated by column chromatography on silica gel (elution with light petroleum–ether, 12 : 1), affording 390 mg (71%) of ester XXVII, n_D^{20} 1.4394. For $C_{16}H_{32}O_2$ (256.4) calculated: 74.95% C, 12.58% H; found: 74.79% C, 12.66% H. IR spectrum (liquid film): 1746, 1468, 1440, 1382, 1190 cm^{-1} ; mass spectrum (*m/e*): 256 (M^+), 225, 213, 199, 157, 143, 129, 101, 88 (base peak).

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