# INFRARED SPECTRA OF COMPOUNDS WITH THE METHOXYMETHYL PROTECTING GROUP

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Infrared spectra of a series of compounds containing the $CH_3OCH_2O$— (MOM—O—) group have been studied. All the spectra exhibit three characteristic strong absorption bands due to coupled stretching vibrations of C—O—C—O—C grouping in the region 1 200—1 000 $cm^{-1}$.

The methoxymethyl (MOM) group gains recently importance as a hydroxyl-protecting group[1]. It has been successfully employed in many syntheses also in our Laboratory[2-11]. Since rapid identification of this group was needed during the synthetic work, we developed a detection method based on the infrared spectroscopy.

We have extended the series of the already prepared and measured compounds by known[12] (*VI*, *VII* and *XIII*), as well as new (*I*, *II*, *V*, *XII*, *XIV*, *XX*, *XXXI* and *XLII*) compounds, prepared by simple reaction sequences. The $CH_3OCH_2O$ group was introduced mainly by reaction of the parent hydroxy derivative with chloromethyl methyl ether in the presence of base[12] (compounds *II*, *V*, *XII* and *XX*), the only exception being 1-octadecanol which was treated with dimethoxymethane using iodotrimethylsilane as catalyst[13]. Most of the 55 compounds measured are steroids containing the $CH_3OCH_2O$ group in position 3 (27 compounds) or 25 (10 compounds).

Infrared bands due to the $CH_3OCH_2O$ group belong to several types of vibrations[14-20]. Analytically significant bands have been found in the region 1 200 to 1 000 $cm^{-1}$. All spectra measured by us exhibited three very strong bands due to coupled stretching vibrations of the C—O—C—O—C grouping (Table I) whose wavenumbers and intensities (comparable with intensities of C=O stretching vibration bands) are in the following ranges; antisymmetric vibration band at 1 144 to 1 153 $cm^{-1}$ ($E$ = 160–300 $mol^{-1}$ l $cm^{-1}$), symmetric vibration band 1 094 to 1 112 $cm^{-1}$ ($E$ = 210–380 $mol^{-1}$ l $cm^{-1}$) and antisymmetric vibration band at 1 039–1 052 $cm^{-1}$ ($E$ = 310–700 $mol^{-1}$ l $cm^{-1}$). The approximate intensity ratio of the respective bands is 2 : 3 : 5 (Table I). The remaining symmetrical C—O—C—O—C vibration that appears at about 850 $cm^{-1}$ is very weak.

TABLE I

Characteristic IR bands for the methoxymethoxy ethers *I*—*LV*

| Compound[a] | $\nu_{(asym)}$[b] | $\nu_{(sym)}$[b] | $\nu_{(asym)}$[b] | $\delta_{(OCH_2O)}$[b] | $\nu_{(C=O)}$[b] |
|---|---|---|---|---|---|
| *I* | 1 047(310) | 1 111(280) | 1 148(165) | 919(115) | — |
| *II* | 1 043(395) | 1 112(320) | 1 149(280) | 922(115) | — |
| *III*[c] | 1 048(425) | 1 111(350) | 1 147(160) | 921(120) | — |
| *IV*[c] | 1 052(685) | 1 104(225) | 1 153(360) | 923(115) | — |
| *V* | 1 047(590) | 1 094(205) | 1 144(215) | 916(115) | — |
| *VI*[d] | 1 046(540) | 1 106(280) | 1 150(215) | 914(100) | — |
| *VII*[d] | 1 042(515) | 1 107(280) | 1 146(190) | 914(105) | — |
| *VIII*[e] | 1 047(420) | 1 107(235) | 1 150(220) | 915(100) | 1 706(345) |
| *IX*[e] | 1 045(555) | 1 106(320) | 1 147(645) | 915(100) | 1 715(450) |
| *X*[e] | 1 047(425) | 1 102(215) | 1 146(180) | 918(105) | 1 706(305) |
| *XI*[e] | 1 057(400) | 1 101(165) | 1 148(420) | 918(105) | 1 713(280) |
| *XII* | 1 051(555) | 1 107(240) | 1 147(290) | 917(120) | — |
| *XIII*[d] | 1 049(530) | 1 108(360) | 1 150(300) | 920(110) | — |
| *XIV* | 1 039(565) | 1 107(350) | 1 150(280) | 918(100) | — |
| *XV*[f] | 1 044(570) | 1 109(350) | 1 150(295) | 919(105) | — |
| *XVI*[g] | 1 048(650) | 1 108(355) | 1 150(300) | 919(110) | — |
| *XVII*[g,h] | 1 040(560) | 1 102(340) | 1 148(295) | 912(100) | — |
| *XVIII*[f] | 1 050(450) | 1 111(280) | 1 152(235) | 918(110) | — |
| *XIX*[g] | 1 048(465) | 1 108(320) | 1 150(275) | 917(125) | 1 728(380) |
| *XX* | 1 043(740) | 1 108(365) | 1 149(295) | 917(110) | 1 741(775) |
| *XXI*[i] | 1 047(665) | 1 109(370) | 1 150(340) | 918(115) | 1 708(560) |
| *XXII*[j] | 1 044(610) | 1 104(385) | 1 148(345) | 915(100) | 1 720(305) |
| *XXIII*[h,i] | 1 042(330) | 1 106(330) | 1 149(255) | 912(105) | 1 727(240) |
| *XXIV*[h,j] | 1 040(590) | 1 104(345) | 1 148(275) | 913(115) | 1 720(200) |
| *XXV*[h,i] | 1 038(610) | 1 100(320) | 1 146(285) | 909(105) | 1 703(195) |
| *XXVI*[h,j] | 1 040(560) | 1 105(305) | 1 148(255) | 913(100) | 1 716(200) |
| *XXVII*[h,i] | 1 038(420) | 1 101(215) | 1 146(185) | 903(105) | 1 704(250) |
| *XXVIII*[h,j] | 1 036(580) | 1 100(330) | 1 148(270) | 910(105) | 1 715(315) |
| *XXIX*[i] | 1 034(405) | 1 102(215) | 1 148(165) | 912(110) | 1 722(240) |
| *XXX*[h,j] | 1 042(560) | 1 105(295) | 1 149(250) | 913(105) | 1 738(205) |
| *XXXI* | 1 045(560) | 1 106(310) | 1 148(250) | 916(115) | 1 736(455) |
| *XXXII*[f] | 1 048(660) | 1 108(375) | 1 150(455) | 920(120) | 1 736(670) |
| *XXXIII*[g] | 1 044(670) | 1 109(375) | 1 150(425) | 919(110) | 1 741(535) |
| *XXXIV*[k] | 1 038(485) | 1 108(275) | 1 150(305) | 916(100) | 1 742(430) |
| *XXXV*[k] | 1 048(450) | 1 108(280) | 1 151(375) | 917(100) | 1 743(425) |
| *XXXVI*[e,h] | 1 042(615) | 1 103(350) | 1 150(665) | 912(100) | 1 706(455) |
| *XXXVII*[f] | 1 038(450) | 1 106(275) | 1 156(300) | 914(120) | 1 760(825) |
| *XXXVIII*[f] | 1 044(480) | 1 106(260) | 1 149(270) | 916(100) | 1 763(670) |
| *XXXIX*[l] | 1 048(435) | 1 110(275) | 1 150(245) | 918(105) | — |
| *XL*[f] | 1 043(515) | 1 108(315) | 1 149(305) | 916(120) | — |
| *XLI*[g] | 1 041(470) | 1 106(310) | 1 149(315) | 914(105) | — |

TABLE I
(*Continued*)

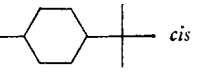
| Compound[a] | $\nu_{(asym)}$[b] | $\nu_{(sym)}$[b] | $\nu_{(asym)}$[b] | $\delta_{(OCH_2O)}$[b] | $\nu_{(C=O)}$[b] |
|---|---|---|---|---|---|
| *XLII* | 1 045(645) | 1 107(395) | 1 150(305) | 916(185) | — |
| *XLIII*[k] | 1 048(460) | 1 107(315) | 1 150(220) | 918(125) | — |
| *XLIV*[e] | 1 047(535) | 1 109(320) | 1 152(295) | 917(110) | 1 708(390) |
| *XLV*[c] | 1 048(560) | 1 110(330) | 1 150(570) | 918(100) | 1 716(405) |
| *XLVI*[c] | 1 040(325) | 1 111(250) | 1 149(190) | 920(105) | — |
| *XLVII*[c] | 1 040(355) | 1 110(275) | 1 148(260) | 921(105) | — |
| *XLVIII*[m] | 1 050(390) | 1 112(340) | 1 150(255) | 921(130) | — |
| *IL*[m] | 1 047(375) | 1 113(330) | 1 150(240) | 921(115) | — |
| *L*[c] | 1 044(370) | 1 110(265) | 1 150(215) | 920(120) | — |
| *LI*[c] | 1 045(365) | 1 110(255) | 1 150(210) | 921(125) | — |
| *LII*[c] | 1 044(335) | 1 110(220) | 1 149(190) | 920(100) | — |
| *LIII*[c] | 1 044(350) | 1 110(220) | 1 149(190) | 920(105) | — |
| *LIV*[c] | 1 048(440) | 1 100(145) | 1 150(220) | 923(110) | — |
| *LV*[c] | 1 046(460) | 1 100(150) | 1 150(215) | 923(100) | — |

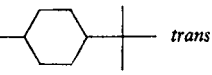
[a] Measured on a Perkin–Elmer 580 spectrometer, cell thickness 0·01 cm, in tetrachloromethane, $c = 0{\cdot}1$ mol $l^{-1}$, unless stated otherwise; [b] wavenumbers in $cm^{-1}$, numbers in parentheses are molar absorption coefficients in 1 $mol^{-1}$ $cm^{-1}$; [c] preparation of the compound described in ref.[4]; [d] preparation in ref.[8]; [e] preparation in ref.[9]; [f] preparation in ref.[3]; [g] preparation in ref.[8]; [h] measured in chloroform; [i] preparation in ref.[6]; [j] preparation in ref.[7]; [k] preparation in ref.[11]; [l] preparation in ref.[10]; [m] preparation in ref.[2].

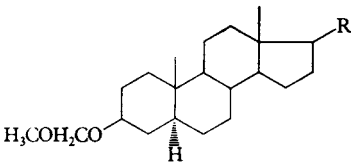
In the spectra of compounds with another single C—O bond, the C—O stretching vibration band of this bond may overlap with some of the three main bands of the C—O—C—O—C grouping. Such an overlap increases the intensity of the band in question, as *e.g.* in the case of the ester *XXXII* where the band of the first antisymmetric vibration overlaps with the C—O stretching vibration band of the ester group. Spectrum of the corresponding ester *LVIII* which does not contain the $CH_3OCH_2O$ grouping, exhibits a C—O stretching vibration band at 1 156 $cm^{-1}$ ($E = 200$ $mol^{-1}$ l $cm^{-1}$). A similar situation exists with the homologous ester *XXXIII* (the corresponding derivative *LIX* has a C—O band at 1 155 $cm^{-1}$ ($E = 135$ $mol^{-1}$ l $cm^{-1}$)). In the spectrum of the secondary alcohol *XIV* and the primary alcohol *XVI* the C—O stretching vibration band overlaps with the band of the third, antisymmetric, vibration of the C—O—C—O—C grouping; for the respective model alcohols *LVI* and *LVII* the C—O band occurs at 1 047 $cm^{-1}$ ($E = 115$ $mol^{-1}$ l $cm^{-1}$) and 1 045 $cm^{-1}$ ($E = 90$ $mol^{-1}$ l $cm^{-1}$).

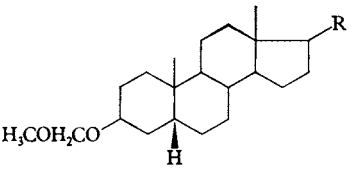
$CH_3OCH_2OR$

*I*, R = $(CH_2)_{17}CH_3$
*II*, R = $CH_2CH_2CH_2Cl$
*III*, R = $CH_2CH_2CH_2I$
*IV*, R = $CH_2C{\equiv}CH$

*V*, R =  *cis*

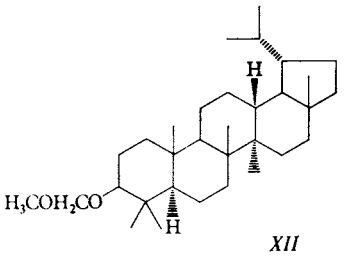
*VI*, R =  *trans*



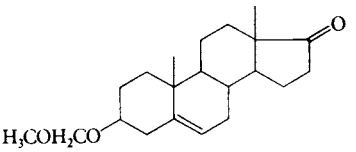


*VII*, R = $CH(CH_3)CH_2CH_2CH_2CH(CH_3)_2$
*VIII*, R = $COCH_3$
*IX*, R = $C(CH_3){=}CHCOOCH_2CH_3$ (20*E*)

*X*, R = $COCH_3$
*XI*, R = $C(CH_3){=}CHCOOCH_2CH_3$ (20*E*)



*XII*

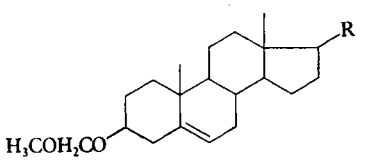


*XX*

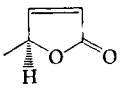
Spectra of all the studied compounds containing the $CH_3OCH_2O$ group display also another band at 923–914 $cm^{-1}$ ($E$ = 100–185 $mol^{-1}$ l $cm^{-1}$), probably due to rocking vibration of the methylene in the O—$CH_2$—O grouping[18]. This assignment is confirmed also by spectra of compounds *LX*–*LXV* in which one or both hydrogen atoms of the methylene group are replaced by a methylene group. These compounds were prepared by reaction of the corresponding alcohols with unsaturated ethers (ethoxyethylene, 2-methoxypropene), catalyzed with pyridinium *p*-toluenesulfonate[21]. Their spectra exhibit no rocking vibration band; the substitution also affects the position and intensity ratios of the C—O—C—O—C stretching vibration bands (Table II).

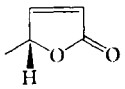
## EXPERIMENTAL

Melting points were determined on a Boetius melting point microscope (G.D.R.). Optical rotations were measured in chloroform on a Perkin–Elmer 141 MC instrument, $^1H$ NMR spectra on a Tesla BS-467 (60 MHz) spectrometer in deuteriochloroform with tetramethylsilane as



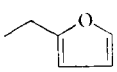
*XIII*, R = $CH(CH_3)CH_2CH_2CH_2CH(CH_3)_2$
*XIV*, R = OH
*XV*, R = $CH_2OH$
*XVI*, R = $CH_2CH_2OH$
*XVII*, R = $CH_2CH(OH)C{\equiv}CCH_2OH$
*XVIII*, R = CHO
*XIX*, R = $CH_2CHO$
*XXI*, R = $COCH_3$
*XXII*, R = $CH_2COCH_3$
*XXIII*, R = $COCH_2Cl$
*XXIV*, R = $CH_2COCH_2Cl$
*XXV*, R = $COCH_2Br$
*XXVI*, R = $CH_2COCH_2Br$
*XXVII*, R = $COCH_2OH$
*XXVIII*, R = $CH_2COCH_2OH$
*XXXIX*, R = $COCH_2OMes$
*XXX*, R = $CH_2COCH_2OMes$
*XXXI*, R = OAc
*XXXII*, R = $COOCH_3$
*XXXIII*, R = $CH_2COOCH_3$
*XXXIV*, R = $CH_2CH_2COOCH_3$
*XXXV*, R = $CH_2CH(COOCH_3)_2$
*XXXVI*, R = $C(CH_3){=}CHCOOCH_2CH_3$ (20*E*)

*XXXVII*, R = 

*XXXVIII*, R = 

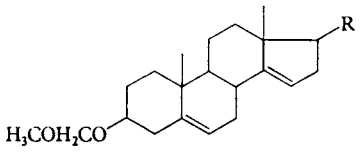
*XXXIX*, R = $C(CH_3){=}CHCN$ (20*E*)

*XL*, R = 

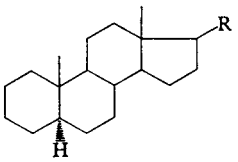
*XLI*, R = 

*XLII*, R = OTos

*XLIII*, R = $CH_2OTos$



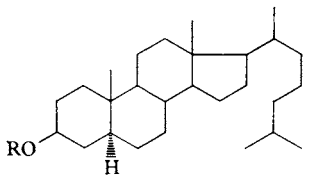

*XLIV*, R = $COCH_3$
*XLV*, R = $C(CH_3)$=$CHCOOCH_2CH_3$ (20*E*)



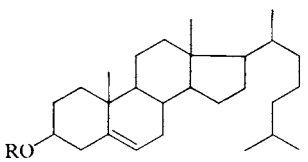

*XLVI*, R = $CH$=$CHCH_2CH_2CH_2OCH_2OCH_3$ (20*Z*)
*XLVII*, R = $C$≡$CCH_2CH_2CH_2OCH_2OCH_3$
*XLVIII*, R = $CH(OH)CH_2CH_2CH_2CH_2OCH_2OCH_3$ (20*R*)
*IL*, R = $CH(OH)CH_2CH_2CH_2CH_2OCH_2OCH_3$ (20*S*)
*L*, R = $CH_2CH(OH)CH_2CH_2CH_2OCH_2OCH_3$ (22*R*)
*LI*, R = $CH_2CH(OH)CH_2CH_2CH_2OCH_2OCH_3$ (22*S*)
*LII*, R = $CH(OH)CH(OH)CH_2CH_2CH_2OCH_2OCH_3$ (20*R*, 22*S*)
*LIII*, R = $CH(OH)CH(OH)CH_2CH_2CH_2OCH_2OCH_3$ (20*S*, 22*R*)
*LIV*, R = $CH_2CH(OH)C$≡$CCH_2OCH_2OCH_3$ (22*R*)
*LV*, R = $CH_2CH(OH)C$≡$CCH_2OCH_2OCH_3$ (22*S*)
*LVI*, R = $OH$
*LVII*, R = $CH_2CH_2OH$
*LVIII*, R = $COOCH_3$
*LIX*, R = $CH_2COOCH_3$

$CH_3(CH_2)_{16}CH_2OR$

*LX*, R = $CH(CH_3)OCH_2CH_3$
*LXI*, R = $C(CH_3)_2OCH_3$




*LXII*, R = $CH(CH_3)OCH_2CH_3$
*LXIII*, R = $C(CH_3)_2OCH_3$




*LXIV*, R = $CH(CH_3)OCH_2CH_3$
*LXV*, R = $C(CH_3)_2OCH_3$

internal standard, unless stated otherwise. Chemical shifts are given in ppm ($\delta$-scale), coupling constants ($J$) and signal widths ($W$) in Hz. All values were obtained by first order analysis. Column chromatography was performed on silica gel according to Pitra (60—120 μm), thin-layer chromatography on silica gel G according to Stahl (Woelm). Solutions of the compounds in organic solvents were dried over anhydrous sodium sulfate and taken down at about 2 kPa. Analytical samples were dried over phosphorus pentoxide at 40°C and 26 Pa for 12 h.

1-Methoxymethoxyoctadecanol (*I*)

Iodotrimethylsilane (60 mg) was added to a solution of 1-octadecanol (541 mg; 2 mmol) in dimethoxymethane (3 ml). After stirring for 2 h at room temperature in an argon atmosphere, the mixture was partitioned between ether and water, the organic layer was separated, washed with 5% aqueous sodium thiosulfate and water, and the solvent was evaporated. Chromatography of the residue on a column of silica gel (50 g) in light petroleum–ether (99 : 1) afforded 443 mg (70%) of compound *I*, m.p. 26—27°C (reported[22] m.p. 28—29°C). $^1$H NMR spectrum: 4·61 s (2 H, O—$CH_2$—O), 3·52 bt (2 H, $C_{(1)}$—H, $J$ = 6·5), 3·35 s (3 H, —$OCH_3$), 0·85 m (3 H, $C_{(18)}$—H).

3-Chloro-1-methoxymethoxypropane (*II*)

Chloromethyl methyl ether (9·1 ml; 0·12 mol) was added dropwise at +10°C during 20 min to a stirred solution of 1-chloro-3-hydroxypropane (8·4 ml; 0·10 mol) and N,N-dimethylaniline (14·7 ml; 0·12 mol) in benzene (36 ml). After stirring for 12 h at room temperature, the mixture was diluted with ether (150 ml), washed successively with dilute (1 : 4) hydrochloric acid, water, dilute (1 : 1) aqueous ammonia and water, and dried over sodium sulfate. Magnesium oxide (50 mg) was added and most of the solvents were evaporated under normal pressure. Distillation of the residue through a 10 cm Vigreux column afforded compound *II*, b.p. 50·5—51·5°C/1·86 kPa. $^1$H NMR spectrum: 4·60 s (2 H, O—$CH_2$—O), 3·65 t (4 H, $C_{(1)}$—$H_2$ and $C_{(3)}$—$H_2$, $J$ = 6), 3·34 s (3 H, $OCH_3$), 2·02 p (2 H, $C_{(2)}$—$H_2$, $J$ = 6). For $C_5H_{11}ClO_2$ (133·6) calculated: 43·33% C, 8·00% H, 25·58% Cl; found: 43·03% C, 8·21% H, 25·28% Cl.

TABLE II

Characteristic IR bands of compounds containing the $OCH(CH_3)OCH_2CH_3$ or $OC(CH_3)_2OCH_3$ groupings

| Compound[a] | $\nu_{(asym)}$[b] | $\nu_{(sym)}$[b] | $\nu_{(asym)}$[b] |
|---|---|---|---|
| *LX* | 1 060(155) | 1 102(205) | 1 134(240) |
| *LXI* | 1 060(165) | 1 078(175) | 1 154(125) |
| *LXII* | 1 037(220) | 1 098(210) | 1 133(215) |
| *LXIII* | 1 036(410) | 1 072(190) | 1 149(135) |
| *LXIV* | 1 045(235) | 1 110(215) | 1 130(245) |
| *LXV* | 1 042(430) | 1 076(225) | 1 150(155) |

[a] Measured in tetrachloromethane, $c$ = 0·1 mol $l^{-1}$, on a Perkin–Elmer 580 instrument, cell thickness 0·01 cm; [b] wavenumbers in $cm^{-1}$, numbers in parentheses denote molar absorption coefficients in $l\ mol^{-1}\ cm^{-1}$.

*cis*-4-Tert-butyl-1-methoxymethoxycyclohexane (*V*)

Diisopropylethylamine (0·35 ml; 2 mmol) and chloromethyl methyl ether (0·11 ml; 1·5 mmol) were added to a solution of *cis*-4-tert-butylcyclohexanol (156 mg; 1 mmol) in dichloromethane (2·5 ml). After stirring for 4 h at room temperature, the solution was poured into water and the product was taken up in ether. The ethereal layer was washed with dilute hydrochloric acid, water, potassium hydrogen carbonate solution and water, and the solvent was evaporated. Chromatography of the residue on a column of silica gel (20 g) in light petroleum–ether (99 : 1) afforded 150 mg (75%) of the oily product *V*. $^1$H NMR spectrum: 4·66 s (2 H, O—$CH_2$—O), 3·82 m (1 H, $C_{(1)}$—H, $W = 11$), 3·37 s (3 H, —$OCH_3$), 0·83 s (9 H, $C(CH_3)_3$). For $C_{12}H_{24}O_2$ (200·3) calculated: 71·95% C, 12·08% H; found: 71·68% C, 12·04% H.

3β-Methoxymethoxylupane (*XII*)

Diisopropylethylamine (0·21 ml; 1·2 mmol) and chloromethyl ether (0·06 ml; 0·8 mmol) were added to a solution of dihydrolupeol (171 mg; 0·4 mmol) in a mixture of benzene (1·5 ml) and dichloromethane (1·5 ml). After stirring at room temperature for 12 h, the mixture was poured in water and the product was taken up in ether. The extract was washed with dilute hydrochloric acid, water, potassium hydrogen carbonate solutin and water. The solvent was evaporated and the residue was chromatographed on a column of silica gel (20 g) in light petroleum–ether (99 : 1) to give 162 mg (86%) of the ether *XII*, m.p. 156–158°C (light petroleum), $[\alpha]_D$ −4° (*c* 0·3). $^1$H NMR spectrum: 4·72 and 4·58 AB system (2 H, O—$CH_2$—O, $J_{AB} = 7$), 3·35 s (3 H, $OCH_3$), 3·05 m (1 H, $C_{(3)}$—H), 1·03 s (3 H, $C_{(8)}$—$CH_3$), 0·95 s (3 H, $C_{(23)}$—H), 0·91 s (3 H, $C_{(27)}$—H), 0·85 s (3 H, $C_{(25)}$—H), 0·78 s (3 H, $C_{(24)}$—H), 0·75 s (3 H, $C_{(28)}$—H). For $C_{32}H_{54}O_2$ (470·8) calculated: 81·64% C, 11·56% H; found: 81·85% C, 11·90% H.

3β-Methoxymethoxy-5-androsten-17β-ol (*XIV*)

A 70% benzene solution of sodium dihydro-bis(2-methoxyethoxy)aluminate (5 ml; 18 mmol) was added to a solution of the ketone *XX* (5 g; 15 mmol) in ether (100 ml). The stirred mixture was refluxed under argon for 2 h, cooled and poured into water. The organic phase was washed with dilute hydrochloric acid, brine, potassium hydrogen carbonate solution and water. Crystallization from ether afforded 2·7 g (55%) of the alcohol *XIV*, m.p. 145–146°C, $[\alpha]_D$ −60° (*c* 0·2). $^1$H NMR spectrum: 5·33 bd (1 H, $C_{(6)}$—H, $J = 4·5$), 4·65 s (2 H, O—$CH_2$—O), 3·43 m (1 H, $C_{(3)}$—H, $W = 40$), 3·35 s (3 H, $OCH_3$), 1·02 s (3 H, $C_{(19)}$—H), 0·75 s (3 H, $C_{(18)}$—H). For $C_{21}H_{34}O_3$ (334·5) calculated: 75·41% C, 10·25% H; found: 75·59% C, 10·52% H.

3β-Methoxymethoxy-5-androsten-17-one (*XX*)

N,N-Dimethylaniline (15 ml; 118 mmol) and chloromethyl methyl ether (8·8 ml; 116 mmol) were added to a solution of 3β-hydroxy-5-androsten-17-one (19·0 g; 70 mmol) in a mixture of benzene (200 ml) and dichloromethane (40 ml). The mixture was stirred for 12 h at room temperature, poured into water and the organic phase was washed with dilute hydrochloric acid, water, potassium hydrogen carbonate solution and water. After evaporation of major part of the solvents, the residue was mixed with light petroleum and the separated product was collected on filter. Yield 17·5 g of the ketone *XX* (75%), m.p. 124–125°C, $[\alpha]_D$ 0° (*c* 0·4). $^1$H NMR spectrum: 5·36 bd (1 H, $C_{(6)}$—H, $J = 4·5$), 4·64 s (2 H, O—$CH_2$—O), 3·32 s (3 H, $OCH_3$), 0·99 s (3 H, $C_{(19)}$—H), 0·83 s (3 H, $C_{(18)}$—H). For $C_{21}H_{32}O_3$ (332·5) calculated: 75·86% C, 9·70% H; found: 75·62% C, 9·59% H.

3β-Methoxymethoxy-5-androsten-17β-ol 17-Acetate (*XXXI*)

Acetic anhydride (0·5 ml) was added to a solution of the alcohol *XIV* (200 mg; 0·6 mmol) in pyridine (2 ml). After standing for 24 h at room temperature, the mixture was poured on ice, the solid was filtered, washed with water, dried *in vacuo* (about 20 kPa) over phosphorus pentoxide and crystallized from light petroleum, yielding 180 mg (80%) of the acetate *XXI*, m.p. 105–108°C, $[\alpha]_D$ −61° (*c* 0·4). $^1$H NMR spectrum: 5·33 bd (1 H, $C_{(6)}$—H), 4·67 s (2 H, O—$CH_2$—O), 4·60 m (1 H, $C_{(17)}$—H, $W = 20$), 3·35 s (3 H, $OCH_3$), 2·02 s (3 H, $CH_3COO$), 1·00 s (3 H, $C_{(19)}$—H), 0·79 s (3 H, $C_{(18)}$—H). For $C_{23}H_{36}O_4$ (376·5) calculated: 73·37% C, 9·64% H; found: 73·69% C, 9·57% H.

3β-Methoxymethoxy-5-androsten-17β-ol 17-*p*-Toluenesulfonate (*XLII*)

*p*-Toluenesulfonyl chloride (3 g; 10 mmol) was added to an ice-cooled and stirred solution of the alcohol *XIV* (1·5 g; 4·5 mmol) in pyridine (20 ml). The mixture was set aside overnight at room temperature, poured on ice, the product was collected on filter, washed with water, dissolved in dichloromethane and diluted with benzene. The solution was washed with a potassium hydrogen carbonate solution and water, and the solvents were evaporated. Crystallization of the residue from dichloromethane–ether afforded 1·4 g (64%) of the *p*-toluenesulfonate *XLII*, m.p. 161–162°C, $[\alpha]_D$ −63° (*c* 0·5). $^1$H NMR spectrum: 7·80 m (2 H, arom. H), 7·33 m (2 H, arom. H), 5·30 m (1 H, $C_{(6)}$—H), 4·65 s (2 H, O—$CH_2$—O), 4·25 m (1 H, $C_{(17)}$—H), 3·38 m (1 H, $C_{(3)}$—H), 3·33 s (3 H, $OCH_3$), 2·43 s (3 H, arom. $CH_3$), 0·98 s (3 H, $C_{(19)}$—H), 0·80 s (3 H, $C_{(18)}$—H). For $C_{28}H_{40}O_5S$ (488·7) calculated: 68·82% C, 8·25% H, 6·56% S; found: 68·58% C, 8·30% H, 6·54% S.

1-(1-Ethoxyethoxy)octadecane (*LX*)

Pyridinium *p*-toluenesulfonate (75 mg; 0·3 mmol) was added to a solution of 1-octadecanol (271 mg; 1 mmol) in dichloromethane (5 ml). After cooling to 0°C, ethoxyethylene (0·3 ml; 3·1 mmol) was added, the mixture was stirred for 2 h at 0°C and diluted with ether (100 ml). The solution was washed with saturated aqueous solution of ammonium sulfate and taken down. The residue was chromatographed on a column of silica gel (40 g) in light petroleum–benzene (60 : 40) to give 300 mg (88%) of the oily *LX*. $^1$H NMR spectrum: 4·66 q (1 H, O—CH—O, $J = 5·2$), 3·17–3·80 m (4 H, $C_{(1)}$—H, and $OCH_2$—). For $C_{22}H_{46}O_2$ (342·6) calculated: 77·13% C, 13·53% H; found: 77·42% C, 13·49% H.

3β-(1-Ethoxyethoxy)-5α-cholestane (*LXII*)

The ether *LXII* was prepared from 5α-cholestan-3β-ol (389 mg; 1 mmol) as described for preparation of the ether *LX* from 1-octadecanol; yield 347 mg (75%) of *LXII* as a mixture of diastereoisomers, m.p. 38–48°C (methanol), $[\alpha]_D$ +21° (*c* 0·3). $^1$H NMR spectrum: 4·77 q (1 H, O—CH—O, $J = 5·3$), 3·20–3·78 m ($C_{(3)}$—H and $OCH_2CH_3$), 1·29 d (3 H, CH—$CH_3$, $J = 5·3$), 1·18 t (3 H, $OCH_2CH_3$, $J = 7$), 0·85 d (6 H, $C_{(26)}$—$H_3$ and $C_{(27)}$—$H_3$), 0·79 s (3 H, $C_{(19)}$—H), 0·64 s (3 H, $C_{(18)}$—H). For $C_{31}H_{56}O_2$ (460·8) calculated: 80·81% C, 12·25% H; found: 80·68% C, 12·36% H.

3β-(1-Ethoxyethoxy)-5-cholestene (*LXIV*)

The title compound was prepared from cholesterol (387 mg; 1 mmol) as described for the preparation of *LX* from 1-octadecanol; yield 352 mg (77%) of the diastereoisomeric mixture *LXIV*, m.p. 46–56°C (methanol), $[\alpha]_D$ −30° (*c* 0·4). $^1$H NMR spectrum: 5·33 bd (1 H, $C_{(6)}$—H, $J = 4·5$),

4·76 q (1 H, O—CH—O, $J$ = 5·2), 3·61 m (2 H, $OCH_2CH_3$), 3·37 m (1 H, $C_{(3)}$—H), 1·30 d (3 H, CH—$CH_3$, $J$ = 5·2), 1·19 t (3 H, $OCH_2CH_3$, $J$ = 7·1), 1·00 s (3 H, $C_{(19)}$—H), 0·86 d (6 H, $C_{(26)}$—$H_3$ and $C_{(27)}$—$H_3$, $J$ = 6), 0·67 s (3 H, $C_{(18)}$—H). For $C_{31}H_{54}O_2$ (458·8) calculated: 81·16% C, 11·86% H; found: 81·27% C, 11·69% H.

1-(2-Methoxyisopropoxy)octadecane (*LXI*)

Pyridinium *p*-toluenesulfonate (75 mg; 0·3 mmol) and 2-methoxypropene (0·3 ml; 3·1 mmol) were added to a solution of 1-octadecanol (271 mg; 1 mmol) in dichloromethane (5 ml). The mixture was stirred at room temperature for 2 h, diluted with ether (100 ml), washed with water and dried over anhydrous potassium carbonate and taken down. The residue was chromatographed on a column of silica gel (40 g; saturated with ammonia vapour for 24 h) in light petroleum–ether (99 : 1) to afford 250 mg (73%) of the oily *LXI*. $^1$H NMR spectrum (tetrachloromethane): 3·25 bt (2 H, $C_{(1)}$—H, $J$ = 6·5), 3·05 s (3 H, $OCH_3$). For $C_{22}H_{46}O_2$ (342·6) calculated: 77·13% C, 13·53% H; found: 77·31% C, 13·43% H.

3β-(2-Methoxyisopropoxy)-5α-cholestane (*LXIII*)

The title compound (409 mg; 89%) was prepared from 5α-cholestan-3β-ol (389 mg; 1 mmol) as described for preparation of the ether *LXI* from 1-octadecanol, m.p. 96–99°C, $[\alpha]_D$ +17° (*c* 0·3; dioxane). $^1$H NMR spectrum (tetrachloromethane): 3·45 m (1 H, $C_{(3)}$—H, $W$ = 36), 3·09 s (3 H, $OCH_3$), 1·22 s (6 H, O—$C(CH_3)_2$—O), 0·84 d (6 H, $C_{(26)}$—$H_3$ and $C_{(27)}$—$H_3$, $J$ = 6·5), 0·79 s (3 H, $C_{(19)}$—H), 0·63 s (3 H, $C_{(18)}$—H). For $C_{31}H_{56}O_2$ (460·8) calculated: 80·81% C, 12·25% H; found: 80·57% C, 12·02% H.

3β-(2-Methoxyisopropoxy)-5-cholestene (*LXV*)

The ether *LXV* was prepared from cholesterol (387 mg; 1 mmol) in the same manner as the ether *XLI* from 1-octadecanol; yield 225 mg (60%), m.p. 126–129°C, $[\alpha]_D$ −28° (*c* 0·3; dioxane). $^1$H NMR spectrum (tetrachloromethane): 5·39 bd (1 H, $C_{(6)}$—H, $J$ = 4·5), 3·44 m (1 H, $C_{(3)}$—H, $W$ = 35), 3·10 s (3 H, $OCH_3$), 1·24 s (6 H, O—$C(CH_3)_2$—O), 0·97 s (3 H, $C_{(19)}$—H), 0·85 d (6 H, $C_{(26)}$—$H_3$ and $C_{(27)}$—$H_3$), 0·66 s (3 H, $C_{(18)}$—H). For $C_{31}H_{54}O_2$ (458·8) calculated: 81·16% C, 11·86% H; found: 80·96% C, 11·96% H.

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