INDUCTIVE EFFECT IN EI-MASS SPECTRA OF SOME 5,6-DIHALOGENIDES AND 5,6-HALOHYDRINS OF 5α-CHOLESTAN-3β-OL AND 3β-ACETOXY-5α-CHOLESTANE*

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Received December 8th, 1981

Partial EI-mass spectra of 3β-hydroxy- and 3β-acetoxy-5α-cholestanes substituted in positions 5α-, 6β- or 5α,6β- with a hydroxyl group or halogen atoms (fluorine, chlorine, bromine) are presented. The molecular ions of 5α,6β-disubstituted derivatives of 3β-hydroxy-5α-cholestane (or of its 3-acetate) are considerably more stable than the corresponding monosubstituted derivatives if at least one of the pair of the vicinal substituents is chlorine or fluorine. This increase in stability, most striking in 5α- and 6β-fluoro compounds, is explained by the inductive effect.

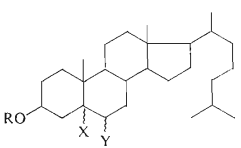
One of the obstacles to a wider use of mass spectrometry as an analytical method is the thermal lability of some substances. In a previous paper[1] we referred on the possibility of using this method for the diagnosis of one such relatively unstable type of substances, *i.e.* steroidal dihalogenides and halohydrins. In this paper we describe the mass spectrometry of 5,6-disubstituted cholesterol derivatives *IX* to *XXXIX*, the thermal lability of which is higher than in the formerly mentioned dihalogenides: while the pyrolysis products of the latter compounds were conjugated dienes, in the case of substances of type *IX* an easy formation of aromatic compounds of the type of anthrasteroid[2] *XLIII* may be expected.

The substrates were prepared by standard procedures[3,4], *i.e.* predominantly by addition of suitable reagents to cholesterol derivatives and, if needed, by further transformation of these products. The required fluoro chloride *XIV* was prepared analogously as fluoro bromide *XVIII*: we exposed cholesteryl acetate to chlorine in the presence of silver fluoroborate and separated the addition products after hydrolysis of the acetoxy group (the chromatographic separation of the product from reaction mixture is easier in the series of hydroxy derivatives). The structure of the product *XIV* follows from its ^{1}H NMR spectrum, where a strong coupling of the fluorine atom with the geminal hydrogen atom ($J_{gem} = 50$ Hz) and the protons on $C_{(19)}$ ($J_{19,F} = 4{\cdot}5$ H_2) is observed. On addition of bromine chloride to [6-^{2}H]-

* Part CCLXXV in the series On Steroids; Part CCLXXIV: This Journal *47*, 2768 (1982).

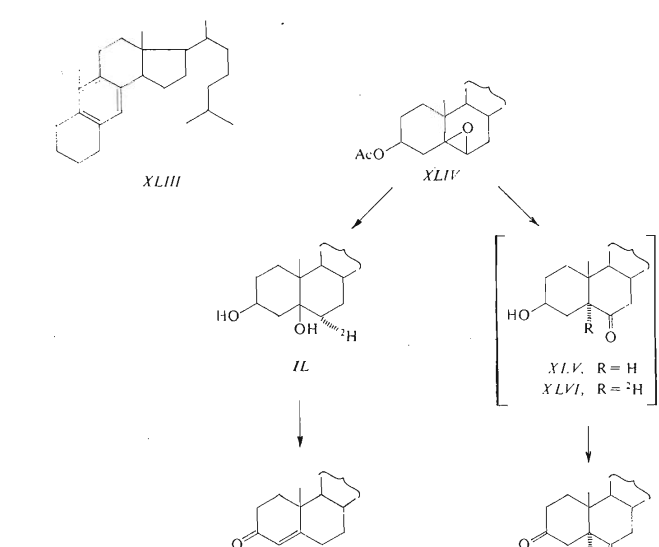
-cholesterol[5] (*XLII*) and [7,7-$^2H_2$]-cholesterol[6] (*XLIII*) corresponding labelled bromo chlorides *XXIII* and *XXIV*, respectively, were prepared.

For comparison the known diol *XL* was also prepared from 5,6β-oxido-5β-cholestan-3β-ol[7] (*XLIV*) with lithium aluminum hydride. This procedure was chosen because it permitted the labelling of the position 5 with deuterium, using lithium aluminum deuteride. However, it was found that the formation of 6β-hydroxy derivative of the 5α-series under these conditions is not merely a case of diaxial opening of the epoxide: the product (*XLI*, 30%) contained 2 atoms of deuterium in the molecule, which could not be exchanged by protic reagents, but oxidation of compound *XLI* gave the known 5α-cholestane-3,6-dione[8] (*XLVIII*) which contained 1 atom of deuterium in the molecule. This finding may be interpreted suggesting that the reaction of the hydride reagent with the epoxide proceeds *via* 6-oxo intermediate *XLV* or *XLVI*, while the hydride (or deuteride) ion is transferred predominantly by an intermolecular mechanism (see the mass spectrum of compound *XLI*). The main product (*IL*, 70%) was identical with 5β-cholestane-3β,5-diol the oxidation of which afforded 6α-deuterated cholestenone (*L*).



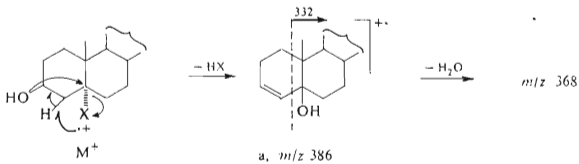
I, R = H, X = α-F, Y = H
II, R = H, X = α-Cl, Y = H
III, R = H, X = α-Br, Y = H
IV, R = Ac, X = α-Cl, Y = H
V, R = Ac, X = α-Br, Y = H
VI, R = Ac, X = α-OH, Y = H
VII, R = Ac, X = α-H, Y = β-Br
VIII, R = Ac, X = α-H, Y = α-Br
IX, R = H, X = α-Cl, X β-Cl
X, R = Ac, X = α-Cl, Y = β-Cl
XI, R = H, X = α-Br, Y = β-Br
XII, R = H, X = β-Br, Y = α-Br
XIII, R = Ac, X = α-Br, Y = β-Br
XIV, R = H, X = α-Cl, Y = β-F
XV, R = Ac, X = α-Cl, Y = β-F
XVI, R = H, X = α-F, Y = β-Br
XVII, R = H, X = α-F, Y = α-Br
XVIII, R = H, X = α-Br, Y = β-F
XIX, R = Ac, X = α-F, Y = β-Br
XX, R = Ac, X = α-Br, X = β-F
XXI, R = H, X = α-Cl, Y = β-Br

XXII, R = H, X = α-Br, Y = β-Cl
XXIII, R = H, X = αBr, Y = β-Cl, 6α-^2H
XXIV, R = H, X = α-Br, Y = β-Cl, 7,7-$^2H_2$
XXV, R = Ac, X = α-Cl, Y = β-Br
XXVI, R = Ac, X = α-Br, Y = β-Cl
XXVII, R = H, X = α-F, Y = β-OH
XXVIII, R = H, X = α-OH, Y = β-F
XXIX, R = H, X = α-F, Y = β-OCH_3
XXX, R = Ac, X = α-F, Y = β-OH
XXXI, R = Ac, X = α-OH, Y = β-F
XXXII, R = H, X = α-Cl, Y = β-OH
XXXIII, R = H, X = α-OH, Y = β-Cl
XXXIV, R = Ac, X = α-Cl, Y = β-OH
XXXV, R = Ac, X = β-OH, Y = α-Cl
XXXVI, R = H, X = α-Br, Y = β-OH
XXXVII, R = H, X = α-OH, Y = β-Br
XXXVIII, R = Ac, X = α-Br, Y = β-OH
XXXIX, R = Ac, X = α-OH, Y = β-Br
XL, R = H, X = α-H, Y = β-OH
XLI, R = H, X = α-^2H, Y = β-OH, 6α-^2H
XLII, E = Ac, X = α-H, Y = β-OH



The mass spectra of 5-halogeno-5α-cholesten-3β-ols *I*–*III*, the same as the spectra of acetates *IV*–*VII*, differ considerably in dependence on the character of the 5α-substituent. Fluoride *I* – in contrast to chloride *II* and bromide *III* – under electron impact forms a very stable molecular ion, which eliminates H_2O and HF very unwillingly. In this case the D-ring cleavage (with loss of $C_{11}H_{23}$ or $C_{11}H_{22}$), accompanied by intensive metastable transitions (m^+ 155·2 and 156·4), is much more important than these eliminations. The ions m/z 251 and 252 thus formed eliminate a molecule of HF or a radical F· and water. The mass spectra of chloride *II* and bromide *III* (similarly as the mass spectrum of 5α-cholestane-3β,5-diol[9]) display a very unstable molecular ion (1·5 and 0·07% relative abundance), which splits off a hydrogen halide molecule easily. The ion $[M—HX]^+$ (m/z 386) evidently possess neither the structure of the molecular ion of cholesterol or of 4-cholesten-3-ol, which would be a product of simple 1,2-elimination of hydrogen halide. This follows from the comparison of relative abundances of ions m/z 386 and 368 in the

mass spectra of all found substances (relative abundance in brackets) :5-chloro-5α--cholestan-3β-ol m/z 386 (50), m/z 368 (100), 5-bromo-5α-cholestan-3β-ol m/z 386 (30), m/z 368 (100), cholesterol[10] M^+ 386 (100), m/z 368 (20), 4-cholesten-3β-ol[11] M^+ 386 (100), m/z 368 (95). As can be seen, the ion m/z 386 $(M-HX)$ eliminates a water molecule much more easily than the M^+ of both cholestenols. If the structure of the molecular ion of 4-cholesten-3β-ol with a double bond in the allylic position to the hydroxyl is assumed to be the most favourable structure (for H_2O elimination) that could be formed by elimination of HX from the molecular ion *II* or *III*, then it is evident that in the decomposition of M^+ of these compounds a more complex mechanism must be involved than the simple sequence of eliminations of HCl and H_2O. Therefore we assume that at least in a certain portion of the molecular ions of halogenides *II* and *III* – participation of the OH group in the elimination of hydrogen halide takes place, leading to a migration of the hydroxyl group into position 5 (Scheme 1). A similar rearrangement of hydroxyl was already observed in the series

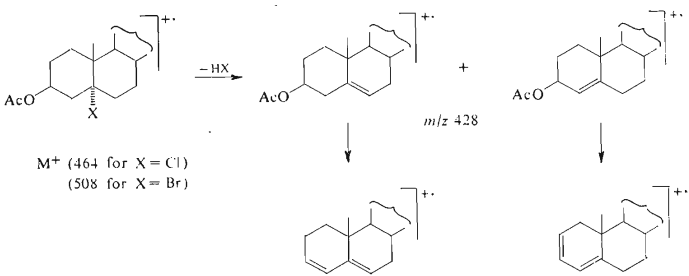


SCHEME 1

of $C_{(4)}$-alkylated cholesterols[12] and 4,4-dimethyl-A-homocholestan-3β-ols[13,14]. The elimination of the hydroxyl from $C_{(5)}$ proceeds easily, as follows, for example, from the mass spectrum of 5α-cholestan-3β,5-diol[9](relative abundance M^+ 2%, $[M-H_2O]^+$ 100%), or its 3β-acetate *VI* (M^+ 6·6%, $[M-H_2O]^+$ 84%).

In the case of acetates *IV* and *V* a similar mechanism of HX elimination under participation of the CH_3COO-group is not possible (large volume, sterical hindrance). A non-specific 1,2-elimination of hydrogen halide, (see below) gives rise to ions m/z 428 with the structure of molecular ions of cholesteryl acetate and 3β-acetoxy--4-cholestene. Their mass spectra do not contain an observable M^+; accordingly the ions m/z 428 in the spectra of acetate *IV* and *V* easily eliminate acetic acid, under formation of dominant ions m/z 368 (Scheme 2), which are stabilized by the system of conjugated double bonds.

Indirect evidence for the hypothesis that the loss of HX from the molecular ions of compounds *IV* and *V* proceeds *via* 1,2-elimination and not *via* 1,3- or 1,4-elimination is given by the mass spectrum of 3β-acetoxy-5α-cholestan-5-ol (*VI*). The ion m/z 428, formed by 1,3- or 1,4-elimination of H_2O (ref.[15]) (loss of 5α-hydroxyl)



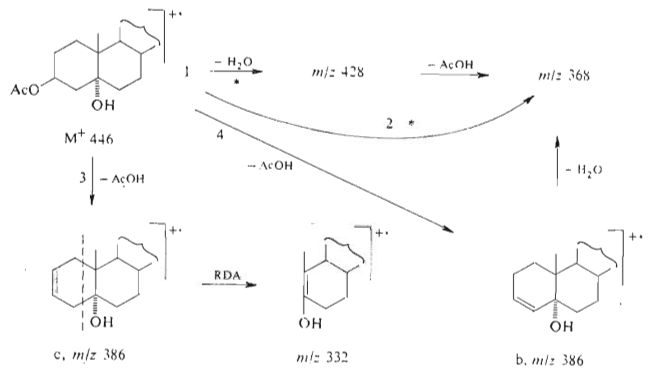
SCHEME 2

from the molecular ion of *VI* does not contain a double bond (Scheme 3, path 1) which would favour the elimination of CH_3COOH. Therefore the molecular ion of *VI* is very stable (84% relative abundance). On the contrary, the ions m/z 428 formed on elimination of HX from the molecular ions of compounds *IV* and *V* are unstable and they undergo 1,2-elimination of acetic acid immediately, to give ions m/z 368, with a system of conjugated double bonds.

Elimination of CH_3COOH from the molecular ion of acetate *VI* gives rise to the unstable ions *b* and *c*, m/z 386 (Scheme 3), which decompose in various ways – in dependence on the position of the double bond formed: the ion *b* loses a molecule of water (path 2; this process is accompanied by a high metastable peak, corresponding to simultaneous elimination of CH_3COOH and H_2O: $m^* = 303{\cdot}6$), while the ion *c* loses a molecule of butadiene, affording the prominent ion m/z 332 (path 3).

Isomeric 6-bromo derivatives *VII* and *VIII* show a far higher stability of their molecular ions than 5-bromo derivative *V*. While 5α-Br is eliminated from M^+ of *III* or *V* in the form of HBr, the 6β-Br is lost (in addition to the alternative elimination of CH_3COOH) from M^+ of *VII* partly as $Br^{\cdot}$ radical; the more strongly bonded Br at the carbon atom $C_{(6)}$ of *VIII* is lost predominantly as $Br^{\cdot}$ radical from the ion $[M-CH_3COOH]^+$ (and not from M^+), to give the dominant ion m/z 369. The D-ring cleavage (loss of 155 μ) also competes with the elimination reactions of the molecular ion of 6β-bromide *VIII*.

The mass spectrum of dichloride *IX* differs from the spectrum of monochloride *II* by a dramatic increase of the molecular ion stability (relative abundance 100%, or 1·5%, respectively). The most important elimination process of the molecular ion *IX* is the loss of Cl_2 (without a metastable transition); an alternative fragmentation path of M^+ the D-ring cleavage with loss of 154 or 155 ů (m^+ 198·7 and 200·5)



SCHEME 3

proceeds to the same extent. Similarly, the molecular ion of acetate *X* undergoes eliminations (loss of $CH_3COOH + Cl_2$) as well as skeletal cleavage (ion $[M-154]^+$ and the products of the C-ring cleavage – prominent ions *m/z* 247, 248 and 249). The molecular ion of dibromide *XI* was not observed at all. The dominant ion in its mass spectrum, *m/z* 366, is formed by elimination of 2 HBr + H_2O. The prominent ions *m/z* 211 and 253 arise from loss of $C_{11}H_{23}$ (D-ring cleavage) or C_8H_{17} (loss of the side chain) from ion *m/z* 366. Similarly as in the series of monohalogenides *II–V*, in dihalogenides *IX–XI* and *XIII* a lower stability of molecular ions of 3β-ols *IX* and *XI* was also observed, when compared with the M^+-stability of their acetates *X* and *XIII*. From this it may be concluded that the mentioned participation of OH group in the elimination of HX, proposed to explain the fragmentations of M^+ of monohalogenides *II* and *III*, is involved also in the elimination of HX from M^+ of hydroxyhalogenides *IX* and *XI*. The diequatorial dibromide *XII* undergoes somewhat different fragmentation: even though here any participation of 3β-OH in the 5α-Br elimination cannot take place, its M^+ is also very unstable (0·2% relative abundance), probably due to the favoured elimination of HOBr. In addition, all other possible eliminations also apply during the decomposition of M^+: loss of Br$^\cdot$, HBr, Br_2, HBr + H_2O, HBr + Br$^\cdot$, 2 HBr + H_2O (base peak *m/z* 366) and Br$^\cdot$ + H_2O (ion *m/z* 368; m^+ 350·8). The mass spectrum of the acetate of diaxial dibromide *XIII* is dominated by the ions $[M-(Br_2 + CH_3COOH)]^+$ and $[M-(2\,HBr + CH_3.COOH)]^+$ which are formed by decomposition of less abundant ions of second generation: $[M-(HBr + CH_3COOH)]^+$ and $[M-(Br^\cdot + CH_3COOH)]^+$. The first

generation ions are very unstable, as well as the molecular ion, the peaks of which are hardly observable.

On the contrary, the molecular ion of chloro fluoride *XIV* practically does not undergo elimination of substituents: the only important process of its decomposition is the D-ring cleavage (loss of 154 or 155 u, m^+ 184·6 and 185·9). The M^+ of acetate *XV* behaves in a similar manner: the loss of 154 u (m^+ 223·2 and 221·8) predominates here in the D-ring cleavage. A similar resistance towards eliminations is also shown by M^+ of fluoro bromide *XVI* which, by the usual D-ring cleavage, loses 154 or 155 u to the same yield. The mass spectrum of 5α,6α-fluoro bromide *XVII* is distinguishable from the spectrum of the diaxial isomer *XVI* merely by a higher abundance of ion m/z 385 $[M-(Br^{\bullet} + HF)]$ and by the prevalence of the loss of 155 over 154 u (ions m/z 329 and 331) from M^+ in the D-ring cleavage. The molecular ion of 5-bromo-6-fluoride *XVIII* shows a considerably lower stability and it undergoes eliminations more easily than M^+ of 5-fluoro-6-bromide *XVI*. This is in agreement with the general observation in the series of 5,6-dihalogeno--cholestan-3β-ols, that halogen bound to $C_{(5)}$ is more easily eliminated than the same halogen on $C_{(6)}$. The base ion m/z 366 in the mass spectrum of compound *XVIII*, product of elimination of HBr, HF and H_2O, further loses its side chain (113 u) or it undergoes the D-ring cleavage (prominent ion m/z 211).

The mass spectrum of 5α-fluoro-6β-bromoacetate *XIX* is dominated by the molecular ion, as well as that of 5α-bromo-6β-fluoroacetate *XX*. The main fragmentation path for the molecular ions of both acetates is the D-ring cleavage, proceeding rather with loss of $C_{11}H_{22}$ than of $C_{11}H_{23}$ and accompanied by a very intensive metastable transition. The ions formed by loss of one substituent from M^+ (by elimination of CH_3COOH, HBr or $B^{\bullet}$) probably undergo immediately further decomposition and are therefore less abundant. More important are the ions of the second and third generation, formed by successive elimination of two or three substituents in the form of CH_3COOH, HBr ($Br^{\bullet}$) and HF ($F^{\bullet}$) in various order and combinations. Among them the most noteworthy is the ion $[M-(CH_3COOH + Br^{\bullet})]^+$ (m/z 387): it is accompanied in both spectra by an intensive metastable transition ($m^*_{527\to387}$ = = 384·2), although the process involves undoubtedly a splitting off of two particles. The D-ring cleavage in ions m/z 387 and 386 accompanied by a loss of $C_{11}H_{22}$ or $C_{11}H_{23}$ is characteristic only of the mass spectrum of *XX* (and not *XIX*).

The mass spectrum of chlorobromide *XXI* contains also an abundant metastable ion m^+ 296·0 corresponding to a two step process: elimination of HCl and Br· radical from M^+. The molecular ion of compound *XXI* and bromochloride *XXII* loses both halogens either in the form of BrCl or HCl + HBr. While in the decomposition of M^+ of *XXI* all three paths are of similar importance, in the case of *XXII* the elimination of HBr + HCl is preferred. The mass spectra of [6α-^{2}H]-5-bromo--6β-chloro-5α-cholestan-3β-ol (*XXIII*) and [7,7-$^2H_2$]-5-bromo-6β-chloro-5α-cholestan-3β-ol (*XXIV*) were also measured. A shift of the peak m/z 420 (M − HBr) by 2

mass units in the spectrum of compound *XXIV* and a partial shift (about 70%) by 1 unit in the spectrum of *XXIII* were also observed. From these results it follows that loss of HBr proceeds as unspecific 1,2-elimination (with the hydrogen coming predominantly from $C_{(4)}$) and that it does not procced as 1,3-elimination. The mass spectra of acetoxy-chloro bromide *XXV* and of its isomer *XXVI* are dominated by the ion *m/z* 368 formed on elimination of BrCl + CH_3COOH from M^+. The 5-chloro isomer *XXV* is characterized by a more stable molecular ion and by the fact that the elimination of HBr from M^+ prevails over the loss of the radical $Br^\bullet$ (in compound *XXVI* – on the contrary – the expulsion of $Br^\bullet$ is preferred).

The very stable molecular ion of fluorohydrin *XXVII* (the same as of 6-methyl ether *XXIX*) practically undergoes the D-ring cleavage only (by loss of $C_{11}H_{22}$, $C_{11}H_{23}$, $C_{10}H_{20}$). The isomeric fluorohydrin *XXVIII* is also characterized by a relatively stable molecular ion which, however, undergoes water elimination to about the same extent as the D-ring cleavage. The same fragmentation path (loss of 155 u) is preferred in the decomposition of M^+ of acetate *XXX*, while the less stable M^+ of the isomeric acetate *XXXI* preferentially eliminates successively H_2O, CH_3COOH and CH_3. The D-ring cleavage takes place here only in the fragment *m/z* 386 ($M - H_2O - CH_3COOH$) to form ions *m/z* 231 and 232 (base peak).

The molecular ions of isomeric chlorohydrins *XXXII* and *XXXIII* (and acetates *XXXIV* and *XXXV*) very easily undergo eliminations of substituents and their abundance is considerably lower than in corresponding fluorhydrins. For chlorohydrins *XXXII* and *XXXIII* the ions *m/z* 402 ($M - HCl$) and 384 ($M - HCl - H_2O$) are of diagnostic value: the first one forms the base peak in the mass spectrum of *XXXII*, the second in the spectrum of its isomer. The hardly observable molecular ions of acetates *XXXIV* and *XXXV* easily eliminate all three substituents under formation of the base ion *m/z* 366 (in the case of the 5β-isomer *XXXV* it is the dominant ion). Labelling of compound *XXXV* with (O^2—H)-ethanol (exchange of H—D to about 50%) showed that *a*) the ion *m/z* 420 is a fragment ion and not the M^+ of the pyrolysis product (it was shifted by 1 unit, the same as M^+ 480), and *b*) that by elimination of CH_3COOH the hydrogen atom from OH is not lost even when both groups are in *syn*-diaxial position.

The molecular peaks in the mass spectra of isomeric bromohydrins *XXXVI* and *XXXVII* were not observed. The base peak in both cases is the ion *m/z* 366 – a product of elimination of HBr + 2 H_2O. The diagnostically important ion $[M - HBr]^+$ (*m/z* 402) occurs only in the mass spectrum of the isomer *XXXVI*. The molecular ions of corresponding acetates *XXXVIII* and *XXXIX* are somewhat more stable. The most abundant ions of their mass spectra arise from the elimination of HBr + + AcOH (*XXXIX*) or HBr + AcOH + H_2O (*XXXIX*). Elimination of CH_3COOH + $Br^\cdot$ is more important in the fragmentation of 5-bromo isomer only.

Inductive Effect

By the analysis and comparison of the mass spectra of the compounds studied it was observed that the stability of the molecular ions of 5α-chlorides, 5α-bromides and 5α-ols in the series of 3β-cholestanol and 3β-acetoxycholestane increased considerably with introduction of chlorine – and still more fluorine – into the vicinal position 6β. The same unexpected phenomenon was also observed with their isomers: the stability of the molecular ions 5α-fluoro-6β (or 6α)-bromides and 6β-ols of this series is far higher than that of corresponding substances without fluorine in the molecule. In the case of the pair fluorohydrin *XXVII* – diol *XL* it may be shown that the higher stability of the molecular ion of the first compound cannot be due simply to a lack of the 5α-hydrogen atom, which could be required for the elimination of water: from the mass spectrum of 5α-deuterio analogue *XLI* of diol *XL* it follows (since the elimination of water from its M^+ proceeds with label retention) that the 5α-hydrogen does not take part in the elimination of water and therefore its mere lack cannot suppress its course (*i.e.* increase the stability of M^+). We consider that the increase in stability of molecular ions by introduction of fluorine or chlorine atom into a position vicinal to the substituents Br, Cl or OH may be explained by means of the inductive effect. The atom of fluorine or chlorine with their inductive effect bring about homogenisation (and shortening) of the polarized bond of the vicinal electronegative and sufficiently polarisable substituent. If the most easily eliminable substituent is affected in this way, this inductive effect will result in increased stability of the molecular ion.

The contribution of the molecular ion current (*i.e.* of all the molecular group ions) to the total ion current which is taken starting from m/z 366 (% of $\sum_{366}$ T.I.C.) was determined (Table I). This value was found to reflect best the increase in molecular ion stability towards eliminations as a result of the inductive effect investigated. In Table I relative abundances of M^+ (in % of base peak) and the ion current in % of $\sum_{366}$ T.I.C. of some halogenides and halohydrins of 3β-cholestanol and its acetate are compared. A considerable increase in the stability of the molecular ion is observed consistently in every triad of compounds, going from 5α-substituted 3β-cholestanols to their corresponding 6β-chloro and 6β-fluoro derivatives (first part of Table I). In the second part of Table I the effect of 5α-fluorine on the stability of M^+ of 6β(α)--bromides and 6β-ols is demonstrated. An increase in the strength of the $C_{(6)}$-Br- or $C_{(6)}$-OH bond due to the inductive effect of 5α-chlorine cannot result in corresponding increase in the stability of M^+ since the $C_{(6)}$-Br and $C_{(5)}$-OH bonds even without this inductive effect are stronger than the very labile $C_{(5)}$-Cl bond (see the mass spectrum of chloride *II*). Therefore, the introduction of Cl into position $C_{(5)}$ leads rather to decrease in the M^+ stability.

EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. The analytical samples were dried at 20°C and 53·3 Pa over phosphorous pentoxide for 8 h. Optical rotations

TABLE I

The effect of 6β-halogen (part A) and 5α-halogen (part B) on relative abundance of molecular ions of 3β,5α,6β (and α)-trisubstituted 5α-cholestanes

Compound	Substitution			Relative abundance of M^+	
	3β	5α	6β[a]	% b.p.	% $\sum$[b]
			Effect of 6β-halogen		
II	OH	Cl	—	4·3	0·8
IX	OH	Cl	Cl	100	27·5
XIV	OH	Cl	F	100	83
IV	OAc	Cl	—	17·7	15·4
X	OAc	Cl	Cl	100	58·2
XV	OAc	Cl	F	100	81·5
III	OH	Br	—	0·1	0·05
XXII	OH	Br	Cl	3·3	2·0
XVIII	OH	Br	F	11	8·2
V	OAc	Br	—	0·03	0·06
XXVI	OAc	Br	Cl	3·6	4·7
XX	OAc	Br	F	100	34·4
Ref.[9]	OH	OH	—	2·3	1·4
XXXIII	OH	OH	Cl	6·7	2·5
XXVIII	OH	OH	F	54	16·9
VI	OAc	OH	—	6·6	2·3
XXXI	OAc	OH	F	23	8·9
			Effect of 5α-halogen		
VIII	OAc	—	6α-Br	9·3	9·5
XVII	OH	F	6α-Br	96	61·7
VII	OAc	—	Br	5·7	7
XXV	OAc	Cl	Br	4·2	5·6
XIX	OAc	F	Br	100	53·3
XL	OH	—	OH	12·3	10·8
XXXII	OH	Cl	OH	25	8·2
XXVII	OH	F	OH	100	73·8
XLII	OAc	—	OH	6·8	2
XXX	OAc	F	OH	100	38

[a] Except for compounds *VIII* and *XVII*; [b] % of $\sum_{366}$ T.I.C.

and the IR spectra were measured in chloroform, the ^{1}H NMR spectra in deuteriochloroform on a Tesla 60 instrument, the chemical shifts are given in δ-scale (ppm, tetramethylsilane as internal standard).

5-Chloro-6β-fluoro-5α-cholestan-3β-ol (*XIV*)

Silver fluoroborate (2·7 g) was added to a stirred solution of cholesteryl acetate (1 g) in dimethoxyethane (20 ml) and chlorine gas was slowly introduced into the mixture. After 20 min at room temperature the mixture was filtered through a layer of sodium sulfate which was washed with ether, the filtrate was washed with a sodium thiosulfate solution, sodium chloride, aqueous sodium carbonate and water. After drying over sodium sulfate and filtering the filtrate was evaporated in a vacuum. The residue was dissolved in 10 ml of chloroform and 100 ml of methanol which contained 2 ml of hydrochloric acid. After 20 h the mixture was concentrated under reduced pressure to 1/4 ot its volume, diluted with ethyl acetate and washed with water. The dried sample was concentrated and applied onto a silica gel column (100 g). The fraction containing the substance with the same polarity as cholesterol was collected (430 mg) and repeatedly crystallized from a mixture of ethyl acetate and methanol. M.p. 137—138°C (150 mg), $[\alpha]_D^{20}$ −26° (*c* 0·9), ^{1}H NMR spectrum: 0·66 (s, 3 H, 18-H), 0·85 (d, J = 6 Hz, 6 H, 26,27-H). 1·20 (d, J = 4·6 Hz, 3 H, 19-H), 4·11 (mt, 1 H, 3-H), 4·57 (dt, $J_{F,6}$ = 50 Hz, $J_{6,7\alpha} = J_{6,7\beta}$ = 2·5 Hz). For $C_{27}H_{40}ClFO$ (441·1) calculated: 73·51% C, 10·51% H; found: 73·25% C, 10·37% H.

3β-Acetoxy-5-chloro-6β-fluoro-5α-cholestane (*XV*)

Hydroxy derivative (*XIV*; 100 mg) was dissolved in 1 ml of pyridine and 1 ml of acetic anhydride, After 20 h the mixture was diluted with 10 ml of methanol and allowed to stand for 1 h. The solution was evaporated in a vacuum and the residue crystallized from a mixture of ethyl acetate and methanol to give acetate *XV*, m.p. 109—111°C, $[\alpha]_D^{20}$ −28° (*c* 1·2); ^{1}H NMR spectrum: 0·68 (s, 3 H, 18-J), 0·85 (d, J = 6 Hz, 6 H, 26,27-H), 1·22 (d, J = 4·5 Hz, 3 H, 19-H), 2·01 (s, H CH_3CO), 4·58 (dt, $J_{6,F}$ = 50 Hz, $J_{6,7\beta} = J_{6,7\alpha}$ = 2·5 Hz, 1 H, 6-H), 5·30 (mt, 1 H, 3-H) ppm. For $C_{29}H_{48}ClFO_2$ (483·1) calculated: 72·09% C, 10·01% H; found: 71·80% C, 9·93% H.

[5,6α-$^2H_2$]-5α-Cholestane-3β,6β-diol (*XLI*)

5,6β-Oxido-5β-cholestan-3β-ol (100 mg) was added to a solution of about 100 mg of lithium aluminum deuteride in 2 ml of tetrahydrofuran and the mixture was refluxed under nitrogen for 2 h. The excessive reagent was decomposed with a minimum amount of water, the mixture was saturated with anhydrous sodium sulfate and the organic components were extracted with ether. The ethereal extract was applied onto a silica gel thin-layer plate and developed with 50% ether in benzene. The zone corresponding to 5α-cholestane-3β,6β-diol (*XL*, R_F = 0·35) was eluted with ether, to give diol *XLI* (30 mg), m.p. 188—190°C, undepressed on admixture of an authentic sample of compound *XL*. ^{1}H NMR spectrum: 0·68 (s, 3 H, 19-H), 0·85 (d, J = 6 H_2, 6 H, 26 a 27-H), 1·02 (s, 3 H, 19-H), 3·64 (mt, $W_{1/2}$ = 22 Hz, 1 H, 3-H) and 3·78 (t, J = 2·5 Hz, 0·5 H, 6-H) ppm. Oxidation of compound *XLI* gave dione *XLVIII* which after exchange in 1% potassium methoxide afforded 5α-cholestane-3,6-dione (*XLVII*).

[6α-^{2}H]-5β-Cholestane-3β,5-diol (*IL*)

The non-polar product from the preceding chromatography on thin layers (*IL*, 70 mg) was eluted with ether, m.p. 146—149°C, without depression when admixed with an authentic sample.

^{1}H NMR spectrum: 0·63 (s, 3 H, 18-H), 0·85 (d, J = 6 Hz, 6 H, 26 and 27-H), 0·92 (s, 3 H, 19-H), 3·40 (bs, 2 H, the signal disappears after addition of ^2H_2O), 4·12 (mt, $W_{1/2}$ = 8 Hz, 1 H, 3-H) ppm. Mass spectrum: $M^{+\cdot}$ = 305 m/z.

[6α-^{2}H]-4-Cholesten-3-one (*L*)

Compound *IL* (30 mg) was dissolved in 2 ml of acetone and oxidized with Jones's reagent at room temperature. After 5 min the mixture was poured onto a solution of potassium hydrogen carbonate, the product was extracted with ether and washed with a dilute sodium chloride solution, dried over sodium sulfate and evaporated. The residue was refluxed for 5 h in xylene, under nitrogen, then applied onto a silica gel thin-layer plate which was developed with benzene. The main product (21 mg) was identical with cholestenone, its mass spectrum ($M^{+\cdot}$ = 385) was compatible with the structure of *L*. IR spectrum (CCl_4): 2 175 (C—O), 1 679 and 1 619 (C=C—C=O) cm^{-1}.

Mass Spectra

The mass spectra were measured on a double focussing mass spectrometer AEI MS 902 (associated Electric Industries, Manchester, G.B.). The samples were introduced by direct inlet into the ion source heated at 130—150°C. The mass spectra were recorded at resolving power of 1 000 and electron energy of 70 eV.

Partial mass spectra (m/z > 200) of compounds are given below. The masses and the corresponding relative abundances in percents of the base peak (in brackets) are presented:

I: 213 (13), 215 (22), 217 (12), 231 (18), 232 (14), 233 (41), 234 (21), 251 (56), 252 (69), 266 (17), 368 (6), 371 (9), 373 (6), 381 (18), 388 (36), M^+ 406 (100), 407 (31).

II: 213 (21), 247 (18), 255 (18), 275 (26), 301 (15), 353 (26), 366 (11), 368 (100), 369 (32), 371 (15), 384 (8), 386 (52), 387 (18), 404 (6), M^+ 422 (1·5).

III: 213 (25), 247 (25), 255 (25), 260 (21), 275 (15), 301 (12), 326 (5), 353 (30), 368 (100), 369 (32), 371 (10), 386 (30), 387 (11), 448 (1·5), 450 (1·5), $M^{+\cdot}$ 466 (0·1).

IV: 213 (12), 214 (9), 215 (11), 247 (7), 249 (5), 255 (9), 260 (5), 274 (7), 310 (4), 353 (13), 368 (100), 369 (33), 428 (9), $M^{+\cdot}$ 464 (18), 465 (5·8), 466 (6·9).

V: 213 (3), 247 (5), 255 (4), 260 (3), 353 (9), 368 (100), 369 (31), 384 (1), 385 (0·6), $M^{+\cdot}$ 508 (0·03), 510 (0·03).

VI: 213 (26), 214 (26), 215 (26), 227 (8), 228 (24), 229 (7). 246 (4), 255 (8), 260 (3), 273 (16), 274 (24), 288 (13), 332 (55), 333 (15), 353 (30), 354 (9), 368 (100), 369 (30), 386 (11), 413 (4), 428 (84), 429 (27), M^+ 446 (6·6).

VII: 213 (28), 215 (26), 229 (16), 247 (26), 255 (26), 260 (25), 274 (5), 275 (6), 293 (10), 295 (10) 315 (4), 326 (4), 353 (25), 368 (100), 369 (50), 428 (4), 429 (3), 433 (3), 435 (3), 448 (2), 450 (2) $M^{+\cdot}$ 508 (5·7), 510 (6).

VIII: 213 (11), 215 (20), 229 (24), 249 (10), 293 (14), 295 (15), 310 (7), 353 (5), 354 (5), 355 (5), 356 (5), 368 (53), 369 (100), 370 (32), 428 (2), 429 (4), 433 (5), 435 (5), 448 (9), 450 (9), $M^{+\cdot}$ 508(10), 510 (10).

IX: 211 (28), 213 (47), 227 (21), 229 (24), 231 (31), 247 (47), 249 (38), 265 (52), 266 (48), 267 (36), 275 (24), 301 (55), 302 (60), 303 (43), 304 (38), 316 (10), 318 (7), 351 (8), 353 (15), 366 (21), 367 (28), 368 (35), 369 (16), 371 (16), 384 (38), 385 (40), 386 (62), 387 (24), 402(5), 405 (14), 420 (26), 421 (12), 422 (12), M^+ 456 (100), 457 (31), 458 (69).

X: 213 (11), 247 (34), 248 (21), 249 (31), 263 (11), 283 (9), 285 (7), 289 (5), 303 (8), 344 (22), 346 (16), 366 (8), 367 (16), 368 (43), 384 (6), 387 (8), 402 (14), 403 (8), 404 (6), 423 (3), 427(7), 438 (5), 440 (3), 462 (6), 463 (2·3), 464 (2·5), M^+ 498 (100), 499 (34), 500 (70), 501 (23), 502 (15),

XI: 211 (49), 212 (19), 213 (14), 226 (13), 229 (12), 239 (10), 247 (22), 253 (55), 254 (13), 255 (11), 260 (11), 261 (11), 271 (5), 275 (5), 342 (5), 351 (11), 353 (9), 366 (100), 367 (31), 368 (39), 384 (30), 385 (10), 386 (8), 446 (3·3), 448 (3·7), 464 (0·3), 466 (0·3).

XII: 211 (32), 247 (25), 253 (18), 255 (15), 257 (16), 275 (17), 333 (11,) 335 (16), 337 (8), 351 (9), 353 (13), 364 (17), 366 (100), 367 (47), 368 (66), 369 (28), 384 (25), 385 (20), 386 (37), 431 (4), 433 (9), 435 (6), 446 (26), 447 (16), 448 (47), 449 (24), 450 (26), 464 (3), 465 (5), 466 (3), 467 (5), 526 (0·7), 528 (1·2), 530 (0·7), M^+ 544 (0·1), 546 (0·2), 548 (0·1).

XIII: 211 (24), 212 (10), 213 (13), 247 (28), 251 (19), 253 (38), 255 (30), 257 (30), 260 (11), 279 (15), 283 (8), 333 (7), 335 (8), 349 (4), 351 (9), 353 (16), 354 (5), 355 (4), 364 (9), 366 (61), 367 (30), 368 (100), 369 (30), 384 (16), 385 (9), 393 (3), 395 (3), 426 (3), 427 (3), 431 (1), 433 (2), 435 (1), 446 (4), 447 (6), 448 (8), 449 (6), 450 (4), 491 (0·7), 493 (0·7), 506 (0·5), 507 (1), 508 (0·6), 509 (1), M^+ 586 (0·03), 588 (0·06), 590 (0·02).

XIV: 231 (21), 233 (20), 247 (11), 249 (18), 250 (12), 267 (11), 285 (62), 286 (77), 287 (33), 288 (29), 300 (18), 404 (5), 405 (3), M^+ 440 (100), 441 (33), 442 (40).

XV: 231 (20), 232 (13), 233 (20), 247 (9), 253 (10), 267 (19), 327 (28), 328 (55), 329 (19), 330 (19), 342 (12), 368 (11), 386 (8), 422 (9), 446 (2), M^+ 482 (100), 483 (33), 484 (38).

XVI: 213 (68), 231 (72), 249 (39), 329 (82), 330 (82), 331 (92), 332 (79), 344 (18), 346 (18), 366 (10), 367 (24), 368 (17), 369 (10), 371 (9), 384 (29), 385 (38), 386 (31), 387 (13), 404 (7), 405 (12), M^+ 484 (99), 486 (100).

XVII: 211 (18), 213 (27), 227 (14), 229 (16), 231 (35), 233 (17), 245 (15), 247 (13), 249 (30), 251 (12), 311 (13), 313 (10), 329 (93), 330 (71), 331 (100), 332 (66), 344 (11), 346 (11), 367 (18), 385 (29), 386 (12), 405 (15), 406 (9), M^+ 484 (96), 485 (96), 486 (96), 487 (29).

XVIII: 211 (70), 226 (18), 253 (30), 291 (7), 351 (14), 366 (100), 367 (43), 368 (23), 371 (6) 384 (16), 385 (15), 386 (12), 387 (7), 389 (6), 404 (6), 405 (5), 431 (4), 433 (4·6), 446 (9), 448 (11) 464 (1·5), 466 (2·5), M^+ 484 (11), 486 (11).

XIX: 213 (15), 229 (9), 231 (7), 233 (8), 247 (8), 293 (7), 311 (7), 313 (7), 367 (18), 368 (13), 371 (17), 372 (36), 373 (24), 374 (34), 386 (11), 387 (12), 388 (11), 446 (2), 447 (2), 466 (9), 468 (9), M^+ 526 (98), 527 (33), 528 (100) 529 (33),

XX: 211 (14), 213 (19), 217 (15), 219 (11), 227 (15), 231 (65), 232 (50), 233 (92), 247 (50), 273 (16), 291 (6), 292 (8), 293 (9), 311 (26), 313 (27), 333 (8), 367 (29), 368 (33), 371 (40), 372 (60), 373 (42), 374 (58), 386 (31), 387 (54), 427 (5), 431 (2·5), 446 (10), 447 (10), 448 (9), 451 (7), 453 (7), 466 (8), 468 (8), M^+ 526 (100), 528 (100).

XXI: 213 (38), 227 (18), 229 (29), 231 (38), 245 (20), 247 (31), 255 (22), 271 (15), 273 (20), 274 (14), 275 (40), 301 (33), 345 (8), 346 (8), 347 (12), 348 (10), 353 (26), 366 (37), 367 (40), 368 (42), 369 (23), 371 (24), 384 (57), 385 (75), 386 (100), 387 (36), 420 (6), 421 (6), 464 (3), 466 (3), M^+ 500 (21), 502 (29).

XXII: 211 (20), 213 (22), 229 (44), 231 (18), 247 (44), 253 (25), 255 (15), 260 (23), 261 (26), 271 (23), 275 (30), 301 (25), 307 (14), 327 (5), 326 (7), 342 (13), 351 (14), 353 (15), 366 (100), 367 (48), 368 (38), 369 (22), 371 (12), 384 (92), 385 (65), 386 (59), 387 (22), 402 (5), 403 (10), 404 (5), 405 (9), 465 (5), 467 (5), M^+ 500 (3·3), 502 (4·5).

XXIII: 211 (39), 212 (76), 213 (35), 247 (23), 253 (41), 254 (52), 275 (12), 351 (6), 352 (10), 353 (9), 354 (8), 366 (49), 367 (100), 368 (46), 384 (18), 385 (39), 386 (27), 387 (26), 402 (2·4), 403 (3·3), 404 (6), 405 (3·6), 406 (3·6), 420 (2), 421 (4), 422 (9), 423 (4), 424 (3·3), 446 (3·3), 448 (3·6), 466 (4), 468 (4), $M^{+\cdot}$ 501 (3), 503 (3·9).

XXIV: 231 (33), 247 (29), 262 (15), 263 (18), 275 (30), 303 (15), 310 (15), 344 (12), 367 (36), 368 (24), 369 (21), 370 (22), 371 (20), 384 (12), 385 (20), 386 (100), 387 (62), 388 (42), 404 (5·6), 405 (6), 407 (8·4), 422 (9), 423 (9), 424 (5), 467 (3·6), 469 (3·2), $M^{+\cdot}$ 502 (2), 504 (2·6).

XXV: 213 (30), 227 (12), 247 (27), 255 (17), 260 (20), 291 (6), 293 (7), 353 (18), 366 (14), 367 (32), 368 (100), 384 (14), 403 (7), 427 (7), $M^{+\cdot}$ 542 (3·6), 544 (4·8).

XXVI: 213 (11), 227 (6), 247 (13), 249 (7), 253 (7), 255 (8), 260 (5), 263 (7), 349 (11), 351 (6), 353 (10), 366 (25), 367 (28), 368 (100), 369 (31), 384 (14), 385 (7), 402 (8), 403 (22), 404 (9), 405 (8), 426 (2·5), 427 (5), 446 (2), 447 (3), 448 (3), 449 (2), 462 (2), 463 (4), 464 (2), 465 (1·7), M^{+} 542 (3·6), 544 (5).

XXVII: 211 (9), 213 (8), 229 (18), 231 (14), 247 (7), 249 (24), 250 (52), 264 (13), 267 (97), 268 (46) 282 (26), 369 (4), 384 (3), 387 (2), 389 (2), $M^{+\cdot}$ 422 (100).

XXVIII: 217 (20), 229 (23), 231 (38), 232 (29), 233 (23), 245 (18), 246 (18), 247 (20), 249 (70), 250 (96), 264 (26), 267 (63), 268 (27), 271 (17), 282 (14), 351 (8), 366 (8), 369 (18), 384 (46), 386 (13), 389 (22), 402 (20), 404 (100), M^{+} 422 (50).

XXIX: 211 (18), 213 (13), 227 (12), 229 (18), 231 (20), 245 (14), 249 (45), 250 (74), 261 (15), 264 (30), 281 (92), 282 (34), 296 (27), 369 (5), 383 (7), 384 (12), 402 (13), 404 (38), 416 (7), M^{+} 436 (100).

XXX: 211 (15), 229 (34), 231 (18), 249 (17), 250 (29), 292 (32), 306 (7), 309 (100), 310 (37), 324 (19), 351 (4), 355 (3), 356 (4), 366 (12), 369 (17), 384 (50), 385 (16), 386 (8), 404 (18), 426 (2), 444 (8), 446 (7), $M^{+\cdot}$ 464 (76).

XXXI: 217 (23), 236 (72), 237 (92), 238 (58), 246 (50), 264 (8), 273 (13), 291 (16), 292 (32), 301 (5), 306 (7), 309 (6), 310 (4), 366 (10), 371 (38), 384 (13), 386 (100), 387 (30), 404 (11), 446 (76), M^{+} 464 (23).

XXXII: 211 (21), 229 (24), 230 (16), 231 (11), 245 (12), 247 (32), 248 (18), 265 (12), 266 (12), 271 (15), 289 (27), 331 (10), 351 (8), 358 (7), 366 (32), 367 (18), 369 (26), 384 (75), 385 (37), 386 (13), 387 (15), 402 (100), 403 (36), 420 (25), 421 (8), 422 (9), $M^{+\cdot}$ 438 (25), 439 (7·5), 440 (8·3).

XXXIII: 211 (20), 213 (13), 227 (17), 229 (18), 245 (18), 247 (25), 253 (13), 261 (19), 265 (16), 266 (17), 271 (20), 331 (15), 351 (15), 358 (20), 366 (25), 367 (21), 384 (100), 369 (37), 385 (50), 402 (70), 405 (9), 420 (28), 421 (9), 422 (11), $M^{+\cdot}$ 438 (7).

XXXIV: 211 (43), 229 (23), 247 (31), 253 (69), 271 (30), 313 (13), 331 (61), 351 (25), 356 (21), 366 (100), 367 (32), 368 (25), 369 (32), 384 (69), 402 (17), 426 (9), 429 (12), 444 (14), 462 (0·7), M^{+} 480 (0·4).

XXXV: 211 (14), 247 (8), 253 (8), 301 (3), 351 (7), 366 (100), 367 (37), 368 (16), 384 (32), 385 (14), 402 (26), 403 (9), 404 (10), 420 (12), 421 (4), 422 (4·6), 426 (3·4), 427 (2), 462 (1), $M^{+\cdot}$ 480 (0·1).
XXXVI: 211 (73), 226 (18), 229 (12), 247 (20), 253 (43), 279 (8), 351 (16), 366 (100), 367 (34), 368 (19), 369 (14), 384 (24), 402 (8), 431 (0·7), 433 (0·7), 446 (3·2), 448 (3·2), 464 (0·7), 466 (0·8).

XXXVII: 211 (82), 226 (16), 239 (9), 247 (12), 253 (45), 279 (9), 351 (14), 366 (100), 367 (30), 368 (21), 369 (19), 384 (46).

XXXVIII: 211 (29), 229 (15), 247 (13), 253 (29), 271 (12), 289 (6), 290 (7), 331 (15), 351 (14), 356 (7), 366 (100), 367 (40), 368 (25), 369 (25), 384 (88), 385 (58), 426 (11), 427 (6), 444 (20), 445 (8), 446 (6), 448 (5), 464 (2), 466 (2·2), $M^{+\cdot}$ 524 (0·2), 526 (0·2).

XXXIX: 211 (16), 227 (10), 229 (14), 247 (15), 253 (25), 271 (13), 288 (9), 289 (6), 340 (9), 351 (16), 356 (13), 366 (54), 367 (23), 368 (12), 369 (19), 384 (100), 385 (34), 426 (5), 427 (3·4), 445 (5·4), M^{+} 524 (0·3), 526 (0·3).

XL: 213 (21), 214 (9), 215 (12), 228 (17), 229 (14), 231 (24), 232 (33), 233 (18), 246 (21), 247 (14), 368 (9), 371 (12), 386 (100), $M^{+\cdot}$ 404 (12).

XLI: 214 (21), 215 (17), 216 (15), 217 (9), 229 (16), 230 (19), 231 (11), 232 (25), 233 (50), 234 (45), 235 (17), 247 (26), 248 (27), 303 (6), 354 (6), 355 (4), 369 (6·5), 370 (6), 372 (9), 373 (8), 387 (100), 388 (100), 389 (28), $M^{+\cdot}$ 405 (10), 406 (10), 407 (3).

XLII: 213 (26), 214 (16), 215 (12), 228 (34), 231 (12), 255 (15), 274 (39), 288 (20), 353 (8), 368 (79), 369 (26), 371 (9), 386 (33), 428 (100), 429 (34), M^{+} 446 (7).

IL: 202 (6), 206 (4), 214 (3), 220 (5), 232 (3), 247 (3), 315 (4·4), 318 (6), 333 (100), 369 (2·4), 372 (2·2), 387 (2·4), $M^{+\cdot}$ 405 (3·7).

L: 230 (52), 245 (12), 247 (12), 260 (18), 261 (34), 272 (12), 300 (12), 328 (10), 332 (11), 333 (13), 343 (31), 370 (11), 384 (8), $M^{+\cdot}$ 385 (100), 386 (40).

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Translated by Ž. Procházka.