MASS SPECTRA OF 4,4-DIMETHYL-A-HOMO-4a,6-CHOLESTADIEN--3-OLS, 4,4-DIMETHYL-A-HOMO-5-CHOLESTENE-3,4a-DIOLS AND THEIR DERIVATIVES*

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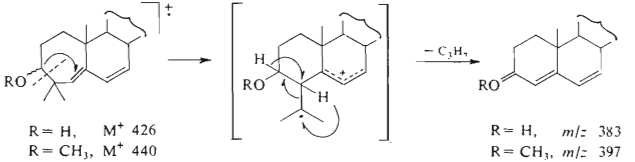
Partial electron impact induced mass spectra are given of 3α-hydroxy-, 3β-hydroxy-, 3β-methoxy-, 3α-acetoxy- and 3β-acetoxy-4,4-dimethyl-A-homo-4a,6-cholestadienes, 3α,5α-epoxy-4,4-dimethyl-A-homo-5-cholestene, isomeric 4,4-dimethyl-A-homo-5-cholestene-3α(β),4aα(β)-diols, their 3-acetoxy derivatives and 3-methyl ethers. The fragmentation of the molecular ions of these substances involves the usual elimination of substituents (in the form of H_2O, CH_3OH, CH_3COOH, CH_2CO), but the most abundant and characteristic ions are products of the contraction of ring A (to a six- or five-membered one), accompanied by expulsion of a framgent containing the carbon atom $C_{(4)}$ with both methyls.

The mass spectral behaviour of steroidal compounds with non-classical A-homo-skeleton has not been studied in detail so far. In connection with our stereochemical studies of 4,4-dimethyl-A-homocholestane derivatives[1-4] we also examincd the electron impact induced fragmentation in the series of 4,4-dimethyl-A-homocholestane derivatives with oxygen-containing substituents[2,5] in the positions 3,4a or 5, and of 3- or 4a-oxygenated derivatives of 4,4-dimethyl-4a,5-epoxy-A-homocholestane[1] or 4,4-dimethyl-3,5-epoxy-A-homocholestane[4]. This study deals with mass spectral fragmentation of Δ^5 and $\Delta^{4a,6}$-unsaturated derivatives of 4,4-dimethyl-A-homocholestane series with oxygen-containing function in positions 3 and 4a.

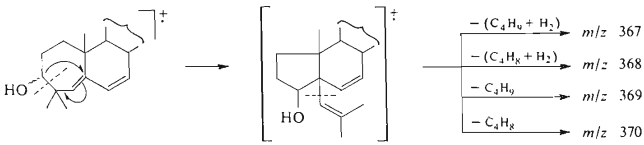


R = H, M^+ 426
R = CH_3, M^+ 440

R = H, *m/z* 383
R = CH_3, *m/z* 397

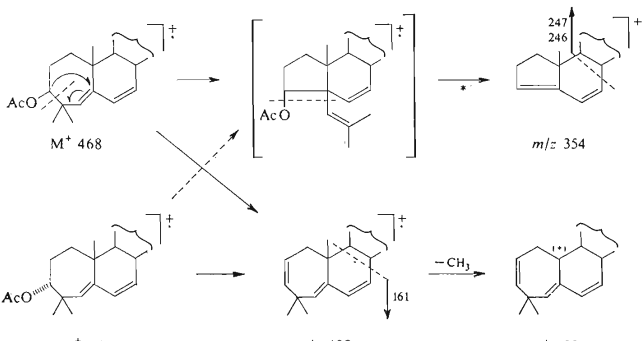
SCHEME 1

* Part CCLXXIV in the series On Steroids; Part CCLXXIII: This Journal *47*, 2530 (1982).



SCHEME 2

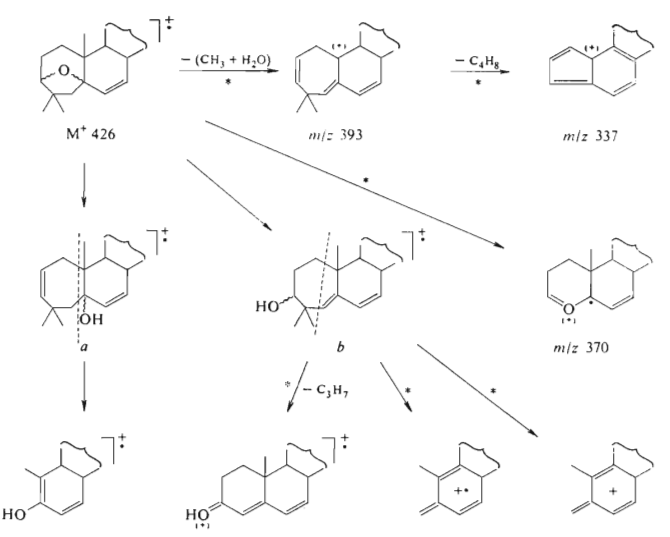
The mass spectra of unsaturated alcohols *I* and *II* are dominated by ion m/z 383 which is formed on losing a species C_3H_7 from the molecular ion (Scheme 1). The preferred allylic cleavage of the $C_{(3)}$—$C_{(4)}$ bond and the high stability of the resulting oxonium ion m/z 383 clearly are the reasons for its high predominance in the spectrum. The proposed mechanism of hydrogen transfer in this process was deduced from the analogy with the formation of the same ion in the mass spectrum of 4a--deuterated diol *XXI*. Alternative splitting off of the fragment C_4 (with or without loss of H_2) leads to the formation of a characteristic group of ions, m/z 367, 369 and 370 (Scheme 2). Ion m/z 294, formed on loss of the side chain C_8H_{18} from ion $[M-H_2O]^+$ is of diagnostic value, because it appears only in the mass spectrum of the β-isomer *II*. Ion m/z 397, the only important ion in the mass spectrum of methyl ether *III* is formed in the same way as the homologous ion m/z 383.



SCHEME 3

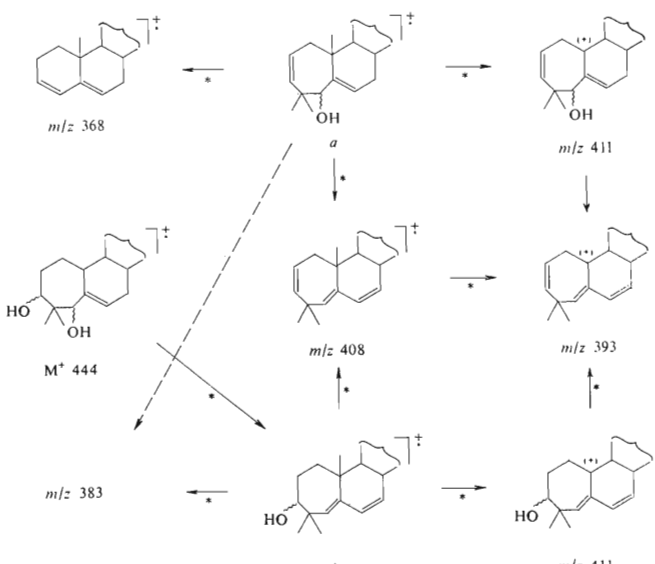
The decomposition of molecular ions of isomeric acetates *IV* and *V* takes place by two competing fragmentation paths (Scheme 3): the first one begins with the elimination of CH_3COOH by McLafferty rearrangement[6] (ion *m/z* 409, *m** 355·7), and the second by the expulsion of a species $C_6H_{10}O_2$ under contraction of ring A (ion *m/z* 354, very abundant *m** 267·8). While the first path is common for both isomers, *IV* and *V*, the second one is important merely for the fragmentation of the β-isomer *V* (ion *m/z* 354 forms the base peak). On the contrary, the spectrum of α-acetoxy derivative *IV* is dominated by the ion *m/z* 408, which affords – by B-ring cleavage – ion *m/z* 161 (*m** 63·5). Analogous cleavage of ion *m/z* 354 gives rise to ions *m/z* 246 and 247 (*m** 172·3 or 170·9), while the loss of the side chain leads to the formation of ion *m/z* 241 (*m** 164·1).

The molecular ion of the unsaturated epoxide *VI* decomposes only to a low extent, by several almost equivalent paths: simultaneous elimination of a water molecule and of a $CH_3^{\bullet}$ radical (an abundant metastable peak at *m** 362·5 was observed) gives rise to the ion *m/z* 393, which loses a species C_4H_8 (*m** 289·0) to give ion *m/z* 337



SCHEME 4

(Scheme 4). On elimination of C_4H_8 from M^+ (m^* 321·4) the most abundant ion m/z 370 is formed, which is further stabilized by expulsion of a radical $CH_3^{\bullet}$ (m^* 340·6). The ion *a* (Scheme 4), formed by splitting of the O-bridge on the carbon atom $C_{(3)}$ is further decomposed to afford ion m/z 330, while the of ion *b*, formed by cleavage of the epoxide bond on the side near to $C_{(5)}$ atom to decomposes, ions m/z 383 (see also Scheme 1) and m/z 325 and 326.



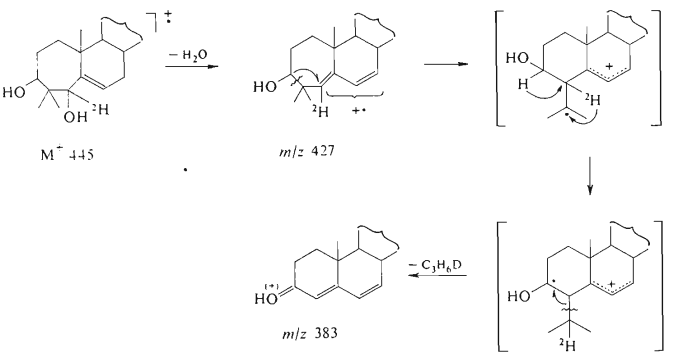
SCHEME 5

The molecular ion of diols *VII*–*X* easily undergoes elimination of a water molecule under formation of both possible products – ions *a* and *b* (Scheme 5). From a comparison with the mass spectra of unsaturated alcohols *I* and *II* it is evident that ion m/z 383 is the main product of fragmentation of ion *b*. A comparison with the mass spectra of deuterated compounds *XXI*, *XXII* and *XXIV* contributed to the elucidation of the origin and the mechanism of formation of the ion m/z 383. It was found that in this process the carbon atom $C_{(4)}$ is eliminated together with both its methyl groups and with the hydrogen atom coming predominantly from the carbon

atom $C_{(4a)}$ (Scheme 6). A partial shift of ion m/z 383 in the spectrum of compound *XXI* to m/z 384 permits an alternative mechanism to be considered, which – on the contrary – is important for the fragmentation of acetates *XI*–*XIV* and methylethers *XV* and *XVI* (as follows from the shifts of ions m/z 383 by 1 mass unit in the mass spectrum of deuterated acetate *XXII*).

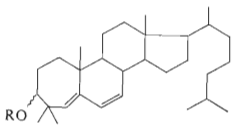
The prominent ion m/z 368 is formed by a loss of a species C_3H_6O from the ion m/z 426 (m^* 317·9). In this case, too, the expulsion of the carbon atom $C_{(4)}$ with both methyls takes place (in the mass spectrum of compound *XXIV* the peak m/z 368 is not shifted). Ion *a* (Scheme 5) and not ion *b*, is probably the precursor of ion m/z 368, because otherwise ion m/z 368 should also be observed in the mass spectra of compounds *I* and *II*, the molecular ions of which have the structure of ion *b*. After splitting of the $C_{(4)}-C_{(4a)}$ bond a recombination of the six-membered ring A (Scheme 7) with a 3,4-annellated system is assumed, which is cleaved under formation of the double bond in the ion m/z 368.

The molecular ions of acetates *XI*–*XIV* and of methyl ethers *XV* and *XVI* are also very unstable and they eliminate a molecule of CH_3COOH or CH_3OH easily to give ion *a*, m/z 426, which – the same as in the fragmentation of diols *VII*–*X* – affords the ions m/z 411, 408, 393, 383 and 368 (Scheme 5). The ion m/z 354 is formed on expulsion of the species C_4H_8O from ion *a* (the corresponding metastable ion m^* 294·2 found in the spectra of acetates *XI* and *XII* and methyl ether *XV*). The loss of the atom $C_{(4)}$ with both methyl groups in this process was confirmed by comparison with the mass spectrum of 4,4-[$^2H_6$]-dimethylanalogue *XXV* (no shift of the peak m/z 354). One of the possible ways of formation for the ion m/z 354 is presented in Scheme 8.

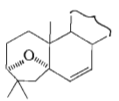


SCHEME 6

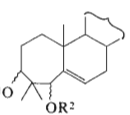
The shift of the ion m/z 383 by one mass unit in the mass spectrum of the deuterated acetate *XXII* shows that this ion is formed in the mass spectra of acetates *XI*–*XIV* by a different mechanism than in the fragmentation of M^+ of diols *VII*–*X* (a similar shift in the spectrum of deuterated diol *XXI* was not observed). The ion *b* cannot be a precursor of the ion m/z 383 (Scheme 4), unless we assume an unfavored elimination of ketene from the 3-acetoxy group together with the 4a-hydroxy group. On the contrary, the McLafferty 1,2-elimination of CH_3COOH under formation of ion *a* is a



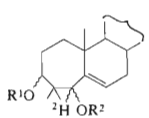
I, R = H, 3α
II, R = 3β
III, R = CH_3, 3β
IV, R = Ac, 3α
V, R = Ac, 3α



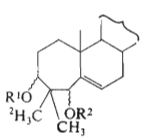
VI



$R^1 = R^2 = H$:	$R^1 = Ac$, $R^2 = H$:	$R^1 = CH_3$, $R^2 = H$:	$R^1 = R^2 = Ac$
VII, 3α, 4aβ	*XI*, 3α, 4aβ	*XV*, 3α, 4aβ	*XVII*, 3α, 4aβ
VIII, 3β, 4aα	*XII*, 3β, 4aα	*XVI*, 3β, 4aα	*XVIII*, 3β, 4aα
IX, 3α, 4aα	*XIII*, 3α, 4aα		*XIX*, 3α, 4aα
X, 3β, 4aβ	*XIV*, 3β, 4aβ		*XX*, 3β, 4aβ

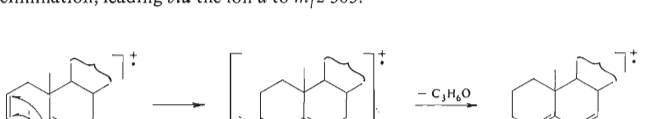


XXI, $R^1 = R^2 = H$; 3α, 4aβ
XXII, $R^1 = Ac$, $R^2 = H$; 3β, 4aβ
XXIII, $R^1 = R^2 = Ac$; 3β, 4aβ

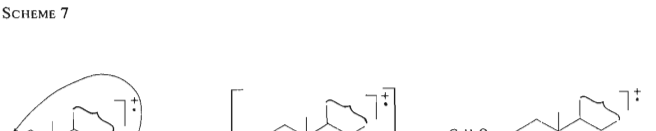


XXIV, $R^1 = R^2 = H$; 3β, 4aα
XXV, $R^1 = Ac$, $R^2 = H$; 3β, 4aα

highly favoured process, so that in this case the ion *a* must be the precursor of the ion *m/z* 383 (Scheme 9). The analogous elimination of CH_3OH from M^+ of methyl ethers *XV* and *XVI* is not as clearly preferred as the elimination of CH_3COOH from M^+ of acetates *XI*–*XIV*, and therefore the alternative 1,4-elimination of the 4a-hydroxyl effectively competes with it. The product of the last elimination, the ion *m/z* 440, is further decomposed as well as M^+ of compound *III* (Scheme 1) to give ion *m/z* 397 (*m** 358·2 found in the spectrum of compound *XV*). The lower population of this ion in the spectrum of the 3β-isomer *XVI* is probably due to a closer space interaction of the 3β-methoxy group with the 19-methyl group which favours its elimination, leading *via* the ion *a* to *m/z* 383.



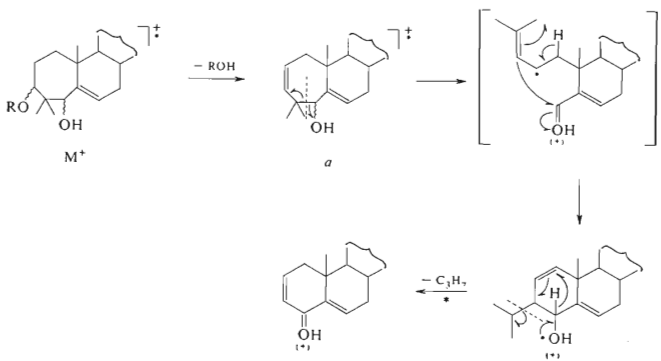
SCHEME 7



SCHEME 8

The ions *m/z* 397 and 398 in the mass spectra of acetate *XI*–*XIV* are of different origin, as is evident from their shift by 6 mass units in the spectrum of the 4,4-[$^2H_6$]-dimethyl analogue *XXV*. Both ions are probably formed from ion *a* on expulsion of C_2H_4 or C_2H_5 (carbon atoms $C_{(1)}$—$C_{(2)}$) after allylic cleavage of the $C_{(1)}$—$C_{(10)}$ bond with contraction of the A ring.

The mass spectra of acetates *XII* and *XIII* were also measured in the presence of $C_2H_5O^2H$ (exchange of the active hydrogen for deuterium took place to about 50%). From the shift of the peak *m/z* 426 it was calculated that during the elimination of CH_3COOH about 30% of active hydrogen was lost. Hence, the elimination of CH_3COOH does not proceed merely by the usual McLafferty rearrangement (under formation of ion *a*), but evidently with participation of the 4a-hydroxyl as well.



SCHEME 9

It seems that this mechanism is responsible for the exceptionally low stability of the molecular ions of hydroxy acetates *XI*–*XIV*, which should otherwise be higher than the stability of M^+ of diacetoxy derivatives *XVII*–*XX*. In fact, the abundance of M^+ of diacetates *XVII*–*XX* is 2, 8, 28 and 40 times higher than the abundance of the molecular ions of hydroxy acetates *XI*–*XIV*.

The molecular ions of diacetoxy derivatives *XVII*–*XX* eliminate CH_3COOH and CH_2CO to give ion *m/z* 426 which is further decomposed by the same pathways as the same ion in the mass spectra of hydroxy acetates *XI*–*XIV* (to form ions *m/z* 411, 408, 393, 383, 368, 354, 247 and 161). The prominent ion *m/z* 354 is formed by elimination of $C_6H_{10}O_2$ from the ion $(M-CH_3COOH)^+$, *m/z* 468 (at least in the mass spectra of compounds *XVIII* and *XX* where the corresponding metastable ion *m** 267·8 was observed). If the ion *m/z* 468 in the spectra of diacetoxy derivatives *XVII*–*XX* is formed by the elimination of 4a-acetoxy group, it should have the structure of the molecular ion of compound *IV* or *V*. However, this observation is opposed by the fact that the ion *m/z* 354 dominates the spectrum of 3α,4aα-diacetoxy derivative *XIX*, and, on the contrary, in the spectra of 3β,4aα- and 3β,4aβ-diacetoxy derivatives *XVIII* and *XX* it attains the relative abundance of only 20 or 30%, respectively, while (according to a comparison with the mass spectra of unsaturated acetates *IV* and *V* its population should be highest in the mass spectra of 3β-diacetates. Hence, the exceptionally high abundance of the ion *m/z* 354 in the mass spectrum of 3α,4aα-diacetate *XIX* (and also 3α,4aα-hydroxy acetate *XIII*) cannot be explained on the basis of either of the proposed fragmentation schemes. It seems that, in the

case of 3α,4aα-isomers *XIII* and *XIX*, the exceptional possibility for both functional groups to get close one to another (on that side of the molecular ion where no interaction with 19-methyl takes place) plays an important role. This space accessibility then conditions the course of a preferred elimination of both functional groups, leading to the ion m/z 354.

From these results it is evident that the main fragmentation paths of Δ^5-unsaturated derivatives of 4,4-dimethyl-A-homocholestane generally involve the contraction of ring A to a six- or five-membered ring, while the expelled fragment always contains the carbon atom $C_{(4)}$ with both methyl groups.

EXPERIMENTAL

The mass spectra were measured on a double focussing mass spectrometer AEI 902 (Associated Electric Industries, Manchester, G.B.). The samples were introduced by direct inlet into the ion source heated at 150–160°C. The low-resolution mass spectra were recorded at a resolving power 1 000 and electron energy 70 eV. The high-resolution measurements were carried out at resolving power $m_1/(m_1 - m_2) = 10\,000$. The accurate masses found range within ±3 ppm of the theoretical value. The syntheses of compounds *I–XX* were described earlier[2–4]. 4aα-Deuterio-4,4-dimethyl-A-homo-5-cholestene-3α,4aβ-diol (*XXI*) was prepared on reduction of 3α-acetoxy-4,4-dimethyl-A-homo-5-cholesten-4a-one[7] with lithium aluminum deuteride in boiling dioxane. 3β-Acetoxy-4aα-deuterio-4,4-dimethyl-A-homo-5-cholesten-4aβ-ol (*XXII*) and 3β,4aβ-diacetoxy-4aα-deuterio-4,4-dimethyl-A-homo-5-cholestene (*XXIII*) were prepared by acetylation of 4aα-deuterio-4,4-dimethyl-A-homo-5-cholestene-3β,4aβ-diol which was obtained on reduction of 3β-acetoxy-4,4-dimethyl-A-homo-5-cholesten-4a-one[7] with lithium aluminum deuteride in boiling dioxane. 3β-Acetoxy-4,4-[$^2H_6$]-dimethyl-A-homo-5-cholesten-4aα-ol (*XXV*) was prepared by acid catalysed opening of 3β-acetoxy-4,4-[$^2H_6$]-dimethyl-4aα,5-epoxy-A-homo-5α-cholestane[1] with hydrobromic acid in chloroform. The reductive saponification of the 3β-acetoxy group in compound *XXV* with lithium aluminum hydride in ether afforded diol *XXIV*.

Partial mass spectra (most abundant peaks from the upper part of the spectrum) of compounds *I–XXV* are given. The masses and the corresponding relative abundances (in brackets) in percents of base peak are presented. The elemental composition corresponding to the accurate mass found (if determined) follows in brackets the relative abundance:

I: 159 (26·, $C_{12}H_{15}$); 161 (5·6, $C_{12}H_{17}$); 247 (4, $C_{18}H_{31}$); 367 (4·3); 368 (2·3); 369 (2·5); 370 (3·4); 383 (100, $C_{27}H_{43}O$); 393 (3); 408 (3); M^+ 426 (4·4, $C_{30}H_{50}O$).

II: 161 (29·5, $C_{12}H_{15}$); 247 (9·3); 295 (12); 325 (3·2, $C_{24}H_{37}$); 367 (6, $C_{26}H_{39}O$); 368 (5·5, $C_{26}H_{40}O$); 369 (4·3, $C_{26}H_{41}O$); 370 (6·4, $C_{26}H_{42}O$); 383 (100, $C_{27}H_{43}O$); 393 (4·3); 408 (21·6); M^+ 426 (8·2, $C_{30}H_{50}O$).

III: 159 (10, $C_{12}H_{15}$); 199 (3); 247 (1·7); 367 (5); 393 (2·6); 397 (100, $C_{28}H_{45}O$); 408 (3·3); 425 (1); M^+ 440 (4·2, $C_{31}H_{52}O$).

IV: 161 (36); 241 (6); 246 (6); 247 (13·4); 253 (5); 295 (9); 300 (9·6); 325 (3·2); 354 (12, $C_{26}H_{42}$); 365 (5·4); 367 (5); 383 (23, $C_{27}H_{43}O$); 393 (20); 408 (100); 425 (3); 426 (3); M^+ 468 (24, $C_{32}H_{52}O_2$).

V: 161 (60. $C_{12}H_{15}$); 241 (18,$C_{18}H_{25}$); 246 (32, $C_{18}H_{30}$); 247 (48, $C_{18}H_{31}$); 253 (3·4); 295 (6); 300 (3·4); 325 (3·3); 354 (100, $C_{26}H_{42}$); 365 (3); 367 (4); 381 (7); 383 (11); 393 (13); 408 (78); 425 (2); 426 (1·8); 453 (1·6); M^+ 468 (20, $C_{32}H_{52}O_2$).

VI: 199 (19); 206 (14); 295 (6); 313 (13, $C_{22}H_{33}O$); 325 (15, $C_{24}H_{37}$); 326 (13, $C_{24}H_{38}$); 330 (10, $C_{23}H_{38}O$); 337 (10, $C_{25}H_{37}$); 341 (8·3, $C_{25}H_{41}$); 351 (6·5, $C_{26}H_{39}$); 355 (3·6); 367 (19, $C_{27}H_{43}$); 369 (14·4, $C_{26}H_{41}O$); 370 (100, $C_{26}H_{42}O$); 383 (41, $C_{27}H_{43}O$); 393 (98. $C_{29}H_{45}$); 408 (13); 411 (6); M^+ 426 (93, $C_{30}H_{50}O$).

VII 247 (33, $C_{28}H_{31}$); 295 (10); 313 (15, $C_{22}H_{33}O$); 315 (8·4); 332 (8); 341 (8·4); 344 (14, $C_{24}H_{40}O$); 345 (15·4, $C_{24}H_{41}O$); 353 (19); 354 (23, $C_{26}H_{42}$); 355 (14·6); 368 (77, $C_{27}H_{44}$); 369 (33); 370 (22); 383 (92, $C_{27}H_{43}O$); 393 (13·4); 397 (10); 398 (8); 408 (38·4); 411 (77); 426 (100); M^+ 444 (1·5, $C_{30}H_{52}O_2$).

VIII: 247 (37); 313 (17); 315 (12); 327 (14); 341 (13); 343 (10·6); 344 (15); 345 (21); 353 (16); 354 (23); 355 (17); 359 (15); 368 (67); 369 (28); 370 (19); 383 (53); 393 (11); 397 (13); 398 (10); 408 (32); 411 (70); 426 (100); M^+ 444 (15, $C_{30}H_{52}O_2$).

IX: 247 (35); 313 (15; 315 (9); 327 (11); 341 (10); 343 (8); 344 (13); 345 (15); 353 (14); 354 (22); 355 (15); 359 (11); 368 (56); 369 (26); 370 (18); 383 (100); 393 (11); 397 (11); 398 (8); 408 (29); 411 (59); 426 (82); M^+ 444 (9, $C_{30}H_{52}O_2$).

X: 247 (26); 313 (14); 315 (9); 327 (6·5); 341 (7); 343 (7); 344 (15); 345 (15); 353 (14); 354 (21); 355 (12); 368 (70); 369 (28); 370 (20); 383 (33); 393 (8); 397 (10); 298 (8), 408 (33); 411 (67); 426 (100); M^+ 444 (2·8).

XI: 231 (20); 247 (45, $C_{18}H_{31}$); 295 (11); 313 (16, $C_{22}H_{33}O$); 315 (10, $C_{22}H_{35}O$); 344 (17, $C_{24}H_{40}O$); 345 (17, $C_{24}H_{41}O$); 353 (15, $C_{26}H_{41}$); 354 (24, $C_{26}H_{42}$); 368 (78, $C_{27}H_{44}$); 369 (31); 370 (19); 383 (20, $C_{27}H_{43}O$); 393 (10); 397 (9); 398 (9); 408 (36); 411 (72); 426 (100); 468 (1·2); 468 (0·3); M^+ 486 (0·3).

XII: 247 (15); 313 (7); 315 (5); 344 (9); 345 (9·4); 354 (17); 368 (53); 370 (21); 383 (13); 393 (5); 397 (12); 398 (11·5); 408 (26); 411 (45); 426 (100); 468 (1·2); M^+ 486 (2·6).

XIII: 247 (32); 295 (6); 313 (12); 343 (9); 344 (14); 345 (13); 353 (14); 354 (96); 368 (57); 370 (15); 383 (21); 393 (11); 397 (9); 398 (7); 408 (39); 411 (64); 426 (100); 468 (4); M^+ 486 (1).

XIV: 247 (21); 295 (6); 313 (8); 344 (10); 345 (11); 353 (13); 354 (27); 368 (71); 383 (15); 393 (8); 397 (6); 398 (6); 408 (37); 411 (58); 426 (100); 468 (2); M^+ 486 (0·8).

XV: 247 (13); 295 (4); 313 (7); 315 (4); 344 (9); 345 (9); 353 (8); 354 (14); 355 (8)8; 368 (60); 383 (12); 393 (6); 397 (63, $C_{28}H_{45}O$); 408 (27); 411 (43); 426 (100); 440 (8); M^+ 458 (2, $C_{31}H_{54}.O_2$).

XVI: 247 (16); 295 (5·5); 313 (9); 315 (6); 344 (10·5, $C_{24}H_{40}O$); 345 (11), $C_{24}H_{41}O$); 353 (11·3, $C_{26}H_{41}$); 354 (17, $C_{26}H_{42}$); 355 (10); 358 (70, $C_{27}H_{44}$); 383 (13, $C_{27}H_{43}O$); 393 (7); 397 (18, $C_{28}H_{45}O$); 408 (27); 411 (53); 426 (100); 440 (3); M^+ (0·4, $C_{31}H_{54}O_2$).

XVII: 247 (18); 295 (5); 313 (6); 327 (8); 354 (70,$C_{26}H_{42}$); 368 (23, $C_{27}H_{44}$); 383 (14, $C_{27}H_{43}.O$); 393 (14); 408 (86); 411 (38); 426 (100); 453 (3·4); 468 (44); 486 (19); 513 (2); M^+ 528 (12, $C_{34}H_{56}O_4$).

XVIII: 247 (25); 275 (10); 295 (8); 313 (7); 327 (28); 354 (41, $C_{26}H_{42}$); 368 (20); 370 (9); 372 (8); 383 (10); 393 (21); 408 (90); 411 (27); 126 (100, $C_{30}H_{50}O$); 453 (10); 468 (42, $C_{32}H_{52}O_2$); 486 (34, $C_{32}H_{54}O_3$); 513 (2); M^+ 528 (12, $C_{34}H_{56}O_4$).

XIX: 241 (11); 246 (19); 247 (30); 327 (10); 354 (100, $C_{26}H_{42}$); 367 (6); 368 (7); 369 (6); 370 (7); 381 (7); 383 (7); 393 (12); 408 (53); 411 (11); 425 (17); 426 (47); 468 (22); 486 (3·3); M^+ 528 (2, $C_{34}H_{56}O_4$).

XX: 247 (13); 295 (3); 313 (5); 327 (9); 344 (7); 345 (7); 354 (20); 368 (38); 383 (10); 393 (9); 408 (46); 411 (40); 426 (100); 453 (4); 468 (29); 486 (30), M^+ 528 (14, $C_{34}H_{56}O_4$).

XXI: 247 (27); 296 (6); 314 (9); 345 (12); 346 (9·5); 354 (15); 355 (16·6); 356 (9); 368 (10); 369 (86); 370 (37); 383 (100); 385 (48); 394 (13·5); 397 (9); 408 (8); 409 (50), 411 (6·6); 412 (52); 427 (86); M^+ 445 (1·4).

XXII: 247 (20); 296 (6); 314 (9); 345 (13); 346 (11); 354 (20); 355 (19); 369 (100); 384 (16); 394 (10); 397 (7); 409 (41); 412 (56); 427 (96); 454 (1·5); 469 (1·2); M^+ 487 (0·4).

XXIII: 247 (40); 328 (21); 354 (49); 355 (20); 369 (57); 370 (29); 371 (21); 384 (23); 394 (25); 408 (28); 409 (86); 410 (32); 412 (62); 426 (20); 427 (100); 428 (35); 469 (17); 487 (17); M^+ 529 (4·5).

XXIV: 247 (44); 313 (11); 315 (15); 319 (11); 327 (15); 341 (12); 343 (14); 344 (18, $C_{24}H_{40}O$); 345 (16); 346 (15); 353 (17); 354 (30), $C_{26}H_{42}$); 355 (20); 359 (19); 368 (72); 369 (29); 370 (21); 383 (49); 399 (8); 403 (14); 404 (10); 414 (39); 417 (60); 432 (100); M^+ 450 (16).

XXV: 170 (23); 171 (22); 247 (21); 301 (8); 315 (6); 319 (7·5); 344 (9); 353 (13); 354 (21); 355 (11); 368 (58); 369 (23); 370 (15); 383 (11); 399 (6); 403 (7); 404 (6); 413 (8); 414 (41); 415 (15); 416 (10); 417 (49); 430 (10); 431 (19); 432 (100); M^+ 486 (1).

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