MASS SPECTROMETRIC FRAGMENTATION OF TRITERPENOID DERIVATIVES WITH OXABICYCLOOCTANE AND OXABICYCLOHEPTANE RING E ARRANGEMENT*

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The character of the mass spectra of triterpenoids derived from 20β,28-epoxy-18α,19β*H*-ursane (*I*) is determined by the structure of the ring E. Fragmentation always takes place in ring E. Two types of fragmentation were found during which ring D is either preserved or cleaved. The type of fragmentation depends on the substitution at the positions $C_{(21)}$ and $C_{(22)}$.

In the preceding paper[1] we discussed the structure elucidation and the reactivity of derivatives of 20β,28-epoxy-18α,19β*H*-ursane (*I*). In connection with structure determination of these compounds the mass spectra of compounds *II*–*XVIII* were studied and the results of these measurements are summarized in this paper (Table I). All compounds measured contain in their ring E an oxabicyclo[2,2,2]octane or oxabicyclo[2,2,1]heptane system (anhydride *II* of oxabicyclo[3,2,2]nonane), part of which is always the same tetrahydropyran ring *cis* annelated with ring D. The individual compounds differ only by the bridge over this tetrahydropyran ring between the positions 17 and 20; this bridge determines the character of the fragmentation.

EXPERIMENTAL

The measurement was carried out on a Varian MAT 311 spectrometer. The energy of the ionizing electrons was 70 eV and the ionizing electron current was 1 mA; the temperature of the ion source was 200°C and the temperature of the direct inlet system was 150–200°C. The high resolution measurements were carried out with an error not exceeding 5 p.p.m.

RESULTS AND DISCUSSION

The compounds measured can be divided into two groups depending on the type of bridging of the tetrahydropyran ring at the positions $C_{(17)}$ and $C_{(20)}$. The type *A* (compounds *II*–*X*): The group forming the bridge is eliminated in the form of a neutral molecule (or neutral molecules), while ring D remains uncleaved (Scheme 1).

* Part L in the series Triterpenes; Part IL: This Journal *41*, 1200 (1976).

TABLE I

Ions of the Substances Measured

Small letters indicate the type of ion, see Schemes 1 and 2.

II	(Anhydride of 3β-acetoxy-21,22-seco-20β,28-epoxy-18α,19β*H*-ursane-21,22-dioic acid): *m/e* 528 ($C_{32}H_{48}O_6$, 0·1%, M), 500 ($C_{31}H_{48}O_5$, 1·6%, *b*), 456 ($C_{30}H_{48}O_3$, 15·0%, *f*), 440 ($C_{29}H_{44}O_3$, 8·7%, *b*), 425 ($C_{28}H_{41}O_3$, 7·9%, 440-CH_3), 396 ($C_{28}H_{44}O$, 3·5%, *f*), 384 ($C_{26}H_{40}O_2$, 30·7%, *g*), 324 ($C_{24}H_{36}$, 7·9%, *g*), 189 ($C_{14}H_{21}$, 52·8%)[a], 43 (100%)[b]
III	(3β-Hydroxy-20β,28-epoxy-21-oxa-18α,19β*H*-ursan-22-one): *m/e* 458 ($C_{29}H_{46}O_4$, 5·8%, M), 440 ($C_{29}H_{44}O_3$, 5·2%, *b*), 425 ($C_{28}H_{41}O_3$, 7·0%, 440-CH_3), 414 ($C_{28}H_{46}O_2$, 12·8%, *f*), 396 ($C_{28}H_{44}O$, 7·0%, *f*), 342 ($C_{24}H_{38}O$, 32·6%, *g*), 324 ($C_{24}H_{36}$, 7·6%, *g*), 189 ($C_{14}H_{21}$, 59·3%), 43 (100%)
IV	(3β-Acetoxy-20β,28-epoxy-21-oxa-18α,19β*H*-ursan-22-one): *m/e* 500 ($C_{31}H_{48}O_5$, 1·0%, M), 456 ($C_{30}H_{48}O_3$, 15·2%, *f*), 440 ($C_{29}H_{44}O_3$, 9·5%, *b*), 425 ($C_{28}H_{41}O_3$, 8·6%, 440-CH_3), 396 ($C_{28}H_{44}O$, 2·9%, *f*), 384 ($C_{26}H_{40}O_2$, 28·6%, *g*), 324 ($C_{24}H_{36}$, 6·2%, *g*), 189 ($C_{14}H_{21}$, 47·1%), 43 (100%)
V	(20β,28-epoxy-21-oxa-18α,19β*H*-urs-2-en-22-one): *m/e* 440 ($C_{29}H_{44}O_3$, 10·8%, M), 425 ($C_{28}H_{41}O_3$, 12·8%, 440-CH_3), 396 ($C_{28}H_{44}O$, 22·1%, *f*), 324 ($C_{24}H_{36}$, 41·2%, *g*), 189 ($C_{14}H_{21}$, 60·8%), 43 (100%)
VI	(3β-Hydroxy-20β,28-epoxy-*E*(21)-nor-18α,19β*H*-ursan-22-one): *m/e* 442 ($C_{29}H_{46}O_3$, 4·4%, M), 414 ($C_{28}H_{46}O_2$, 27·9%, *f*), 396 ($C_{28}H_{44}O$, 15·2%, *f*), 342 ($C_{24}H_{38}O$, 54·4%, *g*), 324 ($C_{24}H_{36}$, 7·6%, *g*), 189 ($C_{14}H_{21}$, 38·0%), 43 (100%)
VII	(3β-Acetoxy-20β,28-epoxy-*E*(21)-nor-18α,19β*H*-ursan-22-one): *m/e* 484 ($C_{31}H_{48}O_4$, 0·1%, M), 456 ($C_{30}H_{48}O_3$, 15·3%, *f*), 396 ($C_{28}H_{44}O$, 5·9%, *f*), 384 ($C_{26}H_{40}O_2$, 24·7%, *g*), 324 ($C_{24}H_{36}$, 11·8%, *g*), 189 ($C_{14}H_{21}$, 56·5%), 43 (100%)
VIII	(3β,22ξ-Dihydroxy-20β,28-epoxy-*E*(21)-nor-18α,19β*H*-ursane-22ξ-carboxyloic acid): *m/e* 488 ($C_{30}H_{48}O_5$, 4·4%, M), 414 ($C_{28}H_{46}O_2$, 6·0%, *f*), 396 ($C_{28}H_{44}O$, 5·5%, *f*), 342 ($C_{24}H_{38}O$, 11·7%, *g*), 324 ($C_{24}H_{36}$, 4·4%, *g*), 189 ($C_{14}H_{21}$, 20·1%), 43 (100%)
IX	(3β,22ξ-Diacetoxy-20β,28-epoxy-*E*(21)-nor-18α,19β*H*-ursane-22ξ-carboxyloic acid): *m/e* 572 ($C_{34}H_{52}O_7$, 0·3%, M), 456 ($C_{30}H_{48}O_3$, 8·2%, *f*), 396 ($C_{28}H_{44}O$, 2·3%, *f*), 384 ($C_{26}H_{40}O_2$, 8·8%, *g*), 324 ($C_{24}H_{36}$, 3·8%, *g*), 189 ($C_{14}H_{21}$, 22·0%), 43 (100%)
X	(Methyl 3β-acetoxy-22ξ-hydroxy-20β,28-epoxy-*E*(21)-nor-18α,19β*H*-ursane-22ξ-carboxylate): *m/e* 544 ($C_{33}H_{52}O_6$, 43·6%, M), 484 ($C_{31}H_{48}O_4$, 23·1%, c), 456 ($C_{30}H_{48}O_3$, 68·0%, *f*), 396 ($C_{28}H_{44}O$, 34·6%, *f*), 384 ($C_{26}H_{40}O_2$, 83·3%, *g*), 324 ($C_{24}H_{36}$, 42·3%, *g*), 189 ($C_{14}H_{21}$, 91·7%), 43 (100%)
XI	(20β,28-Epoxy-*E*(21)-nor-18α,19β*H*-ursane-3β,22α-diol): *m/e* 444 ($C_{29}H_{48}O_3$, 100%, M), 426 ($C_{29}H_{46}O_2$, 8·1%, *j*), 301 ($C_{22}H_{37}$, 8·8%, *n*), 189 ($C_{14}H_{21}$, 18·9%), 125 ($C_7H_9O_2$, 82·4%, *o*), 43 (45·9%)
XII	(3β-Acetoxy-20β,28-epoxy-*E*(21)-nor-18α,19β*H*-ursan-22α-ol): *m/e* 486 ($C_{31}H_{50}O_4$, 56·7%, M), 426 ($C_{29}H_{46}O_2$, 10·3%, *j*), 301 ($C_{22}H_{37}$, 12·4%, *n*), 189 ($C_{14}H_{21}$, 28·9%), 125 ($C_7H_9O_2$, 100%, *o*), 43 (64·9%)

TABLE I

(*Continued*)

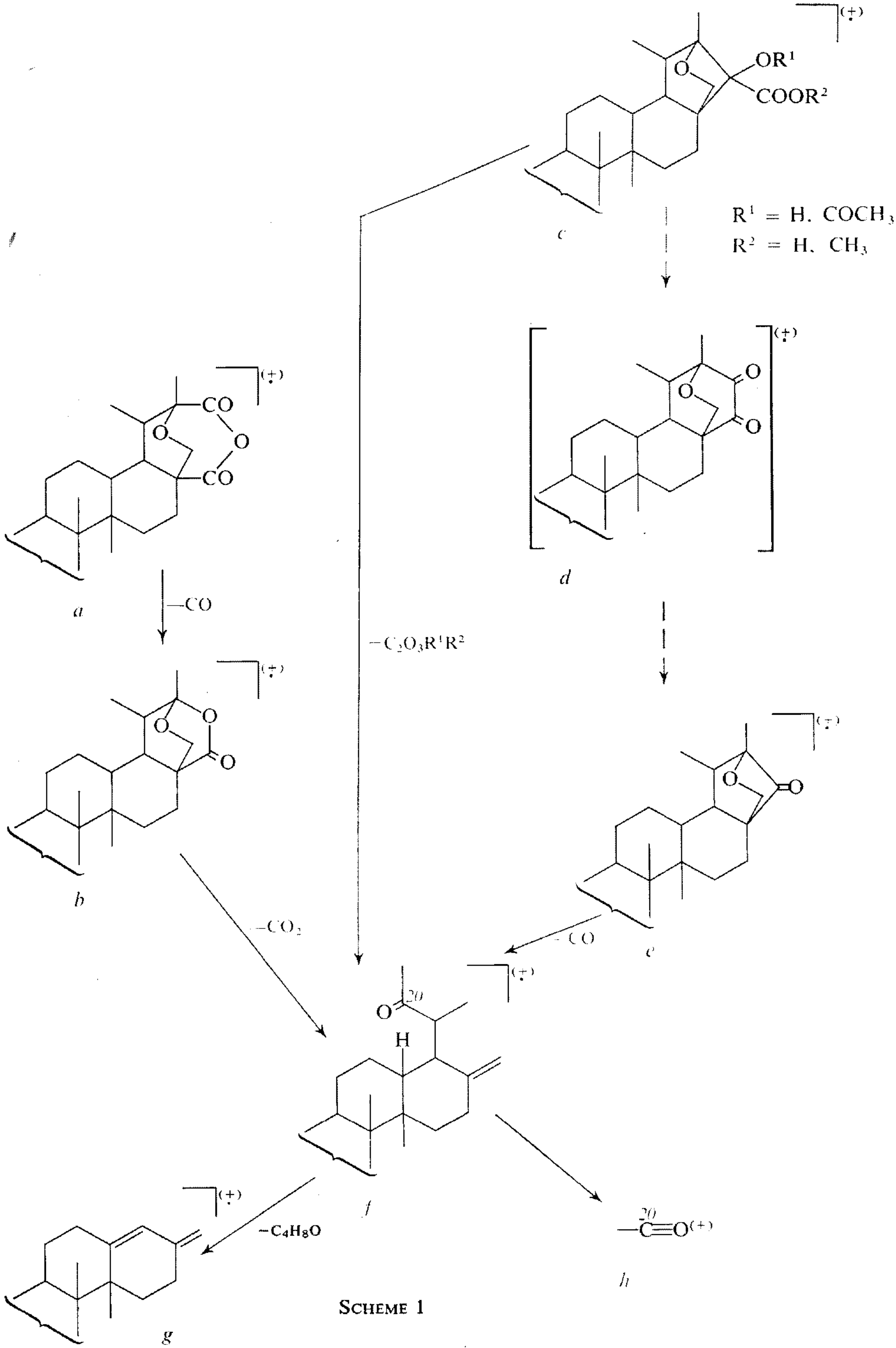
XIII	(3β,22α-Diacetoxy-20β,28-epoxy-*E*(21)-nor-18α,19β*H*-ursane): *m/e* 528 ($C_{33}H_{52}O_5$, 35·5%, M), 486 ($C_{31}H_{50}O_4$, 56·5%, *j*), 468 ($C_{31}H_{48}O_3$, 8·1%, *i*), 426 ($C_{29}H_{46}O_2$, 10·5%, *j*), 301 ($C_{22}H_{37}$, 11·3%, *n*), 189 ($C_{14}H_{21}$, 49·2%), 125 ($C_7H_9O_2$, 87·1%, *o*), 43 (100%)
XIV	(3β-Acetoxy-20β,28-epoxy-*E*(21)-nor-18α,19β*H*-ursan-22β-ol): *m/e* 486 ($C_{31}H_{50}O_4$, 94·4%, M), 426 ($C_{29}H_{46}O_2$, 3·3%, *j*), 301 ($C_{22}H_{37}$, 11·1%, *n*), 189 ($C_{14}H_{21}$, 26·7%), 125 ($C_7H_9O_2$, 100%, *o*), 43 (96·7%)
XV	(3β,22β-Diacetoxy-20β,28-epoxy-*E*(21)-nor-18α,19β*H*-ursane): *m/e* 528 ($C_{33}H_{52}O_5$, 51·3%, M), 486 ($C_{31}H_{50}O_4$, 60·0%, *j*), 468 ($C_{31}H_{48}O_3$, 3·8%, *i*), 426 ($C_{29}H_{46}O_2$, 3·8%, *j*), 301 ($C_{22}H_{37}$, 7·5%, *n*), 189 ($C_{14}H_{21}$, 25·0%), 125 ($C_7H_9O_2$, 48·8%, *o*), 43 (100%)
XVI	(22ξ-Hydroxymethyl-20β,28-epoxy-*E*(21)-nor-18α,19β*H*-ursane-3β,22ξ-diol): *m/e* 474 ($C_{30}H_{50}O_4$, 1·5%, M), 456 ($C_{30}H_{48}O_3$, 16·2%, *k*), 438 ($C_{30}H_{46}O_2$, 11·1%, *l*), 410 ($C_{29}H_{46}O$, 12·1%, *m*), 395 ($C_{28}H_{43}O$, 12·1%, 410-CH_3), 301 ($C_{22}H_{37}$, 9·1%, *n*), 189 ($C_{14}H_{21}$, 90·9%), 109 (C_7H_9O, 100%, *p*), 43 (66·7%)
XVII	(3β-Acetoxy-22ξ-acetoxymethyl-20β,28-epoxy-*E*(21)-nor-18α,19β*H*-ursan-22ξ-ol): *m/e*558 ($C_{34}H_{54}O_6$, 0·2%, M), 498 ($C_{32}H_{50}O_4$, 34·3%, *k*), 438 ($C_{30}H_{46}O_2$, 37·3%, *l*), 410 ($C_{29}H_{46}O$, 2·9%, *m*), 395 ($C_{28}H_{43}O$, 26·5%, 410-CH_3), 301 ($C_{22}H_{37}$, 5·9%, *n*), 189 ($C_{14}H_{21}$, 71·6%), 109 (C_7H_9O, 56·9%, *p*), 43 (100%)
XVIII	(3β-Acetoxy-20β,28-epoxy-18α,19β*H*-ursan-21-one): *m/e* 498 ($C_{32}H_{50}O_4$, 0·7%, M), 470 ($C_{31}H_{50}O_3$, 1·8%, *m*), 438 ($C_{30}H_{46}O_2$, 0·7%, *l*), 410 ($C_{29}H_{46}O$, 0·8%, *m*), 395 ($C_{28}H_{43}O$, 1·7%, 410-CH_3), 361 ($C_{24}H_{41}O_2$, 1·1%, *n*), 301 ($C_{22}H_{37}$, 9·0%, *n*), 189 ($C_{14}H_{21}$, 7·9%), 109 (C_7H_9O, 100%, *p*), 43 (25·8%)

[a] Ion characteristic of pentacyclic triterpenoids[2]. [b] Mixture of ions C_3H_7, C_2H_3O from ring E of compounds of type *A* and C_2H_3O from ring A of 3β-acetoxy derivatives.

Type *B* (compounds *XI*–*XVIII*): The group forming the bridge is not eliminated and ring D is cleaved (Scheme 2). The following groups are eliminated: —CO—O—CO—, —O—CO—, —CO—, —C(OH)(COOH)—, —C($OCOCH_3$).(COOH)— and —C(OH)($COOCH_3$)—. The following groups are not eliminated: —CH(OH)—, —CH($OCOCH_3$), —C(OH)(CH_2OH)—, —C(OH)(CH_2OCOCH_3)—, and —$COCH_2$—.

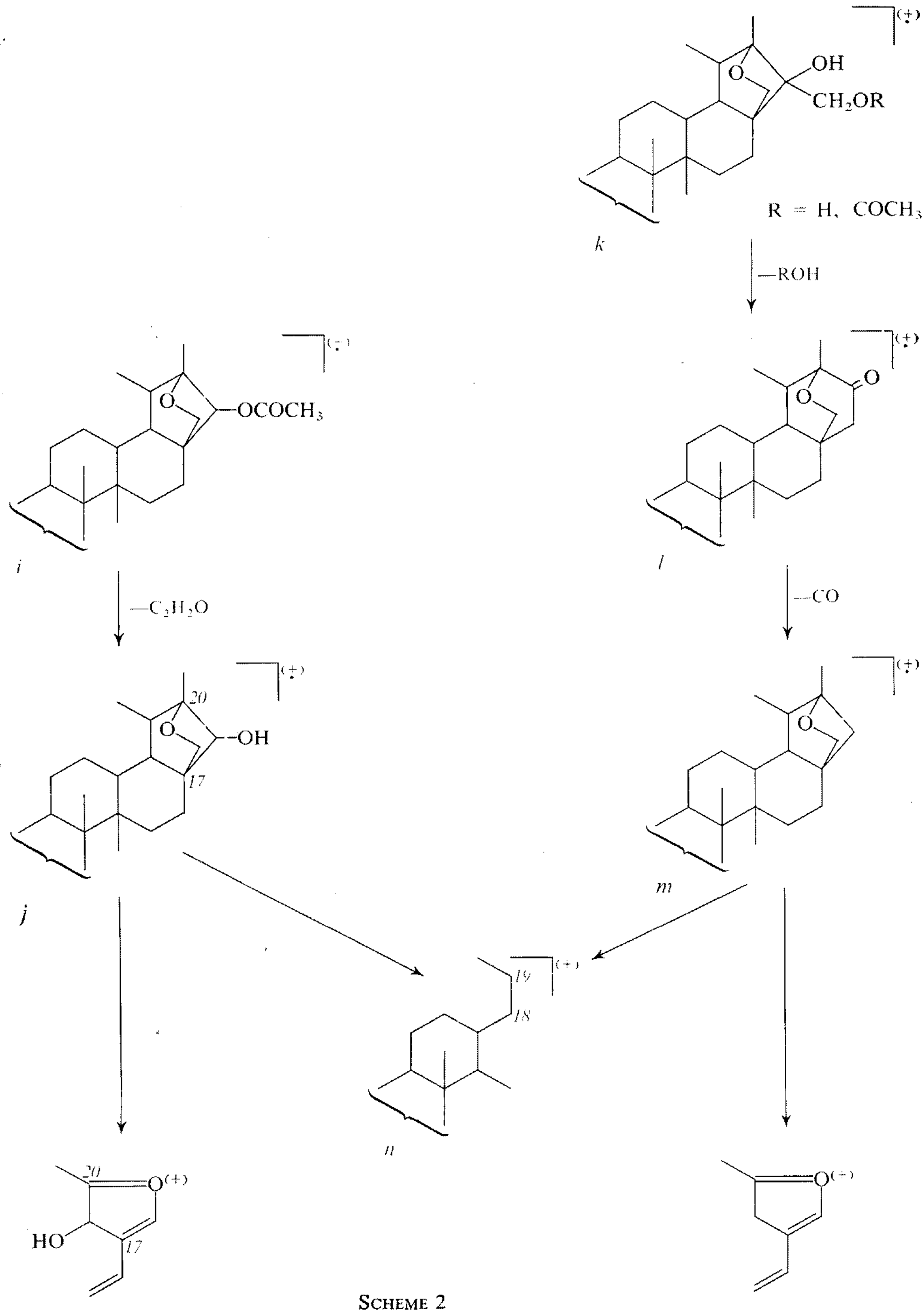
FRAGMENTATION OF COMPOUNDS OF TYPE *A* (*II*–*X*)

The elimination of the group bridging the tetrahydropyran ring aims at the ion *f* which is fragmented both simply to the ion *h* (*m/e* 43) and to the ion *g* by the elimination of C_4H_8O through McLafferty's rearrangement. The substituent in the



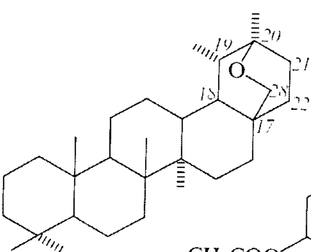
OR¹
COOR²
R^1 = H, $COCH_3$
R^2 = H, CH_3
c
d
a
−CO
b
$-C_2O_3R^1R^2$
e
−CO
$-CO_2$
f
$-C_4H_8O$
g
h

SCHEME 1

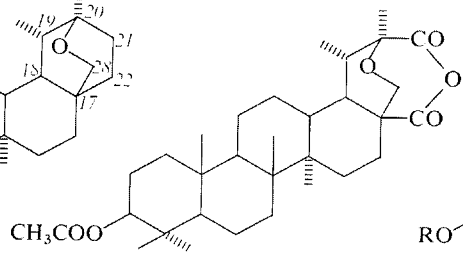

OH
CH₂OR
R = H, COCH₃
k
—ROH
OCOCH₃
i
l
—C₂H₂O
—CO
20
OH
17
j
m
19
18
n
20
O(+)
HO
17
o
O(+)
p

SCHEME 2

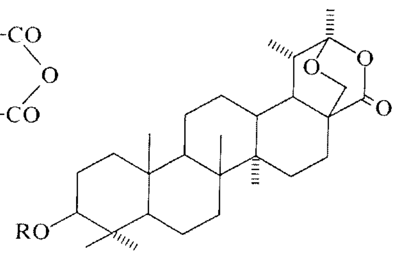
position 3β, together with the hydrogen from the neighbouring position, is eliminated as water or acetic acid at the level of fragments *b*, *f* and *g*. The elimination of water or acetic acid from the molecular ion was observed only with substances *III*, *IV* and *X*.



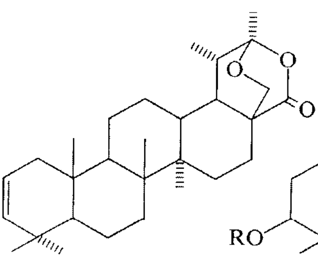
I



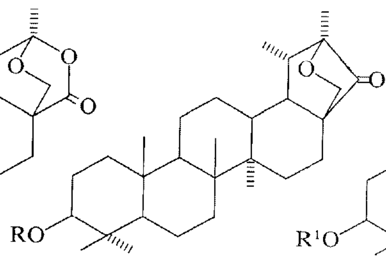
II



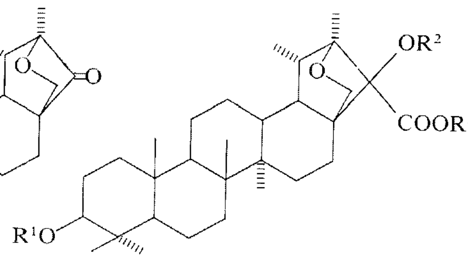
III, R = H
IV, R = $COCH_3$



V



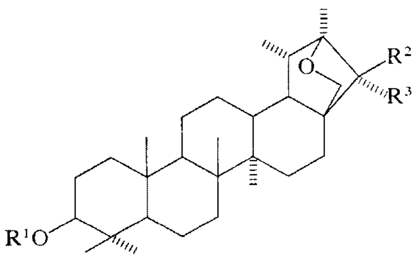
VI, R = H
VII, R = $COCH_3$



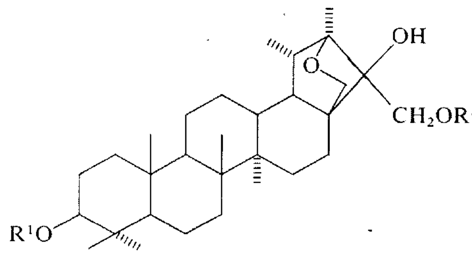
VIII, $R^1 = R^2 = R^3 = H$
IX, $R^1 = R^2 = COCH_3$, $R^3 = H$
X, $R^1 = COCH_3$, $R^2 = H$, $R^3 = CH_3$

Fragmentation of Compounds of Type *B* (*XI*–*XVIII*)

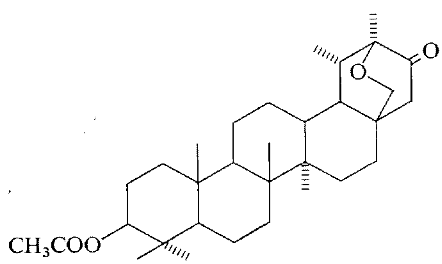
The ion *j* or *m* is common to all substances of this type. It may represent the molecular ion or a fragment. It is cleaved at the tetrahydropyran ring and ring D under two hydrogen atoms transfer, giving rise to ions *n* and *o* or *p*. During this the charge on the oxygen heteroatom of ring E prevails and the ions *o* and *p* are by one order of magnitude more intensive than the ion *n*. The ion *j* as a fragment is formed from the ion *i* by elimination of CH_2CO. The ion *m* is formed from the ion *k* by elimination of H_2O + CO or CH_3COOH + CO, from ion *l* by elimination of CO. The elimination of water or acetic acid from ring A is mostly restricted to the molecular ion. Compounds *XIII* and *XV* are exceptions in which elimination of acetic acid takes place also from the fragment *j*, and also compound *XVIII* is an exception in which acetic acid is eliminated also from fragments *m* and *n*. The pair of the $C_{(22)}$ epimeric hydroxy derivatives *XII* and *XIV* and their acetyl derivatives *XIII* and *XV* have the same *m*/*e* values and approximately equal relative intensities of the corresponding ions in low-resolution records. Supposing that the ion *l*, formed from the ion *k*, possesses the same structure as the molecular ion of compound *XVIII*, the decomposition of the ion *c* may be visualized in an analogous manner. However, the ion *d* was not found in the spectra and the corresponding substance could not be prepared.



XI, $R^1 = R^2 = H$, $R^3 = OH$
XII, $R^1 = COCH_3$, $R^2 = H$, $R^3 = OH$
XIII, $R^1 = COCH_3$, $R^2 = H$, $R^3 = OCOCH_3$
XIV, $R^1 = COCH_3$, $R^2 = OH$, $R^3 = H$
XV, $R^1 = COCH_3$, $R^2 = OCOCH_3$, $R = H$



XVI, $R^1 = R^2 = H$
XVII, $R^1 = R^2 = COCH_3$



XVIII

The measurement of the metastable ions by the DADI (direct analysis of daughter ions) technique confirmed the $a \rightarrow b$ transition for substance *II* (type *A*), the sequence $b \rightarrow f \rightarrow g$ for substance *V* (type *A*), and the decomposition $l \rightarrow m \rightarrow n$ (and $m \rightarrow p$) for compound *XVIII* (type *B*).

REFERENCES

1. Klinotová E., Beneš J., Vokoun J., Vystrčil A.: This Journal *41*, 271 (1976).
2. Budzikiewicz H., Djerassi C., Williams D. H.: *Structure Elucidation of Natural Products by Mass Spectrometry*, Vol. 2, p. 137. Holden-Day, San Francisco, London, Amsterdam 1964.

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