

# MASS SPECTRA OF $18\alpha,19\beta H$ -URSANE DERIVATIVES WITH A LACTONE ARRANGEMENT OF THE RING E\*

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The character of the mass spectra of a series of 25  $18\alpha,19\beta H$ -ursane derivatives with a six-membered or five-membered lactone bridge in the ring E does not depend, surprisingly, on the substitution in the ring E. In all instances of  $3\beta$ -acetoxy- and  $3\beta$ -hydroxy derivatives the dominant ions of the spectrum are formed by the loss of the methyl radical and the ethylene molecule, while the lactone ring and further oxygen-containing functions in the ring E are not fragmented.

In our preceding studies<sup>1,2</sup> the series of  $18\alpha,19\beta H$ -ursane derivatives was prepared and investigated, with an oxabicyclo[2,2,1]heptane and oxabicyclo[2,2,2]octane arrangement of the ring E, *I–XVI*. The character of their mass spectra was unexpectedly in agreement with the spectra of isomeric lactones *XVII–XXIII*, which were prepared in the preceding study<sup>3</sup>. In this connection the mass spectra of compounds *I–XXV* were studied and the results of these measurements are presented in this paper in Table I. The substances measured differ in the arrangement of the lactone in the ring E: a) Substances with a six-membered lactone ring and oxabicyclo[2,2,2]-octane arrangement, *I–IV* and *XIV–XVI*; b) substances with a five-membered lactone ring and oxabicyclo[2,2,1]heptane arrangement, *V–XIII*; and c) substances with a five-membered lactone ring and oxabicyclo[3,2,1]octane arrangement, *XVII–XXIII*. In addition to this the substances mentioned differ by substitution in the rings A and E.

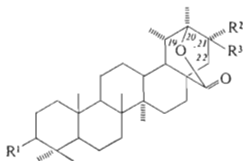
## EXPERIMENTAL

The measurements were carried out on a Varian MAT 311 mass 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 120–200°C. The high resolution measurements were carried out with an error not exceeding 10 ppm. The deuterated diacetate *XXIV* was prepared from monoacetate *XIX* and hexadeuterio acetic anhydride.

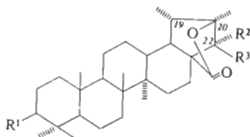
\* Part LXIV in the series Triterpenes; Part LXIII: This Journal 45, 2710 (1980).

## RESULTS AND DISCUSSION

The whole series of the substances measured (*I-XXIII*) had the same character of the mass spectrum, without regard to the arrangement of the lactone bridge in the ring E or the substitution in the ring A and E. At the same time the whole series differs distinctly by its fragmentation from that of analogous derivatives with an ether bridge in the ring E (ref.<sup>4</sup>). In the majority of cases the molecular ions have a low relative abundance (<1%). The dominant ions of all the spectra measured



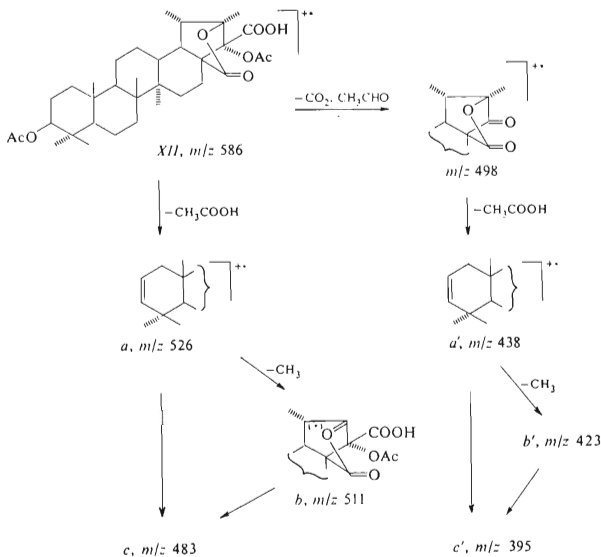
- I*,  $R^1 = \text{OAc}$ ,  $R^2 + R^3 = \text{O}$   
*II*,  $R^1 = \text{OH}$ ,  $R^2 + R^3 = \text{O}$   
*III*,  $R^1 = \text{OAc}$ ,  $R^2 = \text{OAc}$ ,  $R^3 = \text{H}$   
*IV*,  $R^1 = \text{OH}$ ,  $R^2 = \text{OH}$ ,  $R^3 = \text{H}$



- V*,  $R^1 = \text{OAc}$ ,  $R^2 + R^3 = \text{O}$   
*VI*,  $R^1 = \text{OAc}$ ,  $R^2 = \text{OH}$ ,  $R^3 = \text{H}$   
*VII*,  $R^1 = \text{OAc}$ ,  $R^2 = \text{OAc}$ ,  $R^3 = \text{H}$   
*VIII*,  $R^1 = \text{OAc}$ ,  $R^2 + R^3 = \text{NOH}$   
*IX*,  $R^1 = \text{OAc}$ ,  $R^2 = \text{OAc}$ ,  $R^3 = \text{COOCH}_3$   
*X*,  $R^1 = \text{OAc}$ ,  $R^2 = \text{OH}$ ,  $R^3 = \text{COOCH}_3$   
*XI*,  $R^1 = \text{OH}$ ,  $R^2 = \text{OH}$ ,  $R^3 = \text{COOCH}_3$   
*XII*,  $R^1 = \text{OAc}$ ,  $R^2 = \text{OAc}$ ,  $R^3 = \text{COOH}$   
*XIII*,  $R^1 = \text{OH}$ ,  $R^2 = \text{OH}$ ,  $R^3 = \text{COOH}$

are the ions of the type *a*, *b*, *c* (Table I and Scheme 1). The ion *a* is formed from the molecular ion by loss of acetic acid molecule from the ring A in 3 $\beta$ -acetoxy derivatives, or by loss of water in 3 $\beta$ -hydroxy derivatives. In Scheme 1 the ion *a* is repre-

sented, the structure of which corresponds to the formation from acetate. The ion *b* is formed from the ion *a* by loss of a methyl radical and the ion *c* is formed from the ion *b* by loss of a molecule of ethylene. The measurement of metastable ions using the DADI technique (direct analysis of daughter ions) confirmed the genesis of ions  $a \rightarrow b \rightarrow c$ , but also  $a \rightarrow c$ . The stability of the substituents in the ring E is also very remarkable. The stability of the acetoxy group in the position 20 was proved by means of deuteriodiacetate **XXIV** where acetic acid is split off only from the ring A, while the deuterated acetoxy group in the position 20 is preserved in all fragments, although the necessary hydrogen atom in the position  $\alpha$  has a  $\beta$ -configuration.



SCHEME 1

The typical fragmentation for the whole series of our substances **I–XXIII** is shown by the example of the acetoxy acid **XII** (Scheme 1). The molecular ion of this substance  $m/z$  586 is fragmented in two ways. The first of them is described above (ions *a*, *b*, *c*). In the second a molecule of carbon dioxide and acetaldehyde is eli-

TABLE I

Ions of Measured Compounds (the letters indicate the type of ion, see Scheme 1)

*I:*  $m/z$  512 ( $C_{32}H_{48}O_5$ , 0.2%, M), 497 ( $C_{31}H_{45}O_5$ , 1%), 452 ( $C_{30}H_{44}O_3$ , 42%, a), 437 ( $C_{29}H_{41}O_3$ , 27%, b), 409 ( $C_{27}H_{37}O_3$ , 69%, c), 189 ( $C_{14}H_{21}$ , 40%), 43 (100%).

*II:*  $m/z$  470 ( $C_{30}H_{46}O_4$ , 13%, M), 468 ( $C_{30}H_{44}O_4$ , 25%), 452 ( $C_{30}H_{44}O_3$ , 50%, a), 437 ( $C_{29}H_{41}O_3$ , 20%, b), 409 ( $C_{27}H_{37}O_3$ , 54%, c), 189 ( $C_{14}H_{21}$ , 100%).

*III:*  $m/z$  556 ( $C_{34}H_{52}O_6$ , 0.3%, M), 496 ( $C_{32}H_{48}O_4$ , 39%, a), 481 ( $C_{31}H_{45}O_4$ , 12%, b), 453 ( $C_{29}H_{41}O_4$ , 61%, c), 189 ( $C_{14}H_{21}$ , 40%), 43 (100%).

*IV:*  $m/z$  472 ( $C_{30}H_{48}O_4$ , 0.2%, M), 470 ( $C_{30}H_{46}O_4$ , 0.5%), 454 ( $C_{30}H_{46}O_3$ , 52%, a), 439 ( $C_{29}H_{43}O_3$ , 20%, b), 411 ( $C_{27}H_{39}O_3$ , 90%, c), 207 ( $C_{14}H_{23}O$ , 12%), 189 ( $C_{14}H_{21}$ , 81%), 28 (100%).

*V:*  $m/z$  498 ( $C_{31}H_{46}O_5$ , 0.1%, M), 483 ( $C_{30}H_{43}O_5$ , 0.2%), 470 ( $C_{29}H_{42}O_5$ , 0.3%), 454 ( $C_{30}H_{46}O_3$ , 3.5%), 442 ( $C_{29}H_{46}O_3$ , 23%), 438 ( $C_{29}H_{42}O_3$ , 25%, a), 423 ( $C_{28}H_{39}O_3$ , 12%, b), 411 (1.5%), 395 ( $C_{26}H_{35}O_3$ , 30%, c), 189 ( $C_{14}H_{21}$ , 48%), 43 (100%).

*VI:*  $m/z$  500 ( $C_{31}H_{48}O_5$ , 0.1% M), 454 ( $C_{29}H_{42}O_4$ , 4.5%), 440 ( $C_{29}H_{44}O_3$ , 45%, a), 425 ( $C_{28}H_{41}O_3$ , 18%, b), 411 ( $C_{26}H_{35}O_4$ , 4%), 397 ( $C_{26}H_{37}O_3$ , 67%, c), 189 ( $C_{14}H_{21}$ , 78%), 43 (100%).

*VII:*  $m/z$  542 ( $C_{33}H_{50}O_6$ , 0.5%, M), 482 ( $C_{31}H_{46}O_4$ , 51%, a), 467 ( $C_{30}H_{43}O_4$ , 21%, b), 439 ( $C_{28}H_{39}O_4$ , 70%, c), 189 ( $C_{14}H_{21}$ , 80%), 43 (100%).

*VIII:*  $m/z$  513 ( $C_{31}H_{47}O_5N$ , 0.5%, M), 469 ( $C_{30}H_{47}NO_3$ , 6%), 453 ( $C_{29}H_{43}NO_3$ , 26%, a), 438 ( $C_{28}H_{40}NO_3$ , 12%, b), 437 (12%), 422 (6%), 410 (8%), 395 (24%), 393 (25%), 189 (53%), 43 (100%).

*IX:*  $m/z$  600 ( $C_{35}H_{52}O_8$ , 0.1%, M), 556 (0.2%), 540 ( $C_{33}H_{48}O_6$ , 22%, a), 525 ( $C_{32}H_{45}O_6$ , 12%, b), 497 ( $C_{30}H_{41}O_6$ , 40%, c), 189 ( $C_{14}H_{21}$ , 22%), 43 (100%).

*X:*  $m/z$  558 ( $C_{33}H_{50}O_7$ , 0.5%, M), 498 ( $C_{31}H_{46}O_5$ , 64%, a), 483 ( $C_{30}H_{43}O_5$ , 22%, b), 455 ( $C_{28}H_{39}O_5$ , 100%, c), 189 ( $C_{14}H_{21}$ , 73%), 43 (100%).

*XI:*  $m/z$  516 ( $C_{31}H_{48}O_6$ , 0.5%, M), 498 ( $C_{31}H_{46}O_5$ , 13%, a), 483 ( $C_{30}H_{43}O_5$ , 7%, b), 473 (8%), 455 ( $C_{28}H_{39}O_5$ , 25%, c), 452 (10%), 207 ( $C_{14}H_{23}O$ , 37%), 189 ( $C_{14}H_{21}$ , 100%).

*XII:*  $m/z$  586 (0%, M), 526 ( $C_{32}H_{46}O_6$ , 12%, a), 511 ( $C_{31}H_{43}O_6$ , 5%, b), 498 ( $C_{31}H_{46}O_5$ , 2%), 483 ( $C_{29}H_{39}O_6$ , 19%, c), 442 ( $C_{29}H_{46}O_3$ , 20%), 438 ( $C_{29}H_{42}O_3$ , 18%), 423 ( $C_{28}H_{39}O_3$ , 13%), 395 ( $C_{26}H_{35}O_3$ , 25%), 189 ( $C_{14}H_{21}$ , 51%), 43 (100%).

*XIII:*  $m/z$  502 ( $C_{30}H_{46}O_6$ , 0.2%, M), 498 (3%), 484 ( $C_{30}H_{44}O_5$ , 36%, a), 469 ( $C_{29}H_{41}O_5$ , 25%, b), 455 (7%), 441 ( $C_{27}H_{37}O_5$ , 85%, c), 207 ( $C_{14}H_{23}O$ , 21%), 189 ( $C_{14}H_{21}$ , 100%).

TABLE I  
(Continued)

XIV:  $m/z$  514 ( $C_{31}H_{46}O_6$ , 0.1%, M), 470 (1.2%), 454 ( $C_{29}H_{42}O_4$ , 56%, a),  
439 ( $C_{28}H_{39}O_4$ , 31%, b), 426 ( $C_{25}H_{46}O_5$ , 3.5%), 421 ( $C_{28}H_{37}O_3$ , 2%),  
411 ( $C_{26}H_{35}O_4$ , 40%, c), 206 ( $C_{15}H_{26}$ , 41%), 189 ( $C_{14}H_{21}$ , 100%).

XV:  $m/z$  472 ( $C_{29}H_{44}O_5$ , 2.5%, M), 470 ( $C_{29}H_{42}O_5$ , 5%), 454 ( $C_{29}H_{42}O_4$ , 72%, a),  
439 ( $C_{28}H_{39}O_4$ , 30%, b), 411 ( $C_{26}H_{35}O_4$ , 27%, c), 207 ( $C_{14}H_{23}O$ , 43%), 189 ( $C_{14}H_{21}$ , 100%).

XVI:  $m/z$  514 ( $C_{31}H_{46}O_6$ , 0.5%, M), 454 ( $C_{29}H_{42}O_4$ , 29%, a), 439 ( $C_{28}H_{39}O_4$ , 22%, b),  
411 ( $C_{26}H_{35}O_4$ , 23%, c), 206 ( $C_{15}H_{26}$ , 37%), 189 ( $C_{14}H_{21}$ , 92%), 43 (100%).

XVII:  $m/z$  512 (0.5%, M), 452 ( $C_{30}H_{44}O_3$ , 22%, a), 437 ( $C_{29}H_{41}O_3$ , 19%, b),  
409 ( $C_{27}H_{37}O_3$ , 20%, c), 273 ( $C_{17}H_{21}O_3$ , 11%), 189 ( $C_{14}H_{21}$ , 86%), 43 (100%).

XVIII:  $m/z$  470 ( $C_{30}H_{46}O_4$ , 0.5%, M), 452 ( $C_{30}H_{44}O_3$ , 46%, a), 437 ( $C_{29}H_{41}O_3$ , 24%, b),  
409 ( $C_{27}H_{37}O_3$ , 16%, c), 273 ( $C_{17}H_{21}O_3$ , 10%), 207 ( $C_{14}H_{23}O$ , 46%), 189 ( $C_{14}H_{21}$ , 100%).

XIX:  $m/z$  514 (0.3%, M), 496 ( $C_{32}H_{48}O_4$ , 3%), 481 ( $C_{31}H_{45}O_4$ , 3%),  
454 ( $C_{30}H_{46}O_3$ , 21%, a), 439 ( $C_{29}H_{43}O_3$ , 11%, b), 411 ( $C_{27}H_{39}O_3$ , 19%, c), 372 (8.2%),  
275 ( $C_{17}H_{23}O_3$ , 7%), 189 ( $C_{14}H_{21}$ , 39%), 43 (100%).

XX:  $m/z$  556 (0.2%, M), 496 ( $C_{32}H_{48}O_4$ , 47%, a), 481 ( $C_{31}H_{45}O_4$ , 21%, b),  
453 ( $C_{29}H_{41}O_4$ , 35%, c), 427 (6%), 414 (15%), 393 (8%), 385 (5%), 365 (5%),  
317 ( $C_{19}H_{25}O_4$ , 5%), 189 ( $C_{14}H_{21}$ , 60%), 43 (100%).

XXI:  $m/z$  527 ( $C_{32}H_{49}NO_5$ , 5%, M), 511 (20%), 467 ( $C_{30}H_{45}NO_3$ , 28%, a),  
452 ( $C_{29}H_{42}NO_3$ , 14%, b), 450 (37%), 436 (10%), 434 (8%), 424 ( $C_{27}H_{38}NO_3$ , 12%, c),  
263 (19%), 189 ( $C_{14}H_{21}$ , 55%), 43 (100%).

XXII:  $m/z$  514 (1%), 496 (1%), 481 (0.5%), 454 ( $C_{30}H_{46}O_3$ , 100%, a), 439 ( $C_{29}H_{43}O_3$ , 45%, b),  
411 (76%, c), 372 (20%), 275 (10%), 189 (91%), 43 (85%).

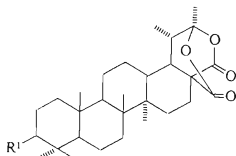
XXIII:  $m/z$  556 (0.3%, M), 496 ( $C_{32}H_{48}O_4$ , 35%, a), 481 ( $C_{31}H_{45}O_4$ , 25%, b),  
453 ( $C_{29}H_{41}O_4$ , 42%, c), 427 (5%), 414 (6%), 189 (51%), 43 (100%).

XXIV:  $m/z$  559 (0.2%, M), 499 ( $C_{32}H_{45}D_3O_4$ , 35%, a), 484 ( $C_{31}H_{42}D_3O_4$ , 16%, b),  
456 ( $C_{29}H_{38}D_3O_4$ , 18%, c), 417 (5%), 189 (49%), 43 (100%).

XXV:  $m/z$  440 ( $C_{30}H_{48}O_2$ , 15%, M), 425 ( $C_{29}H_{45}O_2$ , 16%), 384 ( $C_{26}H_{40}O_2$ , 5%)  
191 ( $C_{14}H_{23}$ , 100%).

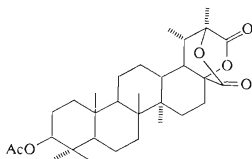
XXVI:  $m/z$  468 ( $C_{30}H_{44}O_4$ , 27%, M), 453 ( $C_{29}H_{41}O_4$ , 11%), 450 ( $C_{30}H_{42}O_3$ , 8%),  
440 ( $C_{29}H_{44}O_3$ , 4%), 435 ( $C_{29}H_{39}O_3$ , 5%), 425 ( $C_{28}H_{41}O_3$ , 11%), 205 ( $C_{14}H_{21}O$ , 33%),  
55 (100%).

XXVII:  $m/z$  471 (0.8%, M), 453 ( $C_{30}H_{43}O_3D$ , 28%, a), 438 ( $C_{29}H_{40}DO_3$ , 16%, b),  
410 ( $C_{27}H_{36}DO_3$ , 13%, c), 207 ( $C_{14}H_{23}O$ , 37%), 189 ( $C_{14}H_{21}$ , 100%).

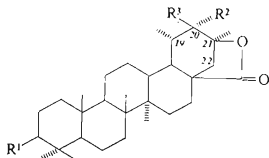


*XVII*,  $R^1 = \text{OAc}$

*XV*,  $R^1 = \text{OH}$



*XVI*



*XVII*,  $R^1 = \text{OAc}$ ,  $R^2 + R^3 = \text{O}$

*XVIII*,  $R^1 = \text{OH}$ ,  $R^2 + R^3 = \text{O}$

*XIX*,  $R^1 = \text{OAc}$ ,  $R^2 = \text{H}$ ,  $R^3 = \text{OH}$

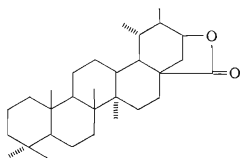
*XX*,  $R^1 = \text{OAc}$ ,  $R^2 = \text{H}_3$ ,  $R^3 = \text{OAc}$

*XXI*,  $R^1 = \text{OAc}$ ,  $R^2 + R^3 = \text{NOH}$

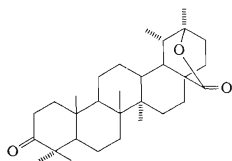
*XXII*,  $R^1 = \text{OAc}$ ,  $R^2 = \text{OH}$ ,  $R^3 = \text{H}$

*XXIII*,  $R^1 = \text{OAc}$ ,  $R^2 = \text{OAc}$ ,  $R^3 = \text{H}$

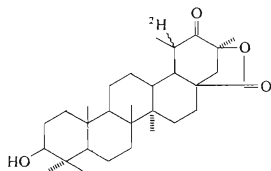
*XXIV*,  $R^1 = \text{OAc}$ ,  $R^2 = \text{H}$ ,  $R^3 = \text{OCOCd}_3$



*XXV*



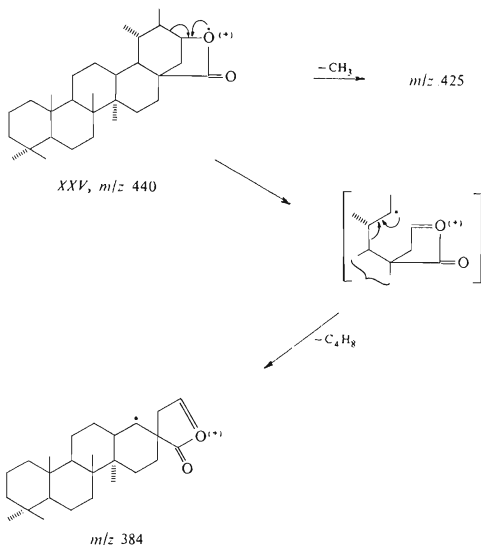
*XXVI*



*XXVII*

minated first thermally from the molecular ion, under formation of ion  $m/z$  498 (which is simultaneously the molecular ion of ketone *V*), which is further fragmented in the described manner (ions  $a'$ ,  $b'$ ,  $c'$ ). The pyrolytic decomposition of the acetoxy acid *XII* was already observed earlier<sup>2</sup>. Other ions of the spectrum, at higher masses, are not very distinct. In compounds *XVII*–*XX* the ions  $m/z$  273 (in 20-oxo derivatives),  $m/z$  275 (in 20-hydroxy derivatives), or  $m/z$  317 (in 20-acetoxy derivatives) may be observed which are formed by the cleavage of the rings B and C. In all instances the known abundant ions  $m/z$  189 or 207 (in 3-acetoxy, or 3-hydroxy derivatives) are present in the spectrum, belonging to the rings A and B (ref.<sup>5</sup>).

Knowing only the mass spectra of compounds *I*–*XVI*, we assumed that the fragmentation is affected by the ethereal oxygen atom of the lactone ring, *i.e.* that the bonds are split which attach the side chain to the lactone ring in the vicinity of the ethereal oxygen atom. Such a type of fragmentation would be common for lactones, ref.<sup>6,7</sup>. In our case it would represent the splitting off of the methyl group from the position 20 (in derivatives *I*–*IV* and *XIV*–*XVI*), or 21 (in derivatives *V*–*XIII*),



SCHEME 2

or the cleavage of the bond between the carbon atoms 19 and 20. In this type of fragmentation it could be assumed that the eliminated ethylene originates in all instances from the carbon atom 19 and the methyl group attached to it. Under the assumption of the validity of this theory we expected in isomeric lactones *XVII–XXIII* a completely different fragmentation, analogous as in the model derivative<sup>8</sup> *XXV* (Scheme 2). Here the cleavage of the bond between the carbon atoms 20 and 21 takes place under the splitting off of molecule  $C_4H_8$  and formation of ion  $m/z$  384. Since lactones *XVII–XXIII* do not split in this way, but analogously as lactones *I–XVI*, we prepared 19-deuterio derivative<sup>3</sup> *XXVII* and 3-oxo derivative<sup>3</sup> *XXVI* in order to find out the origin of the eliminated ethylene. From the spectrum of compound *XXVII* it is evident that ethylene does not originate from carbon 19, and deuterium remains on the fragment of the type *C*. In the spectrum of oxo-derivative *XXVI* the ion *c* is completely absent and ethylene is not split off at all. This means that the oxo group in the position 3 does not enable the usual fragmentation.

On the basis of the data presented it may be considered that the molecule of the eliminated ethylene does not originate in the ring *E*, but from some other site on the skeleton, the determination of which would be only speculative without systematic labelling with deuterium.

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