MASS SPECTROMETRY OF GIBBERELLINS

III. FEATURES OF THE FRAGMENTATION OF 3 α-HYDROXY AND 3-KETO DERIVATIVES OF THE GIBBERELLIN SERIES

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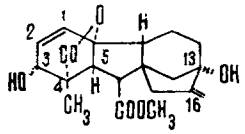
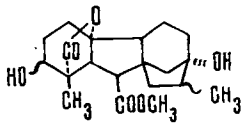
In preceding communications [1, 2] the characteristic features of the fragmentation of the most important gibberellins and some of their derivatives under electron impact have been discussed. In the present communication we show the influence of the nature and stereochemistry of substituents in ring A on the fragmentation of synthetic derivatives of gibberellins A_3 and A_1.

Influence of the Configuration of the Hydroxyl at C_3. The results of a comparison of the mass spectra of the methyl esters of gibberellin A_3 (I) (see [1]) and its 3 α-epimer (II) show the complete identity of their fragmentation pathways (the fragmentations of their 0,0-d_2 analogs are also similar). The intensities of the peaks of the molecular ions referred to the intensities of the main peaks at m/e 136 in (I) and (II) are also the same. In the region of high mass numbers, differences in the intensities of the most considerable peaks are again small, with the exception of peaks due to the elimination of the lactone ring (Table 1, ions d and e). This process of elimination is accompanied by the splitting out of two atoms of hydrogen, one of which apparently comes from the hydroxyl at C_3, since the corresponding peaks in the spectra of the 0,0-d_2 analogs are displaced by only 1 m.u.





I 3β-OH, 3α-H

II 3α-OH, 3β-H

III and III' 3β-OH, 3α-H, C_{16}- epimers

IV and IV' 3α-OH, 3β-H, C_{16}- epimers

The high intensities of the ions d and e in the spectrum of (II) as compared with the spectrum of (I) possibly reflects a greater steric hindrance of the epimer (II), in which the C_3-hydroxyl and the lactone grouping are on the same side of the plane of ring A. At the same time, intensities of the dehydration peaks (ions *a*) in both epimers are approximately the same. In a consideration of molecular models of (I) and (II) it can be seen that the

TABLE 1

Epimer	Ratio I_1 / I_{M^+}				
	M−H_2O (*a*) *m/e* 342	M−CO_2−2H (*b*) *m/e* 314	M−$COOCH_3$ (*c*) *m/e* 301	M−CO_2−2H−OH (*d*) *m/e* 297	M−CO_2−2H−$COOCH_3$ (*e*) *m/e* 255
I	0,74	0,62	1,23	1,54	0,93
II	0,63	0,73	1,36	2,55	3,30

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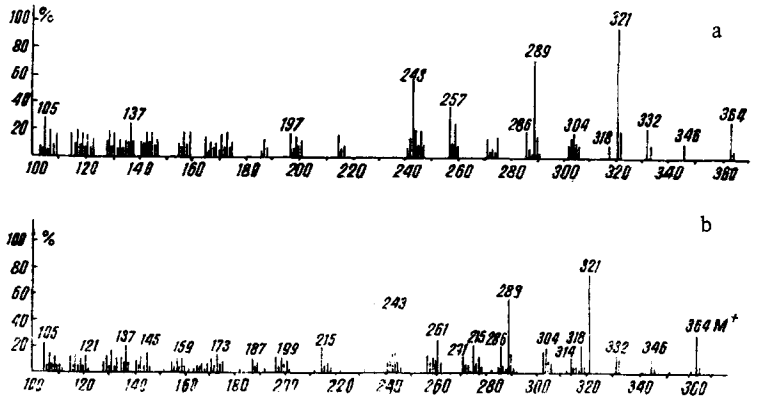
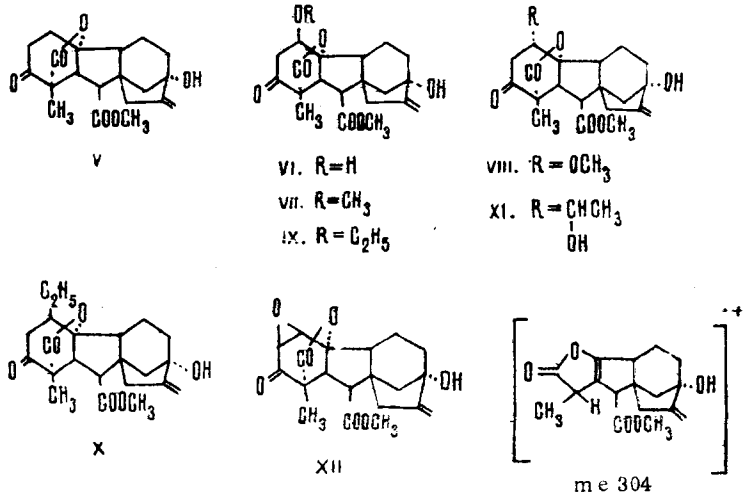


Fig. 1. Mass spectra of the tetrahydro derivatives (III) (a) and (IV) (b).

1,3-elimination of water [3], which must take place with the participation of the hydrogen of the C_{18}-methyl group is equiprobable for both epimers, and the somewhat greater intensity of the ion *a* in the spectrum of (I) is apparently due to the additional possibility of the 1,3-elimination of water with the participation of the proton at C_5.

In the tetrahydro derivatives epimeric at C_3, (III), and (III') and (IV) and (IV'), the greatest difference in the region of high masses is observed for the pair of ions due to the elimination of the lactone ring ($M - CO_2 - 2H$, m/e 318): the I_{318}/I_{M^+} y ratio for the β-epimers (III) and (III') is approximately half that for the α-epimers (IV) and (IV'), while the difference in the intensities of the dehydration peaks are small in all cases. The main direction of fragmentation is connected with the elimination of the saturated ring D (series of M − 43 peaks). In Fig. 1, curves a and b give the spectra of the epimers (III) and (IV); the spectra of (III') and (IV') are similar.

Influence of a Carbonyl Group at C_3. In the mass spectra of the methyl ester of 3-dehydrogibberellin A_1 (V) and its analogs (VI-XI) having substituents at C_1, appreciable peaks are observed with m/e 304 and 303. In the spectra of the 13-O-d analogs of compounds (V), (VII), and (VIII) these peaks are shifted by 1 m.u., and likewise only by 1 m.u. in the spectra of the $O,O\text{-}d_2$ analogs of the dihydroxy keto esters (VI) and (XI) in which the second hydroxy group is attached to ring A.



These facts show that a special fragmentation pathway exists for 3-keto derivatives, which is connected with the splitting out of the C_1—C_2—C_3 fragment; in compound (IX) and (X) this route is confirmed by the presence of the corresponding metastable ions (m* 230.6 and 235.6). As can be seen from Table 2, the most intensive peaks with m/e 304 and 303 proved to be those in compounds (VII) and (XI) to which,on the basis of NMR and CD characteristics [3] the 1α orientation of the substituent has been ascribed. The formation of an ion with

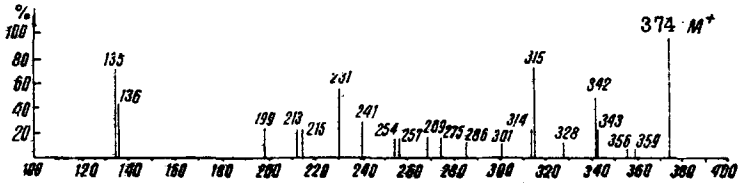


Fig. 2. Mass spectrum of the epoxy ketone (XII).

TABLE 2

Compound	Main ions (m/e and intensity, % of the main peak)					
	M+	M−CH_3OH	M−(H) $COOCH_3$	M−(2H)−CO_2	M−(C_1−C_2−C_3)	Others
V	360(47)	328(100)	301(42)	316(13) 314(13)	304(16) 303(21)	135(40)
VI	376(100)	344(60)	317(68)	—	304(13) 303(15)	135(66)
VII	390(100)	358(86)	331(50)	—	304(22) 303(22)	135(30)
VIII	390(64)	358(70)	331(14)	—	304(100) 303(70)	135(22)
IX	404(40)	372(100)	354(31)	360(20)	304(54) 303(30)	135(50)
X	388(60)	356(67)	329(40)	344(28) 342(24)	304(72) 303(56)	135(100)
XI	404(50)	372(0,35)	345(15) 344(15)	360(15) 358(26)	304(100) 303(30)	135(55)

m/e 304 can be represented as the result of the elimination of a molecule of ketene or its equivalent from the 3-keto derivatives. The type of fragmentation shown does not appear in the mass spectrum of the epoxy ketone (XII) (see Fig. 2).

EXPERIMENTAL METHOD

For the method of obtaining compounds (II) (mp 172-174°C), (III) (mp 235-238°C), (III') (mp 257-261°C), (IV) (mp 168-170°C), and (IV') (mp 198-202°C) see [4]; for the isolation of compounds (V-IX) and (XI and XII) see [3]. Compound (X) (amorphous) was obtained from the corresponding 3-hydroxy compound (see [5]) by the action of chromium trioxide in pyridine with the subsequent purification of the oxidation product by preparative TLC on silica gel.

The mass spectra were taken on an LKB 9000 instrument with the direct introduction of the samples into the ion source (70 eV, 190-230°C). The intensity figures given represent the means of several measurements.

SUMMARY

In the mass spectrum of the 3 α-epimer of the methyl ester of gibberellin A_3 there is an increased intensity of the peaks connected with the elimination of the lactone ring. For the 3-keto derivatives of the gibberellin A_1 series with substituents at C_1 the formation of ions corresponding to the splitting out of the C_1–C_2–C_3 fragment is characteristic.

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