# MASS SPECTRA OF ANTIBIOTICS, DEOXYNIGERICIN AND NIGERICIN

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Summary : Mass spectrometric investigations of the sodium salt of a nigericin-type antibiotic, described earlier, and named deoxynigericin, permitted the elucidation of its structure. A comparison of the mass spectra of the sodium salts of nigericin and deoxynigericin afforded a better understanding of the mass spectral behaviour of this type of compound.

The mass spectra of antibiotics related to monensin were reported by Chamberlin and Agtarap (1). We applied this method to compound II which was found to have a structure similar to nigericin (2).

The structure of deoxynigericin[x], compound II, a new antibiotic was elucidated by mass spectrometry.

## DISCUSSION

Mass spectra of sodium salts I and II, as shown in Figure 1, yield nearly identical fragmentation patterns.

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[x] The structure of compound II based on X-ray crystallography was reported by French authors while this paper was in preparation. (3a,b)

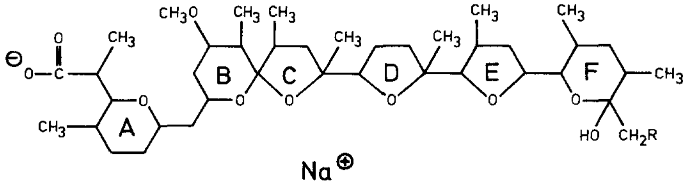
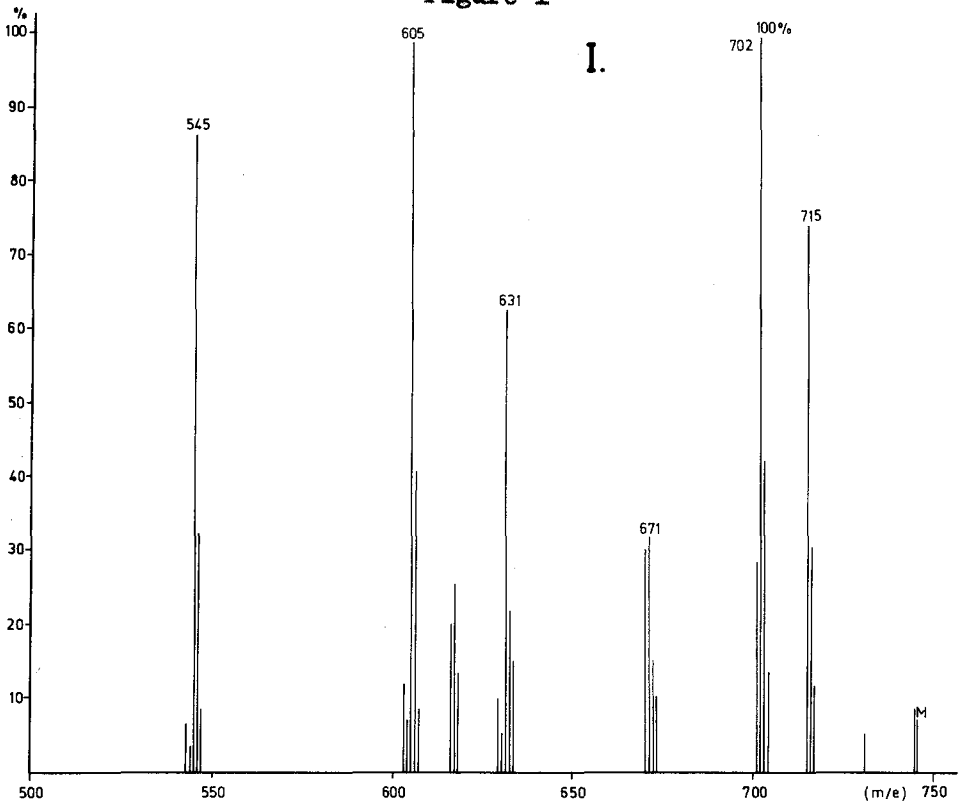
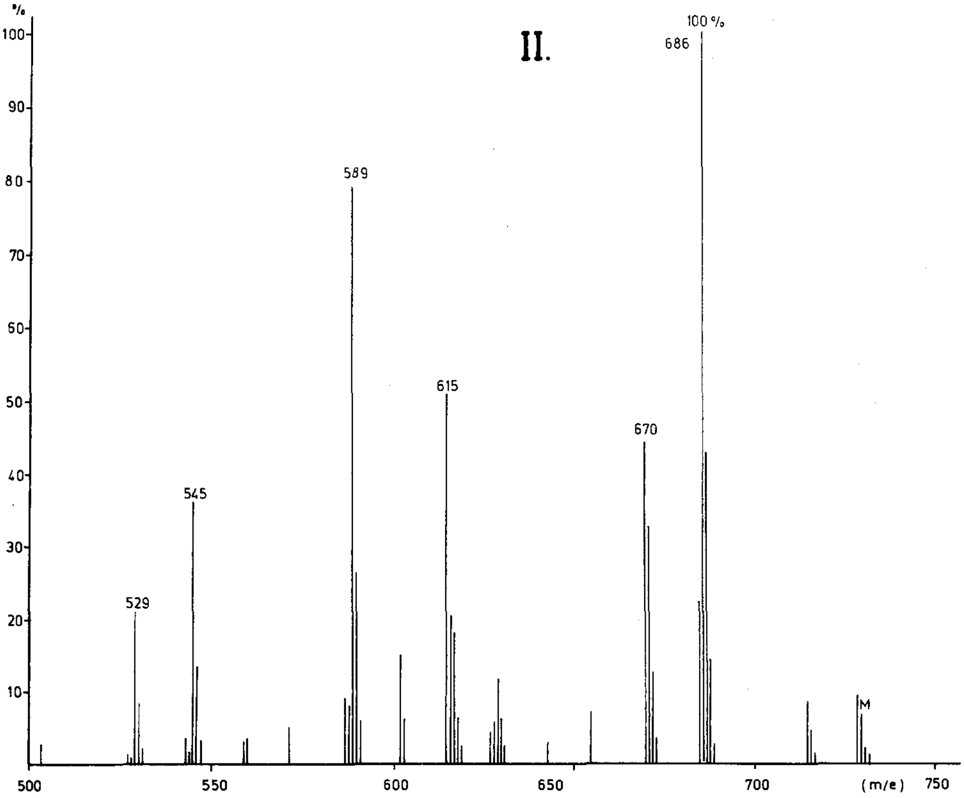


**Figure 1**



a.) Mass spectrum of the sodium salt of nigericin (I); M=746

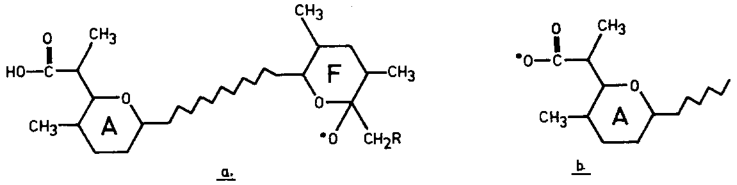


b.) Mass spectrum of the sodium salt of desoxynigericin (II); M=730

Accordingly several ions which appeared at the same mass number or at mass numbers differing in 16 mass units in the two spectra permits postulation of their structures.

The ionic structure of these compounds in solid state (4) suggests that the radical site and the cation site of the molecular-ions will be fairly separated. The hydrogen bond between the carboxyl and the ring F - hydroxyl group (4) in crystalline state suggests that both should be considered as probable radical sites on electron impact (Scheme 1).

**Scheme 1**[x]



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[x] 〰 **means on all schemes the whole remaining part of molecules I and II (containing sodium too).**

**I:R=OH nigericin-sodium salt; II:R=H desoxynigericin-sodium salt**

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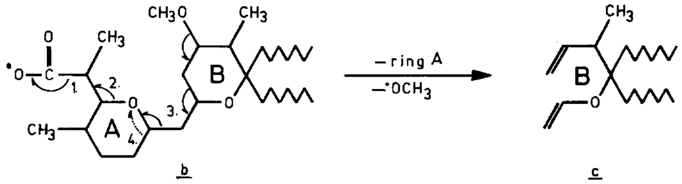
The M - 31 peak in the spectrum of I is fully absent in II, indicating that this ion arises from the loss of $-CH_2OH$ from ring F via structure a. Only two additional ions of considerable abundance are derived from structure a, ions m/e=671 and m/e=545.

The ion m/e=671 arises by the loss of an $RCH_2-COO^{\bullet}$, a similar cleavage of structure b yields the ion m/e=670. These fissions result from the high stability of the neutral products formed. A metastable peak $m^{*}$=615,5 observed in the spectrum of II can be ordered to these processes.

As shown in Figure 1 only a part of the peak at m/e=545 from I can have the structure described by Chamberlin and Agtarap (1) which may be derived from structure a. Another part of this peak appearing at m/e=529 in the spectrum of II arises via a process shown in Scheme 2 from structure b giving ion c.

**Scheme 2**



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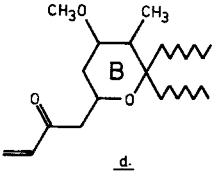
The process leading from m/e=560 (ion formed by cleavage 3.) to m/e=529 is indicated by a metastable peak $m^*$=499,5.

Cleavage 1. in Scheme 2 ($M - CO_2$) is responsible for the base peak in both spectra.

The second most intense peak in the spectra of I and II will be formed at m/e=605 and m/e=589, respectively, if cleavage 4. follows cleavages 1. and 2. instead of cleavage 3. A metastable ion $m^*$=505,5 is found due to this fragmentation (686 → 589) in the spectrum of II.

An ion of higher abundance is considered to arise from the ion $M - CO_2$ via a double hydrogen rearrangement to the neutral part. This ion can be described as having structure d (Scheme 3). The corresponding peak is found in the spectra of I and II at m/e=631 and m/e=615, respectively. A metastable peak $m^{*}$=551,5 from II (686 → 615) seems to be in agreement with this assumption.

**Scheme 3**



d.

All other ions are less abundant so they do not seem to have any structural significance.

## EXPERIMENTAL

Mass spectra were taken with a Varian MAT SM 1 mass spectrometer at resolution 1500, ionizing voltage 70 eV, accelerating voltage 8 kV. Evaporation temperatures were 270°C and 200°C for I and II, respectively.

The sodium salt of nigericin was authentic sample prepared in our Institute.

The sodium salt of deoxynigericin was obtained as described in reference (2). A further purification of the sample was achieved by repeating the chromatographic separation (2).

## Acknowledgement

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## REFERENCES

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