Identification of 1,4-Benzoxazin-3-ones in Maize Extracts by Gas-Liquid Chromatography and Mass Spectrometry

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ABSTRACT

Gas-liquid chromatography-mass spectrometry (GLC-MS) has been used for the separation, detection, and identification of 1,4-benzoxazin-3-ones (hydroxamic acids and lactams) and benzoxazolinones found in maize (Zea mays L.) extracts. Compounds of interest were partitioned into ethyl acetate from aqueous maize seedling extracts. For analysis by GLC-MS, trimethylsilyl derivatives were prepared, chromatographed on a column of 3% OV-1, and detected in the mass spectrometer. Mass spectra were obtained for all peaks present in extracts of four maize lines. A data comparison system was developed for relating unidentified spectra to the spectra of the reference compounds. Based on spectral comparisons, three hydroxamic acids (2,4-dihydroxy-2H-1,4-benzoxazin-3(4H)-one; 2,4-dihydroxy-2H-1,4-benzoxazin-3(4H)-one; and 2,4-dihydroxy-2H-1,4-benzoxazin-3(4H)-one), three lactams (2-hydroxy-2H-1,4-benzoxazin-3(4H)-one; 2,7-dihydroxy-2H-1,4-benzoxazin-3(4H)-one; 1,2-dihydroxy-2H-1,4-benzoxazin-3(4H)-one; and 2,4-dihydroxy-2H-1,4-benzoxazin-3(4H)-one), one benzoxazolinone (6-methoxybenzoxazolinone), and two organic acids (malic and acetic) were identified in the extracts. In addition, one other hydroxamic acid and one other related compound were tentatively identified based on mass spectral evidence.

The existence of naturally occurring 1,4-benzoxazin-3-ones was first reported by Virtanen and his co-workers who identified two hydroxamic acids, DIBOA3-glucoside (Fig. 1, Ia) from rye (6) and DIMBOA-glucoside (IIa) from wheat and maize (20). These glucosides were enzymically hydrolyzed to yield DIBOA (Va) and DIMBOA (Vc), respectively (19, 20). The aglucones were unstable and could be converted to their corresponding benzoxazolinones.

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5. Abbreviations: BOA: benzoxazolinone; MBOA: 6-methoxybenzoxazolinone; M3BOA: 6,7-dimethoxybenzoxazolinone; DIBOA: 2,4-dihydroxy-2H-1,4-benzoxazin-3(4H)-one; DIMBOA: 2,4-dihydroxy-2H-1,4-benzoxazin-3(4H)-one; TRIBOA: 2,4,7-trihydroxy-2H-1,4-benzoxazin-3(4H)-one; DIBOA: 2,4-dihydroxy-2H-1,4-benzoxazin-3(4H)-one; HBAO: 2-hydroxy-2H-1,4-benzoxazin-3(4H)-one; 7-OH HBAO: 2,7-dihydroxy-2H-1,4-benzoxazin-3(4H)-one; HMBOA: 2-hydroxy-7-methoxy-2H-1,4-benzoxazin-3(4H)-one; BSTFA: N,N-bis(trimethylsilyl)-trifluoroacetamide; TMS: trimethylsilyl.

BOA (VIa) and MBOA (VIc), by heating in water (17). More recently, several additional glucosides of 1,4-benzoxazin-3-ones have been reported from wheat, maize, rye, and Coix (3, 7, 9-11, 15). Structures of the benzoxazolinones and 1,4-benzoxazin-3-ones which have been reported from plant extracts are shown in Figure 1.

Separation of cyclic hydroxamates and benzoxazolinones in plant extracts has been accomplished by paper, thin layer, and column chromatography with detection by ferric chloride spray reagent and/or UV spectroscopy (5, 6, 10, 11, 16, 18-20). These methods are time-consuming and do not differentiate readily between the compounds of interest and other compounds which have similar physical properties (4, 11). GLC-MS has been used for the identification of three benzoxazolinones found in plant extracts (14). However, 1,4-benzoxazin-3-ones (lactams) were not detected by this method.

As part of our examination of the possible role of DIMBOA in the resistance of maize to soft rot bacteria (2), we undertook to develop a rapid and sensitive procedure for the separation, detection, and identification of hydroxamates, lactams, and other compounds in maize extracts.

MATERIALS AND METHODS

UV spectra were recorded with a Cary model 155 spectrophotometer. Mass spectra were obtained with an MS-9 mass spectrometer (direct probe; ionization voltage, 70 ev; acceleration voltage, 8 kv). Additional mass spectra were obtained by GLC-MS with a Varian Aerograph model 2700 gas chromatograph connected to a Du Pont 21-491B mass spectrometer (ionization voltage, 70 ev; acceleration voltage, 1.4 kv). The inlet lines to the mass spectrometer were maintained at 250 C and the source at 200 C. The column used for GLC was all glass (1.8 m x 2 mm) with a liquid phase of 3% OV-1 on Varaport 30 (100-120 mesh). Analytical GLC was performed using DC-11 columns in a Hewlett-Packard model 7620A gas chromatograph under the conditions described in the accompanying paper (21). The retention times reported in this paper are for the DC-11 column.

Growth of Plants and Preparation of Maize Extracts. Seeds of Zea mays L. (lines Oh45, Oh43, W64A X WI17, and Jacques XJ177) were planted in Vermiculite and grown, harvested, and extracted as described previously (2).

GLC of Reference Compounds and Maize Extracts. Samples (either reference compounds or maize extracts) were dissolved in absolute ethanol. A portion was placed in a small vial and the ethanol was removed under N2. Before injection, BSTFA was added, mixed with the sample, and the mixture was heated to 65

6. Mention of companies or commercial products does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.
to 70°C for 20 min. Usually, a 2-μl portion was injected into the column for analytical GLC. For GLC-MS, similar procedures were used except that the volume of sample injected was modified as necessary.

Identification of GLC Peaks. Identification of most GLC peaks was made on the basis of co-chromatography with reference compounds on a DC-11 column and by comparison of the mass spectrum of the TMS derivatives obtained by GLC-MS with the mass spectrum of the same derivative of the reference compound. Computer programs were written for molecular formula determination, for the computation of relative intensities of fragments in mass spectra, and for the comparison of spectra (i.e. number of common fragments and correlation coefficient of the relative intensities of those common fragments).

RESULTS

TMS Mass Spectra of 1,4-Benzoxazin-3-ones and Benzoxazolinone Reference Compounds. In these spectra, fragments at m/e 73 and 147 (TMS fragments) were excluded from consideration as base peak. Each of the three benzoxazolinones gave two GLC peaks (isomers) with virtually identical mass spectra and in each case only the spectrum of the second GLC peak is reported. TMS-HBOA (IVa): m/e 309 (100%), 294 (28%), 280 (11%), 266 (25%), 220 (10%), 208 (15%), 192 (25%), 191 (16%), 147 (58%). TMS-HMBOA (IVc): m/e 339 (55%), 324 (14%), 310 (7%), 296 (11%), 250 (20%), 238 (13%), 222 (100%), 206 (19%), 194 (31%), 191 (45%), 147 (102%). A second field-free region metastable ion was observed confirming the 339 to 222 transition.

TMS-DIBOA (Va): m/e 325 (14%), 310 (45%), 297 (10%), 253 (10%), 208 (50%), 192 (47%), 191 (33%), 179 (40%), 164 (75%), 147 (115%), 136 (100%).

TMS-DIMBOA (Vc): m/e 355 (26%), 340 (19%), 327 (7%), 296 (19%), 238 (85%), 194 (100%), 191 (46%), 147 (121%).

TMS-DIM2BOA (Vd): m/e 385 (55%), 370 (32%), 357 (7%), 339 (14%), 326 (11%), 268 (94%), 237 (100%), 191 (50%), 147 (51%).

TMS-BOA (Vla): m/e 207 (56%), 192 (100%), 164 (86%), 149 (11%), 100 (34%).

TMS-MBOA (Vlc): m/e 237 (53%), 222 (8%), 194 (100%), 179 (3%), 164 (11%), 136 (9%), 100 (11%).

TMS-M2BOA (Vid): m/e 267 (61%), 252 (31%), 237 (100%), 222 (21%), 194 (9%), 151 (6%), 100 (9%).

Identification of 1,4-Benzoxazin-3-ones and Benzoxazolinones in Maize Extracts. GLC peaks in the ethyl acetate extract of maize inbred Oh45 had the same retention times as authentic samples of TMS-HBOA, TMS-DIBOA, TMS-HMBOA, TMS-DIMBOA, and TMS-DIM2BOA (Table I; see also Fig. 1A in ref. 21). When samples of the extract were coinjected with each reference compound, the reference material co-chromatographed with the GLC peak in question from the extract. Mass spectra obtained for those peaks in the extracts of Oh45 have all of the same major fragments as the corresponding reference compound (Table I). The number of common fragments in any two spectra and the correlation coefficient (r) of relative intensities of those common fragments were used to compare the spectra from maize extracts with those of the reference compounds (Table I).

For example, the mass spectrum of the GLC peak from the maize extract which eluted at 9.9 min was most similar to the mass spectrum of TMS-HBOA and this GLC peak was thus identified as TMS-HBOA by co-chromatography and its mass spectrum (27 of 29 possible peak matches with the reference compound, r = 0.86). The presence of the other 1,4-benzoxazin-3-ones in the extract was confirmed by the comparison of the mass spectra with

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Footnote: 1 GLC and UV comparisons of the O-methyl and N-methyl isomers of MBOA (13) with the TMS isomers indicated that GLC peak 1 appears to be O-TMS-MBOA and GLC peak 2 the N-TMS derivative.
GLC-MS of Maize Extracts

TABLE I. Comparison of mass spectra of the TMS derivatives of components in maize extracts with spectra of silylated reference compounds.

<table>
<thead>
<tr>
<th>PEAKS FROM MAIZE EXTRACTS</th>
<th>REFERENCE COMPOUNDS</th>
</tr>
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<tbody>
<tr>
<td>A (min) B (m/e) N(a)</td>
<td>Malate HBOA MBOA DIBOA Aconitate HMBOA DIMBOA DIM2BOA Most Probable</td>
</tr>
<tr>
<td>5.5 335 24</td>
<td>20** (b) 5 0 4 6 6 5 5 TMS-Malate</td>
</tr>
<tr>
<td>5.6 237 8</td>
<td>1 1 7** 3 1 6 8 8 TMS-HBOA</td>
</tr>
<tr>
<td>9.9 309 28</td>
<td>5 27** 2 19** 4 14** 12** 11** TMS-HBOA</td>
</tr>
<tr>
<td>19.4 237 8</td>
<td>0 2 8** 3 0 5 7* 7 TMS-MBOA</td>
</tr>
<tr>
<td>20.7 325 39</td>
<td>6 18** 5 30** 5 16* 18* 18 TMS-DIBOA</td>
</tr>
<tr>
<td>22.8 390 35</td>
<td>4 6 1 5 26** 5 6 5 TMS-Aconitate</td>
</tr>
<tr>
<td>26.2 339 51</td>
<td>7** 20** 8 23* 4 32** 26** 22 TMS-HBOA</td>
</tr>
<tr>
<td>29.0 327 57</td>
<td>6 16 9** 20 5 22 27* 26 A</td>
</tr>
<tr>
<td>31.3 397 45</td>
<td>7** 19 8** 14** 6 16* 17** 21* B</td>
</tr>
<tr>
<td>34.0 355 32</td>
<td>5 10** 8 13* 4 18 30** 22 TMS-DIBOA</td>
</tr>
<tr>
<td>38.4 413 27</td>
<td>5 11** 3 9** 4 10 13 14 C</td>
</tr>
<tr>
<td>38.7 385 29</td>
<td>2 9* 5 0* 4 12* 17 27** TMS-DIM2BOA</td>
</tr>
</tbody>
</table>

(a) Spectra were compared using all fragments which were greater than 5 percent of the base peak and greater than m/e 80. The number of fragments meeting these criteria is designated N.

(b) Each number in the table represents the number of observed matches between the fragments of the reference spectra and fragments observed in the spectra obtained from peaks in maize extracts. The number of asterisks represent the correlation coefficient (r) obtained by regression of the relative intensities of the common fragments of one spectrum with the relative intensities of the same fragments in the other spectrum being compared: ** (r > 0.90); *** (0.70 < r < 0.90); ** (0.40 < r < 0.70); and no asterisks represent r < 0.40. Correlation coefficients are not reported for spectral comparisons where six or less common fragments were found. Generally, spectra which met the arbitrarily selected criteria of 12 peak matches and a correlation coefficient greater than 0.7 were considered highly related.

(c) Identification was based on GLC retention times, mass spectral molecular ions, the number of fragments in common with reference spectra, and the value of the correlation coefficient obtained. Those GLC peaks which are not identified by comparison with reference spectra are designated Compounds A, B and C. (See text).

The reference compounds: DIBOA (30 of 36 matches, r = 0.95); HMBOA (32 of 32 matches, r = 0.91); DIBOA (30 of 34 matches, r = 0.91); DIM2BOA (27 of 48 matches, r = 0.99) as shown in Table I.

GLC evidence was found for the presence of small amounts of the benzoxazolinone, MBOA, in the extracts of each maize line examined (see Fig. 1B in ref. 21). The amount of MBOA found was proportional to the amount of DIBOA present in the extract and may have been generated during extraction. The presence of both peaks of TMS-MBOA in the chromatograms was confirmed by mass spectra obtained by GLC-MS (Table I). TMS-MBOA peak 2 elutes just ahead of TMS-DIBOA. A GLC peak (TMS-Malate) was present in extracts prepared at pH 3.0 and interfered with the detection of TMS-MBOA peak 1. Malate was not detected in extracts prepared at pH 5.0, thus allowing the detection of peak 1 of TMS-MBOA (Table I). No evidence for either peak of TMS-BOA or TMS-M2BOA was obtained by co-chromatography or GLC-MS.

As can be seen from Table I, there is a considerable amount of interrelatedness in the spectra of the 1,4-benzoxazin-3-ones. For example, HBOA from the extract was significantly related to DIBOA, HMBOA, and DIMBOA as well as HBOA (based on the criteria of 12 peak matches and r > 0.7). Because of the high degree of structural similarity among the 1,4-benzoxazin-3-ones some degree of mass spectral relatedness could be expected; however, HBOA (and each 1,4-benzoxazin-3-one) showed little similarity to any of the other nonbenzoxazinone reference compounds.

The GLC peaks in the Oh45 extract corresponding to HBOA, DIBOA, DIMBOA, and DIM2BOA were virtually pure (based on peak symmetry and similar numbers of total fragments [N in Table I]). HMBOA gave a symmetrical peak; N was 51 for the peak in the Oh45 extract and only 32 for the reference compound. The "extraneous" fragments were all in the low mass range (< m/e 180) and were the result of an increase in the relative intensity of the low mass fragments. For example, the relative intensity of the fragment at m/e 134 was 5% in the spectrum of the reference compound, but 20% in Oh45. All fragments in the low mass range were much more intense in the maize extracts than in the reference. The apparent impurity is probably due to a difference in the method of obtaining the spectra (i.e. on the front side of the peak for the extracts versus at the apex for the reference). The five 1,4-benzoxazin-3-one peaks in the Oh45 extract are pure or nearly pure. These same peaks were also pure in extracts of W64A × W117. Extracts of one variety, Jacques JX177, had the TMS-DIM2BOA peak partially contaminated with another component (compound C; see next section). Oh43 had a GLC peak which had nearly the same retention time as TMS-DIM2BOA; however, mass spectral analysis showed that the peak did not contain TMS-DIM2BOA and confirmed an earlier report of the absence of DIM2BOA in extracts of this inbred (12).

GLC-MS Evidence for the Existence of Additional Hydroxamic Acids and Related Compounds in Maize Extracts. Mass spectra were obtained from other GLC peaks in the extracts which appeared to be related to one or more of the 1,4-benzoxazin-3-ones based on the criteria of common fragments and correlation coefficient (Table I). These GLC peaks eluted at 29.0, 31.3, and 38.4 min and are designated A, B, and C, respectively.

The mass spectrum of B has a molecular ion and base peak at m/e 397 and a strong M-117 fragment (Fig. 2B). This loss of 117 (COOTMS) is a characteristic of all five 1,4-benzoxazin-3-one reference compounds but not of the benzoxazolinones. By assuming the same saturation number (rings + double bonds) as for benzoxazolinones and 1,4-benzoxazin-3-ones (i.e. 6), two plausible molecular formulas were obtained which can be differentiated on the basis of the isotope peaks as shown in Table II. The M+2 peak is diagnostic for the number of TMS groups (Si atoms), clearly indicating that the molecular formula of the unsilylated...
compound is C₈H₇NO₄. Of the known 1,4-benzoxazin-3-ones (Fig. 1), only IVb and Va have the correct formula and Va (DIBOA) can be ruled out because it has only two reactive hydrogens. Structure IVb (7-OH HBOA) is consistent with the mass spectral data obtained for B. A reference sample of 7-OH HBOA was obtained from J. Hofman and the mass spectrum of B was identical to that of TMS₇-7-OH HBOA (19 out of 20 matches, r = 0.75), thus confirming the identification.

The mass spectrum of C is shown in Figure 2C. This spectrum also has a prominent loss of 117 from the molecular ion which is common to all of the 1,4-benzoxazin-3-ones studied. Since the molecular ion (at m/e 413) is 16 mass units above that of lactam IVb (compound B), it is probable that C is the hydroxamic acid Vb. The molecular formula obtained from the isotope peak data for the unsilylated compound is C₈H₇NO₄ (Table II) and the only known 1,4-benzoxazin-3-one which is consistent with this formula is Vb (TRIBOA). The fragmentation pattern of C is consistent with structure Vb.

| Table II. Determination of molecular formulae of compounds A, B and C (a) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Compound | Intensity of M + 2 Peak (b) | TMS groups | Molecular Formula (c) | Saturation Number (d) |
| Vlc | 5.0 | 5.32 | 1 | 9 | 9 | 6 |
| IvC | 11.2 | 10.88 | 2 | 17 | 1 | 4 |
| Vc | 12.0 | 11.09 | 2 | 9 | 9 | 6 |
| A | 13.9 | 14.51 | 1 | 12 | 17 | 5 |
| B | 17.8 | 12.05 | 2 | 12 | 15 | 6 |
| C | 18.1 | 12.62 | 2 | 12 | 15 | 6 |

(a) Formulae were obtained based on these constraints: (1) Molecular ion (327, 397 and 413 for A, B and C respectively); (2) saturation number equal to six for B and C and four to seven for A; and (3) upper limit of formula C₁₀H₇N₂O₄Si for A, B and C. Only the most plausible formulae are presented.

(b) Relative intensity of molecular ion taken as 100.

(c) Residual formula after removal of the contribution of the TMS groups.

(d) Sum of the number of rings + double bonds in the indicated formula.

Fig. 2. Mass spectra of TMS derivatives of three additional components in maize extracts. Compounds A, B, and C eluted at 29.0, 31.3 and 38.4 min, respectively, on the DC-11 column. All fragments with relative intensities larger than 10% of the corresponding base peak are plotted.
The mass spectrum of A (Fig. 2A) has a base peak at m/e 194, which is the same as the base peak of MBS-MBOA and MBS-DIMBOA. The spectrum does not show the typical loss of 117 from the molecular ion nor the intense fragment at m/e 147 which are characteristic of all 1,4-benzoxazin-3-ones. The spectrum shows a prominent ion at m/e 238 (M-SH) indicating the possible presence of a phenolic TMS group. However, none of the seven 1,4-benzoxazin-3-ones has a strong M-SH peak. The isotope peak data indicate the presence of two or three TMS groups; three can be ruled out by the residual molecular formula (C,HNO) which is too small to be related to any benzoazinone. The two plausible formulas obtained both have a mol wt of 183 (28 mass units less than DIMBOA); however, one has a saturation number of 5 and the other 6 (Table II). The formula C,H,NO is unlikely since all 1,4-benzoxazin-3-ones have at least seven hydrogens. However, the other formula, C,H,NO, is identical to that of DIMBOA less C=0 and also the mass spectrum of A is more closely related to DIMBOA (27 of 37 matches, r = 0.56) than to any other reference compound. Hence, A probably has a saturation number of 5 instead of 6 due to the loss of one double bond (as C=0) from the benzoazinone structure. Although no further work was carried out to characterize A, structure VII or its isomeric form VIII appears to be consistent with the mass spectral data.

Identification of Other Components in Maize Extracts. Mass spectra were also obtained of GLC peaks with retention times of 5.5 and 22.8 min min. These spectra were not closely related to any of the spectra of the benzoazolinones or 1,4-benzoxazin-3-ones (Table I). These GLC peaks were identified as the organic acids acetonate and lactate by both co-chromatography with reference compounds and comparison of the mass spectra obtained by GLC-MS with the spectra of the reference compounds (Table I). These findings are in agreement with an earlier report that acetonate and lactate were the two most abundant organic acids present in extracts of maize seedlings (1).

DISCUSSION

The cyclic hydroxamates DIBOA, DIMBOA, and DIM3BOA and the lactams HIBOA, 7-OH HIBOA, and HMBOA can now be identified as TMS derivatives from maize extracts by their mass spectra obtained by a single GLC-MS run. The GLC-MS method has the following advantages over previous procedures: an increased sensitivity (100 ng can be detected), a reduced time of analysis (at least nine compounds can be identified in a single run), and an increased amount of information obtained about purity and structural properties of compounds (molecular ions and fragmentation patterns).

A data comparison system was developed for relating unidentified spectra to the spectra of known 1,4-benzoxazin-3-ones (Table I). With this system, an unknown spectrum can be quickly compared with a library of spectra and similarities between the unknown and each reference spectrum can be put on a quantitative basis. Two criteria used in this study to determine similarities between an unidentified spectrum and a given reference spectrum were: the number of fragments in common, and the correlation coefficient (r) of the relative intensities of the common fragments. These two criteria were used to confirm the presence of 1,4-benzoxazin-3-ones in the maize extracts.

The usefulness of GLC-MS and the data comparison system for the identification of other compounds in maize extracts was demonstrated with three unidentified GLC peaks (A, B, and C). Based on spectral similarities, these three were selected as compounds related to one or more of the 1,4-benzoxazin-3-one standards (Table I). Two of these unidentified GLC peaks are a lactam-hydroxamate pair, TMS2-7-OH HIBOA (B) and TMS3-TRIBOA (C). The mass spectrum of the third GLC peak (Fig. 2A) was found to have the same base peak as TMS3-DIMBOA (m/e 194) and may be a breakdown product of DIMBOA. This reaction product could be formed in vivo or after the aqueous extract was prepared.

The 1,4-benzoxazin-3-ones and benzoazolinones present in plant extracts can now be separated by GLC and identified by GLC-MS. A quantitative GLC procedure for the direct determination of cyclic hydroxamates and lactams in maize extracts has now been developed and is described in reference 21.

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