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HERBIVORE-INDUCED PLANT VOLATILES IN THE LEAVES OF *Ziziphus jujuba* FROM CHINA

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Chinese jujube, *Ziziphus jujuba* Mill., belonging to the family Rhamnaceae, is an important fruit crop in China and contains 700 cultivars [1]. Among cultivars, *Z. jujuba* Mill. cv. Muzao is an endemic, economic fruit cultivar distributed mainly in the hilly jujube production area of the Losses Plateau, the Yellow River Canyon, located between Shanxi and Shaanxi Provinces in China, and occupies about 65% of total cultivation (300,000 ha) of jujube in the region [2, 3].

Herbivore-induced plant volatiles (HIPVs) play an important role in tritrophic interactions among plants, herbivores, and their natural enemies. Plants employ indirect defense by attracting natural enemies of herbivores (parasitoids or predators) after herbivore damage [4] and direct defense by repelling herbivores [5–9]. To date, there are no related reports about HIPVs of jujube, and this experiment is the first to identify compounds induced by herbivory in any cultivar of jujube.

We studied the volatiles of the leaves of *Z. jujuba* Mill. cv. Muzao using solid phase microextraction (SP-ME) and GC-MS. The volatile compounds were identified and their percentages of the total volatile profile per treatment are presented in Table 1. The components are listed in order of their retention indices calculated on an apolar stationary phase.

Ten grams of the healthy leaves, herbivore-infested (by larvae *Ancylis sativa* Liu, Lepidoptera: Tortricidae) leaves, and artificially damaged leaves were placed in three different sample vials, respectively, at laboratory conditions (25 ± 1°C, RH 65%). Volatile constituents were collected for 2 h using SPME with a 100 μm polydimethylsiloxane (PDMS) fibre. The SPME samples were analyzed by a TraceDSQ GC-MS instrument (Thermo Scientific, USA) with a 30 m quartz capillary column (SE-54), internal diameter 0.25 mm, stationary phase thickness 0.25 μm (5% phenylmethylsilicone). The flow rate of helium (carrier gas) was 1 mL/min. The column temperature was kept at 50°C for 3 min and then programmed to 220°C at a rate of 8°C /min, keeping constant at 220°C for 20 min. Injector and detector (FID) temperatures were 250°C. Volume injected, 1 μL of the oil; split ratio, 1:50. The MS operating parameters were as follows: ionization potential, 70 eV; ion source, EI.

The contents of oil components were calculated from areas of GC peaks without correction coefficients. The identification of the isolated volatile compounds was achieved by comparing obtained mass spectra of unknown peaks with those stored in the NIST.02 (US National Institute of Standards and Technology) mass spectral electronic libraries.

We identified 23 compounds representing 92.36% of the total volatile constituents in healthy leaves of *Z. jujube*. The major compounds of healthy leaves by percentage were *Z*-ocimene (39.97%), 1,1-dimethyl-3-methylene-2-ethenyl-cyclohexane acetate (35.77%), methoxy-phenyl-oxime (4.55%), and *α*-farnesene (3.09%).

From herbivore-infested leaves, we identified 21 compounds representing 90.32% of the total volatile constituents. 1,1-Dimethyl-3-methylene-2-ethenyl-cyclohexane acetate (27.31%) was the major component, followed by 4-hexen-1-ol acetate (23.85%), *Z*-ocimene (19.29%), methoxy-phenyl-oxime (4.04%), and *α*-phellandrene (3.14%). In comparison with the volatile composition of healthy and artificialy damaged leaves, 4-hexen-1-ol acetate was unique to herbivore-infested leaves, and the content of *α*-phellandrene increased remarkably, while 1,1-dimethyl-3-methylene-2-ethenyl-cyclohexane acetate and *Z*-ocimene were sharply reduced.

Twenty-five compounds representing 95.43% of the total volatile constituents in artificially damaged leaves were characterized. 1,1-Dimethyl-3-methylene-2-ethenyl-cyclohexane acetate (35.67%), *Z*-ocimene (28.88%), *α*-farnesene (7.77%), *cis*-3-hexenyl acetate (7.18%), and methoxy-phenyl-oxime (4.57%) were found to be the most abundant constituents. The percentages of *cis*-3-hexenyl acetate and *α*-farnesene increased in artificially damaged leaves, while the percentage of *Z*-ocimene was significantly decreased in comparison with the volatile composition of healthy leaves.

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TABLE 1. Volatile Compounds of the Healthy, Herbivore-infested and Artificialy Damaged Leaves of *Ziziphus jujuba* in North Shaanxi, China, %

Compound[a]	RI[b]	Healthy[c]	Herbivore infested[c]	Artificialdamage[c]
Camphene	620	0.77	0.95	0.52
β-Pinene	705	0.15	0.26	–
α-Phellandrene	740	0.96	3.14	0.62
α-Pinene	843	1.46	1.52	0.83
D-Sylvestrene	910	–	0.96	0.62
Eucalyptol	954	0.55	1.73	0.93
2,2-Dimethyl-3-vinyl-bicyclo[2.2.1]heptane	980	0.15	–	–
(2-Dodecen-1-yl)succinic anhydride	981	–	–	0.15
E-Ocimene	1001	1.43	–	–
3,6,6-Trimethyl-bicyclo[3.1.1]hept-2-ene	1002	–	0.55	1.03
Z-Ocimene	1060	39.97	19.29	28.88
1,1-Dimethyl-3-methylene-2-ethenyl-cyclohexane	1217	35.77	27.31	35.67
cis-3-Hexenyl acetate	1285	1.62	–	7.18
4-Hexen-1-ol acetate	1292	–	23.85	–
E,Z-2,6-Dimethyl-2,4,6-octatriene	1407	0.69	0.15	0.80
Cyclopropane,trimethyl(2-methyl-1-propenylidene)-	1468	–	0.52	–
Z-3-Hexen-1-ol	1505	0.12	1.8	0.50
E,E-2,6-Dimethyl-1,3,5,7-octatetraene	1622	0.34	0.2	0.27
cis-3-Hexenyl butyrate	1663	–	0.95	0.90
cis-3-Hexenyl isovalerate	1691	0.25	1.47	–
n-Valeric acid *cis*-3-hexen-1-yl ester	1693	–	–	2.02
Acetic acid	1699	0.21	–	0.14
Oxirane,2-(hexyn-1-yl)-3-methoxymethylene-	1741	0.39	–	–
(6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)methanol	1741	–	–	0.48
3,7-Dimethyl-1,6-octadien-3-ol	1900	0.12	0.21	0.35
3,6-Dimethoxy-9-(2-phenylethynyl)-fluoren-9-ol	1978	0.19	0.40	0.17
Benzoic acid methyl ester	2081	0.32	–	0.23
2,6-Dimethyl-6-(4-methyl-3-pentenyl)bicyclo[3.1.1]hept-2-ene	2302	–	–	0.23
α-Farnesene	2355	3.09	1.02	7.76
Methoxy-phenyl-oxime	2406	4.55	4.04	4.57
Methyl salicylate	2427	0.29	–	0.13
E-3-(4,8-Dimethyl-3,7-nonadienyl)furan	2483	0.30	–	0.45
4-Methoxybenzaldehyde	2957	–	0.19	–
Total		92.36	90.32	95.43

[a]Compounds listed in order of their RI. [b]RI: retention indices observed. [c]%: Relative percentage obtained from peak area. –: not determined.

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