Synthesis of 
(±)-(10-2H, 11-2H2, 12-2H3) Jasmonic Acid
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(±)-(10-2H, 11-2H2, 12-2H3)Jasmonic Acid,
Plant Growth Regulator, Synthesis, Mass Spectra
(±)-(10-2H, 11-2H2, 12-2H3)Jasmonic acid has
been synthesized starting from racemic jasmonic acid
via 2-formylmethyl-3-methoxycarbonylmethylcyclopentanone by reaction with
(1-2H, 2-2H2, 3-2H3)propyldenedetriphenylphosphorane followed by saponification of the labelled
methyl jasmonate.

Introduction
Jasmonic acid (JA) and methyl jasmonate (JA-Me, I) are naturally occurring substances in
plants. They are representatives of a group of plant growth regulators [1]. The exact quantification
of JA in plant materials is of great interest for further studies on transportation, metabolism and
endogenous importance of JA. Using the GC/MS-SIM method deuterium-labelled JA should be
good internal standard. Therefore this report describes a simple way for the preparation of
(methyl ester of) (10-2H, 11-2H2, 12-2H3)JA. MS-spectrum is compared to that of JA.

Material and Methods
(1-2H2, 2-2H2, 3-2H3)Iodopropane (99.8% pure) was obtained from Isocommerz Handelsgesell-

Ozonolysis
To (±)-methyl jasmonate (5 g, 22 mmol) in 100 ml CH2Cl2, O3 was introduced at ∼15 °C until
the color of the mixture became pale. An excess of ozone was flushed of with N2 and the solution
slowly added to a stirred suspension of Zn powder (7 g) in acetic acid (20 ml) at about 20 °C. Filtration
of the mixture, treatment with water, sodium bicarbonate and drying with anhydrous sodium sulphate gave the crude aldehyde. Further purification was done by column chromatography
(3.5×90 cm) on silica gel (Merck, 0.63–0.2 mm) and solvent mixture n-hexane:ethyl acetate:acetic acid (30:65:5). Aldehyde containing fractions were evaporated giving 2 g (46%) of 2.

Phosphonium salt
(1-2H, 2-2H2, 3-2H3)Propytriphenylphosphonium iodide was prepared according to [2]. Triphenyl-
phosphin (2.62 g, 10 mmol), (1-2H2, 2-2H2, 3-2H3)-
iodopropane (1.77 g, 10 mmol), 1 g K2CO3 in 7 ml
CH3CN were refluxed for 48 h. The mixture was
filtered and after addition of ether the iodide crys-
tallized. Recrystallization from CHCl3/ether gave 2.1 g phosphonium salt (49%, Fp. 201–202 °C).

Wittig reaction
Phosphonium salt (2.1 g) was suspended in 15 ml dry THF, stirred and 1.7 ml of 1.6 M lithium-
umbutyl in n-hexane was added slowly at ∼30 °C. The so prepared deep yellow solution of propylidene-phosphorane was added to 0.44 g aldehyde 2
in 15 ml dry THF at ∼30 °C and further stirred for
15 min. The mixture was purged into 5 N HCl and extracted with ether. After washing with NaHCO3 solution and drying with Na2SO4 evaporation of ether the residue was chromatographed on silica gel with n-hexane and an increasing gradient of ethyl acetate.

Fractions containing methyl jasmonate (3) were collected and evaporated. Methanol (2 ml) and 1 N NaOH (5 ml) were added and the mixture saponified at 60 °C for 2 h. The free acid was recuperated and further chromatographed as described above giving 158 mg (43%) of
(±)-(10-2H, 11-2H2, 12-2H3)JA (4).

Gas chromatography/mass spectrometry
Combined GC/MS was achieved under the following conditions: 50 eV mass spectrometer; steel column (1.5 m×2 mm) containing 3% OV 225 on Gaschrom Q (100–120 mesh); column temp. 180 °C; He 17 ml/min; Rf of methyl esters: 1 = 3.6 min, 3 = 3.6 min, 7-iso-1 = 4.2 min, 7-iso-3 = 4.2 min.

MS of 3: m/z (rel. int.) 230 [M]+ (43%), 212 [M–H2O]+ (6), 199 [M–OCH3]+ (20), 157 [M–CH2COOMe]+ (72), 156 [M–C2H52H]+ (52), 138 (30), 96 [C6H62HO]* (48), 95 [C5H6O]* (43), 84 [C6H5HO]* (100), 83 [C6H5O]* (46).

Conditions for capillary GC were: column (50 m×320 μm) containing PB-1 (film thickness 0.2 μm), column temp. 140 °C, 2 ml/min N2; Rf: 1 = 19.07 min, 3 = 18.75 min, 7-iso-1 = 21.74 min, 7-iso-3 = 21.36 min.

Results and Discussion
Modification of a given natural compound is a rapid tool for synthesizing derivatives. Here we report a short synthesis of deuterium-labelled jas-
monic acid (4), starting from racemic methyl jasmonic acid (±)-JA-Me (1, Fig. 1). Ozonolysis of (±)-JA-Me in dichloromethane at temperatures higher than -20 °C followed by reductive cleavage of the ozonide gave 2-formylmethyl-3-methoxycarbonylcyclopentanone (2) [3, 4], which could be purified by column chromatography.

The aldehyde 2 reacts rapidly with (1-2H,2-2H₂,3-2H₂)propyldene-triphenylphosphorane in THF prepared from the ylide from (1-2H₂,2-2H₂,3-2H₂)propyltriphenylphosphonium iodide. Under the used conditions the newly formed double bond is cis-configurated [4]. A parallel reaction with unlabelled ylide prepared from 1-bromopropane gave a better yield and a higher purity of the crude product. The free acid 4 was obtained by saponification of 3. The final product was methylated with diazomethane and characterized by capillary GC and combined GC/MS. In capillary GC deuterium-labelled JA-Me showed 95% 3 (trans-situated side chains) and 5% 7-iso-3 (cis-situated side chains) (Fig. 2).

Fig. 1. Synthesis of (±)-(10-2H,11-2H₂,12-2H₃)jaemonic acid.

Fig. 2. Composition of product isomers.

Fig. 3. Mass spectra of deuterium-labelled methyl jasmonic acid and methyl jasmonate (JA-Me).
In the mass spectrum of 3 fragments at \( m/z \) 230, 212, 199, 157 indicated the deuterium-labelled side chain compared to those of JA-Me (1) with fragments 224, 206, 193, 151, respectively (Fig. 3). Fragments at 96 and 84 stem from the cyclopentanone part of 3. Compared to those of 1 they showed one unit more, surely, due to a partial McLafferty rearrangement [5].

Retention times of 1 and 3 differ slightly in the capillary GC, because its differences in molecular weights.

For quantification of jasmonic acid by GC/MS-SIM ions at \( m/z \) 230 or 157 of the labelled compound and ions 224 or 151 of non-labelled one, respectively, are recommended.

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