HSR (LONDON),
HOUGHTON STREET REVIEW JOURNAL
ISSN: 2058-5519|Impact factor-15.9
http://houghtonstreetreview.com/index.php/hsr

Molecular Complexes of Jasmonic Acid with Monoammonium Glycyrrhizinate

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doi:https://doi.org/10.5281/zenodo.24506588

ABSTRACT: This article describes the synthesis and spectral characterization of supramolecular complexes formed between monoammonium glycyrrhizinate (MASGA) and jasmonic acid (JA). The complexes were obtained at molar ratios of 2:1, 4:1, and 8:1. The resulting samples were investigated using UV-Vis and IR spectroscopy. The research findings revealed the presence of non-covalent interactions, specifically hydrogen bonding and hydrophobic interactions, between MASGA and jasmonic acid. The reaction yields of the synthesized compounds were 94.5%, 95%, and 92%, respectively. Physicochemical parameters confirm the formation of intermolecular bonds between the reagents and the successful assembly of supramolecular complexes.
Keywords: MASGA, jasmonic acid, supramolecular complex, UV spectroscopy, IR spectroscopy.

INTRODUCTION

Phytohormones play a distinct role as crucial physiological regulators in plant growth, development, and adaptation to various external environmental stress factors. Therefore, investigating the intermolecular interactions between monoammonium glycyrrhizinate (MASGA) and jasmonic acid (JA) is essential not only for elucidating the mechanism of complexation, but also for evaluating the potential of developing novel biologically active supramolecular systems. In complexes formed on the basis of MASGA and jasmonic acid, hydrogen bonds and other intermolecular interactions are expected to occur between the functional groups of the components. Consequently, a new supramolecular system may emerge whose physicochemical properties differ from those of the initial substances. Such structural changes can be detected using modern physicochemical analytical methods, particularly IR and UV spectroscopy, which also allow the identification of the functional groups involved in complexation. From this perspective, synthesizing complexes based on monoammonium glycyrrhizinate (MASGA) and jasmonic acid (JA), determining their structural and spectroscopic properties, and studying the nature of their intermolecular interactions represent pressing challenges in bioorganic and supramolecular chemistry. The findings of this study can contribute to a deeper understanding of the chemical properties of novel biologically active complex systems based on MASGA and jasmonic acid, as well as to assessing their prospects for further biological research.

LITERATURE REVIEW

Jasmonic acid is a widely distributed class of plant growth regulators. It plays a vital role in regulating plant growth and development, stress tolerance, and the synthesis of secondary metabolites.

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To date, more than 30 jasmonate derivatives have been identified, among which the most active representatives are jasmonic acid (JA), the volatile methyl jasmonate (MeJA), and the synthetic jasmonate derivative propyl dihydrojasmonate (PDJ). Jasmonic acid exhibits a broad spectrum of physiological effects, primarily mediating plant stress-resistance responses to protect plants against pathogenic bacteria, herbivorous insects, and abiotic stresses. As an endogenous signaling molecule, it regulates plant growth and development (such as seed germination, flowering, fruit ripening, etc.) and shares functional similarities with abscisic acid. Jasmonic acid and its derivatives can modulate processes such as fruit ripening, viable pollen production, root elongation, tendril coiling, and plant resistance to insects and pathogens [1]. Among other active metabolites of JA are airborne signaling molecules, methyl jasmonate (MeJA) and cis-jasmone (cJA), which act as inter-plant signaling agents that activate defense-related protein-encoding genes and secondary metabolites such as anthocyanins and alkaloids [2]. Jasmonates were initially characterized as growth-inhibiting substances, and exogenously applied jasmonates were shown to promote senescence. However, findings regarding endogenous JA levels indicate that the observed senescence-promoting effect in plants may be associated with the application of high, non-physiological concentrations of JA.

The results obtained from this investigation demonstrate that monoammonium glycyrrhizinate (MASGA) and jasmonic acid (JA) form not merely simple mixtures, but a supramolecular system stabilized by non-covalent interactions. First, the gradual shift in absorption intensity in the UV spectra indicates an alteration in the microenvironment surrounding the chromophore system of jasmonic acid (JA). Second, shifts in the vibrational frequencies corresponding to the –OH, –NH, and –C=O functional groups in the IR spectra confirm the formation of hydrogen bonds and other weak intermolecular interactions. Jasmonates are fatty acid derivatives, with primary representatives including jasmonic acid (JA), methyl jasmonate (MeJA), and the jasmonoyl-isoleucine conjugate (JA-Ile) [4]. Glycyrrhizin derivatives have been recognized as effective carriers for creating supramolecular forms of biologically active substances, capable of enhancing their solubility and storage stability. For a sensitive phytohormone such as jasmonic acid, this approach is theoretically advantageous, as supramolecular encapsulation can improve the resistance of the active compound to external environmental factors. In this context, the present study confirms the complexation between MASGA and JA not only through spectral evidence, but also via high product yields. Therefore, this paper focuses primarily on the spectroscopic evidence of complex formation. Jasmonic acid (JA) and its derivatives—collectively termed jasmonates—are among the simplest phytohormones regulating multifaceted physiological processes, including plant development, growth, and defense responses to various abiotic and biotic stressors [5].

RESEARCH METHODOLOGY

Monoammonium glycyrrhizinate (MASGA) and jasmonic acid (JA) were selected as the objects of study. The complexes were synthesized at three different molar ratios. Specifically, an ethanolic or aqueous-ethanolic solution of jasmonic acid was added dropwise to a pre-prepared solution of MASGA. The resulting reaction mixture was stirred continuously at a constant temperature of 30°C for a specified period. Upon completion of the reaction, the solvents were evaporated using a rotary evaporator, and the obtained products were dried in a drying oven.

RESULTS AND DISCUSSION

During the investigation, supramolecular complexes based on monoammonium glycyrrhizinate (MASGA) and jasmonic acid (JA) were synthesized at three distinct molar ratios. The yields of the

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resulting compounds were 95% at a 2:1 ratio, 93% at a 4:1 ratio, and 92% at an 8:1 ratio. Their melting points were recorded as 188±1°C, 184±1°C, and 182±3°C, respectively.

Shifts in absorption wavelengths and intensities confirm the interaction between jasmonic acid and MASGA, indicating the formation of new complex compounds. IR spectroscopic analysis, the absorption maxima were recorded at 200.0 nm (lgε=5.42), for the 2:1 complex, 260.8 nm (lgε=4.50), for the 4:1 complex, and 260.8 nm (lgε=4.48) for the 8:1 complex (Table 1).

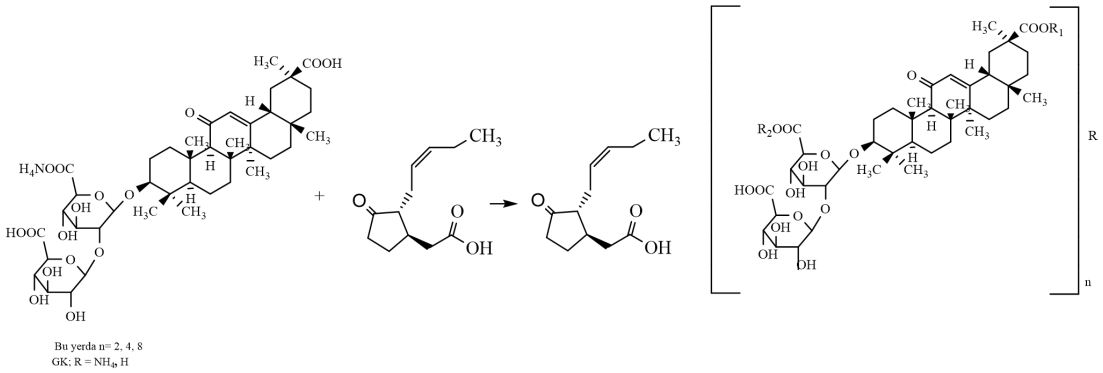

Figure 1. Proposed scheme of supramolecular complex formation between MASGA and jasmonic acid.

No.	Complex	(Tmelt), °C (±3)	Yield, %	UV, lgε (max), nm	IR spectral vibrational frequencies, cm^{-1}
1	MASGA:Jasmonic acid (2:1)	188±1	95	200 (5.42)	ν(OH)=3217, ν(CH, CH_2, CH_3)=2931, ν(C=O)=1710, ν(COO^-)=1594, δ(CH_2, CH_3)=1450–1410, ν(C–O)=1290, 1245, 1180, 1110, 1040, ν(C–O–C)=1040, δ(=CH)=980 cm^{-1}.
2	MASGA:Jasmonic acid (4:1)	184±1	94.5	260.8 (4.50)	ν(OH)=3224, ν(CH, CH_2, CH_3)=2921, ν(C=O)=1706, ν(C=C)=1639, ν(COO^-)=1589, δ(CH_2, CH_3)=1450–1410, ν(C–O)=1290, 1240, 1180, 1110, 1040, ν(C–O–C)=1040, δ(=CH)=980 cm^{-1}.
3	MASGA:Jasmonic acid (8:1)	182±1	96	260.8 (4.48)	ν(OH)=3249, ν(CH, CH_2, CH_3)=2930–2850, ν(C=C)=1637, ν(COO^-)=1589, δ(CH_2, CH_3)=1450–1410, ν(C–O)=1290, 1245, 1180, 1110, 1040, ν(C–O–C)=1040, δ(=CH)=980 cm^{-1}.
4	MASGA	216±2°C	-	260.6 (4.88)	ν(OH, NH_4^+)=3207, ν(CH, CH_2, CH_3)=2930, ν(C=O)=1722, ν(C11=O, C=C)=1657, ν(COO^-)=1589, δ(CH_2, CH_3)=1454, δ(NH_4^+)=1387, δ(CH)=1361,

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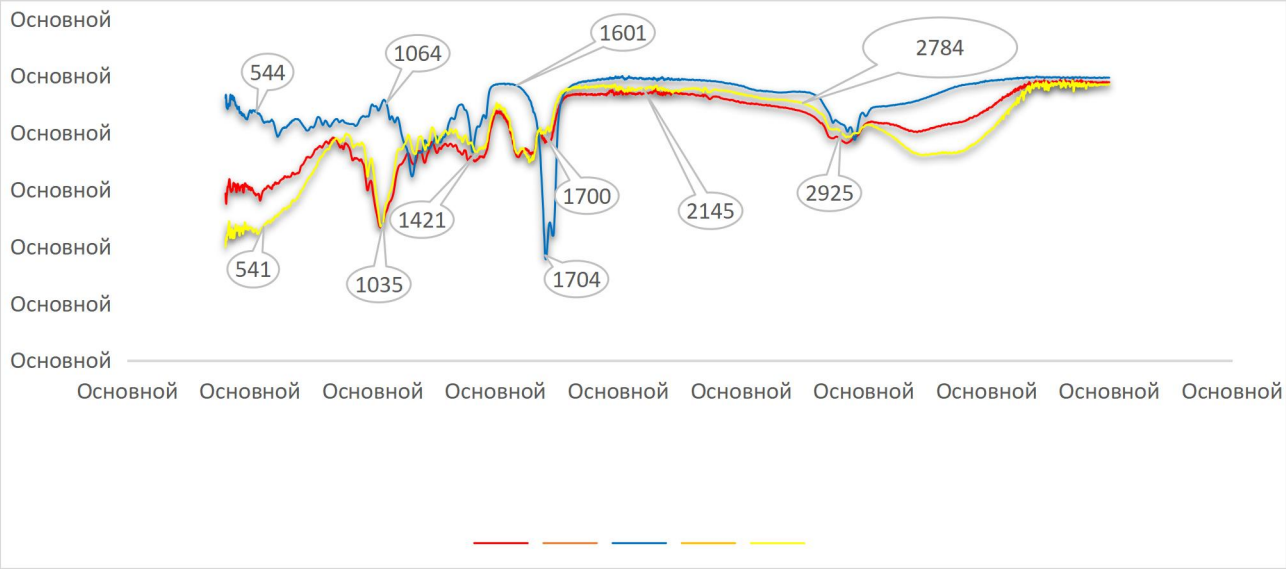
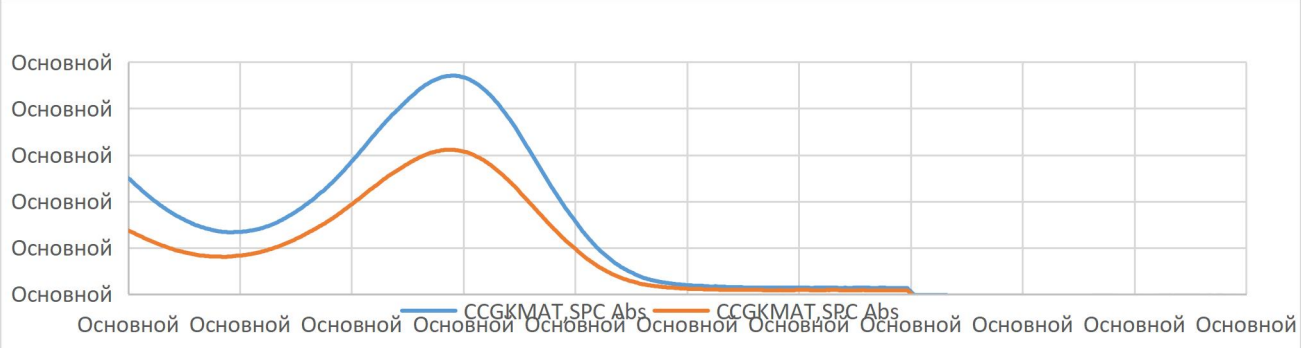
					1306, 1259, 1211, 1166, δ(C–O–C, C–OH)=1166, ν(C–O–C)=1041, δ(=CH)=979.
5	Jasmonic acid	155±2°C	-	228 (4.77)	3007.32 (O–H, =C–H), 2968.89, 2934.07, 2875.19 (CH, CH_2, CH_3), 1732.01 (C=O), 1460.57 (δCH_2, CH_3), 1407.44 (COO^- yoki δOH), 1260, 1215, 1160, 1105, 1045 (C–O), 980–960 (δ=CH) sm^{-1}.

Table 1. Selected physicochemical and spectral characteristics of MASGA and MASGA:Jasmonic



acid supramolecular complexes.

Table 2. IR spectra of MASGA and MASGA:Jasmonic acid supramolecular complexes



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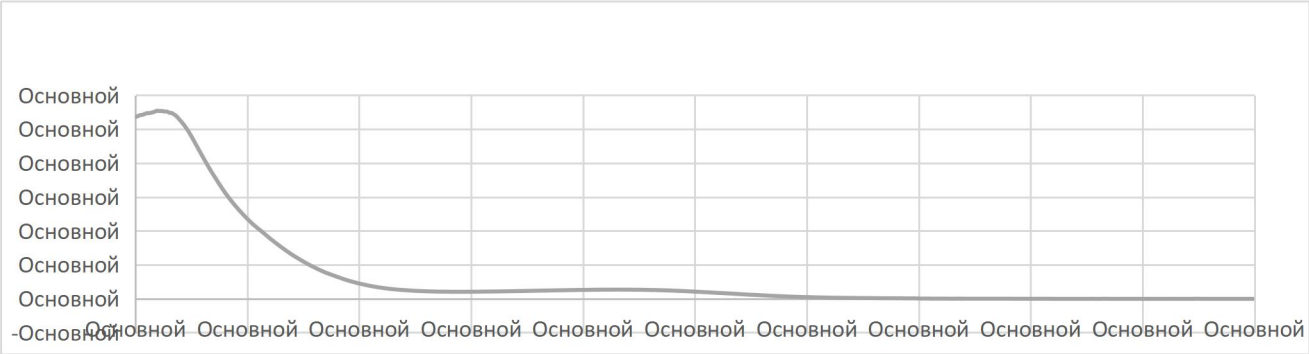

Table 3. UV spectra of MASGA and MASGA:Jasmonic acid (2:1) supramolecular complexes.

Jasmonic acid (JA) was first identified in 1962 as a volatile component of jasmine and has since been recognized as a plant hormone due to its role in mediating diverse biological responses in plants, including defense mechanisms against herbivorous insects or necrotrophic pathogens, wound responses, enhanced synthesis of secondary metabolites, sex determination, and growth regulation [6]. Genetic and molecular studies have demonstrated that the phytohormones jasmonic acid (JA) and methyl jasmonate (MeJA), together with their metabolic intermediates synthesized via the octadecanoid pathway, constitute essential signaling molecules collectively known as jasmonates. They are ubiquitous in the plant kingdom and play pivotal roles in biotic and abiotic stress responses, as well as in processes associated with plant growth and development. Recent studies have also revealed the involvement of jasmonates in plant reproductive health [7]. Under unfavorable environmental conditions, plants modulate their developmental and physiological processes. Such conditions are frequently linked to global warming (climate anomalies), which directly or indirectly leads to a combination of multiple stresses that adversely affect plant growth and productivity. JA serves as a well-established endogenous regulator of stress responses and overall plant growth [8]. Overall, the three core components of JA signaling play critical roles in plant growth, development, and adaptation to biotic or abiotic stresses. Under exogenous application or extreme stress conditions, concentration and timing can influence the transcriptional activity of distinct components within the signaling module. Consequently, manipulating the JA metabolic pathway under stress conditions offers a promising strategy for breeding stress-tolerant agricultural crops [9].Licorice (Glycyrrhiza glabra L. var. glabra, Fabaceae) is recognized as a medicinal plant that synthesizes triterpenoid secondary metabolites, with glycyrrhizin accumulating predominantly in its roots. The effects of methyl jasmonate (MeJA) and salicylic acid (SA) on root growth and glycyrrhizin production were investigated in 65-day-old in vitro-cultured roots. In MeJA-treated roots, increased glycyrrhizin accumulation was accompanied by suppressed root growth, whereas SA enhanced glycyrrhizin content without negatively impacting root growth. Treatment of plantlets with 0.1–2 mM MeJA and 0.1–1 mM SA increased glycyrrhizin production by 3.8- and 4.1-fold, respectively, compared to the control group. These findings support the hypothesis that glycyrrhizin biosynthesis is closely associated with the plant's defense response system.The results of the present study confirm the feasibility of forming supramolecular complexes between monoammonium glycyrrhizinate (MASGA) and jasmonic acid (JA) driven by intermolecular interactions. The formation of hydrogen bonds, electrostatic interactions, and hydrophobic forces

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between the carboxyl groups, glycosidic moieties, and other functional centers of the MASGA molecule and the carboxyl and carbonyl groups of jasmonic acid (JA) plays a decisive role in stabilizing the complex. Investigating the resulting system via spectroscopic techniques enables the identification of shifts in the functional groups of the components and substantiates the nature of complexation.

CONCLUSION.

Supramolecular complexes between monoammonium glycyrrhizinate (MASGA) and jasmonic acid (JA) were successfully synthesized at molar ratios of 2:1, 4:1, and 8:1. UV and IR spectroscopic analyses confirmed the presence of non-covalent interactions between the functional groups of the constituent molecules. These findings demonstrate that MASGA can serve as an effective supramolecular carrier for jasmonic acid (JA). Future studies should focus on a comprehensive evaluation of the solubility, biological activity, and storage stability of these complexes. Furthermore, jasmonic acid-mediated metabolic engineering opens new avenues for protecting agricultural crops against biotic and abiotic stresses. Amid ongoing environmental changes, the mechanisms underlying JA-mediated release of secondary metabolites warrant further investigation across diverse plant systems. Additionally, synthetic biology approaches offer novel strategies for optimizing the production ratios of valuable secondary metabolites.

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