

¹³C- AND PROTON-NMR SPECTRA OF SESQUITERPENOID AND RELATED PHYTOALEXINS

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Abstract - ¹³C- and Proton-NMR spectral data of the title compounds have been appraised.

Interaction between hypersensitive plant tissues and various parasites elaborate small molecular weight substances called phytoalexins¹⁻⁶. These compounds may be primary or secondary metabolites which accumulate to higher levels in the damaged than healthy tissue^{7,8}. Many of these compounds have been implicated in the toxicity of diseased food plants to humans and livestock. Much interest has been shown in recent years to unfold the defense/inhibitory mechanism in plants manifested by phytoalexins.

Phytoalexin production can be triggered⁹⁻³ by many physical factors such as wounding^{14,15}, ultra-violet¹⁶⁻²⁰, chemical elicitors such as heavy metals²¹⁻³⁸, antimetabolites³⁹, DNA interchelating agents⁴⁰, RNA synthesis inhibitors^{41,42}, peptides/proteins⁴³⁻⁵⁰ and many other factors⁵¹⁻⁶⁰.

Phytoalexins, also called stress metabolites may or may not have an antifungal activity and yet they are accumulated in response to infection. Examples for this phenomenon may be the phytoalexins produced by Leguminosae. Thus pterocarpan (antifungal) and coumestans (mostly inactive) are both produced by plants belonging to this family^{5,61}. This has further confused the issue of the role of these substances produced in the host. Structural diversity of phytoalexins isolated from different plant families have helped to understand their biosynthetic derivation and other characteristics on the one hand while on the other it points out the fact that phytoalexins are not a homogeneous class of substances.

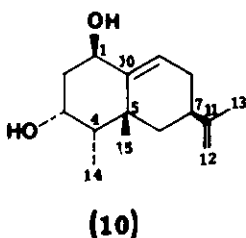
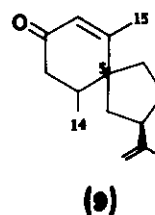
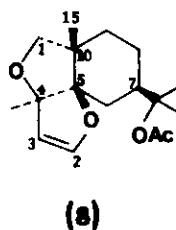
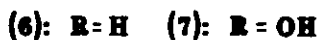
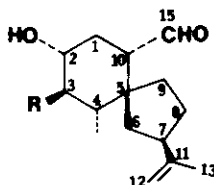
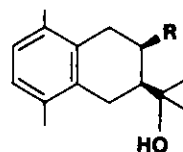
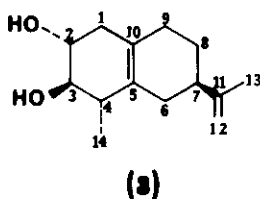
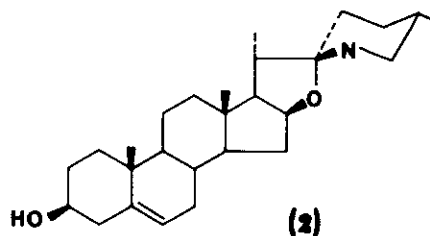
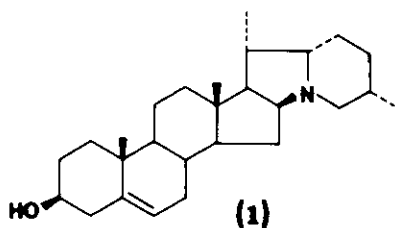
Phytoalexins are indeed produced in very small amounts and their isolation in milligram scale is often, faced with difficulties. This hinders the attainment of spectral data for their identification. Thus a need for accumulation of the published data, on these compounds is most desirable. This is the concern of the present article. We have already accumulated and published ¹H-NMR data on pterocarpan and related phytoalexins³ and here we shall be accumulating ¹H-NMR and ¹³C-NMR data for terpenoid phytoalexins which are mainly derived from members of Solanaceae family of plants.

Because of its economic importance, potato (*S. tuberosum*) has been the centre of attention for chemical and biochemical research. Early work on this tuber, under stress, has reported the presence of usual phenolic compounds^{9-12,62-65}, such as chlorogenic acid, coumaric acid and its derivatives, like scopolin, esculin and umbelliferone. Nonphenolics such as pipecolic acid^{66,67}, sterol⁶⁸ and steroidal alkaloids namely solanidine (1), chaconine and tomatidenol (2) have been reported in potato tubers by mechanical injury⁶⁹⁻⁷⁵. More than twenty five sesquiterpenoid phytoalexins have also been isolated and identified from potato tuber in response to various biotic and abiotic elicitors. Out of these phytoalexins rishitin (3) was the first one to be reported⁷⁴. This was then followed by the isolation of various other sesquiterpenoid stress metabolites such as rishitinol (4), lubimin (6), oxylubimin (7), phytuberin (8), solavetivone (9), capsidiol (10), etc.

Rishitin (3) a representative example of this series of compounds has been induced by compatible and noncompatible race of *P. infestans*. A nonpathogen of potato, *Fusarium solani*, has also been found to induce the formation of rishitin⁷⁵⁻⁷⁸. Rishitin is also produced in response to bacterium⁷⁸, fungal⁷⁹, proteins, lipids⁸⁰, nematocids 1,2-dibromo-3-chloropropane⁸¹, chloramphenicol⁸²⁻⁸³ and sodium fluoride⁷⁹. A DNA fraction from a resistant potato hybrid has also been found to elicit rishitin when applied to a susceptible cultivar⁸⁴.

Because of their biogenetic relationship, none of the above mentioned sesquiterpenes is found alone and therefore most of them are present only in detectable amounts. Yet spectroscopic data for most of these and related compounds has been published in the literature. For example ¹³C-NMR data has been extensively used for identification of these phytoalexins. The relative and absolute configurations of different groups, in these stereochemically important molecules have also been decided by use of nuclear magnetic resonance spectroscopy⁸⁵. Thus ¹H-NMR studies showed that both the hydroxyl groups in rishitin (3) are equatorial and the absolute configuration of this compound has been decided⁸⁵⁻⁸⁷ as shown in structure (3).

The non-equivalence of the methyl groups of 1-hydroxy-1-methylethyl function in rishitinol (4) has been ascribed by its NMR studies. The absolute configuration of this molecule has been assigned by analogy with that of rishitin (3) and occidol (5). Capsidiol (10), another phytoalexin elicited by potato in response to many⁸⁸⁻⁹⁰ fungi was identified by full ¹H-NMR analysis. This compound has trans relationship between the methyl groups attached to C-4 and C-5, as established by ¹H-NMR spectroscopy. This is an exceptional case where methyl groups in an eremophilane type structure are present in a trans fashion, whereas in over one hundred known naturally occurring eremophilanes, these groups are present in a cis relationship. The uniqueness of capsidiol structure was



further confirmed by X-ray analysis and also ^{13}C -NMR data⁹¹⁻⁹³.

Most of these compounds have an isopropyl groups which show characteristic signals for the olefinic groups (1.7-1.9 ppm) and the terminal olefinic protons at 4.6-4.9 ppm. Equivalent or nearly equivalent olefinic protons, as expected, show broad signals lacking fine structure. Spin-spin decoupling has been used to show the weak interaction with methyl protons, by the sharpening of each band upon simultaneous irradiation of the other band. Additional methyl group signals (0.9-1.6 ppm) are also present and their simple or multiple nature is readily distinguished between methyl groups at tertiary or quaternary carbons respectively. The methyl groups appearing in

the range of 1.9-2.3 ppm are indicative of their attachments to sp^2 carbons. For isopropyl groups, the methyl groups are nonequivalent with a small difference in their signals. For their clarification, lanthanide shift reagents are commonly used to identify the nearly equivalent nuclei of this series of compounds⁹⁴.

The olefinic protons range between 5.7-6.8 ppm and their coupling constants not only indicate the substitution on the vicinal carbon atoms but also the nature of functional groups on these carbon atoms. Double irradiation of these signals defines the coupling pattern in these molecules. Deuterium exchange has been helpful in deciding hydroxylic proton signals.

The carbonyl signals in these compounds are important in deciding factors for structure elucidation. The carbonyl protons in lubimin (6) and oxylubimin (7) give rise to multiplets at 3.6 and 3.4 ppm respectively, each with half-width of $>20 H_z$, showing an equatorial hydroxyl group since the carbonyl proton must be axial with two axial neighbours. The remaining carbonyl proton for oxylubimin (7) at 2.98 ppm appears as a doublet of doublets with $J \sim 9$ and $\sim 10 H_z$. An axial-axial vicinal coupling of one of this signal with carbonyl proton at 3.4 ppm and the other with the methine proton is shown by spin decoupling experiments.

An aldehyde function in these compounds such as lubimin (6) and oxylubimin (7) show doublets at 9.74 and 9.78 respectively with $J \sim 3 H_z$. This coupling has helped to locate the aldehyde group at a carbon atom with single proton. Spin-decoupling then located this methine proton at 2.26 and 2.33 ppm respectively. The small coupling constants indicated that the aldehyde function was equatorial while the methine proton was in axial configuration.

¹³C-NMR Spectroscopy:

Sesquiterpenes generally give rise to ¹³C-NMR spectra having separate lines for each carbon and the specific carbon types are readily identified by off resonance decoupling. A remarkable sensitivity of carbon shieldings to molecular geometry and conformation has been observed for capsidiol (10) and related compounds thus establishing their absolute stereochemistry.

Sesquiterpene stress metabolites, show carbonyl, olefinic, carbonyl and alkyl carbons from the position of the signals in their ¹³C-NMR spectra. Thus ketonic carbonyl carbons show signals between 180-200 ppm and are distinguishable from aldehydes by off-resonance decoupling. For capsidiol (10), noise decoupled spectrum showed fifteen signals. Four at the lowest field for olefinic carbons with the fully substituted pair with lower intensities. Similarly one of the high field peaks (40 ppm) has a relatively low intensity, identifying it as a quaternary carbon

signal. Off-resonance spectra showed that 9.5, 21.1 and 32.4 ppm signals arose from methyl carbons, C-14, C-13, and C-15 respectively.

There are deshielding trends caused by *syn*-axial interactions of groups separated by four ^{95,96} bonds and methyl carbons are remarkably sensitive to their special orientation with respect to their γ -neighbours⁹¹. It has also been reported that for methyl carbons, similarly distinctive and directionally opposed, effects are observed in *syn*-axial orientation relative to their δ -neighbours⁹⁵. Thus methyl carbon signals have helped in establishing the vicinal methyl groups C-14 and C-15 in *trans* diaxial position in capsidiol. The C-14 signal being higher due to the neighbouring *gauche* hydroxyl group. From various ¹³C-NMR signal considerations supported by X-ray analysis, absolute configuration of capsidiol has been established as (11) by excellent studies of Stoessel et al^{91,97}.

The signals at 41.4, 48.9, 65.8, 75.8 and 128.9 ppm were assigned to carbons with one proton directly attached to them. The methylene carbons showed up at 31.4, 36.8, 46.4 and 109.0 ppm. The last of these signals was due to the exomethylene carbon while its partner C-11 showed up at 150.3. The signals near 21, 109 and 150 ppm are characteristic of isopropenyl group in this series of compounds. Thus from ¹³C-NMR, capsidiol was shown to have three methyl, three methylene, two-CHOH-, two methine and one quaternary carbon, a trisubstituted double bond and an isopropenyl group accounting for fifteen signals mentioned above.

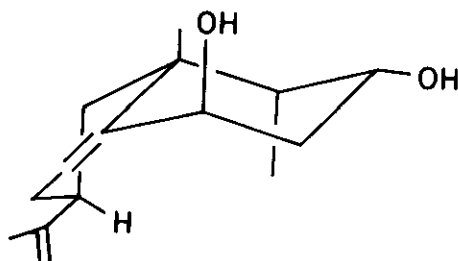
¹³C-NMR, as applied to lubimin (6), helped to characterize a quaternary carbon signal at 46.9 ppm, thus revising a previously proposed structure⁹¹. The isopropenyl carbons appeared at 21.2, 108.8 and 147.3 ppm, while an aldehyde carbon signal appeared at 204.9 ppm. A -CH(OH)- (69.3) ppm, a secondary methyl (16.4 ppm) as well as five methylene carbon signals (25.9, 32.6, 33.3, 40.3 and 41.8 ppm) and three methine carbons (41.8, 47.4 and 58.4 ppm) also were apparent in the ¹³C-NMR spectrum of lubimin. The two equivalent signals at 41.8 ppm were distinguished by off-resonance decoupling. This information along with the ¹H-NMR data defined vetispirane skeleton for lubimin as (6). Subtle structural features like unresolved proton signals for hydroxyisopropyl moiety have also been shown to be resolved in ¹³C-NMR of these compounds. Thus ¹H- and ¹³C-NMR spectroscopy has played a pivotal role in solving problems relating to structural and configurational nature in sesquiterpene stress metabolites.

Stress Agents Referred in the Following Tables

- | | |
|---|--|
| 1. <i>Phytophthora infestans</i> | 2. <i>Fusarium solani</i> |
| 3. <i>Fusarium oxysporum</i> | 4. <i>Verticillium albo-atrum</i> |
| 5. <i>Phoma exigua</i> var. <i>exigua</i> | 6. <i>Phoma exigua</i> var. <i>foveata</i> |
| 7. <i>Erwinia carotovora</i> | 8. <i>Monilinia fructicola</i> |
| 9. <i>Glomerella cingulata</i> | 10. Diseased plant |
| 11. Tobacco mosaic virus | 12. <i>Ceratostomella fimbriata</i> |
| 13. <i>Helicobasidium mompa</i> | 14. <i>Botrytis cinerea</i> |
| 15. <i>Cladosporium cucumerinum</i> | 16. <i>Botryodiplodia theobromae</i> |
| 17. <i>Ceratocystis fimbriata</i> | 18. <i>Botrytis theobromae</i> |
| 19. Black rot mould | 20. Mercuric chloride |
| 21. <i>Piricularia oryzae</i> | 22. U.V. Light |
| 23. 2,2-Dichloro-3,3-dimethylcyclopropane | |

Solvents Referred in the Tables

1. Chloroform-d
2. Carbon tetrachloride



(11)

COMPOUND	PLANT SOURCE	STRESS AGENT	SOLVENT	NMR SHIFTS (ppm)	REF.
Rishitin	Solanum tuberosum	1-9	1	PMR: 1.14, d(J6.5 H ₂), 14-CH ₃ ; 1.75, s, 13-CH ₃ ; 3.18, t(J9H ₂), 3-H; 3.63, br. dd (J9 & 7H ₂), 2-H; 4.64, br. s, 12-H; 4.74, br. s, 12-H.	75, 77, 85, 98-112
			1	CMR: 38.4, C ₁ ; 71.5, C ₂ ; 79.2, C ₃ ; 41.7, C ₄ ; 129, C ₅ ; 31.2, C ₆ ; 40.5, C ₇ ; 26.6, C ₈ ; 29.7, C ₉ ; 124.9, C ₁₀ ; 148.9, C ₁₁ ; 109, C ₁₂ ; 21.1, C ₁₃ ; 16.5, C ₁₄ .	
Rishitinone	Solanum tuberosum	1	2	PMR: 1.76, s, 13-CH ₃ ; 0.76, s, 15-CH ₃ ; 0.84, d(J7H ₂), 14-CH ₃ ; 4.77, br. s, -CH ₂ - 3.65, m, OH	112
			2	CMR: 12.9, 15.5, 20.4 (-CH ₃); 30.2, 39.3, 42.8, 46.0 (-CH ₂); 41.3, 41.5, 56.1, 69.5 (>CH-); 40.7 (>C<); 109.9 (=CH ₂); 147.4 (=C<); 211.1 (>C=O).	
Rishitinol	Solanum tuberosum	1	1	PMR: 1.35, 1.46, 2s, 2xCH ₃ ; 2.19, 2.25, 2s, 2xAr-CH ₃ ; 2.9, OH; 2.91, 2x-CH ₂ -; 4.7, -CHOH; 6.9, 2x-CH<; 6.95, s, 2xAr-H.	113
Lubimin	Solanum tuberosum, egg plant, Datura stramonium	1, 7-9	1	PMR: 0.94, d(J7H ₂), 14-CH ₃ ; 1.68, s, 13-CH ₃ ; 3.65, m, 1H; 4.65, 2H, s, 9.74, 1H, d(J3H ₂).	92, 99, 100, 114-
			1	CMR: 41.8, C ₁ ; 59.3, C ₂ ; 40.3, C ₃ ; 41.0, C ₄ ; 46.9, C ₅ ; 33.3, C ₆ ; 47.4, C ₇ ; 32.6, C ₈ ; 25.9, C ₉ ; 58.4, C ₁₀ ; 147.3, C ₁₁ ; 108.8, C ₁₂ ; 21.2, C ₁₃ ; 16.4, C ₁₄ ; 205, C ₁₅ .	117
Lubiminol	Solanum tuberosum	1	1	PMR: 0.89, d(J6.5 H ₂), 14-CH ₃ ; 1.7, 13-CH ₃ ; 2.49, br. s, 2xOH, 3.28, t(J10H ₂), C ₁₀ -H; 3.6, -CHOH-; 3.9, dd(J10&2.5H ₂), C ₁₅ -H ₂ ; 4.66, br. s, C ₁₂ -H ₂ .	117
			1	CMR: 48.3, C ₁ ; 69.6, C ₂ ; 40.4, C ₃ ; 40.7 or 40.9, C ₄ ; 46.4, C ₅ ; 32.6, C ₆ ; 47.1, C ₇ ; 36.6, C ₈ ; 25.3, C ₉ ; 40.0 or 40.7, C ₁₀ ;	

COMPOUND	PLANT SOURCE	STRESS AGENT	SOLVENT	NMR SHIFTS (ppm)	REF.
Oxylubimin	Solanum tuberosum	1	2	147.5, C ₁₁ ; 107.8, C ₁₂ ; 21.2, C ₁₃ ; 16.1, C ₁₄ ; 63.9, C ₁₅ . PMR: 0.89, d(J7H ₂), 14-CH ₃ ; 1.08, 13-CH ₃ ; 2.38, d.d.d. (J10, 4, 2.5H ₂), C ₁₀ -H; 9.8, d(J2.5H ₂), C ₁₅ -H; 4.75, br.s, C ₁₂ -H ₂ ; 3.01, t(J10H ₂), 3.48, t(J10H ₂), 3.9, br.s. Exch. D ₂ O, -CH(OH).CH(OH)-.	117, 92.93, 100
			2	CMR: 42.2, C ₁ ; 74.1, C ₂ ; 76.8, C ₃ ; 47.1, C ₄ ; 48.3, C ₅ ; 32.7, C ₆ ; 47.3, C ₇ ; 30.5, C ₈ ; 26.8, C ₉ ; 57.6, C ₁₀ ; 147.0, C ₁₁ ; 109.0, C ₁₂ ; 21.2, C ₁₃ ; 11.2, C ₁₄ ; 204, C ₁₅ .	
Cyclodehydroisolubimin	Solanum tuberosum	1	1	PMR: 1.22, s, 14-CH ₃ ; 1.76, s, 13-CH ₃ ; 2.5, br.s. 2H; 3.64, d(J8.9H ₂), 1H; 3.98, m(J8.9H ₂), 1H; 4.74, m, 2H.	118
			1	CMR: 21.2(q); 21.4(q); 30.7(t); 32.9(t); 35.2(t); 45.6(t); 46.0(d); 47.0(d); 52.9(t); 54.6(s); 71.7(t); 83.5(s); 108.9(t); 148.2(s) 210.1(s).	
Isolubimin	Solanum tuberosum	1, 8, 9	1	PMR: 0.90, 14-CH ₃ ; 1.69, br.s, 13-CH ₃ ; 3.70, 15-CH ₂ -; 4.68, 12=CH ₂ .	119
			1	CMR: 50.1, C ₁ ; 211.6, C ₂ ; 46.7, C ₃ ; 43.0, C ₄ ; 46.8, C ₅ ; 40.0, C ₆ ; 47.2, C ₇ ; 32.5, C ₈ ; 25.0, C ₉ ; 42.4, C ₁₀ ; 147.6, C ₁₁ ; 108.6, C ₁₂ ; 21.5, C ₁₃ ; 16.7, C ₁₄ ; 64.3, C ₁₅ .	
10-Epilubimin	Solanum tuberosum	8, 9	1	PMR: 0.94, d(J6.5H ₂), 14-CH ₃ ; 1.72, s, 13-CH ₃ ; 4.68, s, 12=CH ₂ ; 9.81, CHO; 3.69, br, -CH(OH)-.	
			1	CMR: 42.2, C ₁ ; 66.6, C ₂ ; 39.9, C ₃ ; 36.9, C ₄ ; 46.3, C ₅ ; 32.9, C ₆ ; 48.0, C ₇ ; 38.8, C ₈ ; 30.7, C ₉ ; 58.6, C ₁₀ ; 147.6, C ₁₁ ; 108, C ₁₂ ;	120

COMPOUND	PLANT SOURCE	STRESS AGENT	SOLVENT	NMR SHIFTS (ppm)	REF.
10-Epilubiminol	Solanum tuberosum	8	1	21.4, C ₁₃ ; 17.0, C ₁₄ ; 205, C ₁₅ . CMR: 42.1, C ₁ ; 66.6, C ₂ ; 40.4, C ₃ ; 35.4, C ₄ ; 46.4, C ₅ ; 34.0, C ₆ ; 47.9, C ₇ ; 31.2, C ₈ ; 31.3, C ₉ ; 49.1, C ₁₀ ; 148.4, C ₁₁ ; 108.2, C ₁₂ ; 12.5, C ₁₃ ; 17.2, C ₁₄ ; 62.1, C ₁₅ .	110
Solavetivone (Katahdinone)	Solanum tuberosum	1, 8, 9	1	CMR: 40.9, C ₁ ; 46.6, C ₂ ; 32.7, C ₃ ; 34.3, C ₄ ; 50.2, C ₅ ; 166.1, C ₆ ; 125.4, C ₇ ; 198.4, C ₈ ; 43.1, C ₉ ; 39.3, C ₁₀ ; 146.8, C ₁₁ ; 108.9, C ₁₂ ; 20.8, C ₁₃ ; 21.2, C ₁₄ ; 15.9, C ₁₅ .	
11,12-Dihydroxysolavetivone	Solanum tuberosum	1, 8, 9	1	PMR: 0.97, d (J7H ₂), 3H; 1.18, s, 3H; 1.6-2.4, m, 8H; 1.95, d (J1H ₂), 3H; 2.67, m, 2H; 3.43, d (J12H ₂), 1H; 3.55, d (J12H ₂), 1H; 5.76, br, 1H.	122, 124
			1	CMR: 15.9, -CH ₃ ; 21.0, CH ₃ ; 21.7, -CH ₃ ; 27.4, -CH ₂ -; 34.0, -CH ₂ -; 36.9, -CH ₂ -; 38.5, >CH-; 42.8, -CH ₂ -; 46.1, >CH-; 49.9, >C<; 69.3, -OCH ₂ -; 73.6, -O-C<-; 125.4, =CH-; 167.1, =C<; 199.2, >C=O.	
11-Hydroxy-12-O-Glucosyl-oxysolavetivone	Solanum tuberosum	5	1	PMR: 0.96, d (J7H ₂), 3H; 1.21, s, 3H; 1.5-2.4, m, 8H; 1.99, d (J1H ₂), 3H; 2.70, m, 2H; 3.3-4.0, m, -CH ₂ -O; 4.3, d (J7H ₂), 1H; 5.74, br, 1H.	124
Phytuberin	Solanum tuberosum	1, 7	1	PMR: 1.04, 1.44, 1.47, 1.56, 1.99, 5xs, 5x-CH ₃ ; 4.67, d (J2.8H ₂), 1H, =CH-; 6.44, d (J2.8H ₂), 1H, -O-CH=; 3.26, d (J8.5H ₂), 1H; 3.39, d (J8.5H ₂), -CH ₂ -O.	75, 78, 94, 102, 121, 123,
			1	CMR: 74.0, C ₁ ; 146.7, C ₂ ; 105.3, C ₃ ; 93.5, C ₄ ; 95.1, C ₅ ; 29.6, C ₆ ; 44.1, C ₇ ; 22.1, C ₈ ; 34.8, C ₉ ; 45.4, C ₁₀ ; 83.7, C ₁₁ ; 23.7, C ₁₂ ; 23.1, C ₁₃ ; 23.7, C ₁₄ ; 16.7, C ₁₅ ; 170.0, C ₁₆ ; 22.6, C ₁₇ .	125, 126
Phytuberol	Solanum tuberosum	8, 9	1	CMR: 73.8, C ₁ ; 146.9, C ₂ ; 104, C ₃ ; 93.4, C ₄ ; 95, C ₅ ; 29.6, C ₆ ; 46.3, C ₇ ; 21.7, C ₈ ;	

COMPOUND	PLANT SOURCE	STRESS AGENT	SOLVENT	NMR SHIFTS (ppm)	REF.
Ipomeamarone	Ipomoea batatas	12-18	1	34.6, C ₉ ; 45.1, C ₁₀ ; 72.4, C ₁₁ ; 26.7, C ₁₂ ; 27.3, C ₁₃ ; 23.3, C ₁₄ ; 16.6, C ₁₅ . PMR: 7.29, d(J1.8H ₂), 1&4-H, 6.29, d(J1.8H ₂), 2-H; 4.84, m(J6.0, 4.2, 1.8H ₂), 5-H; 1.85, m, 6&7-H; 2.69, q(J<15.8H ₂), 10-H; 2.29, d(J6.2H ₂), 12-H; 1.29, s, 9-CH ₃ ; 0.87, d(J6.0H ₂), 14&15-CH ₃ .	129-140
Ipomeamaranol	Ipomoea batatas	19	1	PMR: 0.86, d, 14-CH ₃ ; 1.33, s, 9-CH ₃ ; 2.71, 10-H; 3.62, 15-CH ₂ OH; 4.91, m, 4-H; 6.37, t, 2-H; 7.37, d, 1-&4-H.	132, 133, 137, 138, 140, 141
4-Hydroxymyosinone	Ipomoea batatas	19	1	PMR: 0.92, d(J6.0H ₂), 9 & 10-CH ₃ ; 1.22, s, 4-CH ₃ ; 2.55, s, 5-CH ₂ ; 2.9, m, 2-CH ₂ ; 1.5-2.4, m, 3-, 7-, 8-H; 6.77, 7.17, 8.08, furylalkanone protons.	139
1-(3'-Furyl)-6,7-dihydroxy-4,8-dimethylnonan-1-one	Ipomoea batatas	20	1	PMR: 0.94, 0.97, d(J7H ₂), 4-, 9-10-CH ₃ ; 2.20, br. s, 6-&7-OH; 2.82, t(J7H ₂), 2-H; 3.14, t(J5H ₂) 7-H; 3.75, m, 6-H; 6.84, m, furyl-H at C ₄ ; 7.56, m, furyl-H at C ₂ ; 8.16, m, furyl-H at C ₁ ; 1.1-2.1, m, 6H, other protons at C ₃ , 4, 5&8.	139
Aubergenone	Egg plant	10	1	PMR: 1.06, s, 15-CH ₃ ; 1.13, d(J7H ₂), 14-CH ₃ ; 1.22, s, 12-&13-CH ₃ ; 2.32, dd(J11&7H ₂), 4-H; 5.84, q(J10H ₂), 1-H; 6.71, q(J10H ₂), 2-H.	116, 142
			1	CMR: 160, C ₁ ; 125.9, C ₂ ; 204.0, C ₃ ; 49.1, C ₄ ; 45.3, C ₅ ; 26.1, C ₆ ; 44.5, C ₇ ; 22.4, C ₈ ; 40.0, C ₉ ; 36.2, C ₁₀ ; 13.4, C ₁₁ ; 72.6, C ₁₂ ; 27.2, C ₁₃ ; 27.6, C ₁₄ ; 20.8, C ₁₅ .	
Glutinosone	Nicotina glutinosa	11	1	PMR: 0.93, d(J6H ₂), 14-CH ₃ ; 1.71, s, 13-CH ₃ ; 3.53, s, OH; 4.35, d(J5H ₂), 3-H;	143-145

COMPOUND	PLANT SOURCE	STRESS AGENT	SOLVENT	NMR SHIFTS (ppm)	REF.
Capsidiol	Capsicum frutescens	1	1	4.72, br.s, 12-CH ₂ ; 5.88, br.s, 1-H. PMR: 0.93, d(J7.1H ₂), 14--CH ₃ ; 1.12, s, 15-CH ₃ ; 1.73, s, 13-CH ₃ ; 4.24, t(J4.6, 4.6&12.4H ₂), 3-H; 4.34, t(H1.9, 2.75, 5.2&11.4), 1-H; 5.94, t(J1.9, 1.9, 6.3H ₂), 9-H; 4.69, 4.72, d(J2H ₂), 12-H. CMR: 75.4, C ₁ ; 36.8, C ₂ ; 65.8, C ₃ ; 48.9, C ₄ ; 40.0, C ₅ ; 46.4, C ₆ ; 41.4, C ₇ ; 31.4, C ₈ ; 128.9, C ₉ ; 141.2, C ₁₀ ; 150.3, C ₁₁ ; 109.0, C ₁₂ ; 21.1, C ₁₃ ; 9.5, C ₁₄ ; 32.4, C ₁₅ .	88, 89, 91, 146-151
9-Oxoneralidol	Solanum melongena	8	1	CMR: 111.6, 144.8, C ₂ ; 73.2, C ₃ ; 41.8, C ₄ ; 23.0, C ₅ ; 122.8, C ₆ ; 129.6, C ₇ ; 55.2, C ₈ ; 198.9, C ₉ ; 129.2, C ₁₀ ; 155.4, C ₁₁ ; 27.6, C ₁₂ ; 27.9, C ₁₃ ; 16.4, C ₁₄ ; 20.7, C ₁₅ .	142
11-Oxyneralidol	Solanum melongena	8	1	PMR: 5.19, d(J1.5H ₂), 1a-H; 5.051, d(J1.5H ₂), 1b-H; 5.936, t(J17.4, 16.6H ₂), 2-H; 5.62, d(J16.0H ₂), 10-H; 5.605, d(J16.0H ₂), 9-H; 2.65, d(J4.5H ₂), 8-H; 5.16, t(J7&1.5H ₂), 6-H; 1.30, s, 3-CH ₃ ; 1.33, s, 12-&15-Me; 1.62, s, 14-Me. CMR: 111.7, C ₁ ; 144.9, C ₂ ; 73.4, C ₃ ; 42.1, C ₄ ; 22.9, C ₅ ; 125.0, C ₆ ; 134.1, C ₇ ; 42.4, C ₈ ; 125.2, C ₉ ; 139.4, C ₁₀ ; 70.6, C ₁₁ ; 29.9, C ₁₂ ; 27.9, C ₁₃ ; 16.2, C ₁₄ ; 29.9, C ₁₅ .	142
9-Oxynerolidol	Solanum melongena	8	1	CMR: 111.7, C ₁ ; 144.9, C ₂ ; 73.5, C ₃ ; 41.8, C ₄ ; 23.0, C ₅ ; 127.7, C ₆ ; 137.0, C ₇ ; 48.1, C ₈ ; 66.0, C ₉ ; 128.4, C ₁₀ ; 131.9, C ₁₁ ; 25.7, C ₁₂ ; 28.1, C ₁₃ ; 16.2, C ₁₄ ; 18.2, C ₁₅ .	142
11-Dehydroneralidol	Solanum melongena	8	1	PMR: 5.195, d(J1.5H ₂), 1a-H; 5.055, d(J1.5H ₂), 1b-H; 5.93, t(J10.5, 17.5H ₂), 2-H; 5.14, d(J15.5, 7.5H ₂), 10-H; 5.610, d(J15.5, 7.5H ₂), 9-H; 2.8, t(J7H ₂), 8-H; 5.16, 6-H; 4.85, m, 12-H; 1.30, s, 13-CH ₃ ;	142

COMPOUND	PLANT SOURCE	STRESS AGENT	SOLVENT	NMR SHIFTS (ppm)	REF.
11-Ethoxynerylol	Solanum melongena	8	1	1.86, s, 15-CH ₃ . PMR: 5.30, d(J1.5H ₂), 1a-H; 5.14, d(J1.5H ₂), 1b-H; 6.08, t(J1.8&10H ₂), 2-H; 5.26, t(J7H ₂), 6-H; 5.6, d, 10-H; 5.58, d, 9-H; 2.72, 8-H; 1.26, s, 13-CH ₃ ; 1.26, s, 12&15-CH ₃ ; 1.60, 14-CH ₃ ; 1.14, t, 0-CH ₂ -CH ₃ ; 3.40, q, -O-CH ₂ -CH ₃ .	142
Calamusenone	Acorus calamus		1	PMR: 1.38, m, 2a-H; 2.54, m, 2b-H; 2.04, m, 3-H; 2.42, m, 4-H; 2.95, d(J17H ₂), 6a-H; 3.17, d(J17H ₂), 6b-H; 2.77, d(J6H ₂), 9-H; 2.68, m, 10-H; 1.85, s, 12-CH ₃ ; 2.04, s, 13-CH ₃ ; 1.08, d(7H ₂), 14-CH ₃ ; 1.07, d, (J7H ₂), 15-CH ₃ .	152
Isocalamusenone	Acorus calamus		1	CMR: 138.78, q, C ₁ ; 34.266, C ₂ ; 31.048, C ₃ ; 45.052, C ₄ ; 137.617, C ₅ ; 27.353, C ₆ ; 134.474, C ₇ ; 204.64, C ₈ ; 48.926, C ₉ ; 33.372, C ₁₀ ; 140.402, C ₁₁ ; 22.546, C ₁₂ ; 23.003, C ₁₃ ; 19.844, C ₁₄ ; 19.733, C ₁₅ .	152
			1	PMR: 2.82, m, 1-H; 1.3-2.0, m, 2-H; 2.2, m, 2-H; 2.78, d(J16H ₂), 6-H; 3.23, d(J16H ₂), 6-H; 2.3, m, 9-H; 2.42, m, 10-H; 1.76, s, 12-CH ₃ ; 1.78, s, 13-CH ₃ ; 0.90, d(J7H ₂), 14-CH ₃ ; 1.62, s, 15-CH ₃ .	
			1	CMR: 53.689, C ₁ ; 37.067, C ₂ ; 23.420, C ₃ ; 135.451, C ₄ ; 132.591, C ₅ ; 27.532, C ₆ ; 135.451, C ₇ ; 209.049, C ₈ ; 47.555, C ₉ ; 30.095, C ₁₀ ; 133.787, C ₁₁ ; 20.623, C ₁₂ ; 21.989, C ₁₃ ; 16.626, C ₁₄ ; 13.948, C ₁₅ .	152
Tropone	Acorus calamus		1	PMR: 7.12, d(J12H ₂), 6-H; 7.02, s, 9-H; 6.94, dd(J12&3H ₂), 7-H; 3.20, br.q(J7H ₂), 4-H; 2.89, m, 2-H; 2.27, m, 3-H; 2.27, s, 14-CH ₃ ; 1.58, m, 3-H; 1.26, d(J7H ₂), 15-CH ₃ . CMR: 186.463, s, C ₈ ; 150.461, s, 148.089,	

COMPOUND	PLANT SOURCE	STRESS AGENT	SOLVENT	NMR SHIFTS (ppm)	REF.
Momilactone - A	Rice	21-23		s, 146.063, s; 140.283, d; 139.337, d; 133.866, d; 44.281, d, C₄; 35.088, t; 30.511, t; 25.557, q; 20.154, q. PMR: 5.85, dd (J10.5&13H₂), Hb; 5.71, d (J5H₂), Hg; 4.98, dd (J1H₂), Hd; 4.95, dd, Hc; 4.84, t (J5H₂), Hh; 2.58-2.69, m, He; 2.32, d, Hj; 2.21, d (J12.5H₂), He or Hf; 2.06, d, He or Hf; 1.90, dd, Hp; 1.80, dd, Hr; 1.75, m, H_s; 1.50-1.65, m, Hn, u, v; 1.52, s, Hk; 1.32, m, Ht; 1.00, s, Hq; 0.90, s, Ha.	20 153- 158

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