^{13}C- AND PROTON-NMR SPECTRA OF SESQUITERPENOID AND RELATED PHYTOALEXINS

Mohammad Afzal and Galib Al-Oriquat
Biochemistry Department, Faculty of Science, Kuwait University, Kuwait

Abstract - ^{13}C- *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 phytoalexins[1-6]. 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 triggered[9-3] by many physical factors such as wounding[14,15], ultraviolet[16-20], chemical elicitors such as heavy metals[21-38], antimetabolites[39], DNA interchelating agents[40], RNA synthesis inhibitors[41,42], peptides/proteins[43-50] and many other factors[51-60].

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 pterocarpans (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.

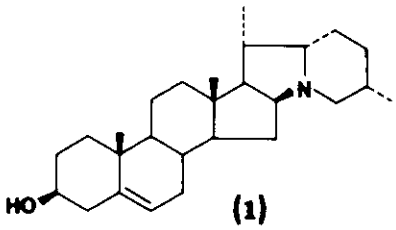
Phytoalexins are indeed produced in very small amounts and their isolation in milligram scale is often, faced with difficulties. This hinders the attainment of spectral data for their identification. Thus a need for accumulation of the published data, on these compounds is most desirable. This is the concern of the present article. We have already accumulated and published ^{1}H-NMR data on pterocarpan and related phytoalexins[3] and here we shall be accumulating ^{1}H-NMR and ^{13}C-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 pehnolic compounds[9-12,62-65], such as chlorgenic acid, couramaric acid and its derivatives, like scopolin, esculin and umbelliferone. Nonphenolics such as pipecolic acid[66,67], sterol[68] and steroidal alkaloids namely solanidine (1), chaconine and tomatidenol (2) have been reported in potato tubers by mechanical injury[69-75]. 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 reported[74]. This was then followed by the isolation of various other sesquiterpernoid stress metabolites such as rishitinol (4), lubimin (6), oxylubimin (7), phytuberin (8), solavetivone (9), capsidiol (10), etc.

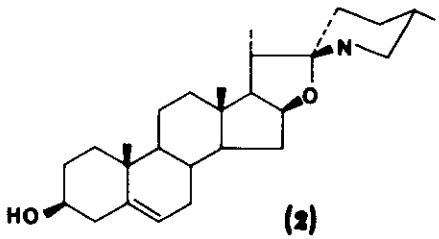
Rishitin (3) a representative example of this series of compounds has been induced by compatible and noncompatible race of P. infestans. A nonpathogen of potato, Fusarium solani, has also been found to induce the formation of rishitin[75-78]. Rishitin is also produced in response to bacterium[78], fungal[79], proteins, lipids[80], nematocids 1,2-dibromo-3-chloropropane[81], chloramphenicol[82-83] and sodium fluoride[79]. A DNA fraction from a resistant potato hybrid has also been found to elicit rishitin when applied to a susceptible cultivar[84].

Because of their biogenetic relationship, none of the above mentioned sesquiternes 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 ^{13}C-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 spectroscopy[85]. Thus ^{1}H-NMR studies showed that both the hydroxyl groups in rishitin (3) are equatorial and the absoluted configuration of this compound has been decided[85-87] as shown in structure (3).

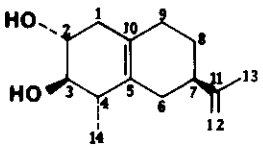
The non-equivalence of the methyl groups of 1-hydroxy-1-methylethyl function in rishitinol (4) has been ascribed by its NMR studies. The absolute configuration of this molecule has been assigned by analogy with that of rishitin (3) and occidol (5). Capsidiol (10), another phytoalexin elicited by potato in response to many[88-90] fungi was identified by full ^{1}H-NMR analysis. This compound has trans relationship between the methyl groups attached to C-4 and C-5, as established by ^{1}H-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



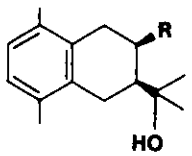
(1)



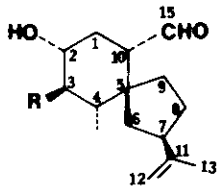
(2)



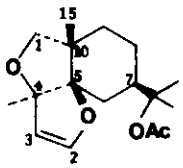
(3)



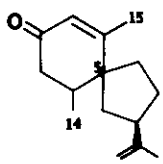
(4): R=OH (5): R=H



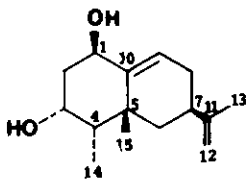
(6): R=H (7): R=OH



(8)



(9)



(10)

further confirmed by X-ray analysis and also ^{13}C-NMR data[91-93].

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 compounds[94].

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 carbinyl signals in these compounds are important in deciding factors for structure elucidation. The carbinyl 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 carbinyl proton must be axial with two axial neighbours. The remaining carbinyl 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 carbinyl 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 aldhyde group at a crabon 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 methin proton was in axial configuration.

^{13}C-NMR Spectroscopy:

Sesquiterpenes generally give rise to ^{13}C-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, carbinyl and alkyl carbons from the position of the signals in their ^{13}C-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-neighbours[91]. 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-neighbours[95]. Thus methyl carbon signals have helped in establisheing the vivinal methyl groups C-14 and C-15 in trans diaxial position in capsidiol. The C-14 signal being higher due to the neighbouring guache hydroxyl group. From various ^{13}C-NMR signal considerations supported by X-ray analysis, absolute configuration of capsidiol has been established as (11) by excellent studies of Stoessl 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 ^{13}C-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.

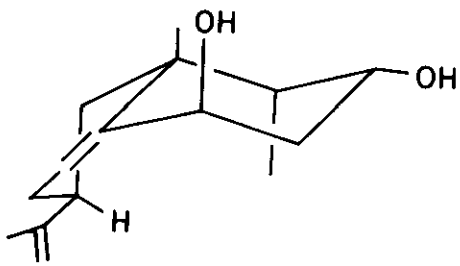
^{13}C-NMR, as applied to lubimin (6), helped to characterize a quaternary carbon signal at 46.9 ppm, thus revising a previously proposed structure[91]. The isopropenyl carbons appeared at 21.2, 108.8 and 147.3 ppm,while an aldehyde carbon signal appeared at 204.9 ppm. A -CH(OH)-(69.3) ppm, a secondary 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 ^{13}C-NMR spectrum of lubimin. The two equivalent signals at 41.8 ppm were distinguished by off-resonance decoupling. This information along with the ^{1}H-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 ^{13}C-NMR of these compounds. Thus ^{1}H- and ^{13}C-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. Phytophthora infestans
2. Fusarium solani
3. Fusarium oxysporum
4. Verticillium albo-atrum
5. Phoma exigua var. exigua
6. Phoma exigua var foveatea
7. Erwinia carotovora
8. Monilinia fructicola
9. Glomerella cingulata
10. Diseased plant
11. Tobacco mosaic virus
12. Ceratostomella fimbriata
13. Helicobasidium mompa
14. Botrytis cinerea
15. Cladosporium cucumerinum
16. Botryodiplodia theobromae
17. Ceratocystis fimbriata
18. Botrytis theobromae
19. Black rot mould
20. Mercuric chloride
21. Piricularia oryzae
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_z),14-CH_3;1.75,s,13-CH_3;3.18,t(J9H_z),3-H;3.63,br.dd(J9 & 7H_z),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_z),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_z),14-CH_3;1.68,s,13-CH_3;3.65,m.1H;4.65,2H,s,9.74,1H,d(J3H_z).	92,99,100,114-117
			1	CMR: 41.8,C_1;69.3,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}.	
Lubiminol	Solanum tuberosum	1	1	PMR:0.89,d(J6.5 H_z),14-CH_3;1.7,13-CH_3;2.49,br.s.2xOH,3.28,t(J10H_z),C_{10}-H;3.6,-CHOH-;3.9,dd(J10&2.5H_z),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.
				147.5,C_{11};107.8,C_{12};21.2,C_{13};16.1, C_{14};63.9,C_{15}.	
Oxylubimin	Solanum tuberosum	1	2	PMR: 0.89,d(J7H_z),14-CH_3;1.08,13-CH_3;2.38,d.d.d.(J10,4,2.5H_z),C_{10}-H;9.8,d(J2.5H_z),C_{15}-H;4.75,br.s, C_{12}-H_2;3.01,t(J10H_z).3.48,t(J10H_z), 3.9,br.s.Exch.D_2O,-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_z),1H; 3.98,m(J8.9H_z),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_z),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.
				21.4,C_{13};17.0,C_{14};205,C_{15}.	
10-Epilubiminol	Solanum tubero-sum	8	1	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 tubero-sum	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 tubero-sum	1,8,9	1	PMR: 0.97,d(J7H_z),3H;1.18,s,3H;1.6-2.4,m,8H;1.95,d(J1H_z),3H;2.67,m,2H; 3.43,d(J12H_z),1H;3.55,d(J12H_z),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 tubero-sum	5	1	PMR:0.96,d(J7H_z),3H;1.21,s,3H;1.5-2.4,m,8H;1.99,d(J1H_z),3H;2.70,m, 2H;3.3-40,m,-CH_2-O;4.3,d(J7H_z),1H; 5.74,br,1H.	124
Phytuberin	Solanum tubero-sum	1,7	1	PMR: 1.04,1.44,1.47,1.56,1.99,5xs, 5x-CH_3;4.67,d(J2.8H_z),1H,=CH-;6.44, d(J2.8H_z),1H,-O-CH=;3.26,d(J8.5H_z), 1H;3.39,d(J8.5H_z),-CH_2-O.	75,78, 94,102, 121, 123, 125, 126
			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}.	
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.
				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}.	
Ipomeamarone	Ipomoea batatas	12-18	1	PMR: 7.29,d(J1.8H_z),1&4-H,6.29,d(J 1.8H_z),2-H;4.84,m(J6.0,4.2,1.8H_z), 5-H;1.85,m,6&7-H;2.69,q(J≤15.8H_z), 10-H;2.29,d(J6.2H_z),12-H;1.29,s,9-CH_3;0.87,d(J6.0H_z),14&15-CH_3.	129-140
Ipomeamaronol	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_2OH;4.91,m,4-H; 6.37,t,2-H;7.37,d,1-&4-H.	132, 133, 137, 138, 140, 141
4-Hydroxymyoporone	Ipomoea batatas	19	1	PMR: 0.92,d(J6.0H_z),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_z),4-,9-10-CH_3; 2.20,br.s,6-&7-OH;2.82,t(J7H_z),2-H; 3.14,t(J5H_z)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_z), 14-CH_3;1.22,s,12-&13-CH_3;2.32,dd (J11&7H_z),4-H;5.84,q(J10H_z),1-H; 6.71,q(J10H_z),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_z),14-CH_3;1.71,s, 13-CH_3;3.53,s,OH;4.35,d(J5H_z),3-H;	143-145

COMPOUND	PLANT SOURCE	STRESS AGENT	SOLVENT	NMR SHIFTS (ppm)	REF.
				4.72,br.s,12-CH_2;5.88,br.s,1-H.	
Capsidiol	Capsicum frutescens	1	1	PMR: 0.93,d(J7.1H_z),14--CH_3;1.12,s,15-CH_3;1.73,s,13-CH_3;4.24,t(J4.6,4.6&12.4H_z),3-H;4.34,t(H1.9,2.75,5.2&11.4),1-H;5.94,t(J1.9,1.9,6.3H_z),9-H;4.69,4.72,d(J2H_z),12-H.	88,89,91,146-151
			1	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}.	
9-Oxonerolidol	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_z),1a-H;5.051,d(J1.5H_z),1b-H;5.936,t(J17.4,16.6H_z),2-H;5.62,d(J16.0H_z),10-H;5.605,d(J16.0H_z),9-H;2.65,d(J4.5H_z),8-H;5.16,t(J7&1.5H_z),6-H;1.30,s,3-CH_3;1.33,s,12-&15-Me;1.62,s,14-Me.	142
			1	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-Dehydronerolidol	Solanum melongena	8	1	PMR: 5.195,d(J1.5H_z),1a-H;5.055,d(J1.5H_z),1b-H;5.93,t(J10.5,17.5H_z),2-H;6.14,d(J15.5,7.5H_z),10-H:5.610,d(J15.5,7.5H_z),9-H;2.8,t(J7H_z),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.
				1.86,s,15-CH_3.	
11-Ethoxynerolidol	Solanum melongena	8	1	PMR: 5.30,d(J1.5H_z),1a-H;5.14,d(J 1.5H_z),1b-H;6.08,t(J18&10H_z),2-H; 5.26,t(J7H_z),6-H;5.6,d,10-H;5.58, d,9-H;2.72,8-H;1.28,s,13-CH_3;1.26, s,12&15-CH_3;1.60,14-CH_3;1.14,t,O-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_z),6a-H;3.17,d(J17H_z),6b-H;2.77,d(J6H_z), 9-H;2.68,m,10-H;1.85,s,12-CH_3;2.04, s,13-CH_3;1.08,d(7H_z),14-CH_3;1.07,d, (J7H_z),15-CH_3.	152
			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}.	
Isocalamusenone	Acorus calamus		1	PMR: 2.82,m,1-H;1.3-2.0,m,2-H;2.2, m,2-H;2.78,d(J16H_z),6-H;3.23,d(J 16H_z),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_z),14-CH_3;1.62,s,15-CH_3.	152
			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}.	
Tropone	Acorus calamus		1	PMR: 7.12,d(J12H_z),6-H;7.02,s,9-H; 6.94,dd(J12&3H_z),7-H;3.20,br.q(J7H_z), 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_z),15-CH_3.	152
				CMR: 186.463,s,C_8;150.461,s,148.089,	

COMPOUND	PLANT SOURCE	STRESS AGENT	SOLVENT	NMR SHIFTS (ppm)	REF.
				s,146.063,s;140.283,d;139.337,d; 133.866,d;44.281,d,C_4;35.088,t; 30.511,t;25.557,q;20.154,q.	
Momilactone - A	Rice	21-23		PMR: 5.85,dd(J10.5&13H_z),Hb;5.71,d ($J5H_z$),Hg;4.98,dd($J1H_z$),Hd;4.95,dd, Hc;4.84,t($J5H_z$),Hh;2.58-2.69,m,He; 2.32,d,Hj;2.21,d($J12.5H_z$),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

REFERENCES

1. M. Afzal and Galib Al-Oriquat, Heterocycles, 1982, 19, 1295.
2. M. Afzal and Galib Al-Oriquat, Acta Chimica Turkiea, 1985, 12, (in press).
3. M. Afzal and Galib Al-Oriquat, Heterocycles, 1986, (in press).
4. I.A.M. Cruickshank, Ann. Rev. Phytopathol., 1963, 1, 351.
5. J.L. Ingham, Bot. Rev., 1972, 38, 343.
6. J. Kuc, Ann. Rev. Phytopathol., 1972, 10, 207.
7. J. Kuc, "Microbial Toxins", Ed. S. Kadis, A. Ciegler and S.J. Ajl, Academic press, 1972, 8, pp. 211.
8. J.D. Bulock, "The Biosynthesis of Natural Products", McGraw-Hill, New York, 1965, p.1
9. I.A.M. Cruickshank and D.R. Perrin, "Biochemistry of Phenolic Compounds", Ed. J.B. Harborn, Academic press, 1964, p. 511.
10. J. Kuc, Ann. Rev. Phytopathol., 1966, 20, 337.
11. R. Rohringer and D.J. Samborski, Ann. Rev. Phytopathol., 1967, 5, 77.
12. A. Stoessl, "Recent Advances in Phytochemistry", Ed. C. Steelinck and V.C. Runeckles, Appleton Century Crofts, New York, 1970, 3, pp. 143.
13. A. Stoessl, J.B. Stothers and E.W.B. Ward, Phytochemistry, 1976, 15, 855.
14. J.A. Hargreaves and J.A. Bailey, Physiol. Plant Pathol., 1978, 13, 89.
15. J.E. Rahe and R.M. Arnold, Canad. J. Bot., 1975, 53, 921.
16. L.A. Hadwiger and M.E. Schwochau, Plant Physiol., 1971, 47, 588.
17. J.L. Ingham, Phytochemistry, 1976, 15, 1489.
18. J.L. Ingham, Canad. J. Bot., 1978, 56, 2230.
19. K.O. Muller, Phytopathol. Z., 1956, 27, 237.
20. P. Langcak, D. Cartwright, D.P. Leworthy, R.J. Pryce and J.P. Ride, Neth. J. Plant Pathol., 1978, 83, 153.
21. J.B. Harborne, T.J. Mabry and H. Mabry, "The Flavonoids", Chapman and Hall, London, 1975.
22. J.A. Hargreaves, Plant Pathol., 1979, 15, 279.
23. R.S. Burden and J.A. Bailey, Phytochemistry, 1975, 14, 1389.
24. R.L. Lyne, J.L. Mulheirn and D.P. Leworthy, J. Chem. Soc. Chem. Comm., 1976, 497.
25. R.L. Lyne and L.J. Mulheirn, Tetrahedron Letters, 1978, 3127.
26. A.R. Ayers, J. Ebel, F. Finelli, N. Berger and P. Albersheim, Plant Physiol., 1976, 57, 751.
27. A.A. Bell and M.N. Christensen, Phytopathol., 1968, 58, 883.
28. A.A. Bell, Phytopathol., 1969, 59, 1119.

29. I.A.M. Cruickshank and D.R. Perrin, Life Science, 1963, 3, 680.
30. D.R. Perrin, Tetrahedron Lett., 1964, 1, 29.
31. W.L. Klarman and J.B. Sangford, Life Science, 1968, 7, 1095.
32. V.J. Higgins and R.L. Millar, Phytopathol., 1968, 58, 1377.
33. F.J. Muehlbauer and C. Sander, Pism. Newsletter, 1975, 7, 32.
34. R.L Lyne and L.J. Mulheirn, Tetrahedron Lett., 1978, 3127.
35. W.Q. Loegering, Hereditas Suppl., 1966, 11, 167.
36. T. Minamikawa and I. Uritani, Arch. Biochem. Biophys., 1964, 108, 573.
37. K.O. Muller, Aust. J. Sci., 1958, 11, 275.
38. G. Loebenstein, S. Rabina and T. Van-Praag, Virology, 1968, 34, 264.
39. J.A. Bailey, Phytochemistry, 1969, 8, 1393.
40. L.A. Hadwiger and M.E. Schwochau, Plant Physiol., 1971, 47, 346.
41. S.L. Van Broembsen and L.A. Hadwiger, Physiol. Plant Pathol., 1972, 2, 207.
42. M.E. Schwochau and L.A. Hadwiger, Arch. Biochem. Biophys., 1969, 134, 34.
43. A.A. Bell and J.T. Presley, Phytopathol., 1969, 59 1147.
44. A.I. Zaki, N.T. Keen and D.C. Erwin, Phytopathol., 1972, 62, 1402.
45. L.A. Hadwiger and M.E. Schwochau, Biochem. Biophys. Res. Comm., 1970, 38, 683.
46. L.A. Hadwiger, A. Jafri, S.L. Van Broembson and R. Eddy, Plant Physiol., 1974, 53, 52.
47. R.A. Dixon and K.W. Fuller, Physiol. Plant Pathol., 1977, 11, 287.
48. M. Stekoll and C.A. West, Plant Physiol., 1978, 61, 38.
49. M. Wade and P. Albersheim, Proc. Nat. Acad. Sci., U.S.A., 1979, 76, 4433.
50. I.A.M. Cruickshank and D.R. Perrin, Life Science, 1969, 7, 449.
51. E.W.B. Ward, C.H. Unwin and A. Stoessle, Canad. J. Bot., 1973, 51, 2327.
52. P.J.G.M. Dewit and P.H.M. Roseboam, Physiol. Plant Pathol., 1980, 16, 391.
53. J.M. Dow and J.A. Callow, Physiol. Plant Pathol., 1979, 15, 27.
54. N.T. Keen and M. Legrand, Physiol. Plant Pathol., 1980, 17, 175.
55. N.T. Keen and M. Long, Physiol. Plant Pathol., 1972, 2, 307.
56. N.T. Keen, Physiol. Plant Pathol., 1971, 1, 265.
57. A.J. Anderson, Phytopathol., 1979, 69, 913.
58. C. Ballou, Adv. in Microbial Physiol., 1976, 14, 93.
59. E. Chalutz and M.A. Stahman, Phytopathol., 1969, 59, 1972.
60. B.A. Cunningham, Scientific American, 1977, 237, 96.
61. T. Hijwegen, Phytochemistry, 1973, 12, 375.
62. I.M. Smith, Plant Pathol., 1971, 1, 85.

63. D.D. Clarke, Proc. Roy. Soc., (London), 1972, 181, 302.

64. N.P. Korableva, E.V. Morozova and L.V. Metlitskii, Chem. Abst., 1974, 80, 118331.

65. A. Kamara, Diss. Abstr. Inter., 1974, 34B, 3033.

66. G. Palfi, Chem. Abstr., 1968, 68, 75798.

67. M.S. McDonald, Z. Pflanzenphysiol., 1974, 73, 371.

68. M.A. Hartmann and P. Benveniste, Phytochemistry, 1974, 13, 2667.

69. R.K. McKee, Ann. Appl. Biol., 1955, 43, 147.

70. S.L. Sinden, Amer. Bot. J., 1972, 49, 368.

71. M.J. Shih and J. Kuc, Phytochemistry, 1974, 13, 997.

72. R. Locci and J. Kuc, Phytopathol., 1967, 57, 1272.

73. O.L. Ozeretskovskaya, M.A. Davydova, N.I. Nasyukova and L.V. Metlitskii, Doki. Bot. Sci., 1967, 196, 5.

74. K. Tomiyama, T. Sakuma, N. Ishizaka, N. Sato, K. Katsui, M. Takasugi and T. Masamune, Phytochemistry, 1971, 61, 174.

75. J.L Yarns, J. Kuc and E.B. Williams, Phytopathol., 1971, 61, 174.

76. N. Sato, K. Tomiyama, N. Katsui and T. Masamune, Ann. Phytopathol. Soc. Japan, 1968, 34, 140, 344.

77. J.L. Varns, W.W. Currier and K. Kuc, Phytopathol., 1971, 61, 968.

78. G.D. Lyon, Physiol. Plant Pathol., 1972, 2, 411.

79. L.V. Metlitskii, Yu. T. Dyakov, O.L. Ozeretskovskaya, L. Yurganova, L.I. Chalova and N.I. Vasyukova, Chem. Abstr., 1971, 75, 45732.

80. T. Ersek, "Symposium on Current Topics in Plant Pathology", Budapest, June, 1974, p.15.

81. K. Komai and S. Sato, J. Agric. Chem. Soc. Japan, 1974, 48, 599.

82. Z. Kiraly, B. Barna and T. Ersek, Nature, 1972, 239, 456.

83. T. Ersek, B. Barna and Z. Kiraly, Acta Phytopathol. Acad. Sci., Hung., 1973. 8, 3.

84. M. Yamamota, Rev. Plant Protect. Res. (Phytopathol. Soc. Japan), 1974, 7, 45.

85. N.Katsui, A. Murai, M. Takasugi, K. Imaizumi, T. Masamune and K. Tomiyama, J. Chem. Soc. Chem. Comm., 1968, 43.

86. S.T. K. Bukhari and R.D. Guthrie, J. Chem. Soc., 1969, 1073.

87. N. Karada and K. Nakanishi, J. Amer. Chem. Soc., 1969, 91, 3989.

88. A. Stoessl, C.H. Unwin and E.W.B. Ward. Phytopathol. Z., 1972, 74, 141.

89. A. Stoessl, C.H. Unwin and E.W.B. Ward, Phytopathol., 1973, 63, 1225.

90. E.W.B. Ward, C.H. Unwin and A. Stoessl, Phytopathol., 1973, 63,1537.

91. G.I. Birnbaum, A. Stoessl, S.H. Grover and J.B. Stothers, Canad. J. Chem., 1974, 52, 993.

92. N. Katsui, A. Matsunaga and T. Masamune, Tetrahedron Lett., 1974, 4483.

93. A. Stoessl, J.B. Stothers and E.W.B. Ward, J. Chem. Soc. Chem. Commun., 1975, 431.

94. D.T. Coxon, R.F. Curtis, K.R. Price and B. Howard, Tetrahedron Lett., 1974, 2363.

95. S.H. Grover, J.P. Guthrie, J.B. Stothers and C.T. Tan, J. Mag. Res., 1973, 10, 227.

96. J.B. Stothers, C.T. Tan and K.C. Teo, Canad. J. Chem., 1973, 51, 2893.

97. A. Stoessl, J.B. Stothers and E.W.B. Ward, Phytochemistry, 1976, 15, 855.

98. K. Tamiyama, T. Sakuma, N. Ishizaka, N. Sato, N. Katsui, M. Takasugi and T. Masamune, Phytopathol., 1968, 58, 115.

99. T. Nakajima, K. Tomiyama and M. Kinugawa, Ann. Phytopathol. Soc. Japan, 1975, 41, 49.

100. T. Horikawa, K. Tomiyama and N. Doke, Phytopathol., 1976, 66, 1186.

101. K. Tomiyama, N. Ishizaka, N. Sato, T. Masamune and N. Katsui, "Biochemical Regulation in Diseased Plants or Injury", Ed. T. Hirani, Kyoritsu Printing Press. Co. Tokyo, 1968, p. 287.

102. M. Shih and J. Kuc, Phytopathol., 1973, 68, 826.

103. N. Ishizaka and K. Tomiyama, Plant Cell Physiol., 1972, 13, 1053.

104. N. Sato, K. Kitazawa and K. Tomiyama, Physiol. Plant Pathol., 1971, 1, 289.

105. N. Sato and K. Tomiyama, Ann. Phytopathol. Soc. Japan, 1969, 35, 202.

106. K. Tomiyama and F. Fukaya, Ann. Phytopathol. Soc. Japan, 1976, 41, 418.

107. E.H. Allen and J. Kuc, Phytopathol., 1968, 58, 776;
T. Masamune, A. Murai, M. Takasugi, A. Matsunaga, N. Katsui, N. Sato, and K. Tomiyama, Bull. Chem. Soc. Japan, 1977, 50, 201.

108. A. Murai, K. Nishizakura, N. Katsui and T. Masamune, Bull. Chem. Soc. Japan, 1977, 50, 1206.

109. J. Beczner, B.M. Lund and C.E. Bayliss, Proc. Amer. Phytopathol. Soc. Abstr., 1975, No. 121.

110. A. Stoessl, J.B. Stothers and E.W.B. Ward, Canad. J. Chem., 1978, 56, 645.

111. M. Katsui, A. Murai, M. Takasugi, K. Imaizumi and T. Masamune, J. Chem. Soc. Chem. Comm., 1968, 43.

112. N. Katsui, F. Yagihashi, A. Murai and T. Masamune, Chem. Lett., 1980, 1455.

113. N. Katsui, A. Matsunaga, K. Imaizumi and T. Masamune, Tetrahedron Letters, 1971, 2, 83.

114. L.V. Metlitskii, O.L. Ozeretskovskaya, N.S. Vul'fson and L.I. Chalova, Doklady Akad. Nauk. S.S.R., 1971, 200, 1970.

115. C.V. Metlitsky, Y.T. Yurganova, L.I. Chalova and N.I. Vasxukova, Ser. Biorogicheskaya Akad. Nauk. S.S.S.R., 1971, 3, 399.

116. A. Stoessl, J.B. Stothers and E.W.B. Ward, J. Chem. Soc. Chem. Comm., 1974, 707 and 709.

117. N. Katsui, A. Matsunaga, H. Kitahara, F. Yagihashi, A. Murai, T. Masamune and N. Sato, Bull. Chem. Soc. Japan, 1977, 50, 1217.

118. D.T. Coxon, K.R. Price, J.B. Stothers and A. Stoessl, J. Chem. Soc. Chem. Comm., 1979, 348.

119. E.B. Kalan and S.F. Osman, Phytochemistry, 1976, 15, 775.

120. N. Katsui, F. Yagihashi, A. Matsunaga, K. Orito, A. Murai and T. Masamune, Chem. Lett., 1977, 723.

121. D.T. Coxon, K.R. Price, B. Howard, S.F. Osman, E.B. Kalan and R.M. Zacharius, Tetrahedron Letters, 1974, 2921.

122. R.C. Anderson and D.M. Gunn, J. Chem. Soc. Chem. Comm., 1977, 27.

123. D.L. Hughes and D.T. Coxon, J. Chem. Soc. Chem. Comm., 1974, 882.

124. A.G. Malmberg and O. Theander, Phytochemistry, 1980, 19, 1730.

125. J. Kuc, Teratology, 1973, 8, 333.

126. D.T. Coxon, K.R. Price, B. Howard and R.F. Curtis, J. Chem. Soc. Perkin I, 1977, 53.

127. W.W. Currier, Diss. Abstr. Int., 1975, 36B, 685.

128. K.R. Price, B. Howard and D.T. Coxon, Physiol. Plant Pathol., 1976, 9, 189.

129. I. Oguni and I. Uritani, Plant Physiol., 1954, 53, 649.

130. I. Oguni and I. Uritani, Plant and Cell Physiol., 1971, 12, 507.

131. I. Uritani, M. Uritani and H. Yamada, Phytopathol., 1960, 50, 30.

132. H. Inoue and I. Uritani, Plant and Cell Physiol., 1979, 20, 1307.

133. N. Kato, H. Imaseki, N. Nakashima, and I. Uritani, Tetrahedron Lett., 1971, 13, 843.

134. N. Suzuki, K. Kasai, Y. Yamazaki, T. Araki, S. Toyoda and T. Takanashi, Bull. Nat. Inst. Agr. Sci. Japan, 1957, 8, 69.

135. M. Hiura, Rept. Gifu Agr. Coll., 1943, 50, 1.

136. T. Kubota and T. Matsuura, J. Chem. Soc. Japan, 1953, 74, 101, 197, 248, and 668.

137. T. Akazawa, I. Uritani and A. Kubata, Arch. Biochem. Biophys., 1960, 88, 150.

138. A.E. Arinze and I.M. Smith, Physiol. Plant Pathol., 1980, 17, 145.

139. L.T. Burka, L. Kuhnert and B.J. Wilson, Tetrahedron Letters, 1974, 4017.

140. D.T.C. Yang, B.J. Wilson and I.M. Harris, Phytochemistry, 1971, 10, 1653.

141. K. Oba, K. Oga, K. Nagai and I. Uritani, Proc. Ann. Meeting of Agr. Chem. Soc. Japan, 1979, 90.

142. A. Stoessl, J. B. Stothers and E.W.B. Ward, Canad. J. Chem., 1975, 53, 335.

143. A. Murai, H. Taketsura and T. Masamune, Bull. Chem. Soc. Japan, 1980, 53, 1049.

144. A. Murai, H. Taketsura, K. Fujisawa, Y. Nakahara, M. Takasugi and T. Massamune, Chem. Lett., 1977, 665.

145. R.S. Burden, J.A. Bailey and G.G. Vincent, Phytochemistry, 1975, 14, 221.

146. M. Gordon, A. Stoessl and J.B. Stothers, Canad. J. Chem., 1973, 51, 748.

147. A. Stoessl, J.R. Robinson, G.L. Rock and E.W.B. Ward, Physiology and Biochem., 1977, 67, 64.

148. R.C. Baker, C.J.W. Brooks and S.A. Hutchinson, J. Chem. Soc. Chem. Commun., 1975, 293.

149. R.C. Baker and C.J.W. Brooks, Phytochemistry, 1976, 15, 689.

150. D.R. Jones, C.H. Unwin an E.W.B. Ward, Phytopathol., 1975, 65, 1286.

151. E.W.B. Ward, C.H. Unwin and A. Stoessl, Canad. J. Bot., 1974, 52, 2481.

152. M. Rohr, P. Naegeli and J.J. Daly, Phytochemistry, 1979, 18, 279.

153. D. Cartwright, P. Langcake, R.T. Pryce and D.P. Leworthy, Nature, 1977, 267, 513.

154. T. Kato, Tetrahedron Lett., 1963, 3861.

155. T. Kato, J. Chem. Soc. Perkin I, 1977, 250.

156. D. Cartwright, P. Langcake, R.J. Pryce, D.P. Leworthy and J.P. Ride, Phytochemistry, 1981, 20, 535.

157. T. Kato, Phytochemistry, 1977, 16, 45.

158. V.K. Harding and J.B. Heale, Physiol. Plant Pathol., 1980, 17, 227.

Received, 16th April, 1986