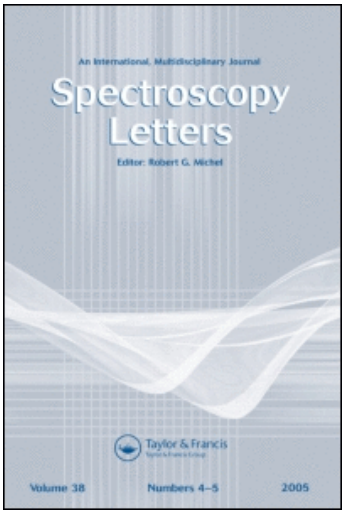

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Stereochemical Study of Desacylguayulin a Using Modern NMR Techniques

Felix J. Parodi[a]; Marcus Nauman[a]; Nikolaus H. Fischer[a]
[a] Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana

To cite this Article Parodi, Felix J. , Nauman, Marcus and Fischer, Nikolaus H.(1987) 'Stereochemical Study of Desacylguayulin a Using Modern NMR Techniques', Spectroscopy Letters, 20: 2, 97 — 103
To link to this Article: DOI: 10.1080/00387018708081531
URL: http://dx.doi.org/10.1080/00387018708081531

SPECTROSCOPY LETTERS, 20(2), 97-103 (1987)

STEREOCHEMICAL STUDY OF DESACYLGUAYULIN A USING MODERN NMR TECHNIQUES

Felix J. Parodi, Marcus Nauman and Nikolaus H. Fischer*
Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803

Key Words: desacylguayulin A; NMR; guayule; stereochemistry; conformation.

ABSTRACT: The relative configuration and solute conformation of desacylguayulin A was established using modern NMR techniques. Application of COSY, NOESY, CONOESY, homo- and heteronuclear J-resolved, DEPT and NOEDIFF allowed assignments of all ^{1}H and ^{13}C NMR resonances.

INTRODUCTION

Parthenium argentatum (guayule), a rubber-producing perennial shrub native to the Chihuahuan desert in south western Texas and northern Mexico. It has been suggested that the economic use of guayule as a source for natural rubber might depend on by-product utilization.[1] Therefore, we have initiated structural and chemical studies of major guayule resin constitutents and their derivatives.

Recently, the molecular structure of Guayulin A, a principle component of the guayule resin[2], was determined by X-ray crystallography[3]. Guayulin A, an

ellicitor of allergic contact dermatitis in sensitized subjects[4] is allegedly a reservoir of the allelopathic cinnamic acid[5].

Saponification of guayulin A provided its parent alcohol, desacylguayulin A. By the use of modern NMR techniques[6,7,8], the stereochemistry and solute conformation of desacylguayulin A were determined. Also, the ^{1}H and ^{13}C nmr assigments are described below.

NMR SPECTRAL ASSIGNMENTS OF DESACYLGUAYULIN A (1)

The assignment of the ^{1}H-nmr spectrum of 1 involved the combined utilization of a complementary COSY spectrum and nuclear Overhauser effects[9,10]. The relative configuration as well as the determination of the major conformation of **1** at ambient temperature was based on a NOEDIFF and 2D-NOESY experiments at 200 MHz, and was confirmed by the CONOESY experiments at 400 MHz. The use of NOEDIFF and NOESY was complementary. Irradiation of "isolated protons" showed a clear NOEDIFF spectrum, while the 2D-NOESY experiment was used to obtain NOE data between protons in the "crowded" region between 1.7 and 2.3 ppm. 2 D-CONOESY at 400 MHz was used as a fast technique to confirm the 2D-COSY spectrum and NOE data provided by the experiments at 200 MHz. The section plot of the 2D J-resolved experiments gave more accurate coupling constants than the 2 D J-resolved plot.

The presence of trans- double bonds in 1 was established primarily from the absence of NOEs between Me-14, Me-15 and the two vinylic protons. NOE between the vinylic protons H-1 and H-5, Me-13 and H-5 and H-8, Me-12 and H-6 and H-7 provided evidence for the conformation in which the cyclopropane ring, vinylic protons as well as the axial proton geminal to a hydroxyl were above the plane, while both vinyl methyls Me-14 and Me-15 were below the plane. Final determination of the conformation was provided by the NOE between other protons as shown in table 1, as well as molecular model considerations based on coupling constants derived from the J-resolved methods.

TABLE 1. ^{1}H-NMR Resonance Assignments and Nuclear Overhauser Effects[a] of 1.

δ[b]	m[c]	^{1}H	1	2α	2β	3α	3β	5	6	7	8	9α	9β	12	13	14	15
4.92	dd	1		+	+			+			+		+				
2.0		2α	+		+	+											
2.15		2β	+	+			+										
2.19		3α		+			+										+
1.9		3β			+	+		+									
4.4	d	5	+		+		+				+		-		+		
1.52	dd	6								+				+			+
0.76	dd	7							+					+			
3.62	ddd	8	+					+					+		+		
1.87	dd	9α														+	
2.71	dd	9β	+					-			+						
1.16	s	12							+	+							
1.22	s	13						+			+						
1.52	d	14										+					
1.66	d	15				+			+								

a NOEDIFF 5 <——> 13 <——> 9 negative; SI=16K; DP = 41L; D1 = 0.2; D2 = 2; NE = 8; NS = 32. Recycle delay=2 sec.
NOESY: SI = 0.5 x 0.5 K; NS = 64; NE = 256, mixing time = 1 sec; (overnight)
CONOESY: SI = 0.5 x 0.5 K; NS = 16; NE = 256; RD = 1; D1 = 1, D9 = 1; (3 hours). Bruker AM 400.

b ppm: relative to TMS. 0.1 mM $CDCl_3$. Bruker WP 200.

c From J-resolved exp: SI = 0.5 x 0.25 K; NS=64 (overnight)
J(Hz): 5,6 = 6,5 = 12; 5,15 = 15,5 = 2.2; 6,7 = 7,6 = 9; 7,8 = 8,7 = 10.5; 8,9α = 9α,8 = 11; 8,9β = 5.3; 14,1 = 1.5; 9α,9β = 13

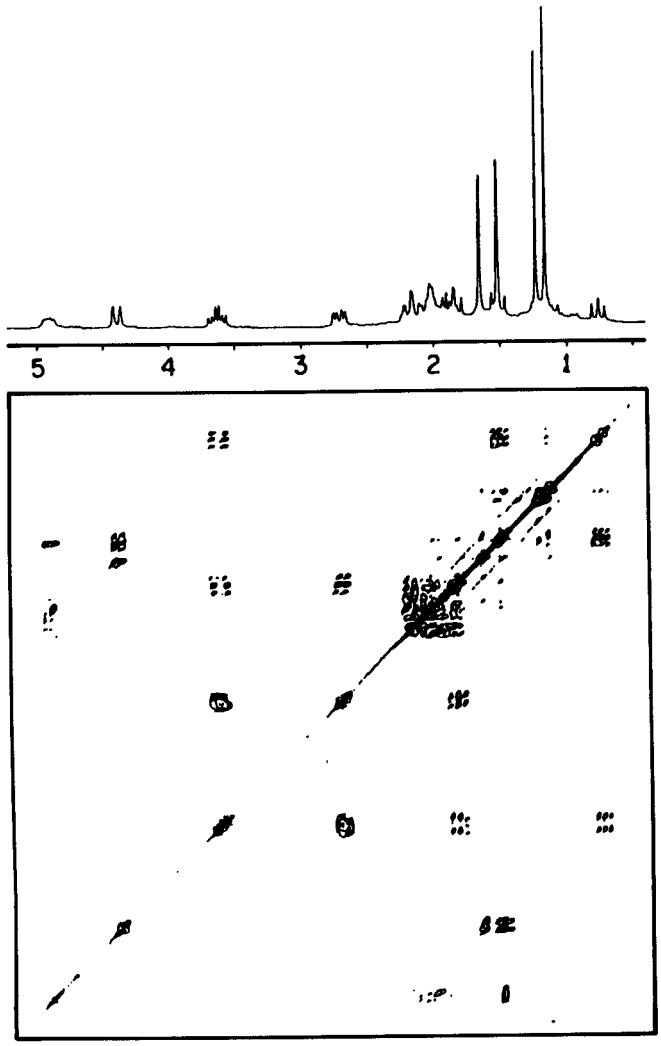

Fig 1. 200 MHz COSY spectrum of desacylguayulin A (1)

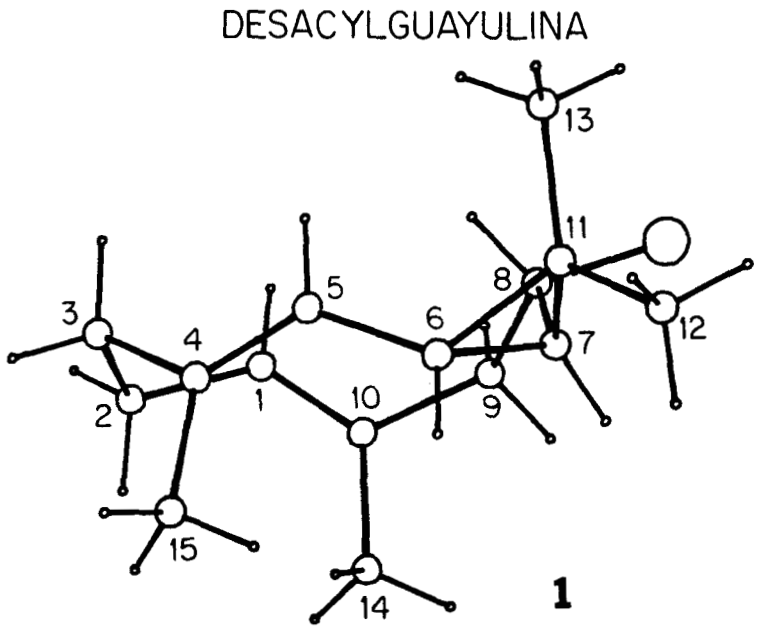

Fig. 2. Stereochemical representation of desacylguayulin A (1).

Assignments for all carbon resonances were provided by the combined utilization of 2D-heteronuclear shift correlation and DEPT experiments.

CONCLUSIONS

The combined utilization of the complementary 2D-NOESY and NOEDIFF experiments as well as the J-resolved experiments provided structural information for the determination of the stereochemistry of desacylguayulin A and confirm the assignments of all proton and carbon resonances provided by the 2D-homonuclear and heteronuclear shift correlation experiments.

ACKNOWLEDGMENTS

We are grateful to the U.S.-Spain Committee for Scientific and

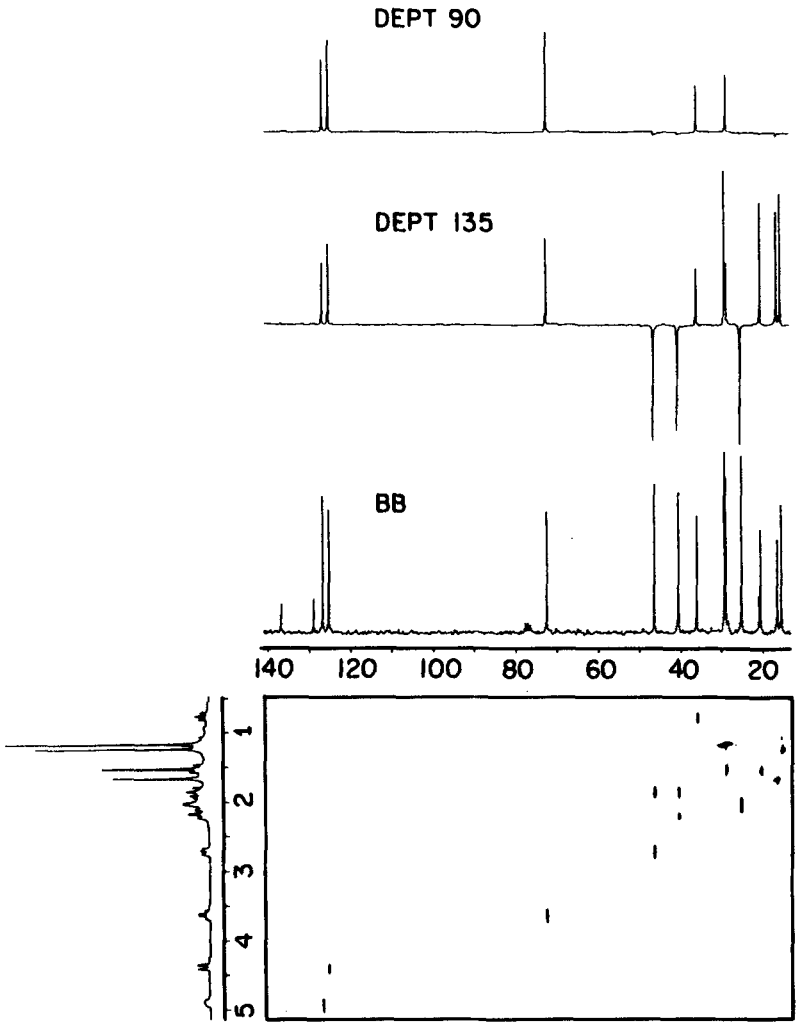

Fig 3. DEPT and H-C correlation of desacylguayulin A[1].

BB and DEPT at 50MHZ; 0.3mM, 3 hours. Jc-H(Hz) based on H-C J-resolved method: SI=256x128w, NS=64 (overnight).
δc 126.5 (d,152,C-1), 25.0 (t,132,C-2), 40.2 (t,132,C-3), 136.6 (s,C-4), 125.2 (d,155,C-5), 35.5 (d,162, C-6), 28.4 (d,160,C-7), 72.1 (d,148,C-8), 46.2 (t,131,C-9), 128.5 (s,C-10), 20.5 (s,C-11), 28.9 (q,126,C-12), 15.2 (q,126,C-13), 20.2 (q,125,C-14), 16.2 (q,125,C-15).

Technological Cooperation (Project No. CCB-8409023) for support of this research.

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Date Received: 10/06/86
Date Accepted: 11/14/86