RANCINAMYCINS I, II, III AND IV
STRUCTURAL STUDIES

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Rancinamycins are secondary metabolites produced by *Streptomyces lincolnensis* in a sulfur-depleted culture medium. The structures (except stereochemistry) of the main components of the rancinamycin-complex were determined by the use of IR, UV, PMR and CMR spectra.

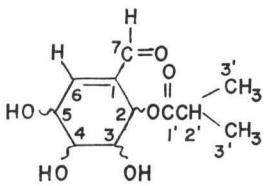
The production, isolation and characterization of rancinamycins I, II, III and IV have been described in a preceding communication.[1] These metabolites, which exhibit *in vitro* activity against Gram-positive and Gram-negative bacteria, are produced by *Streptomyces lincolnensis* in media depleted of sulfur-containing inorganic or organic compounds.

Rancinamycins I, II, III and IV behaved as single entities in several tlc and paper chromatographic systems. Gas chromatographic-mass spectroscopic analysis, however, revealed that each of rancinamycins I, II and III was a mixture of isomeric components[1]. While each isomeric mixture was separated analytically the individual components have not been isolated. The studies reported in this communication, therefore, have been carried out on the isomeric mixtures.

The present paper discusses the structure of the main components of the rancinamycin complex. Possible structures for the minor components and suggestions regarding the biosynthetic origin of rancinamycins are also discussed.

Rancinamycin I

Rancinamycin I was found to be a mixture of five isomeric components, $C_{11}H_{16}O_6$, designated rancinamycins Ia, Ib, Ic, Id and Ie[1]. Rancinamycins Ia and Ib are the main components comprising *ca* 87% of rancinamycin I, while rancinamycins Ic, Id and Ie are present in small amounts (1%, 3% and 8%, respectively). It was felt that the structures of the two major components could be determined from spectral data on the rancinamycin I mixture and its 2,4-dinitrophenylhydrazone** as the small amounts of the minor components would not contribute significantly to spectral data. Consequently, the following discussion is concerned only with discussion of spectral properties as they lead to the elucidation of the structures of rancinamycins Ia (**1**) and Ib (**2**).



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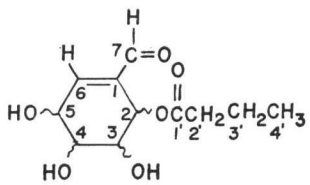

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** CMR and PMR spectra indicate the presence of only two isomeric components in rancinamycin I or rancinamycin I-2,4-dinitrophenylhydrazone.

Table 1. Fragmentation patterns of TMS*-derivatives of rancinamycins I, rancinamycins II and rancinamycins III obtained by gas chromatography-mass spectroscopy

m/e		
Rancinamycins Ia to Ie-TMS	Rancinamycins IIa to IIe-TMS	Rancinamycins IIIa to IIId-TMS
133	133	133
147	147	147
167	167	167
191	191	191
204	204	204
243	243	239
255	255	243
267	267	255
272	272	258
283	283	267
329	329	272
342	343	283
357	357	331
372	372	344
445	459	357
460	474	372
		447
		462

* TMS=trimethylsilyl.

Rancinamycins Ia~Ie form *tris*-trimethylsilyl ether derivatives, $C_{11}H_{18}O_6\cdot[Si(CH_3)_3]_3$, having identical fragmentation patterns in their mass spectra (Table 1). This confirms the isomeric nature of rancinamycins Ia ~Ie and indicates that three of the six oxygens in these compounds are present as hydroxyl groups. IR absorptions at 3400, 1252, 1195~1150 and 1100~1050 cm^{-1} and broad absorptions at δ 4.7~5.3 (due to exchangeable protons) in the PMR spectrum of rancinamycin I (Fig. 1, Table 2) support this conclusion.

Two of the oxygens of rancinamycins Ia and Ib are present as ester groups. Absorptions in the saturated carbon region in the CMR spectrum of rancinamycin I (Table 3) combined with the presence of two ester carbonyl absorptions at δ 172.9 and δ 175.1 indicate the presence of

Table 2. Proton magnetic resonance spectrum of rancinamycin I*.

Chemical shift (δ)	Number of hydrogens	Assignment**
0.9	—	$-CH_3$ (H-4′, **2**)
1.1	—	$-CH_3$ (H-3′, **1**)
1.55	—	$-CH_2-$ (H-3′, **2**)
2.19	—	$-CH_2-$ (H-2′, **2**)
2.42	—	>CH– (H-2′, **1**)
2.52	—	DMSO
3.50	1	>CHOH } (H-3, H-4, H-5, **1** and **2**)
3.75	1	>CHOH }
4.40	1	>CHOH }
4.70~5.30	—	–OH (**1** and **2**)
5.38	1	>CHOC(=O)–(H-2, **1** and **2**)
6.96	1	H>C=C< (H-6, **1** and **2**)
9.48	1	–CH=O (H-7, **1** and **2**)

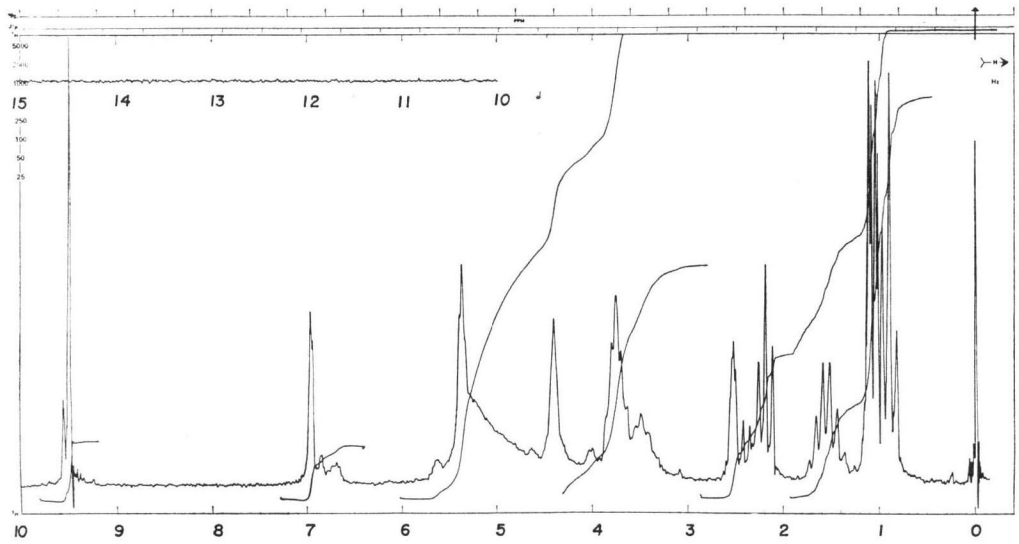
* Spectra were obtained using d_6-dimethylsulfoxide (DMSO) as solvent.
** See structures **1** and **2**.

Table 3. C-13 Nuclear magnetic resonance spectrum of rancinamycin I*.

Chemical shift (Rel. to TMS)	Number of carbons	Multiplicity**	Type of carbon	Assignment***
13.8	1	q	$-CH_3$	(C-4′, **2**)
17.8	1	t	$-CH_2-$	(C-3′, **2**)
18.4	2	q	$-CH_3$	(C-3′, **1**)
33.3	1	d	>CH–	(C-2′, **1**)
36.1	1	t	$-CH_2-$	(C-2′, **2**)
65.3	1	d	>CH–O– }	(C-3, C-4, C-5, **1** or **2**)
66.8	1	d	>CH–O– }	
69.0	1	d	>CH–O– }	
69.5	1	d	>CH–O–	(C-2, **1** or **2**)
136.3	1	s	>C=C<	(C-1, **1** or **2**)
152.9	1	d	H>C=C<	(C-6, **1** or **2**)
172.9	1	s	–C(=O)–O– }	(C-1′, **1** or **2**)
175.1	1	s	–C(=O)–O– }	
191.8	1	d	–C(=O)H	(C-7, **1** or **2**)

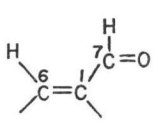
* Spectra were obtained using d_6-dimethylsulfoxide as solvent.
** s, d, t, q designate singlet, doublet, triplet and quartet, respectively.
*** See structures **1** and **2**.

Fig. 1. Proton magnetic resonance spectrum of rancinamycin I (in d_6-dimethylsulfoxide)



$(CH_3)_2CHC\overset{O}{\underset{O-}{<}}$ [δ 18.4 ($2CH_3$, q); δ 33.3 (>CH—, d)] and $CH_3CH_2CH_2C\overset{O}{\underset{O-}{<}}$ [δ 13.8 (CH_3, q); δ 17.8 (β-CH_2, t); δ 36.1 (α-CH_2, t)] in rancinamycin I[2] and consequently rancinamycins Ia and Ib are isomeric esters. On the basis of retention times of their trimethylsilyl derivatives[1], rancinamycin Ia is considered to contain the isobutyrate moiety while rancinamycin Ib is the isomeric *n*-butyrate ester[3,4]. The mass spectra of the TMS derivatives of rancinamycins Ia and Ib show the presence of a strong mass ion peak at *m/e* 372 (M^+—88). This peak is due to the loss of the butyric acids from the rancinamycins Ia or Ib, respectively[5]. IR absorption at 1735 cm^{-1} and PMR data (Table 2; Fig. 1) also support the presence of isobutyrate [δ 1.1 ($2\underline{CH_3}$, d); δ 2.42 (>$\underline{CH}$–, m)] and butyrate [δ 0.9 ($\underline{CH_3}$, t); δ 1.55 (β-$\underline{CH_2}$, m); δ 2.19 (α-$\underline{CH_2}$, t)] esters. CMR doublets at δ 65.3, 66.8, 69.0 and 69.5 (Table 3) indicate the presence of four -CHO-groups. Three of these groups are present as -$\underline{CH}$OH (δ 3.50, 3.75, 4.40; 1 H each) (Table 2) while the fourth (δ 5.38, 1H) is part of the ester grouping.

Rancinamycin I forms a 2,4-dinitrophenylhydrazone (2,4-DNPH). This property, IR carbonyl absorption at 1700 cm^{-1} and CMR (δ 191.8, d) and PMR (δ 9.48, 1H, s) absorptions indicate that the last of the oxygens of rancinamycins Ia and Ib is present as an aldehyde attached to a carbon bearing no hydrogens. UV maxima of rancinamycin I (220 nm) and rancinamycin I-2,4-DNPH (370 nm)[1] indicate an α,β-unsaturated aldehyde. CMR absorptions (δ 136.3, d; δ 152.9, s) (Table 3) and vinyl proton absorption at δ 6.96 (1H, d) in the PMR spectrum of rancinamycin I confirm this conclusion thereby indicating the presence of fragment **3** in rancinamycins Ia and Ib.



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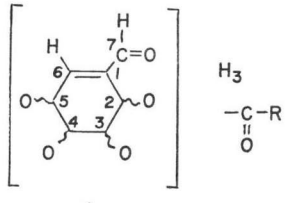
4 R= $(CH_3)_2CH$-

5 R= $CH_3CH_2CH_2$-



The molecular formula ($C_{11}H_{16}O_6$) of rancinamycins Ia or Ib requires the presence of four sites of unsaturation or four rings, or combinations of these systems. The fact that only three sites of unsaturation (vinyl, aldehyde, and ester groupings) are present in rancinamycins Ia or Ib indicates the presence of a cyclic system. This conclusion, in conjunction with NMR data presented thus far, indicate partial structures **4** and **5** for rancinamycins Ia and Ib. Confirmation of these structural assignments and location of the ester groups at C-2 or rancinamycins Ia and Ib were accomplished by CMR and PMR spectral analysis of rancinamycin I-2,4-DNPH.

The physical properties of rancinamycin I-2,4-DNPH[1] and PMR (Table 4; Fig. 2) and CMR (Table 5) spectra indicate that rancinamycin I-2,4-DNPH is a mixture of two isomeric compounds corresponding to rancinamycins Ia and Ib-2,4-DNPH (**6** and **7** respectively).

Table 4. Proton magnetic resonance spectrum of rancinamycin I-2,4-DNPH*

δ (Rel. to TMS)	Number of hydrogens	Multiplicity***	Assignment**
0.9	3	t	$-C_3\underline{H}$ (H-4′, **7**)
1.08	6	d	$-CH\langle^{\underline{CH_3}}_{\underline{CH_3}}$ (H-3′, **6**)
1.56	2	m	$-\underline{CH_2}-CH_3$ (H-3′, **7**)
2.25	2	t	$-\underline{CH_2}-CH_2-CH_3$ (H-2′, **7**)
2.42	1	m	$-CH\langle^{\underline{CH_3}}_{\underline{CH_3}}$ (H-2′, **6**)
2.44			DMSO
3.34			Water
3.72	1	t	$>C\underline{H}OH$ (H-4, **6** and **7**)
3.82	1	t	$>C\underline{H}OH$ (H-3, **6** and **7**)
4.32	1	t	$>C\underline{H}OH$ (H-5, **6** and **7**)
4.67	1	d	$>CHO\underline{H}$ (at C-4, **6** and **7**)
5.06	1	d	$>CHO\underline{H}$ (at C-5, **6** and **7**)
5.32	1	d	$>CHO\underline{H}$ (at C-3, **6** and **7**)
5.68	1	d	$>C\underline{H}-O-\overset{O}{\overset{\|}{C}}-C$ (H-2, **6** and **7**)
6.32	1	d	$\underline{H}>C=C<$ (H-6, **6** and **7**)
7.75	1	d	Aromatic protons
8.25	2	m	Aromatic protons
8.82	1	s	$\underline{H}>C=N-$ (H-7, **6** and **7**)
11.42	1	s	$-N-N\underline{H}-C_6H_5$ (**6** and **7**)

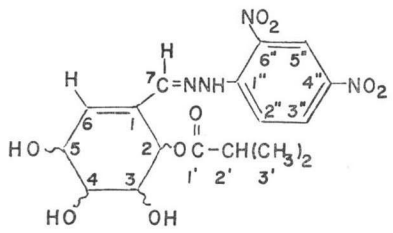
* Spectra obtained using d_6-dimethylsulfoxide (DMSO) as solvent.

** Refer to structures **6** and **7**.

*** s, d, t, q and m designate singlet, doublet, triplet, quartet and multiplet, respectively.

IR absorptions at 1600, 840 and 762 cm^{-1},[1] UV maximum at 370 nm and the aromatic or unsaturated proton and carbon absorptions in the PMR and CMR spectra (Tables 4, 5; Fig. 3) support the presence of the chromophoric system **8** in rancinamycin I-2,4-DNPH.

The presence of three hydroxyls in rancinamycin I-2,4-DNPH is supported by IR (3410, 1331, 1313, 1268 and 1107 cm^{-1}) and by the fact that three protons (doublets at δ 4.67, 5.06 and 5.32) in the PMR spectrum of rancinamycin I-2,4-DNPH exchange with deuterium (Fig. 2). Furthermore decoupling



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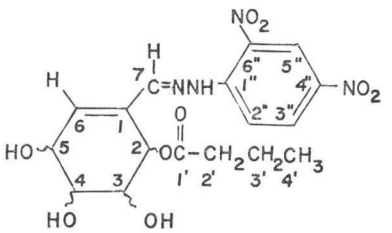

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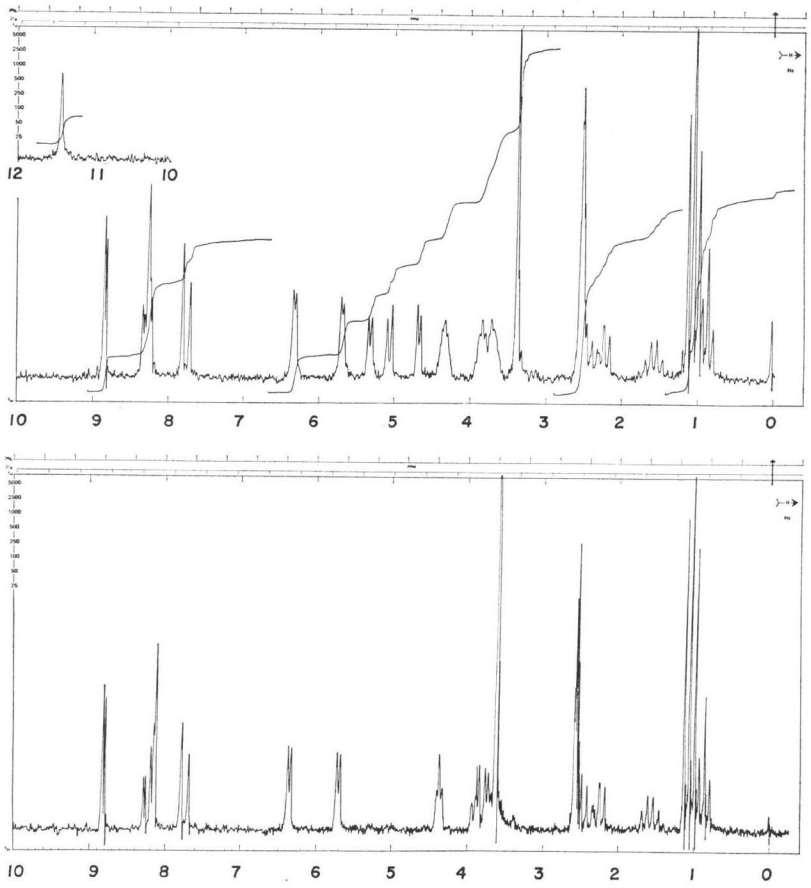
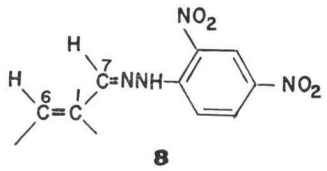
Fig. 2. Proton magnetic resonance spectrum of rancinamycin I-2,4-dinitrophenylhydrazone.
Upper: in d_6-Dimethylsulfoxide Lower: in d_6-Dimethylsulfoxide; D_2O added





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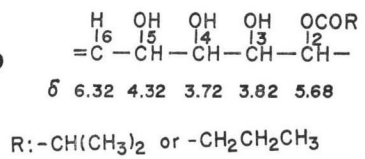

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δ 6.32 4.32 3.72 3.82 5.68

R: $-CH(CH_3)_2$ or $-CH_2CH_2CH_3$

studies indicated that triplets at δ 3.72, 3.82 and 4.32 (1H each), assigned to -CHO-, are coupled with the hydroxyl protons at δ 4.67, 5.32 and 5.06 respectively, thereby indicating the presence of three -CHOH groups.

Absorptions in the saturated-carbon region in the CMR spectrum (Table 5) in conjunction with the presence of the two ester-carbonyl absorptions at δ 172.9 and 175.1 indicate the presence of $(CH_3)_2$–$CHC(=O)O$– (2CH_3 at δ 18.5, q; –$CH<$ at δ 33.3, d) and $CH_3CH_2CH_2C(=O)O$– (CH_3 at δ 13.8, q; β–CH_2 at 18.1, t; α-CH_2 at δ 36.1, t)[9] in rancinamycins Ia and Ib-2,4-DNPH, respectively. PMR data (Table 4; Fig. 2) support the presence of isobutyrate [δ 1.08 (2CH_3, d); δ 2.42 (>CH–, m)] and butyrate [δ 0.9 (CH_3, t); δ, 1.56 ($CH_3CH_2CH_2$–, m); δ 2.25 (–CH_2CH_2–, t)] esters. Spin decoupling studies showed that the protons at δ 0.9, 1.08, 1.56 and 2.25 are not coupled with protons of the rings of rancinamycins

Table 5. C-13 Nuclear magnetic resonance spectrum of rancinamycin I-2,4-DNPH*

Chemical shift (Rel. to TMS)	Number of carbons	Multiplicity***	Type of carbon	Assignment**
13.8	1	q	$-CH_3$	(C-4′, **7**)
18.1	1	t	$-CH_2-$	(C-3′, **7**)
18.5	2	q	$-CH_3$	(C-3′, **6**)
33.3	1	d	>CH–	(C-2′, **6**)
36.1	1	t	$-CH_2-$	(C-2′, **7**)
65.5	1	d	>CH–O–	(C-3; C-4; C-5, **6** and **7**)
68.7	1	d	>CH–O–	
69.0	1	d	>CH–O–	
69.4	1	d	>CH–O–	(C-2, **6** and **7**)
70.1	1	d	>CH–O–	
116.3	1	d	aromatic CH	(C-2″, **6** and **7**)
122.7	1	d	aromatic CH	(C-3″, **6** and **7**)
129.3	1	d	aromatic CH	(C-5″, **6** and **7**)
129.3	1	s	–C=C–	(C-1, **6** and **7**)
131.7	1	s	aromatic C	(C-6″, **6** and **7**)
136.8	1	s	aromatic C	(C-4″, **6** and **7**)
140.5	1	d	H>C=C<	(C-6, **6** and **7**)
144.1	1	s	aromatic C	(C-1″, **6** and **7**)
149.4	1	d	H>C=N–	(C-7, **6** and **7**)
172.9	1	s	–O>C=O	(C-1′, **6** and **7**)
175.1	1	s	–O>C=O	

* Spectra obtained using d_6-dimethylsulfoxide (DMSO as solvent).
** Assignments refer to structures **6** and **7**.
*** s, d, t, q designate singlet, doublet, triplet, and quartet, respectively.

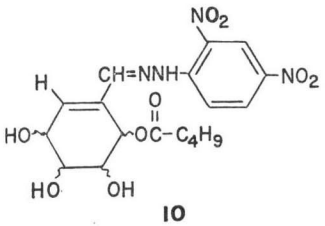
Ia and Ib-2,4-DNPH thereby confirming the presence of the isolated $-O-\underset{\underset{O}{\|}}{C}-CH(CH_3)_2$ and $-O\underset{\underset{O}{\|}}{C}-CH_2-CH_2CH_3$ systems. Furthermore, spin decoupling studies established the presence of fragment **9** in the molecule and the location of the ester moieties at C-2 of rancinamycin Ia-2,4-DNPH and rancinamycin Ib-2,4-DNPH.

Here, as with rancinamycin I, the molecular formula of rancinamycins Ia-2,4-DNPH and Ib-2,4-DNPH necessitate the presence of a six-membered cyclic system and therefore the structures of these compounds are represented by **6** and **7** respectively. The data obtained in this study are insufficient to permit stereochemical assignments at C-2, C-3, C-4 and C-5 of the molecule of rancinamycins Ia or Ib. However, on the basis of biosynthetic considerations and structural relationship of rancinamycins to shikimic acid, possible stereochemistry at C-3, C-4 and C-5 of rancinamycins Ia or Ib is proposed later.

The differences between the isomeric rancinamycins Ic, Id and Ie, unknown at present, are probably due to differences in absolute stereochemistry.

Rancinamycin II

The physical and chemical properties of rancinamycin II have been described earlier[1]. Rancinamycin II was also found to be a mixture of five isomeric compounds designated rancinamycins IIa to IIe. Rancinamycins IIa and IIe are the main components comprising *ca* 86% of rancinamycin II while rancinamycin IIb, IIc and IId are present in 7%, 3% and 4% respectively[1]. The mass spectra of rancinamycins II-TMS (Table 1) have the same molecular ion (*m/e* 474, $C_{12}H_{18}O_6$) and a fragmentation pattern identical to that of rancinamycins Ia-TMS and Ib-TMS for mass ions below *m/e* 372. This suggests that rancinamycins IIa to IIe are higher homologs of rancinamycins Ia and Ib containing an additional $-CH_2-$ group in the ester moiety. The M^+-102 ion present in the mass spectra of rancinamycins II-TMS is attributed to the loss of pentanoic acid from their molecules[5] in contrast to the loss of butyric acid in the case of rancinamycins Ia-TMS and Ib-TMS.



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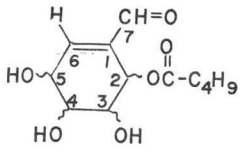

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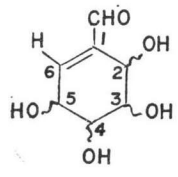
IR spectra of rancinamycin II and rancinamycin II-2,4-DNPH are similar to those of rancinamycin I and rancinamycin I-2,4-DNPH[1]. In addition rancinamycin II and rancinamycin II-2,4-DNPH have UV maxima[1] expected for compounds containing an α,β-unsaturated aldehyde system. The PMR spectrum of rancinamycin II-2,4-DNPH is identical to that of rancinamycin I-2,4-DNPH in all but the region from δ 0.5 to 2.5 (9H)[1]. These results indicate that the structure of rancinamycin II-2,4-DNPH is represented by **10**. The mass spectroscopic analysis described above in conjunction with data discussed earlier suggest that the structure of rancinamycins IIa to IIe is represented by **11**.

The PMR spectrum of rancinamycin II indicates the presence of $-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_3$ and $-\overset{O}{\overset{\|}{C}}-CH_2\underset{CH_3}{\underset{|}{CH}}-CH_3$ or $-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\underset{|}{CH}}-CH_2CH_3$ systems in rancinamycins II. Thus it appears that differences in the acyl group or in stereo-chemistry account for the various rancinamycins II although there is no evidence suggesting stereochemical differences at C-2, C-3, C-4 or C-5.

Rancinamycin III

High resolution mass spectra of rancinamycin III-TMS derivative showed molecular formula of $C_7H_6O_5\cdot[Si(CH_3)_3]_4$[1] indicating the presence of four hydroxyls in rancinamycin III ($C_7H_{10}O_5$). Ran-



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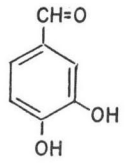

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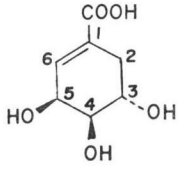

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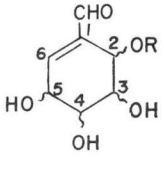


15 I: R= COC_3H_7
II: R= COC_4H_9
III: R= H

cinamycin III, like rancinamycins I and II forms a 2,4-dinitrophenylhydrazone exhibiting a UV maximum at 370 nm, indicative of an α,β-unsaturated carbonyl system. The IR spectrum showed the absence of the ester carbonyl at *ca* 1735 cm^{-1} which characterizes the spectra of rancinamycins I and II. These data support structure **12** for rancinamycin III.

Gas chromatographic-mass spectroscopic analysis of the trimethylsilyl-derivative of rancinamycin III indicated the presence of four isomeric components in rancinamycin III. The TMS-derivatives of all four components, designated rancinamycins IIIa, IIIb, IIIc and IIId (Table 1), had identical molecular weight (462) and fragmentation pattern. The differences between the isomeric rancinamycins IIIa~IIId, unknown at present, are probably due to differences in stereochemistry. As in the case of rancinamycins I and II the stereochemistry at C-2, C-3, C-4 and C-5 of **12** is not known.

Rancinamycin IV

High resolution mass spectroscopy indicated the mol. formula of $C_7H_6O_3$ for rancinamycin IV[1]. Gas chromatographic-mass spectroscopic analysis of the TMS-derivative of rancinamycin IV showed the presence of one component $C_7H_4O_3 \cdot [Si(CH_3)_3]_2$ having a retention time of 4.5 minutes. IR absorption indicate the presence of –OH (3350 cm^{-1}) unsaturated or aromatic carbonyl (1660 cm^{-1}) and an aromatic system (1600, 820, 760 cm^{-1}). Rancinamycin IV, like rancinamycins I, II and III, forms a 2,4-dinitrophenylhydrazone. The PMR spectrum of rancinamycin IV indicates the presence of an aldehyde proton at δ 9.76 (singlet), three aromatic hydrogens at δ 6.96, 7.32 and 7.34 and two exchangeable hydrogens at δ 7.27. The fact that rancinamycin IV forms a *bis*-trimethylsilyl derivative indicates the presence of two hydroxyl groups in the molecule.

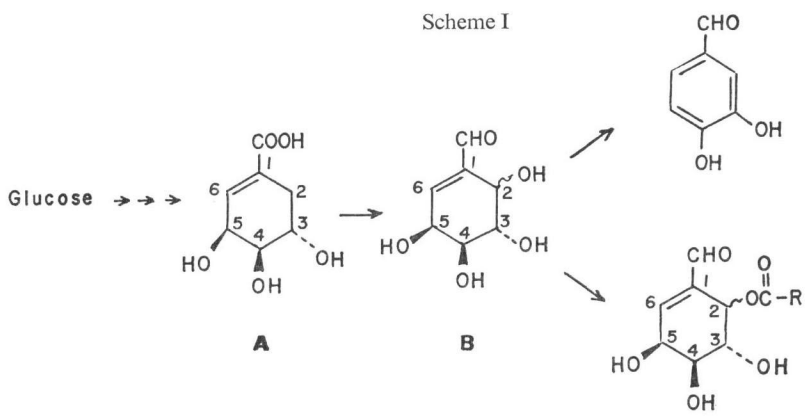
These data suggest that rancinamycin IV is a dihydroxybenzaldehyde. Comparison of PMR spectra[10] of 3,4-dihydroxybenzaldehyde (**13**) and rancinamycin IV indicated that the two compounds are identical.

Biosynthetic Considerations

Pronounced structural similarities between rancinamycins I, II and III and shikimic acid (**14**) suggest that rancinamycins I, II and III (**15**) have a biogenetic origin similar to shikimic acid.

We have reported[1] that *S. lincolnensis*, when grown in a complex medium produces lincomycin only. WITZ *et al.*[11] have shown that tyrosine is a precursor of 4-*n*-propylhygric acid, the amino acid

Scheme I



moiety of lincomycin. Since *S. lincolnensis* produces lincomycin in media containing glucose as the only carbon source, it follows that the organism is able to synthesize aromatic amino acids, specifically tyrosine. This necessitates the production of shikimic acid, the well known intermediate in the biosynthesis of aromatic amino acids[12], by *S. lincolnensis*. We propose that *S. lincolnensis*, when grown in a medium depleted of sulfur-containing compounds, synthesizes rancinamycins I, II and III *via* a pathway (Scheme I) similar to that involved in the biosynthesis of shikimic acid.

Reduction and hydroxylation of shikimic acid (A, Scheme I) would give rancinamycin III (B) which can afford rancinamycins I and II (by acylation) or rancinamycin IV (by dehydration). In view of the close structural relationship between shikimic acid and rancinamycins I, II and III it is reasonable to assume that the chirality of C-3, C-4 and C-5 in the rancinamycins remains the same as it does in shikimic acid. In the conversion of A to B, it is possible that hydroxylation could occur at C-2 or at C-6 of shikimic acid thus giving rise to four possible isomers of rancinamycin III. The problem of stereochemistry at the asymmetric centers including absolute stereochemistry is a subject currently under consideration.

Experimental

Isolation of Rancinamycins I, II, III and IV.

The metabolites were produced, isolated and separated by the procedures described by ARGOUDELIS *et al*[1].

Rancinamycin I, II, III or IV-2,4-Dinitrophenylhydrazones.

The individual 2,4-dinitrophenylhydrazones were prepared by the methods reported by ARGOUDELIS *et al*[1].

Spectroscopic Procedures.

Proton Magnetic Resonance (PMR) Spectroscopy: PMR spectra were recorded on a Varian XL-100-15 spectrometer operating at 100 MHz. All preparations were run in either D_2O or d_6-dimethylsulfoxide (d_6-DMSO) using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (SDSS) or tetramethylsilane (TMS) as internal reference.

Carbon-13 Nuclear Magnetic Resonance Spectroscopy: ^{13}C-NMR spectra were obtained on a pulsed Varian XL-100 operating at 25.16 MHz and locked to the 15.4 MHz ^{2}H-resonance of the solvent dimethylsulfoxide. The protons were decoupled by 800 Hz band width noise modulation centered at δ 4 in the proton spectrum. Off resonance decoupling was centered at δ 0 with the power attenuated to 4 db below 1 watt. The spectrometer was operated by a 24K Nova computer and the 8K 24 bit FIDS were transferred in 4K blocks to an IBM-1800 computer for accumulation, apodization, transformation and storage. All chemical shifts are given in parts per million relative to tetramethylsilane (TMS).

Infrared Spectroscopy: Infrared spectra were obtained in mineral oil suspension on a Digilab Model 14D FOURIER Transform Spectrometer.

Gas Chromatography-Mass Spectroscopy (GC-MS).

Gas chromatographic separation was done on a GC Varian Aerograph series 2700 chromatograph using a 6 ft, 3.8% UCW-98 on 80~100 mesh Diatoport-S column (Hewlett-Packard). The operation was performed isothermally at 185°C. The mass spectra were recorded on a CH7 Massenspectrometer (Varian Met., West Germany) operating at 70 electron volts.

It was found necessary to prepare the trimethylsilyl ethers of rancinamycins in order to obtain volatile compounds satisfactory for gas chromatographic analysis. This was done by reacting 50 μl of a 1 mg/ml solution of a rancinamycin preparation in dimethylformamide with 50 μl of Regisil® (Regis Chemical Co.). The reaction mixture was allowed to stand at room temperature for 30 minutes.

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