electrical forces and the complications caused by acceleration of ions as indicated by a recent study[1] are avoided.

Correlation of the present data with the earlier literature values are in the order which could be accounted for by the significant differences in experimental conditions. For example, the earlier value of k_3 was obtained at 200°, using 100-eV electron energies and a cell accelerating voltage of 5 eV; the deviation is in the right direction.

The six values, for reactions 8–10 and 15–17 are reported here for the first time.

Finally, it might be worth mentioning that the rise of the NO^+ and $c\text{-}C_3H_6^+$ parent ion concentration curves were considerably slower than those of other primary ions studied indicating that the superexcited states of these molecules are relatively long lived with a lifetime in the microsecond region.

A more detailed account will be forthcoming at a later date.

Acknowledgments. The authors thank the National Defence Research Board of Canada for financial support and Drs. R. J. Donovan and J. A. Franklin for assistance.

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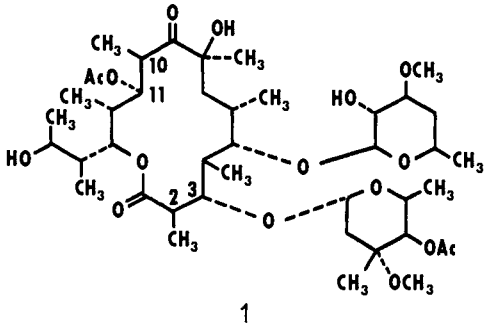
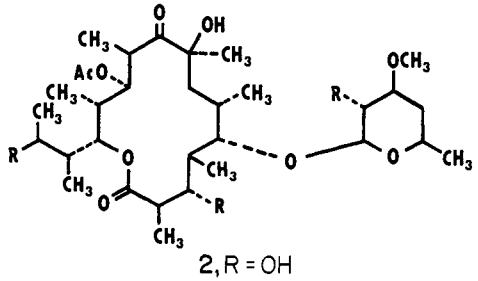
Structure of Lankamycin

Sir:

Evidence obtained in these laboratories has shown that the structure of lankamycin is **1**, differing from the previously proposed structure[1] in that the sugar substitution is reversed; D-chalcose is bound at C-5 and 4-*O*-acetyl-L-arcanose is bound at C-3.



1



2, R = OH
3, R = OAc

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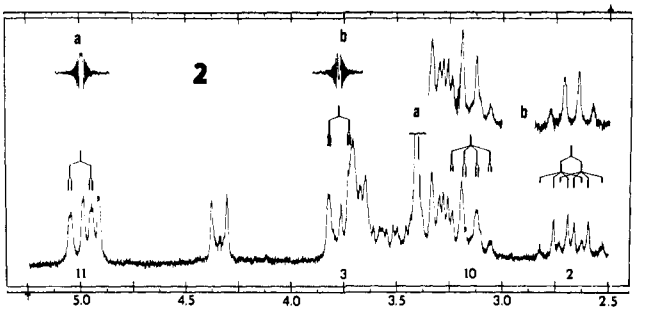

Figure 1. Partial nmr spectra of a $CDCl_3$ solution of darcanolide (**2**). Inserts show the decoupled spectra arising from irradiation at a and b, respectively.

Lankamycin, a neutral macrolide antibiotic[2] isolated from the fermentation broth of various *streptomycetes* species,[3,4] consists of a 14-membered polyhydroxylated lactone ring, 11-acetyllankolide,[1] on which are substituted two deoxy sugars, D-chalcose,[5] shown to be identical with D-lankavose,[5–7] and 4-*O*-acetyl-L-arcanose.[5,8] During mild methanolysis a monoglycoside, darcanolide (**2**), is formed together with methyl 4-*O*-acetyl-L-arcanoside.[1]

The partial nmr spectra of a $CDCl_3$ solution of **2**[9] (Figure 1)[10] reveals the resonances of two protons at 3.15 and 2.68 ppm (δ) both coupled with a single additional ring proton and a methyl group. Detailed analysis of the nmr spectra of related macrolide antibiotics[11] and derivatives[12,13] has shown that the chemical shifts of these protons are indicative of protons α to a carbonyl group (*viz.* H-2 and H-10). Further, the conformation of the aglycone of **1** has been shown to be identical with that proposed for the aglycones of the erythromycins and related monoglycosides.[11–15] Therefore, the 3.15-ppm multiplet is assigned to H-10 on the basis of the small axial–equatorial $J_{10,11}$ coupling (1.5 Hz) and the 2.68 ppm resonance to H-2 by the large diaxial $J_{2,3}$ coupling (9.7 Hz).[16] These assignments were corroborated by spin decoupling experiments (Figure 1, a and b).[10]

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(10) Nmr spectra were determined at 100 MHz using a Varian Associates HA-100 spectrometer. Chemical shifts were obtained by first-order analysis and are reported in ppm (δ) from internal reference TMS. Spin decoupling experiments were performed in frequency sweep using a Hewlett-Packard audiooscillator, Model 200AB.
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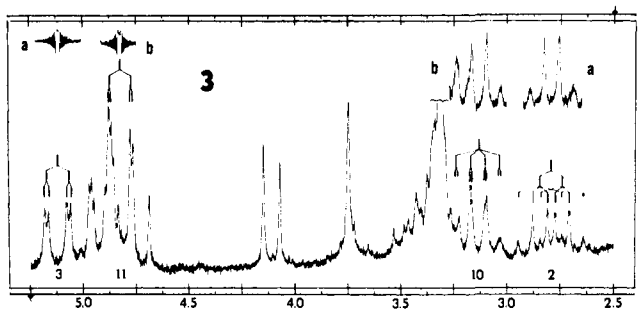

Figure 2. Partial nmr spectra of a $CDCl_3$ solution of triacetyldarcanolide (3). Inserts show the decoupled spectra arising from irradiation at a and b, respectively.

Irradiation of the doublet of doublets resonance at 5.00 ppm, assigned unequivocally to H-11, deshielded by the 11-acetyl group, results in sharpening of the 3.15-ppm quartet (H-10). The chemical shift of H-3 is located by the collapse of the resonance of H-2 when the doublet of doublets at 3.78 ppm is irradiated.

The partial nmr spectra of a $CDCl_3$ solution (Figure 2) of triacetyldarcanolide (**3**),[17] a tetraacetate, prepared from **2** by acetic anhydride–pyridine acetylation, also clearly shows the characteristic resonances of H-2 and H-10 at 2.79 and 3.13 ppm, respectively. Spin decoupling experiments (Figure 2, a and b) locate the chemical shifts of H-3 and H-11 at 5.12 and 4.82 ppm. The large paramagnetic shift of H-3 (−1.34 ppm), which can be accommodated only by acetylation of a geminal 3-hydroxyl group,[18] requires that the D-chalcose residue of **3** be bound at C-5. Since migration of a glycosidically bound sugar during acetylation or acid-catalyzed methanolysis is unlikely and has not been observed with other macrolide antibiotics, the D-chalcose residue must be at C-5 in **2** and **1**, thereby proving the alternate structure.

The glycosidic linkage of D-chalcose in **3** was shown to be β by the coupling constant[19] of the 4.11-ppm anomeric proton ($J_{1',2'}$ = 7.5 Hz, Figure 2). The determination could not be made from the spectra of **1** or **2** since in these compounds H-1′ is also virtually coupled[20] to H-3′ due to the chemical shift proximity of H-2′ and H-3′ (Figure 1). Similarly, analysis of the 220-MHz nmr spectra[21] of **1** revealed an α-glycosidic linkage for 4-*O*-acetyl-L-arcanose ($J_{1'',2a''}$ = 4.5 Hz, $J_{1'',2e''}$ = ~1 Hz). These assignments corroborate previous molecular rotational difference determinations.[22]

The proposed structure is not unexpected in view of the suggested common biosynthetic origin of the various macrolide antibiotics.[23,24] The assignment of structure **1** to lankamycin removes the only discrepancy in the pattern of sugar substitution. All described 14-membered aglycone ring macrolide antibiotics, erythromycin A,[25] B,[26] and C,[27,28] oleandomycin,[29] lankamycin,[1] picromycin,[30,31] narbomycin,[32] and megalomicin A,[33] have now been shown to have a 4,6-dideoxy- or 3,4,6-trideoxy-3-dimethylamino-D-*xylo*-hexopyranose (D-desosamine[34,35] or D-chalose[6,7]) attached to the C-5 secondary hydroxyl *via* a β-glycoside bond;[22] a 2,6-dideoxy-L-hexopyranose of differing stereochemistry (L-cladinose,[36,37] L-mycarose,[37] L-oleandrose,[38] or 4-*O*-acetyl-L-arcanose[8]) is attached to the C-3 secondary hydroxyl, when present, *via* an α-glycoside bond.[22]

Acknowledgments. The authors acknowledge a generous gift of lankamycin from Dr. Ernst Vischer of Ciba Limited, Basle, Switzerland.

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The Stimulated Raman Effect. A New Source of Laser Temperature-Jump Heating[1]

Sir:

The temperature-jump technique is widely used for the study of rapid chemical reactions.[2] In this technique a capacitor is discharged through a cell containing the solution of interest, thereby raising its temperature 1–10° in about 10^{-6} sec. This type of heating can be employed only with solutions of moderately high ionic concentrations. It has been pointed out[3,4] that the use of optical heating with a Q-switched laser is not subject to this limitation. Moreover a laser temperature-jump apparatus can have a heating time of 10^{-8} sec or less by using a cavity-dumped[5] or mode-locked

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