those of II, IV, VI. The difference between the 2 demycarosyl derivatives is assumed to come from the fatty acid moieties at carbon 3. And the differences among 9-dehydromaridomycin I, III, V and among 9-dehydromaridomycin II, IV, VI, all come from the fatty acid moieties at carbon 4″. On the basis of these findings, the structures of maridomycins were proposed as shown in the Figure.

To confirm the proposed structures, the mass fragmentation patterns[4] of each component and their derivatives were inspected (Table III).

Comparison of Maridomycin I and II; Maridomycin I shows molecular peak at 857, which is 14 mass unit greater than that of II. The fragments (1), (2), (3), (4), (9) and (10) correspond to aglycone moieties and show 1 methylene (*m/e* 14) difference between I and II.

The fragments (11), (12), (13) and (14) indicate that they have the same acylsugar moiety.

These mass patterns and the liberation of propionic acid from I with alkali hydrolysis suggest that the propionyl group is located at carbon 3 or 9. The NMR spin decoupling study excludes the possibility of carbon 9. The elimination mechanism of the propionic acid accounts for the fragments (5), (6), (7) and (8).

Thus it was concluded that I has propionyl group at carbon 3 instead of acetyl group at carbon 3 in II.

The mass spectra of I-diacetate (XXXI), I-dipropionate (XXXII), I-9-propionate (XXXIII) and I-2′-propionate (XXXIV) together with their NMR-spectra and *p*Ka′ values support the structure of I.

The structures of other maridomycin components were established analogously as shown in the figure[5].

Zusammenfassung. Strukturaufklärung einer Gruppe von Antibiotika aus der Reihe der Makrolide.

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Antimony Trichloride Catalyzed Reactions on Terpenoids, a Nucleophilic Addition Reaction on Khusinol

Unlike the well-known Lewis acids, aluminium chloride and boron trifluoride, which are extensively used in structural and synthetic organic chemistry, there is no similar record in the literature about the use of antimony trichloride. Limited use of antimony trichloride has, however, been made in the rearrangement of phenolic ethers[1], and as a spray reagent for the identification of isoprenoids[2]. We have recently observed that antimony trichloride, unlike aluminium chloride and boron trifluoride, uniquely catalyses some reactions on terpenoids. In the present communication, an interesting addition of CH_3OH to the methylenic double bond of Khusinol[3] (1) in the presence of catalytic amount of antimony trichloride is described.

Khusinol (I), on warming briefly on water bath with a methanolic solution of antimony trichloride, affords a pale yellow mobile liquid from which a compound was isolated in a pure form (TLC) by column chromatography over alumina, in 90% yield. Chemical and spectroscopic data presented in this paper shows that this compound represents a hydroxy ether (II, $C_{16}H_{28}O_2$). All compounds gave satisfactory elemental analysis.

The IR-spectrum of the compound showed intense bands at 3450 cm^{-1} (hydroxyl group), 1060 (methoxyl group) and at 810 cm^{-1} (trisubstituted double bond). The compound gave a positive tetranitromethane test and the presence of only 1 olefinic linkage was confrimed by

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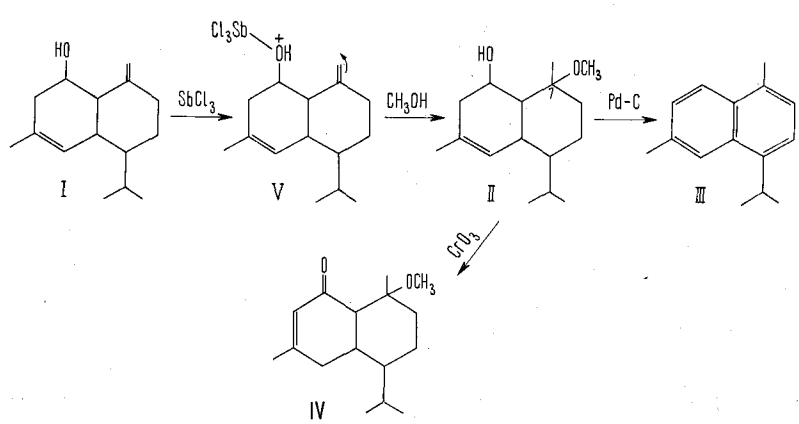

quantitative hydrogenation and peracid titrations. As dehydrogenation of (II) with Pd-C (30%) furnished cadalene (III) in quantitative yields as the only product of dehyrogenation (TLC on silica gel layers impregnated with sym trinitrobenzene, mp and mixture mp of the picrate with an authentic sample 116°) it was clear that the reaction product (II) contained the intact cadinane skeleton.

Oxidation of (II) with Jones reagent afforded a crystalline keto ether (IV, $C_{16}H_{26}O_2$, mp 121°) $\gamma c = O$ 1680 cm^{-1}, λmax 230 nm (This value is lower than expected for this chromophore, but is in good agreement with that observed [λmax 233 nm $\varepsilon 13{,}800$] for the oxidation product[3] of dihydro Khusinol which has an identical chromophore) ε 15,500, whereas prolonged oxidation of (II) with active manganese dioxide afforded only the parent compound back. These observations showed that Jones oxidation of (II) is attended by a double bond shift to afford an α, β-unsaturated ketone (IV). The NMR-spectrum of the oxidation product clearly demonstrates that it should be represented by (IV).

These spectral features and chemical reactions clearly established structure (II) for the reaction product. This structure could also be confirmed by the NMR-spectrum of (II) which displayed 2 doublets (3 H each) at 0.74 and 0.9 δ (J = 6 c/s) assignable to an isopropyl group situated in an assymetric environment. The singlet at 1.29 δ and 3.25 δ could be assigned to C-C-CH_3 and OCH_3, respectively. The broadened singlet at 1.63 δ could be assigned to a C = C-CH_3 grouping. The one proton signals at 4.72 (multiplet) and 5.3 δ (narrow multiplet) are assignable to CHOH and olefinic protons, respectively.

The formation of (II) is obviously not a simple electrophilic addition as this would require the trisubstituted double bond to react first. The formation of (II) can be rationalized[3] as an initial complexing (as in V) followed by proton transfer to yield an incipient carbonium ion at C_7 which may be attacked by the nucleophile in a stepwise or concerted reaction.

Zusammenfassung. Es wird eine neuartige Reaktion an einem Terpen beschrieben.

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Effects of Cyclophosphamide on the Chemical Composition of the Glomerular Basement Membrane and Non-Collagenous Urinary Glycoprotein of the Rat

Cyclophosphamide (Cytoxan) in addition to its uses as an immunosuppressive and anticarcinogenic agent and in treatment of rheumatoid disorders has been widely employed in the therapy of the idiopathic nephrotic syndrome (INS) of childhood, or lipoid nephrosis, with encouraging results[1]. Since this disease is not immunologically mediated[2], but possible the result of metabolic derrangements, and since it has been suggested that proteinuria may result from molecular alterations in the glomerular basement membrane (GBM)[3], it is possible that cyclophosphamide may modify proteinuria by altering the chemical composition of the glomerular capillary wall. We have isolated and characterized a urinary glycoprotein (MUPpg) from normal rat urine which resembles the non-collagenous component of GBM[4,5]. We have also described alterations in the chemical composition of this glycoprotein in nephrotic rats and suggested that increased permeability of the GBM may be associated with biochemical changes in this membrane related urinary glycoprotein (MUPpg). Although cyclophosphamide does not significantly modify proteinuria induced by administration of aminonucleoside promycin (AMP) to rats, it seemed reasonable to evaluate the effects of cyclophosphamide on the chemistry of normal rat GBM and rat urinary glycoprotein.

Materials and methods. Daily 24 h urine specimens were collected for 48 h from 100 normal Sprague-Dawley rats (150 g) for isolation of normal control MUPpg. 30 normal rats from this group (normal control) were sacrificied and their kidneys used for preparation of GBM. The remainder were divided into 2 groups. Group I (35 rats) received daily i.p. injections of cyclophosphamide 10 mg/kg 5 days per week for 6 weeks. Group II (35 rats) received 1 cm^3 of saline i.p. for 5 days per week for 6 weeks.

One week after cessation of injections, daily 24 h urine specimens were collected for 48 h from Groups I and II. The urine from each group was pooled and used for preparation of MUPpg. The rats were sacrificed and the kidneys from each group pooled for isolation of glomerular basement membrane. MUPpg was isolated as previously described[4,5] by DEAE ion exchange chromatography followed by Sephadex G 200 gel filtration. Glomerular basement membrane was isolated by the method of KRAKOWER and GREENSPON[6]. Aliquots of lyophyllized MUPpg and lyophylized GBM from control and both experimental groups of animals were hydrolyzed in 6 *N* HCl for 21 h for amino acid analysis. The NCl was removed by flash evaporation and amino acid analysis was performed on a Beckman amino acid analyzer by the method of SPACKMAN, MOORE and STEIN[7]. Materials were prepared for analysis of carbohydrates by hydrolysis at 110 °C for 4 h followed by chromatography on Whatman No.1 filter paper. Hexose[8], glucose and galactose (glucostat and galactostat enzymatic methods, Worthington Biochemicals) were determined quantitatively on GBM and MUPpg from the control and both experimental groups of animals.

Triplicate studies demonstrated the reproducibility of the carbohydrate analytic methods with the following

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