Tetrahedron. Vol. 25, pp. 3007 to 3015. Pergamon Press 1969. Printed in Great Britain

STUDIES ON JULIMYCINS—IV

THE STRUCTURES OF JULICHROMES $Q_{1\cdot3}$, $Q_{2\cdot3}$, $Q_{1\cdot4}$ AND $Q_{3\cdot4}$

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(*Received in Japan* 20 *December* 1968; *Received in the UK for publication* 9 *February* 1969)

Abstract—Among julichromes isolated from the metabolites of *Streptomyces shiodaensis*, julichromes $Q_{1\cdot3}$, $Q_{2\cdot3}$, $Q_{1\cdot4}$ and $Q_{3\cdot4}$ are established as new asymmetrical bianthraquinonyl derivatives composed of two different yet biogenetically close C_{19}-units. The spectroscopic examinations and the chemical experiments for the confirmation of the structures are described.

IN THE preceding paper,[1] the isolation and purification of julichromes, minor components of julimycin B-complex, were reported. This paper is concerned with the structures of julichromes $Q_{1\cdot3}$, $Q_{2\cdot3}$, $Q_{1\cdot4}$ and $Q_{3\cdot4}$.

Julichrome $Q_{1\cdot3}$ (I)* is isolated from SV fraction[1] as red prisms, m.p. 190–210°, and changes colour to violet with magnesium acetate. Although considerable fluctuation of the yield is observed by fermentation conditions, I is next to julimycin B-II in content.

Recrystallized and dried $Q_{1\cdot3}$ soon adsorbs 2·5 moles of water in the air, and the elementary analysis of the anhydrous sample gave the molecular formula, $C_{38}H_{36}O_{15}$, which was supported by the proton-counting on NMR spectrum and by the analyses of its derivatives.

The NMR spectrum† of I (cf. Fig. 1) evidently indicates that the molecule has an

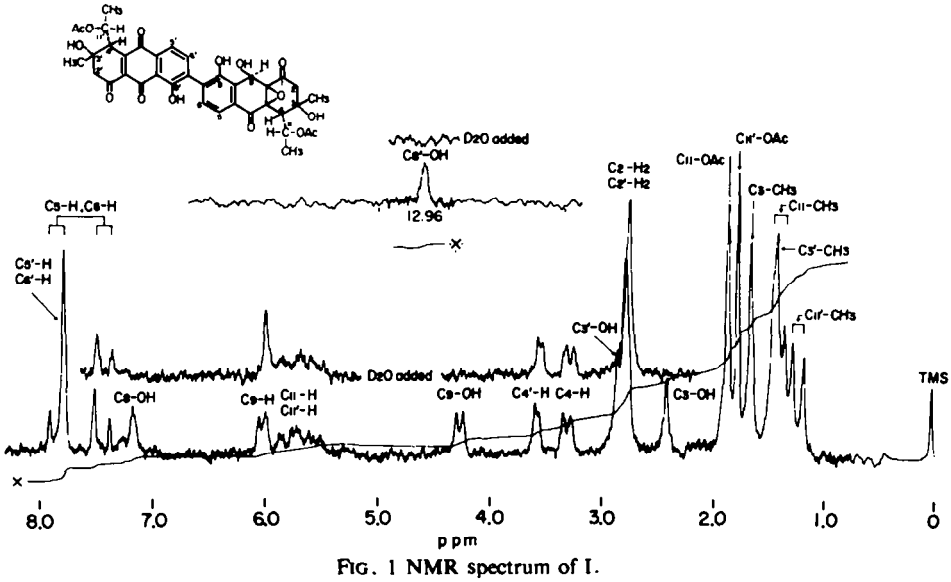


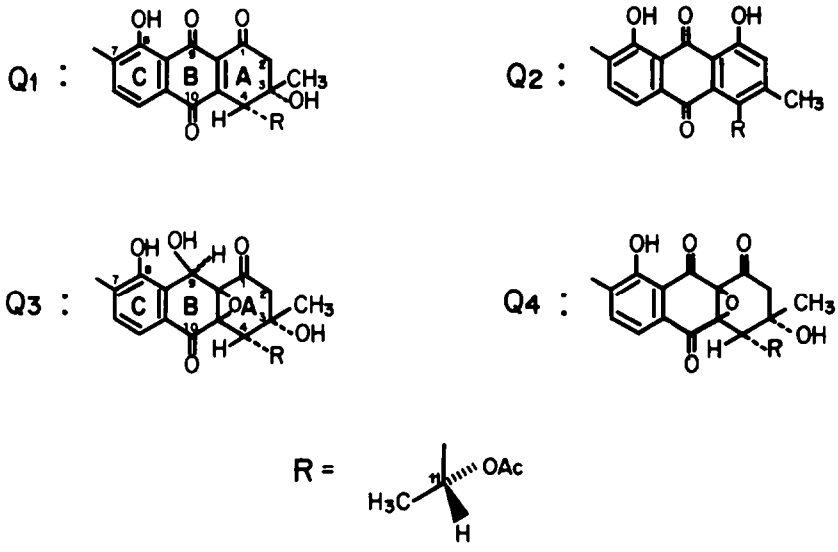
FIG. 1 NMR spectrum of I.

* I was early reported as julimycin SV by Katagiri *et al.*[2]

† NMR spectra were taken on a Varian A-60 spectrometer in $CDCl_3$ using TMS as internal reference. Chemical shifts are expressed in δ (ppm) downfield from TMS.

asymmetrical structure and includes the known Q_1 unit (cf. Chart 1) in comparison with the spectrum of julimycin B-II (Q_1—Q_1).

CHART 1



In order to confirm the presence of Q_1 unit, I was treated with pyridine.[3] As expected, this treatment gave monoanhydro derivative (II), $C_{38}H_{34}O_{14}$, and the product was proved to be identical with julichrome Q_2-3 isolated from B-I fraction.[1] The NMR spectrum of II clearly shows the presence of the signals due to the Q_2 unit in comparison with that of bisanhydro julimycin B-II (Q_2—Q_2).[3] The other observation in the NMR spectrum of II will be mentioned below.

In regard to the unknown Q_3 unit of I, the existence of a peri-hydroxy quinonoid

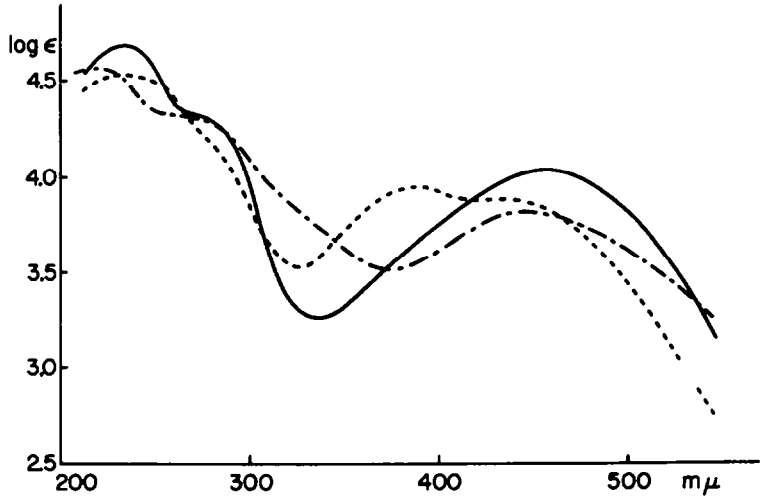


FIG. 2 UV spectra of I (—·—·—), III (– – – –) and julimycin B-II (————) in MeOH.

structure is denied because of the low intensity of UV band at 450 mμ compared with that of julimycin B-II (cf. Fig. 2). This is also supported by the absence of the chelated OH proton signal assignable to Q_3 unit. However, it is likely to assume that this Q_3 unit also has a ring system similar to Q_1 unit on account of its formula, $C_{19}H_{19}O_{18}$.

By the assignment of the NMR spectrum of I (cf. Fig. 1) the substituents on A ring (C_1—C_4) of Q_3 unit should be identical with those of Q_1 unit, though the stereochemistry is uncertain. Moreover, the structure of the C ring, having one phenolic OH group (δ, 7·13 ppm) and two *ortho* protons (δ, 7·47, 7£84 ppm, AB-quartet, J=8·0 c/s), would be the same as Q_1 unit from the biogenetical consideration. The presence of one phenolic OH group was confirmed by the methylation of I and II giving dimethyl and trimethyl ether, respectively.

Regarding the B ring, a quinol structure is most likely from the UV spectrum and analytical data. In fact, the proton signals at 6·03 ppm (doublet, J = 3·0 c/s) and 4·25 ppm (doublet, J = 3·0 c/s) are assignable as belonging to a benzylic secondary OH group. The former doublet was converted to a singlet simultaneously with the disappearance of the latter signal by deuterium exchange experiment, and the methine signal is too low for a proton at any position other than the benzylic C atom. The coupling aspect of $-\underset{|}{\overset{|}{C}}\underline{H}-\underline{O}H$ also suggests that the OH function is taking part in H-bonding and that the C atom adjacent to this benzylic C atom has no proton. If the speculation regarding to the position of the phenolic OH group is correct, the secondary OH group is presumably not located at C_{10} but at C_9, for the phenolic OH proton signal is not observed in the chelated OH region.

One O atom remained to be accounted for and it seems to be located at A/B juncture as an epoxide. Because, both C atoms at the juncture are quartanary from NMR, and

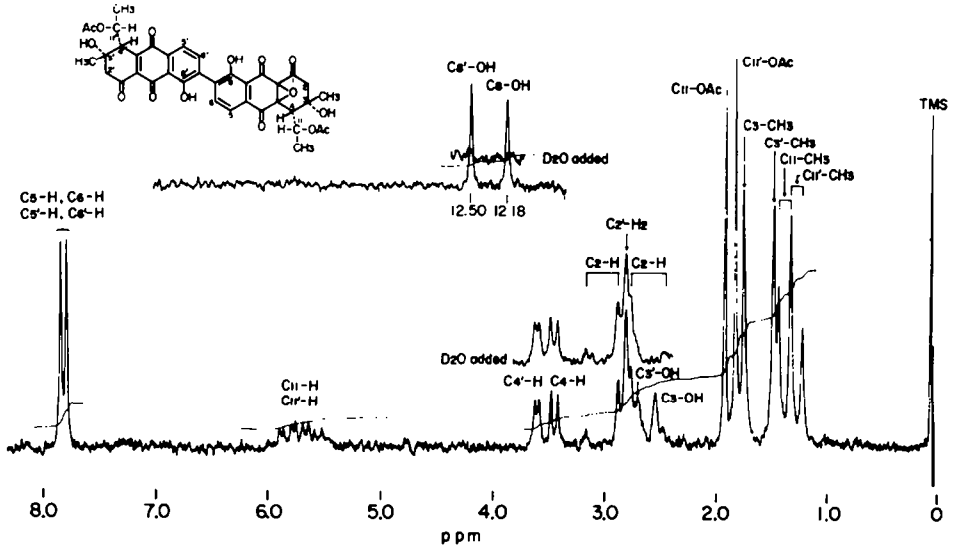


FIG. 3 NMR spectrum of III.

the Q_3 unit resists the aromatization (on heating with pyridine) and air oxidation which might be expected in a true quinol structure.

In order to ascertain the structure of B ring, the secondary OH group was oxidized with potassium bichromate in acetic acid. The product (about 60%) was identified as julichrome $Q_{1\cdot4}$ (III) isolated from B-I fraction[1] by comparison of IR and NMR spectra and of ORD curves.

Compound III shows the molecular formula, $C_{38}H_{34}O_{15}$, and the slightly higher spot than julimycin B-II on continuous development TLC.[1] The NMR spectrum, shown in Fig. 3, clearly indicates the presence of Q_1 unit, the absence of the secondary OH group and the shift of the phenolic OH proton signal into a lower field (12·18 ppm) suggesting the chelation of the OH function to the new CO group at C_9.

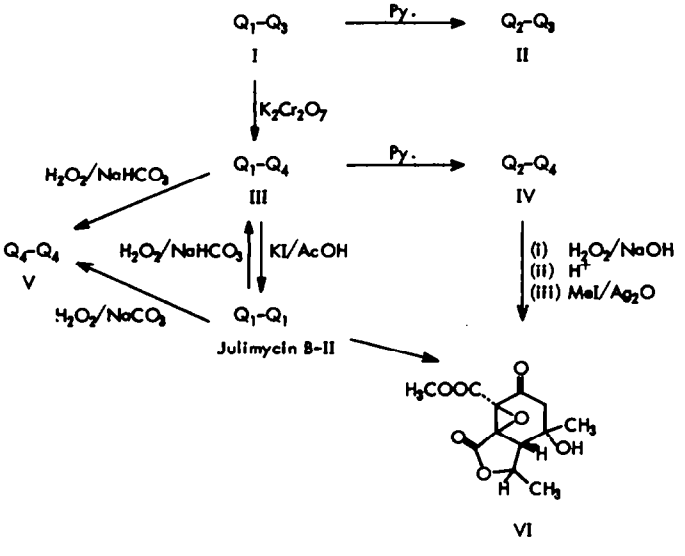
Nevertheless, the intensity of the UV band of III does not change so much at 450 mμ compared with that of I (cf. Fig. 2) supporting the existence of the epoxide ring at A/B juncture. Moreover, the treatment of III with pyridine gave the monoanhydro derivative (IV) as expected.

Thus, the structures of I, II and III were assumed as Q_1—Q_3, Q_2—Q_3 and Q_1—Q_4, respectively (cf. Chart 1), though the stereochemistry is unknown.

In order to confirm the existence of the epoxide ring, III was treated with potassium iodide in acetic acid[4] giving julimycin B-II (Q_1—Q_1) in an excellent yield. Further, the epoxidation of julimycin B-II with hydrogen peroxide gave III and julimycin B-II diepoxide (V) depending on the conditions. V was also obtained by the epoxidation of III. Subsequently, IV was degraded with hydrogen peroxide for the establishment of the configuration of the epoxide ring. The product, isolated as methyl ester (VI), was identical with the authentic specimen obtained from julimycin B-II.[5] Since it is clear that the product came from Q_4 unit and not from Q_2 unit, the configuration of the epoxide of the original pigment must be β.

From these interconversion and degradation experiments summarized in Chart 2, the

CHART 2



VI

stereochemistry of the compounds I, II and III as well as their structures was established except the configuration of C_9—OH in Q_3 unit (the problem will be discussed in the following paper).

Subsequently, the structure of julichrome $Q_{3\cdot4}$ (VII) isolated from SV fraction[1] is discussed. VII neither changes its colour with magnesium acetate nor exhibits chelated CO bands in IR spectrum, and its UV spectrum lacks the λ_{max} at 450 mμ. These observations suggest the absence of the peri-hydroxy quinonoid chromophore in its molecule. Moreover, VII precedes I (Q_1—Q_3) in elution order on TLC[1] as slightly as III (Q_1—Q_4) precedes julimycin B-II (Q_1—Q_1). This evidence, together with its molecular formula, $C_{38}H_{36}O_{16}$, suggests that VII has a structure of Q_3—Q_4.

As expected, the treatment of VII with potassium iodide in acetic acid afforded I, and epoxidation of I gave VII reversely. Further, VII was oxidized to V with potassium bichromate. These experiments shown in Chart 3 clearly confirm the structure of VII.

CHART 3

$$\underset{\text{I}}{Q_1—Q_3} \underset{H_2O_2/NaHCO_3}{\overset{KI/AcOH}{\rightleftharpoons}} \underset{\text{VII}}{Q_3—Q_4} \xrightarrow{K_2Cr_2O_7} \underset{\text{V}}{Q_4—Q_4}$$

The NMR spectra of all these compounds but II reveal the almost overlapping pattern of the signals attributable to each unit. In the case of II, the spectrum showed somewhat abnormal chemical shifts in the protons of Q_3 unit, especially of the substituents at A ring (cf. Table 1). This abnormal behaviour disappeared in the spectrum of trimethyl ether of II.

TABLE 1. THE CHEMICAL SHIFTS OF THE PROTONS ATTRIBUTABLE TO Q_3 UNIT (IN $CDCl_3$)

	II (50 mg/0·4 ml)	II (1 mg/0·4 ml)	I (40 mg/0·4 ml)	VII (22 mg/0·3 ml)
C_2—H_2	2·43 (ppm)	2·60	2·78	2·77
C_3—CH_3	1·38	1·55	1·67	1·65
C_3—OH	2·90		2·30	?
C_4—H	3·20		3·32	3·30
C_{11}—H	5·52		?	?
C_{11}—OAc	1·62	1·73	1·77	1·75
C_{11}—CH_3	1·38	1·38	1·42	1·40
C_9—H	6·05		6·03	5·98
C_9—OH	4·08		4·25	?
C_5—H	7·81		7·84	7·84
C_6—H	7·42		7·46	7·45

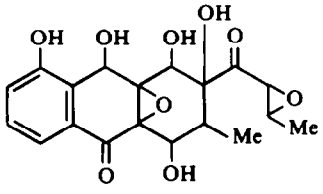
In order to make clear the abnormal spectrum of II, the spectrum was taken in a diluted solution. As shown in Table 1, the signals moved toward normal pattern. Moreover, the osmometric mol. wt. determination of II in chloroform solution gave a result consistent with that of NMR spectrum. As summarized in Table 2, the mol. wt. is varied depending on the concentration, and the experiment evidently indicates that II

is associated into a dimer at a concentration for ordinary NMR spectrum and gradually dissociated on dilution. Thus, it was concluded that the abnormal NMR spectrum of II is not due to the alternation of the conformation at A ring but to an intermolecular interaction.

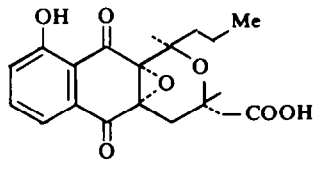
TABLE 2. MOL WT DETERMINATION OF II
(calc. for $C_{38}H_{34}O_{14}$: 714·65)

Sample (mg in 0·5 ml $CHCl_3$)	Mol. wt. (found)
29·022	1411
2·9022	818
0·58044	759

The structures of Q_3 and Q_4 units are closely related to cervicarcin (VIII)[6] and frenolicin (IX),[7] respectively. To our knowledge, however, julichrome is the first example which has such epoxynaphthoquinone moiety coupled with the anthraquinonyl



VIII



IX

moiety. The co-existence of these moieties in a molecule is interesting from the biogenetical point of view.

EXPERIMENTAL*

Julichrome Q_{1-3} (I)

I, recrystallized from MeOH, was hygroscopic and adsorbed 2·5 moles of water in the air. (Found: C, 58·55; H, 5·29; H_2O, 5·51; M.w. (osmometry in acetone). 777. $C_{38}H_{36}O_{15}\cdot 2\frac{1}{2}\ H_2O$ required: C, 58·68; H, 5·31; H_2O, 5·79%; M.w. 777·71). Analysis of the dried sample (at 150°) avoiding moisture gave the following data. (Found: C, 62·51; H, 5·10. $C_{38}H_{36}O_{15}$ requires: C, 62·29; H, 4·95%); IR ν_{max} (Nujol) cm^{-1}: 3615 (w.), 3470 (s.), 1700–1725 (v.s.), 1675 (s.), 1633 (m.); ORD: $|\phi|_{500}$ 0, $|\phi|_{470}$ +3050, $|\phi|_{410}$ +1490, $[\phi]_{359}$ +5820, $[\phi]_{334}$ 0, $[\phi]_{290}$ −17,390; CD: $[\theta]_{534}$ 0, $[\theta]_{500}$ −2640, $[\theta]_{462}$ 0, $[\theta]_{420}$ +2930, $[\theta]_{327}$ +21,200, $[\theta]_{300}$ +8900 (*c*, 0·1096 MeOH).

Dehydration of I *to* II

A soln of 500 mg I in 4 ml pyridine was heated on a steam bath for 2 hr. The pyridine was distilled off *in vacuo*, and the residue was chromatographed on metal free silica gel (5 g) and eluted with $CHCl_3$—MeOH (100 : 1). The eluate was evaporated, and the residue was recrystallized from benzene to give 293 mg II as yellow powder, m.p. 165–190° (dec). The continuous development TLC of the mother liquor gave additional 97 mg pure crop. (Found: C, 63·87; H, 4·81. $C_{38}H_{34}O_{14}$ requires: C, 63·86; H, 4·80%); UV λ_{max}(dioxan) mμ (log ε): 230 (4·54), 268 (4·54), 442 (4·15); IR ν_{max} (Nujol) cm^{-1}: 3480 (m.), 1741 (s.), 1714 (s.), 1690 (m.), 1670 (w.), 1628 (s.); ORD: $|\phi|_{570}$ +10.800, $|\phi|_{420}$ 0, $|\phi|_{352}$ +21.000, $|\phi|_{314}$ −14.900.

* M.ps were determined on hot plate and are uncorrected.

$[\phi]_{272}$ −5400, $[\phi]_{235}$ −19,900, $[\phi]_{218}$ +25,300. CD: $[\theta]_{400}$ 0, $[\theta]_{374}$ −7800, $[\theta]_{356}$ +17,200, $[\theta]_{310}$ 0, $[\theta]_{280}$ −17200, $[\theta]_{254}$ 0, $[\theta]_{210}$ −25,000 (*c*, 0·02258 MeOH).

This product was identical with the specimen isolated from julimycin B-complex in all respects.

Methylation of I (8,8′-O-*dimethyl ether*)

A soln of 100 mg I in 20 ml acetone was refluxed with 5 ml MeI in the presence of excess anhyd Ag_2O. After 2 hr, the mixture was filtered and the filtrate was evaporated to dryness. Recrystallization of the residue from MeOH gave 78 mg dimethyl ether as yellow needles, m.p. 250–260°. (Found: C, 63·01; H, 5·08; MeO, 8·31. $C_{40}H_{40}O_{15}$ requires: C, 63·15; H, 5·30; MeO, 8·16%); UV λ_{max} (dioxan) mμ (log ε): 228·5 (4·54), 375 (3·75).

Methylation of II (1′,8,8′-O-*trimethyl ether*)

A soln of 100 mg II in 20 ml acetone was treated with excess MeI and Ag_2O as described above. The crude product was purified by preparative TLC on metal free silica gel using $CHCl_3$—MeOH (9 : 1) and then by recrystallization from MeOH to afford 61 mg trimethyl ether as yellow needles, m.p. 255°. (Found: C, 64·87; H, 5·37; MeO, 11·91. $C_{41}H_{40}O_{14}$ requires: C, 65·07; H, 5·33; MeO, 12·30%); UV λ_{max} (dioxan) mμ (log ε): 228 (4·54), 268 (4·54), 370 (3·91).

Oxidation of I *with* $K_2Cr_2O_7$ *to* III

A soln of 500 mg II in 15 ml AcOH was heated with vigorous stirring on a boiling water bath, and to the soln a hot soln of 95 mg $K_2Cr_2O_7$ in 6 ml AcOH was added in six portions during 15 min. After additional 3 min, the mixture was poured into 300 ml H_2O and extracted with $CHCl_3$. The $CHCl_3$ soln was washed with H_2O, dried over $MgSO_4$ and evaporated to give 540 mg red product, which was separated by preparative TLC on metal free silica gel ($CHCl_3$—MeOH, 9 : 1). The product from main zone was recrystallized from MeOH to afford 290 mg III as red prisms, m.p. 200–220°. (Found: C, 62·38; H, 4·74. $C_{38}H_{34}O_{15}$ required: C, 62·46; H, 4·69%); IR ν_{max} (Nujol) cm^{-1}: 3600 (w.), 3545 (m.), 3412 (w.), 3293 (w.), 1720–1735 (s.), 1711 (s.), 1669 (m.), 1645 (w.), 1633 (w.); ORD: $[\phi]_{670}$ −450, $[\phi]_{530}$ −1420, $[\phi]_{470}$ +3950, $[\phi]_{422}$ +1970, $[\phi]_{385}$ +6710, $[\phi]_{318}$ −4640, $[\phi]_{279}$ −30,200, $[\phi]_{251}$ +36,900, $[\phi]_{240}$ +16,600; CD: $[\theta]_{570}$ 0, $[\theta]_{494}$ −4600, $[\theta]_{450-400}$ 0, $[\theta]_{348}$ +16,300, $[\theta]_{318}$ +7500, $[\theta]_{298}$ +11,400, $[\theta]_{285}$ 0, $[\theta]_{262}$ −46,600, $[\theta]_{246}$ 0. (*c*, 0·037 dioxan).

This product was identical with julichrome $Q_{1\cdot4}$ isolated from julimycin B-complex.

3,3′-O-*Diacetate of* III

A mixture of 90 mg III, 10 mg *p*-TsOH and 2 ml Ac_2O was stirred at room temp for 2 hr. The reaction mixture was poured into 30 ml H_2O, and the ppts were collected and washed with H_2O. Recrystallization of the ppts from MeOH gave 50 mg diacetate as red prisms, m.p. 210°. (Found: C, 61·76; H, 4·73. $C_{42}H_{38}O_{17}$ requires: C, 61·91; H, 4·70%).

Dehydration of III (IV)

A soln of 290 mg III in 5 ml pyridine was heated on a steam bath at 90° for 1 hr. The pyridine was distilled off *in vacuo*, and the residue was purified by preparative TLC ($CHCl_3$—MeOH 9 : 1) on metal free silica gel. Recrystallization from acetone gave 195 mg IV as fine orange powder, m.p. 210–220°. (Found: C, 63·43; H, 4·64. $C_{38}H_{32}O_{14}\cdot\frac{1}{2}H_2O$ requires: C, 63·24; H, 4·61%). The NMR spectrum clearly shows the signals assignable to Q_2 and Q_4 units.

Conversion of III *to julimycin* B-II

To a soln of 30 mg III in 6 ml AcOH 30 mg KI was added, and the mixture was stirred at room temp for 30 min. The reaction mixture was poured into H_2O and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with H_2O, dried over $MgSO_4$ and evaporated to give 30 mg almost pure product. Recrystallization from ethyl acetate gave 24 mg julimycin B-II. (Found: C, 63·73; H, 4·89. $C_{38}H_{34}O_{14}$ requires: C, 63·86; H, 4·80%); ORD: $[\phi]_{600}$ +2200, $[\phi]_{474}$ +12,600, $[\phi]_{414}$ +4400, $[\phi]_{340}$ +7100, $[\phi]_{280}$ −28,000, $[\phi]_{246}$ +30,600, $[\phi]_{240}$ +26,600 (*c*, 0·03224 MeOH).

This product was identified as julimycin B-II by IR spectrum as well as ORD curve.

Epoxidation of julimycin B-II

(i) *Epoxidation to* III. A soln of 10 mg julimycin B-II in 2·5 ml MeOH and 0·3 ml 30% H_2O_2 was

cooled to −30°, and with stirring 0·3 ml 5% $NaHCO_3$ aq was added at once to the soln. The colour of the soln soon changed to violet. After 30 sec. the reaction mixture was acidified with 10% HCl and extracted with EtOAc. The EtOAc soln was washed with dil NaCl aq, dried over $MgSO_4$ and evaporated. The residue was separated by continuous development TLC on metal free silica gel using $CHCl_3$–MeOH (96:4) to afford 1 mg III, which was identified as the specimen isolated from julimycin B-complex by comparison of IR spectrum and TLC.

(ii) *Epoxidation to* V. To a soln of 50 mg julimycin B-II in 25 ml MeOH 1·5 ml of 30% H_2O_2 was added, and the soln was cooled to -30°. With stirring 0·75 ml 5% Na_2CO_3 aq was added dropwise to the soln. The colour of the soln changed to blue by initial addition but finally became yellow, and then the soln was acidified immediately with 10% HCl. The reaction mixture was treated as described above to afford 48 mg yellow amorphous powder, which was separated by continuous development TLC. The main product (20 mg) obtained from the second zone was recrystallized from $CHCl_3$–ether to give 13 mg V as yellow needles, m.p. >300°. (Found: C, 59·57; H, 4·66. $C_{38}H_{34}O_{16}\cdot H_2O$ requires: C, 59·68; H, 4·75%). Colour reaction with $Mg(OAc)_2$: negative.

Epoxidation of III *to* V

A mixture of 10 mg III, 5 ml MeOH and 0·2 ml 30% H_2O_2 was cooled to −20°, and 0·3 ml 5% $NaHCO_3$ aq was added with stirring to the mixture. After 4 min, the soln, which became pale yellow, was acidified with 10% HCl and treated as above. Recrystallization of main product (4 mg) from $CHCl_3$–ether gave 2·5 mg V, which was identical with above specimen in comparison of IR spectrum and TLC.

Acetylation of V (3,3′-O-*diacetate*)

A soln of 20 mg V in 2 ml Ac_2O was stirred at room temp in the presence of 20 mg *p*-TsOH for 2 hr. Working up as usual gave 20 mg crude acetate as yellow powder, which was purified by continuous development TLC on metal free silica gel using $CHCl_3$–MeOH (99·5:0·5) for 16 hr to give 11 mg pure acetate. For analysis, the acetate was recrystallized from MeOH to afford 6 mg yellow prisms, m.p. 207–215°. (Found: C, 60·92; H, 4.88. $C_{42}H_{38}O_{18}$ requires: C, 60·72; H, 4·61%); NMR δ(ppm): 12·18 ($C_{8,8'}$—OH, 2H, s.); 7·83 ($C_{5,5',6,6'}$—H, 4H, s.); 5·40 ($C_{11,11'}$—H, 2H, m.); 3·95 ($C_{4,4'}$—H, 2H, d. J = 3·5 c/s); 3·09, 2·86 ($C_{2,2'}$—H_2, 4H, AB-type q. J = 18·0 c/s); 2·04 ($C_{3,3'}$—OAc, 6H, s.); 1·95 ($C_{3,3'}$—CH_3, 6H, s.); 1·81 ($C_{11,11'}$—OAc, 6H, s.); 1·26 ($C_{11,11'}$—CH_3, 6H, d. J = 6·5 c/s).

Oxidative degradation of IV *with hydrogen peroxide*

To a suspension of 195 mg IV in 7 ml dioxan and 3·1 ml 30% H_2O_2 3·9 ml 5% NaOH was added dropwise with stirring. The stirring was continued at room temp for 10 min and then at 60° for 10 min. The mixture was acidified with dil HCl, and the excess H_2O_2 was decomposed with PtO_2. After removal of the dioxan *in vacuo*, the residue was dissolved in H_2O and washed with EtOAc. The pH of the H_2O soln was adjusted to about 5·0 with dil NaOH, chromatographed on 10 ml Dowex 50 (x12 proton type) and eluted with H_2O. The eluate was evaporated to dryness *in vacuo* to give 170 mg red syrup, which was methylated by refluxing for 3 hr with MeI and Ag_2O in 8 ml MeOH. The product (157 mg) was chromatographed on 10g silica gel and eluted with $CHCl_3$–MeOH (99·5:0·5–99:1). After elution of yellow oily mixture, 33 mg crystalline product was obtained. It was purified by recrystallization from $CHCl_3$ to afford 9 mg VI as colourless prisms, m.p. 209–210°. (Found: C, 53·64; H, 5·13. $C_{12}H_{14}O_7$ requires: C, 53·33; H, 5·22%); $[\alpha]_D^{24}$ −21·1° ±0·9° (*c*, 0·513 MeOH).

The mixed m.p. determination and the comparison of IR spectra proved that this product is identical with authentic specimen ($[\alpha]_D$ −19·9° ±2°) obtained from julimycin B-II in similar procedure.

Julichrome $Q_{3,4}$ (VII)

Compound VII, isolated from julimycin B-complex, was purified from ether to give yellow amorphous powder. It softens at about 275° but does not melt below 280°. (Found: C, 59·63; H, 5·17; H_2O, 2·29. $C_{38}H_{36}O_{16}\cdot H_2O$ requires: C, 59·53; H, 5·00; H_2O, 2·35%). Analysis of the dried sample (at 120°) avoiding the moisture gave the following data. (Found: C, 60·60; H, 5.13. $C_{38}H_{36}O_{16}$ requires: C, 60·96; H, 4·85%); UV λ_{max} (MeOH) mμ (log ε): 208·5 (4·48), 267 (4·25), 370 (3·94); IR ν_{max} ($CHCl_3$) cm^{-1}: 3584 (w.), 3424 (m.), 1736 (s.), 1698 (s.), 1650 (m.); ORD: $|\phi|_{600}$ 0, $|\phi|_{376}$ +9830, $|\phi|_{314}$ −25,600, $|\phi|_{291}$ −7860, $|\phi|_{269}$ −37,000, $|\phi|_{249}$ 0, $|\phi|_{231}$ −32,400, $|\phi|_{218}$ +24,600; CD: $|\theta|_{380}$ 0, $|\theta|_{336}$ +16,200, $|\theta|_{311}$ 0, $|\theta|_{300}$ −13,000, $|\theta|_{280}$ 0, $|\theta|_{256}$ −32,400, $|\theta|_{240}$ −9730, $|\theta|_{230}$ −19,500, (*c*, 0·762 MeOH).

Compound I *from* VII

To a soln of 10 mg VII in 0·5 ml AcOH 20 mg KI was added, and the mixture was stirred at room temp for 30 min. Working up as usual gave 10 mg I which was identical with authentic specimen in comparison of IR spectra.

Epoxidation of I (VII)

A soln of 100 mg I in 50 ml MeOH and 2 ml H_2O_2 was cooled to −20° (bath temp), and 2 ml of 5% $NaHCO_3$ was added with stirring to the soln. The colour of the soln immediately changed to blue and then to yellow within one min. The soln was acidified with 10% HCl and extracted with EtOAc. The crude orange product was purified by continuous development TLC on metal free silica gel using $CHCl_3$–MeOH (93:7) to give 71 mg VII as yellow amorphous powder. (Found: C, 59·20; H, 4·91. $C_{38}H_{36}O_{16}\cdot H_2O$ requires: C, 59·53; H, 5·00%). The NMR spectrum showed the signals assignable to Q_3 and Q_4 units, and the IR spectrum and ORD curve were identical with those of the above-mentioned specimen isolated from julimycin B-complex.

Oxidation of VII *with potassium bichromate* (V)

A soln of 70 mg VII in 2·1 ml AcOH was heated on boiling water bath, and a hot soln of 14 mg K_2CrO_7 in 0·9 ml AcOH was added with stirring to the soln in 3 portions during 15 min. The reaction mixture was poured into H_2O and extracted with EtOAc. The extract gave 66 mg crude product, which was separated by continuous development TLC ($CHCl_3$–MeOH, 93:7) into 18 mg V and 10 mg unchanged material. V was recrystallized from $CHCl_3$–ether and identical with the sample obtained from julinycin B-II.

Acknowledgements—The authors indebted to Drs. K. Takeda and Y. K. Sawa of this Laboratory for their encouragement. They also thank Dr. T. Kimura and Mr. Kyotani for supplying julichrome Q_{1-3}.

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