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CORIAMYRTIN—XIII

THE REACTIONS OF ISOHYDROCORIAMYRTIN AND ISOCORIAMYRTIN WITH PHENYLHYDRAZINE ANALOGUES

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Abstract—The reactions of excess α-methylphenylhydrazine with isohydrocoriamyrtin (I), isohydrocoriamtrtin-methylphenylhydrazone (VI), or 11-O-methylisohydrocoriamyrtin-methylphenylhydrazone (VIII) produced the derivative III_a which has α-methylphenylhydrazino group at C-11. An analogous derivative V was produced in the reaction of α,α-diphenylhydrazine with isocoriamyrtin (IV). The reactions of 2,4-dinitrophenylhydrazine and *p*-bromophenylhydrazine with I did not yield any product corresponding to III_a.

THE structure of isohydrocoriamyrtin which is produced by the acid catalysed isomerization of dihydrocoriamyrtin was shown to be I in a previous work.[2] This compound gives the 2,4-dinitrophenylhydrazone II, $C_{21}H_{24}O_8N_4$.[2,3] However, the reaction of crude isohydrocoriamyrtin with excess α-methylphenylhydrazine in acetic acid has been reported to provide a derivative, III, $C_{29}H_{34-36}O_3N_4$, which contains two moles of methylphenylhydrazine.[4] This derivative III has been confirmed in the present study to be produced from pure isohydrocoriamyrtin, and the structure has been determined to be III_a, $C_{29}H_{36}O_3N_4$. The analogous reaction of isocoriamyrtin (IV) with α,α-diphenylhydrazine, which yielded V, and the reactions of isohydrocoriamyrtin with other phenylhydrazine analogues have also been investigated.

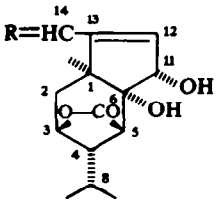
The IR spectrum of III shows retention of the γ-lactone at 1760 cm^{-1}. Therefore, this reaction should involve elimination of one of the two OH groups in isohydrocoriamyrtin. The mono-methylphenylhydrazone (VI), $C_{22}H_{28}O_4N_2$, has been prepared in the reaction of I with one mole of methylphenylhydrazine. The UV (Table 1) and NMR (5·40 τ, d, J = 3 c/s, 11-H; 5·54–5·24 τ, m, 3-H; 4·12 τ, d, J = 3 c/s,

TABLE 1. UV ABSORPTIONS OF ISOHYDROCORIAMYRTIN DERIVATIVES PRODUCED BY THE REACTIONS WITH α-METHYLPHENYLHYDRAZINE

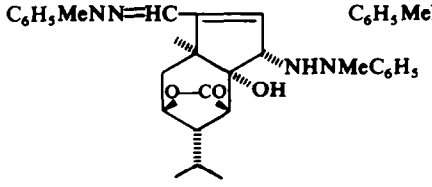
Compounds	Absorption (log ε)			
	226 mμ	248 mμ	305 mμ (shoulder)	328 mμ
III	(4·23)[a]	4·27	4·30	4·49
Methylphenylhydrazine	(3·65)	4·04	(3·27)	(2·08)
III–Methylphenylhydrazine	(4·10)	3·88	4·25	4·49
VI	4·12	3·89	4·24	4·43

[a] No peak is shown where the data are written in the parentheses.

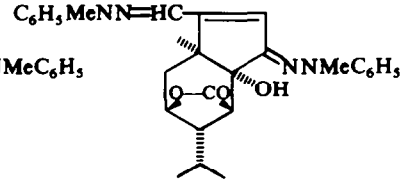
CHART 1



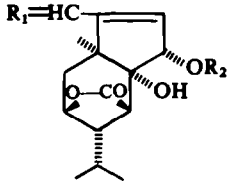
I: R = O
II: R = $NNHC_6H_3(NO_2)_2$
VI: R = $NNMeC_6H_5$
XIII: R = $NNHC_6H_5$



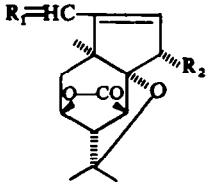
III_a



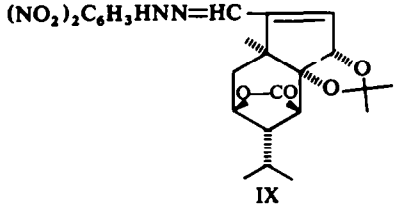
VII



VIII: R_1 = $NNMeC_6H_5$, R_2 = Me
X: R_1 = $NNHC_6H_3(NO_2)_2$, R_2 = Et
XI: R_1 = $NNHC_6H_3(NO_2)_2$, R_2 = Me
XII: R_1 = $NNHC_6H_4Br(p)$, R_2 = Me



IV: R_1 = O, R_2 = OH
V: R_1 = $(C_6H_5)_2NN$, R_2 = $(C_6H_5)_2NNH$



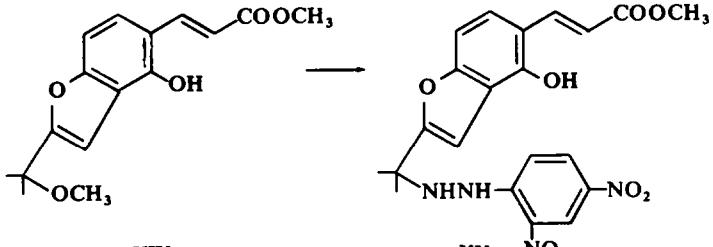
IX

12-H) spectra are in agreement with the structure VI. The reaction of methylphenylhydrazine with VI yielded the derivative III. As shown in the Table, the difference in the intensities of the UV absorptions between III and VI corresponds to one mole of methylphenylhydrazine. These UV spectra indicate that the conjugated system in the mono-methylphenylhydrazone VI is retained in III without any further conjugation. The NMR spectrum of III also shows retention of all protons on the carbon skeleton of isohydrocoriamyrtin including 11-H and 12-H which are exhibited at 6·00 τ (d, J = 3 c/s) and 4·12 τ (d, J = 3 c/s). These spectral evidence excludes the possibility that the structure of III is the 11,14-bis-methylphenylhydrazone VII, or that the attack by the second molecule of methylphenylhydrazine at C-13 accompanied by the allylic rearrangement occurred. Accordingly, the structure of III, except the configuration at C-11, can be represented by III_a which has been confirmed by further evidence as follows. The NMR spectrum of III also shows that there could be 36 protons, among which two disappear on the addition of D_2O. The protons on and around C-11 have been better characterized by the NMR spectrum measured in hexadeuteriodimethylsulfoxide: The signals assignable to 11-H and

12-H are exhibited at 6·25 τ (m) and 4·08 τ (d, J = 3 c/s), of which the former was transformed into a doublet (J = 3 c/s) on the addition of D_2O. A singlet at 4·88 τ and a diffused doublet at 5·10 τ, each of which corresponds to one proton, were shown to be OH and NH protons by disappearance on the addition of D_2O. The NMR spectrum (in $CDCl_3$) of III also exhibits 2-αH and 2-βH at 8·33 τ (d, J = 15 c/s) and 6·39 τ (d.d., J = 15 c/s, J' = 5 c/s) which are shown by isohydrocoriamyrtin at 8·37 τ (d, J = 15 c/s) and 6·90 τ (d.d., J = 15 c/s, J' = 5 c/s) respectively, to indicate the stronger deshielding effect by the C-14 methylphenylhydrazine moiety. The upfield shift of 11-H of III as compared with that of VI is attributable to the substituent at C-11.

The reaction of α,α-diphenylhydrazine with isocoriamyrtin (IV)[2] which does not have a free OH group at C-6 produced an analogous product V. This product, $C_{39}H_{38}O_3N_4$, shows UV absorption peaks at 246, 306 and 334 mμ, IR bands at 3400 (NH) and 1772 (γ-lactone) cm^{-1}, and NMR signals of aromatic protons (3·3–2·4 τ, H_{20}) and of C-11 and C-12 protons at 6·17 τ (d, J = 3 c/s) and 4·28 τ (d, J = 3 c/s) respectively, in agreement with the structure V. The reaction of I with excess diphenylhydrazine, and the reaction of IV with excess methylphenylhydrazine, performed in essentially the same manner as the preparation of III and V yielded oily products. Although these products were not completely purified even by repeated chromatography on silicic acid column, the NMR spectrum of the latter product shows approximately ten aromatic protons.

Although the formation of such a substitution product as III is unusual, there is an example of the substitution of an allylic OMe group in an athamantin derivative XIV by 2,4-dinitrophenylhydrazine in methanolic hydrochloric acid to produce XV, for which a resonance-stabilized carbonium ion as the intermediate has been presumed.[5]

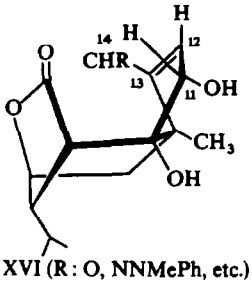


XIV XV

Evidence for the configuration of the methylphenylhydrazino group at C-11 in III has been provided as follows: Methoxylation of VI was carried out in methanol containing a small amount of sulphuric acid, or in a warm mixture of methanol and acetic acid, to produce VIII, $C_{23}H_{30}O_4N_2$, which shows MeO at 6·55 τ, and 11-H at 5·87 τ (d, J = 3 c/s) in the NMR spectrum. The UV and IR spectra are in accord with retention of the other part in the molecule of VI. No other product was isolated, nor detected as a distinct spot on TLC of the mother liquor. Upon the treatment with methylphenylhydrazine in acetic acid, this methoxide VIII gave III as the only isolable product. The spin–spin coupling constants of 11-H ~ 12-H in the NMR spectra of these compounds are the same as that of isohydrocoriamyrtin, and of isohydrocoriamyrtin 2,4-dinitrophenylhydrazone-acetonide (IX)[2] (J = 3 c/s). Stereomodels XVI show that the cyclopentene ring in these compounds is significantly

distorted so as to be considered to induce an appreciable difference of the J value between the dihedral angles 11-αH ~ 12-H and 11-βH ~ 12-H. The coupling constants calculated on the basis of these dihedral angles observed in the Dreiding steromodel, by taking J_0 values as originally proposed by Karplus,[6] are 0·54 c/s and

CHART 3



XVI (R: O, NNMePh, etc.)

2·52 c/s, respectively. Therefore the identity of the coupling constants of 11-H ~ 12-H among VI, VIII and III, and their J values appear to favor retention of the α-configuration of the substituents at C-11, if the Karplus equation is closely applicable for these parts of the molecules. Furthermore, the coincidence of the results in forming III by the two routes, directly from I or VI, and *via* the methoxyl derivative VIII, and also the fact that the methoxylation of VI occurred on the reaction condition analogous to that of the formation of III from VI, are in agreement with the retention of the configuration at C-11 in all of the three steps, VI → III, VI → VIII, and VIII → III, and consequently are indicative of the α-configuration of the methoxyl and the methylphenylhydrazino group at C-11 in VIII and III. Any product presumable to be the C-11 epimer of III and VIII upon these reactions was not detected on TLC. The diphenylhydrazino group at C-11 in V would also be oriented α by the analogy of the reaction with the formation of III, and this configuration is supported by the identity of the coupling constant of 11-H ~ 12-H with that of IV (J = 3 c/s).

The stereospecificity of these substitution reactions at C-11, which occurred in spite of the mechanism which could be presumed to be nucleophilic substitutions *via* cations at C-11, might be attributable to the steric hindrance or the neighbouring group participation by the lactone carbonyl located near C-11 on the β-side.[2] The neighbouring group participation by 6-OH is improbable because it should cause inversion of the configuration at C-11. The invalidity of this participation by 6-OH is also substantiated by the production of 11-diphenylhydrazinoisocoriamyrtin diphenylhydrazone (V) from isocoriamyrtin (IV).

When I or II was treated either at room temperature or at elevated temperature, with a solution of 2,4-dinitrophenylhydrazine in aqueous ethanol containing sulphuric acid, the products were mixtures of II and its 11-ethoxide X, $C_{23}H_{28}O_8N_4$. The NMR spectrum of X shows signals assignable to an OEt group at 8·74τ (t, J = 7 c/s) and 6·28 τ (q, J = 7 c/s) along with the signals which indicate the retention of the other part of the structure II. The UV and IR spectra of X, λ_{max} 259 (4·04), 290 (3·75) and 372 mμ (log ε 4·39); ν_{max} 1765 cm^{-1} are also in agreement with the simple ethoxylation. No other product was detected in appreciable amount on TLC and elution chromatography. This ethoxide was also obtained when II was treated with a warm mixture of ethanol and sulphuric acid, and an equilibrium mixture was produced

when either II or X was warmed with aqueous ethanol containing sulphuric acid. On the treatment of I with 2,4-dinitrophenylhydrazine in methanolic hydrochloric acid, 11-O-methylisohydrocoriamyrtin 2,4-dinitrophenylhydrazone (XI), $C_{22}H_{26}O_8N_4$ alone was obtained. The reactions of I with excess *p*-bromophenylhydrazine either in acetic or methanolic hydrochloric acid has not yielded any compound corresponding to III. The *p*-bromophenylhydrazone prepared by the reaction of equimolar *p*-bromophenylhydrazine with I was hardly purified, but 11-O-methylisohydrocoriamyrtin *p*-bromophenylhydrazone (XII), $C_{22}H_{27}O_4N_2Br$, was obtained by treating I with a warm methanolic solution of *p*-bromophenylhydrazine hydrochloride. The reaction of I with one mole of phenylhydrazine in acetic acid yielded the phenylhydrazone XIII, $C_{21}H_{26}O_4N_2$. However, the reaction of excess phenylhydrazine either with I or the phenylhydrazone XIII in acetic acid resulted in production of tarry mixtures from which no expected product was isolated by chromatography. The treatment of I with excess 2,4-dinitrophenylhydrazine in acetic acid produced II only. The treatment of 11-O-methylisohydrocoriamyrtin methylphenylhydrazone (VIII) with a solution of methylphenylhydrazine in 1% methanolic sulphuric acid resulted in the recovery of VIII. These results show that the substituents in the phenylhydrazine analogues besides the acids used as the catalyst exert marked effects on the substitution reactions at C-11.

EXPERIMENTAL

M.ps are uncorrected. UV spectra were taken in EtOH, and IR spectra in KBr. Unless otherwise stated, NMR spectra were measured in $CDCl_3$ with TMS as an internal standard on a Varian A-60 spectrometer, and coupling constants are shown by c/s. TLC was developed on Silica Gel G acc. to Stahl (E. Merck, 0·25 mm) in $CHCl_3$–MeOH (95:5), which induced satisfactory separation of the C-11 hydroxyl hydrazones from their corresponding C-11 substituted derivatives. The elution chromatography was run on Mallincrodt's silicic acid (100 mesh) in $CHCl_3$. The ratios of the mixed solvents are shown by vol/vol, and the concentrations of the compounds and the acids are shown by grav/vol.

11-*Methylphenylhydrazino-isohydrocoriamyrtin methylphenylhydrazone* (III) *from isohydrocoriamyrtin* (I).

Excess α-methylphenylhydrazine and I (50 mg) in AcOH (0·5 ml) were heated on a boiling water-bath for 10 min, and then kept at room temp overnight. Yellow crystals were filtered off and washed with water (44 mg). Recrystallization from EtOH gave pale yellow crystals of III, m.p. 206–207° (dec); λ_{max} (log ε) 248 (4·27), 305 (shoulder, 4·30), 328 mμ (4·49). ν_{max} 3210 (OH, NH), 1760 (γ-lactone) cm^{-1}; NMR 9·10 (d, J = 6), 8·90 (d, J = 6) (8-Me_2), 8·55 (s, 1-Me), 8·33 (d, J = 15, 2-αH), 6·39 (dd, J = 15, J' = 5, 2-βH), 7·90–7·70 (m, 4-H, 8-H), 7·38 (d, J = 4, 5-H), 6·92 (s), 6·73 (s, MeN × 2), 6·00 (d, J = 3, 11-H), 5·40 (m, 3-H), 4·12 (d, J = 3, 12-H), 3·3–2·5 τ (m, ArH_{10} and 14-H); NMR (in DMSO-D_6) 6·25 (d, J = 3, 11-H), 5·10 (d, J = 5, NH), 4·88 (s, OH), 4·08 τ (d, J = 3, 12-H). (Found: C, 71·13; H, 7·33; N, 11·75. Calc. for $C_{29}H_{36}O_3N_4$. C, 71·28; H, 7·43; N, 11·47%).

Isohydrocoriamyrtin methylphenylhydrazone (VI)

To a soln of I (39·6 mg) in 3 drops of EtOH, 10% soln (0·20 ml) of α-methylphenylhydrazine in AcOH aq (67%) was added. After standing at room temp for 30 min, deposited crystals were filtered off (53·8 mg), and recrystallized from MeOH–water. m.p. 183–185° (dec); λ_{max} (log ε) 248 (3·89), 305 (4·24, shoulder), 328 mμ (4·43); ν_{max} 3540, 3455, 1763 cm^{-1}; NMR 9·09 (d, J = 6), 8·87 (d, J = 6) (8-Me_2), 8·55 (s, 1-Me), 6·70 (s, MeN), 8·34 (d, J = 15, 2-αH), 6·32 (dd, J = 15, J' = 5, 2-βH), 7·30 (d, J = 4, 5-H), 5·40 (d, J = 3, 11-H), 5·54–5·24 (m, 3-H), 4·12 (d, J = 3, 12-H), 3·3–2·6 τ (m, ArH and 14-H). (Found: C, 68·77; H, 7·46; N, 7·05. $C_{22}H_{28}O_4N_2$ requires: C, 68·72; H, 7·34; N, 7·29%).

11-*Diphenylhydrazino-isocoriamyrtin diphenylhydrazone* (V)

Excess α,α-diphenylhydrazine in a mixture of AcOH and water (1:1) was added to a soln of isocoria-

myrtin (55·5 mg) in AcOH, and the reaction mixture was heated on a boiling water-bath for 10 min. After standing at room temp for 30 min, yellow crystals were filtered off (47·2 mg). Recrystallizing twice from EtOH with the aid of charcoal, and once from MeOH, yellow crystals, m.p. 214–215° (dec) were obtained; λ_{max} (log ε) 246 (4·19), 306 (4·31), 334 mμ (4·34); ν_{max} 3400, 1772 cm^{-1}; NMR 8·61 (s), 8·40 (s, 8-Me_2), 8·25 (s, 1-Me), 6·17 (d, J = 3, 11-H), 4·28 (d, J = 3, 12-H), 3·3–2·4 τ (m, ArH_{20}). (Found: C, 76·41; H, 6·55; N, 9·12. $C_{39}H_{38}O_3N_4$ requires: C, 76·69; H, 6·27; N, 9·17%).

11-O-*Methylisohydrocoriamyrtin methylphenylhydrazone* (VIII)

Crystals of VI (53·8 mg) were dissolved in 1% soln of H_2SO_4 in MeOH (0·5 ml). On standing at room temp for a few min, the soln started to deposit crystals which then formed a semi-solid mass. After filtration, the product (37·2 mg) was recrystallized from MeOH to yield colourless needles of VIII, m.p. 179–182° (dec); λ_{max} (log ε) 248 (4·11), 305 (4·24, shoulder), 328 mμ (4·44); ν_{max} 3470, 1764 cm^{-1}; NMR 6·55 (s, 11-OMe), 5·87 (d, J = 3, 11-H), 4·07 τ (d, J = 3, 12-H). (Found: C, 69·18; H, 7·82; N, 6·89. $C_{23}H_{30}O_4N_2$ requires: C, 69·32; H, 7·59; N, 7·03%).

11-*Methylphenylhydrazino-isohydrocoriamyrtin methylphenylhdrazone* (III) *from isohydrocoriamyrtin methylphenylhydrazone* (VI) *and from* 11-O-*methylisohydrocoriamyrtin methylphenylhydrazone* (VIII)

(a) *From* VI. To a soln of VI (4 mg) in AcOH (a drop), 10% soln of α-methylphenylhydrazine in AcOH–water (67%, 3 drops) was added, and the reaction mixture was heated on a boiling water-bath for a few min. After cooling, crystals were filtered off, and recrystallized from EtOH, m.p. 194–198°. The product was identified as III by IR spectra, mixed m.p., and TLC.

(b) *From* VIII. VIII was treated with α-methylphenylhydrazine in analogous way as above, and the product was identified as III by IR comparison, mixed m.p., and TLC.

Isohydrocoriamyrtin phenylhydrazone (XIII)

To a saturated soln of I (49·9 mg) in EtOH, 10% soln of phenylhydrazine in 67% AcOH–water (0·25 ml) was added. On scratching, a semi-solid mixture was effected from which crystals were collected by filtration (62·5 mg). Recrystallization from MeOH provided pale yellow crystals, m.p. 219–220° (dec); λ_{max} (log ε): 248 (3·88), 303 (4·07), 336 mμ (4·35); ν_{max} 3425, 3285, 1765 cm^{-1}. (Found: C, 67·98; H, 7·37; N, 7·41. $C_{21}H_{26}O_4N_2$ requires: C, 68·09; H, 7·07; N, 7·56%).

Isohydrocoriamyrtin 2,4-*dinitrophenylhydrazone* (II)

(a) Isohydrocoriamyrtin (6·3 mg) was added to a warm soln of 2,4-dinitrophenylhydrazine (9 mg) in AcOH (1·5 ml). The resultant soln was heated on a boiling water-bath for 30 min, and then evaporated *in vacuo*. The residue which was shown to be almost a single product on TLC was recrystallized from MeOH to give orange crystals, m.p. 275–278° (dec); λ_{max} (log ε) 260 (4·15), 290 (3·90), 375 mμ (4·49); ν_{max} 3445, 3265, 1765, 1745 cm^{-1}. NMR (DMSO-D_6) 5·63 (d, J = 3, 11-H), 3·81 (d, J = 3, 12-H), −1·48 τ (s, chelated NH). (Found: C, 54·62; H, 5·13; N, 12·18. Calc. for $C_{21}H_{24}O_8N_4$: C, 54·78; H, 5·25; N, 12·17%).

(b) A soln of 2,4-dinitrophenylhydrazine (75 mg) in EtOH–water–H_2SO_4 (14:4:5·6, 2·5 ml) was added to a soln of I (50 mg) in EtOH. The reaction mixture was warmed on a boiling water-bath for 1 min, and left to stand at room temp overnight. Orange-yellow crystals which showed two spots on TLC were filtered off (67 mg), and were chromatographed on a column (1·2 × 11 cm). After fast moving fraction was eluted, slow fraction was collected, and the solvent was distilled. The residue was recrystallized from $CHCl_3$ to yield orange crystals which were identified as II.

11-O-*Ethylisohydrocoriamyrtin* 2,4-*dinitrophenylhydrazone* (X)

(a) The fast moving fraction of the chromatography in the above experiment was distilled, and the residue was recrystallized from MeOH to yield yellow crystals, m.p. 269–271° (dec); λ_{max} (log ε): 259 (4·04), 290 (3·75), 372 mμ (4·39); ν_{max} 3480, 3290, 1765 cm^{-1}; NMR 8·74 (t, J = 7, 11-$OCH_2\underline{CH_3}$), 6·28 (q, J = 7, 11-$OC\underline{H_2}CH_3$), 5·75 (d, J = 3, 11-H), 3·65 (d, J = 3, 12-H), −1·01 τ (s, chelated NH). (Found: C, 56·25; H, 5·93; N, 11·29. $C_{23}H_{28}O_8N_4$ requires: C, 56·55; H, 5·78; N, 11·47%).

(b) A soln of 2,4-dinitrophenylhydrazine in EtOH (6 ml) containing 0·8 ml of H_2SO_4 was added to a soln of I (50 mg) in EtOH, and the mixture was warmed on a boiling water-bath for 5 min. After cooling, yellow crystals were filtered off, and recrystallized from EtOH. This product was identified as X.

(c) A soln of II in EtOH containing H_2SO_4 (10%) was refluxed on a boiling water-bath for 10 min. After cooling, ppt was recrystallized from $CHCl_3$–MeOH to give yellow crystals which were identified as X.

11-O-*Methylisohydrocoriamyrtin* 2,4-*dinitrophenylhydrazone* (XI)

A soln of II (25·5 mg) in 1·5 ml of 20% H_2SO_4–MeOH was heated on a boiling water-bath for 10 min. Deposited yellow crystals were filtered off and washed three times with a small amount of MeOH (21·8 mg). After recrystallization from MeOH, the crystals were chromatographed. Crystals obtained from the eluate in $CHCl_3$ were recrystallized from MeOH to give yellow needles of XI, m.p. 264–265° (dec); ν_{max} 3470, 3270, 1762 cm^{-1}. λ_{max} (log ε) 260 (4·08), 290 (3·81), 375 mμ (4·44). NMR 6·45 (s, OMe), 5·79 (d, J = 3, 11-H), 3·57 τ (d, J = 3, 12-H). (Found: C, 55·52; H, 5·60; N, 11·63. $C_{22}H_{26}O_8N_4$ requires: C, 55·69; H, 5·52; N, 11·81%).

11-O-*Methylisohydrocoriamyrtin* p-*bromophenylhydrazone* (XII)

A soln of *p*-bromophenylhydrazine hydrochloride (5 mg) in MeOH was added to a soln of I (5·3 mg), and 1 hr later, the mixture was concentrated *in vacuo* at room temp to give a crystalline ppt. This crude product was shown by TLC to contain two compounds. The soln of this mixture in 1% H_2SO_4–MeOH was heated on a boiling water-bath for 6 min, and then concentrated *in vacuo* to give a crystalline ppt which showed on TLC to be almost a single product corresponding to the faster spot of the product on the reaction at room temp. A larger amount of this compound was prepared by heating the soln of I and *p*-bromophenylhydrazine hydrochloride in MeOH for 5 min, and the crystalline product which showed on TLC the faster spot only was recrystallized from MeOH–water and subsequently from MeOH, and then chromatographed. The crystals obtained from $CHCl_3$ eluate were recrystallized from MeOH to yield pale yellow needles, m.p. 200–202° (dec); λ_{max} (log ε) 254·5 (3·92), 313 (4·28), 343 mμ (4·41); ν_{max} 3470, 3350, 1767 cm^{-1}; NMR 6·55 (s, OMe), 5·89 (d, J = 3, 11-H), 4·08 τ (d, J = 3, 12-H). (Found: C, 56·88; H, 6·11; N, 5·91. $C_{22}H_{27}O_4N_2Br$ requires: C, 57·02; H, 5·87; N, 6·05%).

Reaction of 11-O-*methylisohydrocoriamyrtin methylphenylhydrazone* (VIII) *with methylphenylhydrazine in* H_2SO_4–MeOH

To a soln of VIII (5·3 mg) in MeOH (5 ml) was added 10% soln of α-methylphenylhydrazine in 1% H_2SO_4–MeOH (0·035 ml). After standing at room temp for 20 min, the soln was concentrated *in vacuo* at room temp, and ppt was filtered off. This ppt was identified as VIII. No product in the appreciable amount was detected on TLC.

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