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1α,2α-EPOXYSCILLIROSIDINE, THE MAIN TOXIC PRINCIPLE OF *HOMERIA GLAUCA* (WOOD AND EVANS) N.E. BR.

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Abstract—The structure of the main toxic principle of *Homeria glauca* (Wood and Evans) N.E. Br. has been established as 1α,2α-epoxyscillirosidine (II; R = H) by its degradation to a 1,4-dien-3-one also prepared from the known scillirosidine (I). NMR and CD measurements were used to determine the full stereochemistry.

HOMERIA GLAUCA (Wood and Evans) N.E. Br. (family Iridaceae) is one of the plants responsible for "tulp poisoning"[1] of live-stock in South Africa. Recently Naudé and Potgieter[2] succeeded in isolating the main toxic principle in a pure crystalline state and studied its pharmacological properties.

It was soon recognized that the main toxic principle was a bufadienolide closely related to scillirosidine (I)[3] and its structure has now been determined as 1α,2α-epoxyscillirosidine (II; R = H) by means of the following chemical and spectroscopic evidence.

The molecular formula was established as $C_{26}H_{32}O_8$. The substance contained an acetoxy group (acetyl determination, IR and NMR evidence) and gave a 6-deacetoxy-derivative. A secondary hydroxy group could be acetylated to give a monoacetate (II; R = Ac). The monoacetate contained at least two further hydroxy groups (active hydrogen determination). Two oxygen atoms are present in an α-pyrone side chain which gave rise to an UV absorption band at 300 mμ (ε 5700), the appropriate IR bands at 1718, 1639, 1538 and 835 cm^{-1} and, in the NMR spectrum, to three protons at low field showing the expected splitting pattern [τ 3·74 (two doublets, J = 10 and 1 c/s), proton at position 23; τ 2·77 (quartet, J = 2·5 and 1 c/s), proton at position 21, and τ 2·13 (two doublets, J = 10 and 2·5 c/s), proton at position 22]. These signals are also observed in the spectrum of scillirosidine. As the NMR spectrum also indicated the presence of two quaternary-attached methyl groups at τ 9·14 and 8·62, and had a two-proton multiplet between τ 6·6–6·9 which showed no

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[1] J. M. Watt and M. G. Breyer-Brandwijk, *The Medicinal and Poisonous Plants of Southern and Eastern Africa* (2nd Ed.) p. 504–513, E. and S. Livingstone Ltd, Edinburgh and London (1962).

[2] T. W. Naudé and D. J. J. Potgieter, *J. S. Afr. Vet. Med. Assoc.* **37**, 73 (1966).

[3] A. von Wartburg and J. Renz, *Helv. Chim. Acta* **42**, 1620 (1959).

downfield shift on acetylation, it was concluded that the toxic principle is a new bufadienolide containing a 1,2-epoxy group.

The chemical behaviour of the new bufadienolide closely paralleled that of scillirosidine (I).[3] The presence of a 3-hydroxy-4-en-6-acetoxy grouping is evident from oxidation and hydrogenation experiments. Oxidation with manganese dioxide in chloroform gave the α,β-unsaturated ketone (III), which had λ_{max} 223 mμ (ε 14,450). The corresponding derivative from scillirosidine had an UV absorption maximum at 227 mμ (ε 16,200); the hypsochromic shift (241 → 227 mμ) has been ascribed[3] to the presence of both the 6β-acetoxy and 8β-hydroxy groups.

On catalytic hydrogenation in ethanol over palladized calcium carbonate, 3 mole of hydrogen were absorbed to give a deacetoxy derivative (IV; R = H) which showed no selective UV absorption. An analysis of the NMR spectrum of the monoacetate (IV; R = Ac) confirmed the presence of a $\Delta^{5(6)}$-double bond (see below).

TABLE 1. (*m/e* with relative intensities in brackets)

3-Dehydroscillirosidine	1α,2α-Epoxy-3-dehydro-scillirosidine	Fragment
396 (100%)	410 (57%)	M-60
378 (28%)	392 (16%)	M-60-18
261 (16%)	275 (26%)	M-195
243 (72%)	257 (100%)	M-213

The absence of protons alpha to hydroxy groups in the NMR spectrum of the α,β-unsaturated ketone (III) indicated that the remaining two hydroxy groups must be tertiary. They must also be both vicinal and cis, since the alcohol (II; R = H) reacted very rapidly with lead tetra-acetate in acetic acid. The oxidation product readily lost the acetoxy group at position 6 to give the fully conjugated dienone (V) showing λ_{max} 285 mμ (ε 17,400) and an IR band at 1740 cm^{-1} of a five-membered ring ketone. The formation of this product established positions 8 and 14 for the above two tertiary hydroxy groups and position 6 for the acetoxy group.

The very close relationship between the new bufadienolide and scillirosidine is clearly evident from a comparison of the IR and mass spectra of their 3-dehydro-derivatives. The two IR spectra are almost superimposable and differ only in bands near 1350 and 900 cm^{-1}. The mass spectra of these two compounds reveal a remarkable similarity. The four most abundant peaks in the higher mass range in the spectrum of the 3-dehydro-derivative (III) occur at 14 mass units ($+O$, $-H_2$) higher than those of the corresponding four most abundant peaks in the spectrum of 3-dehydroscillirosidine (cf. Table 1).

The two-proton multiplet observed in the NMR spectrum of the alcohol (II) between τ 6·6–6·9 is absent in the spectrum of scillirosidine and is due to the α protons of a 1,2-epoxy group.[4] In the spectrum of the 3-dehydro-derivative (III), this multiplet had moved down field to τ 6·3–6·6 and now appeared as a well-resolved pattern of six lines (AB part of an ABX-system; $J_{AB} = 4$, $J_{BX} = 2$, $J_{AX} = 0$ c/s). That one of the protons α to the epoxy group is spin-coupled to the olefinic proton at position

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[4] K. Tori, T. Komeno and T. Nagagawa, *J. Org. Chem.* **29**, 1136 (1964).

[5] C. Lehmann, *Études sur la photochimie de quelques époxycétones dans la série des stéroïdes.* D.Sc. Techn. Thesis, E.T.H. Zürich 1964 and private communication Dr. K. Schaffner, Zürich.

4 (appearing at τ 3·96, J = 2 c/s) was established by a double resonance experiment. Irradiation of the olefinic proton resonance led to a simplification of the pattern to an AB-system ($\Delta\nu_{AB}$ 11, J_{AB} = 4 c/s). The above six resonance lines are also observed in the NMR spectrum of 17β-acetoxy-1α,2α-epoxy-androst-4-en-3-one and also in its 1β,2β-epoxy-isomer.[5]

The new bufadienolide (II) and scillirosidine (I) were inter-related by the following reactions. Treatment of the 3-dehydro-derivative (III) with zinc dust in acetic acid gave two products, one of which, the 1,5-dien-3-one (VI), could be isomerized on alumina or by oxalic acid in ethanol to the other product which proved to be the 1,4-dien-3-one (VII). The structures of these two products followed from their molecular formulae, $C_{24}H_{28}O_5$, and spectroscopic properties. The 1,5-dien-3-one (VI) had λ_{max} 222 mμ (ε 16,100) and the 1,4-dien-3-one (VII) had λ_{max} 243 mμ (ε 14,900). The CD spectra were also determined. The 1,4-dien-3-one (VII) showed the expected negative Cotton effect at 310 (shoulder) mμ ($\Delta\varepsilon_{max}$ = −1·3) for its n–π* transition but the 1,5-dien-3-one (VI) had a positive Cotton effect at 337 mμ (Δε = +1·8). This must be due to homoconjugation between the Δ^5-double bond and the 1-en-3-one chromophore.

In the NMR spectrum of the 1,4-dien-3-one isomer (VII), determined in deuteriochloroform, the olefinic proton at position 1 appeared as a doublet (τ 2·92), spin coupled (J = 10 c/s) with the olefinic proton at position 2 (τ 3·82). The latter proton was further split (2 c/s) as a result of coupling with the proton at position 4 (cf. Ref. 6, p. 123) which appeared at τ 3·90, superimposed on one of the doublets of the proton at position 2. In dimethyl sulphoxide-d_6 solution the corresponding positions were τ 2·80 (proton at position 1), τ 3·96 (proton at position 2) and τ 4·01 (proton at position 4). The 1,5-dien-3-one (VI) is only slightly soluble in deuteriochloroform and its spectrum was determined in dimethyl sulphoxide-d_6 solution. The olefinic proton at position 5 appeared as a multiplet at τ 4·61 and the proton at position 1 at τ 2·94 (J = 10 c/s). The significant feature in the spectrum is the doublet at τ 4·26 (J = 10 c/s) due to the proton at position 2 which is now not further split.

The above 1,4-dien-3-one (VII) could also be prepared from 3-dehydro-6-deacetoxyscillirosidine (VIII)[3] by dehydrogenation with 2,3-dichloro-5,6-dicyano-p-benzoquinone. This interrelationship with scillirosidine also established the stereochemistry of the new bufadienolide (II) at all centres except at positions 1, 2, 3 and 6.

The configuration of the 1,2-epoxy group was determined by CD measurements of the 3-dehydro-derivative (III). The Cotton effect due to the n–π* transition of the α,β-unsaturated keto-group was strongly positive ($\Delta\varepsilon_{max}$ 345 mμ = +5·79 in dioxan). Inspection of Dreiding models and projection in octant diagrams predict a positive Cotton effect for a 1α,2α-epoxy group and a negative effect for its 1β,2β-isomer (cf Fig. 1). It is known[7] that in an α-epoxy-α,β-unsaturated ketone the sign of the Cotton effect of the n–π* transition is determined, in the first place, by the configuration of the epoxy group and also by the chirality of the chromophoric system.

In this particular case ring A is almost planar and the contribution due to the

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[6] N. S. Bhacca and D. H. Williams, *Applications of NMR Spectroscopy in Organic Chemistry*, Holden-Day, San Francisco (1964).

[7] G. Snatzke, *Tetrahedron* 21, 413, 421 (1965).

chirality of the chromophore is relatively small in magnitude in both the α and β epoxy isomers. The sign of the Cotton effect should therefore be strongly negative for a 1β,2β-epoxy-4-en-3-one and strongly positive for a 1α,2α-epoxy-4-en-3-one. This prediction is confirmed by the CD spectra determined on two model substances.[5] The results for dioxan solutions were: 17β-acetoxy-1α,2α-epoxyandrost-4-en-3-one, $\Delta\varepsilon_{max} = +6{\cdot}45$ at 337 mμ and 17β-acetoxy-1β,2β-epoxyandrost-4-en-3-one, $\Delta\varepsilon_{max} = -6{\cdot}70$ at 336 mμ. The configuration of the epoxy group in the alcohol (II; R = H) is thus established as alpha.

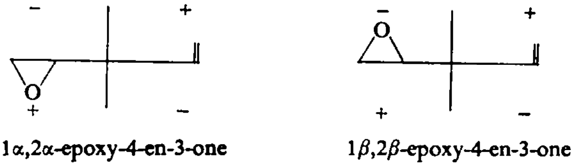


FIG. 1.

The CD spectra of 17β-acetoxy-1α,2α-epoxyandrost-4-en-3-one and the 3-dehydro-derivative (III) determined in ethanol solution are presented in Fig. 2. It is interesting to note that both substances showed three Cotton effects due to π–π* transitions and

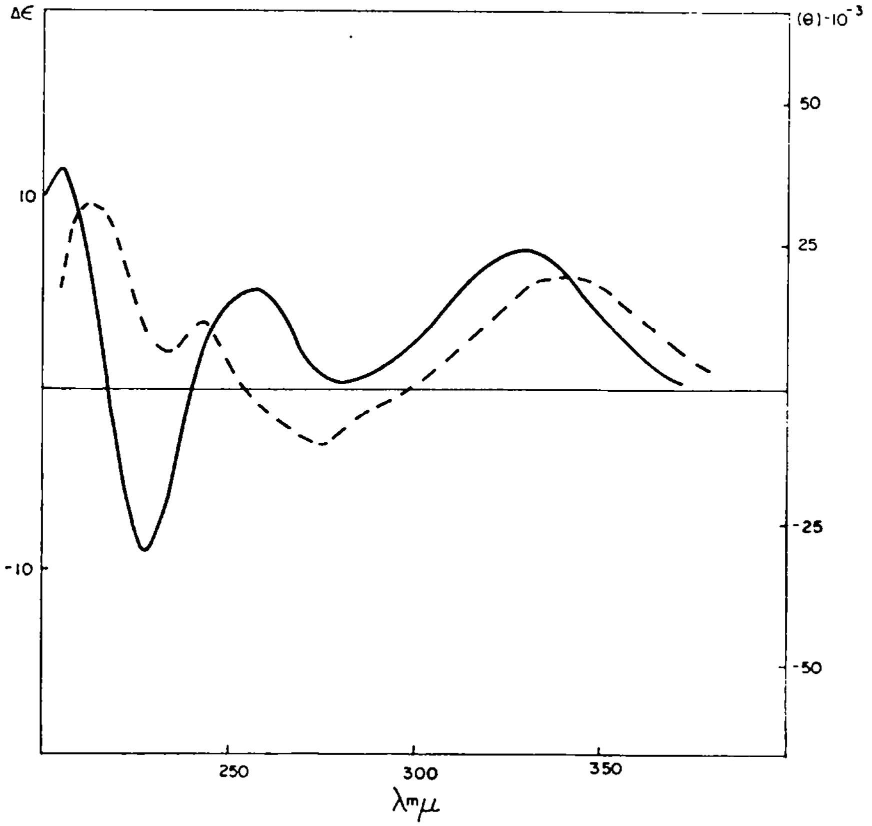
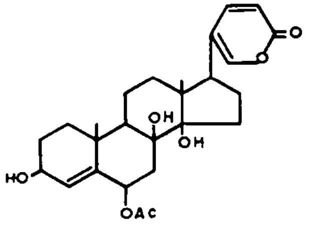


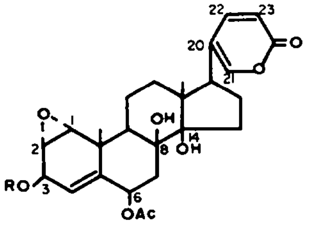
FIG. 2. CD of 17β-acetoxy-1α,2α-epoxyandrost-4-en-3-one [——], and 3-dehydro-1α,2α-epoxy-scillirosidine (III) [– – –].

only the one at lowest wavelength had the same sign in both substances. A further point of interest is the bathochromic shift observed in the CD maxima of the 3-dehydro-derivative compared to those of the model compound. This should be compared with the UV maxima where a hypsochromic shift is observed for the K band [λ_{max} 247·5 mμ for 17β-acetoxy-1α,2α-epoxyandrost-4-en-3-one and λ_{max} 223 mμ for the 3-dehydro-derivative (III)].

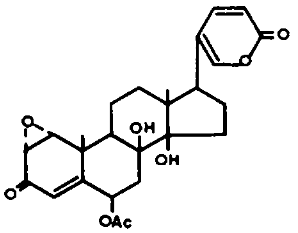
A β-configuration has been assigned to the substituents at positions 3 and 6 on the basis of the following nuclear magnetic resonance evidence. The olefinic proton at position 4 of the alcohol (II) appeared as two doublets centred around τ 4·13 ($J_{3,4}$ = 5, $J_{4,6}$ = 2 c/s) and is therefore coupled with the protons at both positions 3 and 6. The observed splitting ($J_{3,4}$ = 5 c/s) support a 3αH (3βOH) configuration (dihedral angle measured on Dreiding models ca. 30°) rather than a 3βH configuration (dihedral angle ca. 90°).[6]



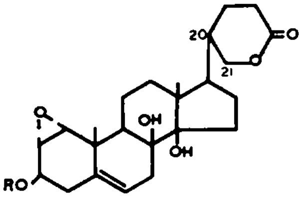
I



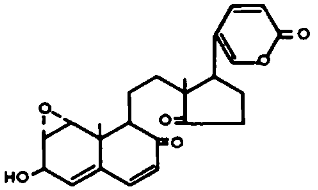
II



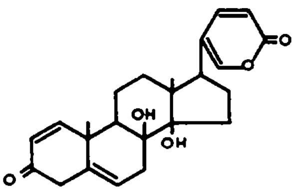
III



IV



V



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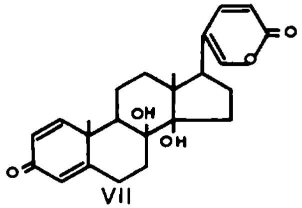
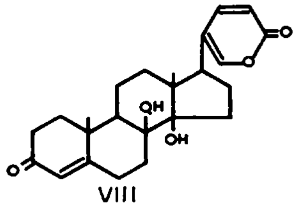


VII



VIII

The angle between the plane of the Δ^4-double bond and the C—H bonds of the allylic protons at position 6 is in both cases $>20°$ and $<170°$ and allylic coupling with protons in both these positions can be expected.[6] In the 3-dehydro-derivative (III), however, the angle between the plane of the Δ^4-double bond and the allylic protons is $<10°$ for 6αH and near 90° for 6βH and one would expect $J_{4,6}$ to have a maximum with a 6βH and zero with a 6α proton. Since no allylic coupling is in fact observed, a 6αH (6βOAc) configuration is preferred.

The structure of the hydrogenation product (IV; R = H) is of interest in view of the fact that a similar hydrogenation product of scillirosidine has been assigned a structure with a $\Delta^{20(22)}$-double bond. In the NMR spectrum of the monoacetate (IV; R = Ac) the two protons at position 21 appear between τ 5·3–6·0, and form the AB part of an ABX pattern due to coupling with a proton at position 20 ($J_{AB} = 11{\cdot}4$, $J_{AX} = 8{\cdot}6$, $J_{BX} = 4{\cdot}2$ c/s). The olefinic proton is placed at position 5 on the following evidence. The protons alpha to the epoxy group at positions 1 and 2 appear as a clear AB quartet at τ 6·9 (J = 4 c/s) showing the absence of further coupling between the protons at positions 2 and 3 (as found for the Δ^4-3-hydroxy compounds of this series). Dreiding models of the 1α,2α-epoxy-Δ^5-3β-acetoxy compound (IV; R = Ac) showed dihedral angles near 90° between the protons at positions 2 and 3 which would explain the absence of vicinal coupling. The 3α proton appeared at τ 5·12 as a triplet (J = 8·4 c/s) coupled to the two protons at position 4. The olefinic proton at position 5 appeared as a poorly resolved triplet at τ 4·48 (J $\sim$ 2·5 c/s).

EXPERIMENTAL

Unless specified to the contrary $[\alpha]_D$ refer to chf, UV absorption spectra to EtOH, and IR absorption spectra to chf solutions. UV spectra (Unicam Model S.P. 500 spectrometer) and IR spectra (Perkin–Elmer Model 237 spectrometer). NMR spectra (Varian A-60 or HA-100 spectrometer in $CDCl_3$ or DMS-d_6 soln). The chemical shifts were measured on the τ-scale relative to TMS (τ10·0); τ-values are estimated to be accurate to ±0·01 ppm, coupling constants to ±0·2 c/s. The CD spectra (dioxan or 96% EtOH soln on a Jasco ORD/UV-5 spectrometer with attachment for CD measurements).[8] Mass spectra (MS-9 double-focussing mass spectrometer using direct insertion). Alumina for chromatography was Bio-Rad Neutral AG7. For TLC on silica gel G. chf containing 2-8% EtOH was used and a 1% solution of ceric sulphate in 4N H_2SO_4 as spray reagent,

1α,2α-*Epoxyscillirosidine* (II; R = H). A sample of the main toxic principle of *Homeria glauca* (Wood and Evans) N.E. Br. was purified by crystallization from EtOH and chf–benzene to give 1α,2α-*epoxyscillirosidine*, m.p. 157–158° (EtOH) and 169–171°/chf–benzene, NMR evidence for ½ mole benzene of crystallization), $[\alpha]_D$ −11° (*c* 1·06), λ_{max} 300 mμ (ε 5700), ν_{max} 1739, 1718, 1639, 1538 and 835 cm^{-1}. (Found: C, 67·8, 67·8; H, 6·8, 6·9; O, 25·4; acetyl, 8·1. $C_{26}H_{32}O_8 \cdot \frac{1}{2}C_6H_6$ requires: C, 68·1; H, 6·9; O, 25·0; acetyl, 8·4%.) The substance gave a blue Lieberman colour test.

3-*Monoacetate* (II; R = Ac). Acetylation of 1α,2α-epoxyscillirosidine (100 mg) in Ac_2O (1 ml) and pyridine (1 ml) for 24 hr at room temp gave the 3-*monoacetate* which was crystallized first from dioxan and then from MeOH, m.p. 209–210°. $[\alpha]_D$ −66° (*c* 0·7). (Found: C, 65·0; H, 6·9; active H, 0·51, 0·49. $C_{28}H_{34}O_9$ requires: C, 65·3; H, 6·7; 2 active H, 0·39%.)

3-*Dehydro*-1α,2α-*epoxyscillirisodine* (III). 1α,2α-Epoxyscillirosidine (51 mg), chf (5 ml) and neutral MnO_2[9] (503 mg) were shaken vigorously for 3·5 hr at room temp. The MnO_2 was filtered

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[8] The Jasco ORD/UV-5 instrument was used with the amplitude calibration recommended by the manufacturer and gave amplitude values of ca. 25% higher than those obtained for measurements on a Dichrograph (Roussel-Jouan), e.g. a sample of 17β-acetoxy-1α,2α-epoxyandrost-4-en-3-one measured for us by Dr. G. Snatzke of Bonn gave $\Delta\varepsilon_{max}$ 337 mμ = +5·06).

[9] O. Maniera, G. Rosenkranz and F. Sondheimer, *J. Chem. Soc.* 2189 (1953).

off and washed with hot chf. The product crystallized from chf–MeOH to give 3-*dehydro*-1α,2α-*epoxyscillirosidine*, m.p. 235–236°, $[\alpha]_D$ +129° (*c* 1·0), λ_{max} 223 and 300 mμ (ε 14,450 and 5850, respectively), ν_{max} 1755, 1720, 1690, 1641, 1543 and 836 cm^{-1}, CD (λ_{max}, Δε) in EtOH: 213 (+9·7), 243 (+3·4), 275 (−3·4), 339 (+5·9); and CD (λ_{max}, Δε) in dioxan: 235 (+4·88), 275–285 (−2·3) and 345 (+5·79). (Found: C, 66·3; H, 6·5. $C_{26}H_{30}O_8$ requires: C, 66·4; H, 6·4%.)

The CD data (λ_{max}, Δε) for 17β-acetoxy-1α,2α-epoxyandrost-4-en-3-one[5] are (a) in EtOH: 205 (+11·5), 228 (−9·1), 256 (+5·25). 330 (+7·25) and (b) in dioxan: 225 (−12·94), 245 (+6·13), and 337 (+6·45).[8]

Hydrogenation of 1α,2α-*epoxyscillirosidine*. Compound II (R = H; 150 mg) was hydrogenated over 5% Pd–$CaCO_3$ (75 mg) in EtOH (25 ml) (3·17 mole H_2 absorbed in 45 min). The crude product was obtained pure only after repeated crystallization from MeOH and AcOEt to give IV (R = H), m.p. 279–282°, ν_{max} 1725 (broad) cm^{-1}. (Found: C, 68·7; H, 8·0. $C_{24}H_{34}O_6$ requires: C, 68·9; H, 8·2%.)

3-*Monoacetate* (IV. R = Ac) Acetylation of the above deacetoxy-derivative (97 mg) in Ac_2O (2 ml) and pyridine (2 ml) for 10 hr at room temp gave the 3-*monoacetate* which was crystallized from AcOEt, m.p. 275–278°, $[\alpha]_D$ +61° (*c* 1·0). (Found: C, 67·6; H, 7·8. $C_{26}H_{36}O_7$ requires: C, 67·8; H, 7·9%.)

6-*Deacetyl*-1α,2α-*epoxyscillirosidine*. A solution of 1α,2α-epoxyscillirosidine (150 mg) in 50% EtOH (30 ml) was adjusted to pH 8–9 by addition of 0·1N $Ba(OH)_2$. Further small quantities of alkali were added at short intervals to keep the pH constant. After 2 hr at room temp the reaction was stopped by bubbling CO_2 through the solution and the product isolated with chf and filtered through a column of silica gel G in 8% EtOH in chf. The main fraction crystallized from dil EtOH to give the 6-*deacetyl-derivative*, m.p. 244–246°, $[\alpha]_D$ −42° (*c* 0·9 in EtOH). (Found: C, 66·9; H, 6·9. $C_{24}H_{30}O_7$ requires: C, 67·0; H, 7·0%.)

Conjugated dienone (V) *from* 1α,2α-*epoxyscillirosidine* (II; R = H). Compound II (R = H; 54 mg) in AcOH (1 ml) was treated for 3 min with a freshly prepared solution of lead tetra-acetate (75 mg) in AcOH (2 ml). The solvent was removed *in vacuo* at 25–30°, the residue dissolved in chf and washed with water. Evaporation of the chf gave a crude product which was dissolved in 1:1 chf–benzene and adsorbed on a column of neutral alumina (2 g). After 16 hr the column was eluted with chf and the main fraction crystallized from AcOEt and from MeOH to give the *conjugated dienone* (V), m.p. 173–174°, $[\alpha]_D$ −187° (*c* 1·2), λ_{max} 285 mμ (ε 17,400), $\nu_{max}^{CHCl_3}$ 1752 sh, 1727, 1673, 1642, 1597 and 1538 cm^{-1}; ν_{max}^{Nujol} 1740, 1712, 1680, 1640, 1603 and 1540 cm^{-1}. (Found: C, 69·9; H, 6·3. $C_{24}H_{26}O_6$ requires C, 70·2; H, 6·4%.)

Reduction of the 3-*dehydro-derivative* (III) *with zinc in acetic acid*. Compound III (152 mg) in AcOH (6 ml) and water (1·8 ml) was vigorously stirred at room temp while Zn dust (330 mg, activated according to Shriner and Neumann[10]) was added in small portions over a period of 3 hr. The mixture was then stirred for 1 hr, filtered, and the solvent removed *in vacuo* at room temp. The product, dissolved in chf. and washed with water until free of all traces of acid, showed mainly two spots on silica gel TLC plates. One of the two major components crystallized (57 mg) from chf–MeOH and was purified by crystallization from acetone to give the 1,5-*dien*-3-*one* (VI), m.p. 227–229°, λ_{max} 222 and 300 mμ (ε 16,100 and 6300 respectively), ν_{max}^{KBr} 1700 (very broad), 1630 and 1540 cm^{-1}, CD (λ_{max}, Δε) in ethanol: 225 (+10·0), 258 (−5·7) and 337 (+1·8). (Found: C, 72·5; H, 7·0. $C_{24}H_{28}O_5$ requires: C, 72·7; H, 7·1%.)

The 1,5-dien-3-one or the above crude mixture could be converted to the other major reduction product of III by (a) adsorption in chf soln on a column of neutral alumina for 36 hr, or (b) treatment in a boiling 0·2% soln of anhydrous oxalic acid in EtOH for 10 hr. The product was in each case purified by chromatography on neutral alumina. Elution with chf and crystallization from MeOH–chf gave the 1,4-*dien*-3-*one* (VII), m.p. 264–266°, $[\alpha]_D$ −22° (*c* 0·9), λ_{max} 243 and 300 mμ (ε 14,900 and 6300 respectively), ν_{max} 1707 (broad), 1660, 1618, 1602 and 1536 cm^{-1}, CD (λ_{max}, Δε) in ethanol: 230 (+16·9), 265 (−8·9) and 310 sh (−1·3). (Found: C, 72·7; H, 7·2. $C_{24}H_{28}O_5$ requires: C, 72·7; H, 7·1%.)

1,4-*dien*-3-*one* (VII) *from scillirosidine* (I). Compound VIII (25 mg, m.p. 263–264°, lit[3] 254–261°, prepared according to von Wartburg and Renz[9]) was treated with 2,3-dichloro-5,6-dicyano-p-benzoquinone (BDH, 22 mg) in boiling Na-dried benzene (10 ml) for 60hr. The reaction mixture

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[10] R. L. Shriner and F. W. Neumann, *Org. Synthesis*, Coll. Vol. III, p. 74, Note 1, John Wiley and Sons Ltd, New York (1955).

was diluted with benzene (20ml) and washed consecutively with a sat Na_2SO_4aq, water, again with Na_2SO_4aq and finally with water. On silica gel TLC plates two spots appeared of approximately equal intensities, one corresponding to the starting material and the other to the product. The mixture was separated on a layer (20 × 20 cm) of silica gel G (30 g, containing 2% of fluorescent indicator Green, Woelm) using 4% EtOH in chf as eluant in a double run. Two well separated bands were visible under UV light. The lower band containing the more polar material was collected and extracted with MeOH. The product was filtered in chf soln through a column of neutral alumina (0·3 g) and crystallized from MeOH to give VII (4 mg), m.p. and mixed m.p. 262–265°. The product was further identified by TLC, IR spectrum and its mass spectrum.

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