Tetrahedron. Vol. 29, pp. 1795 to 1800. Pergamon Press 1973. Printed in Great Britain

THE REACTIONS OF EVONINE AND NEOEVONINE ALKALOIDS OBTAINED FROM *EUONYMUS SIEBOLDIANA* BLUME

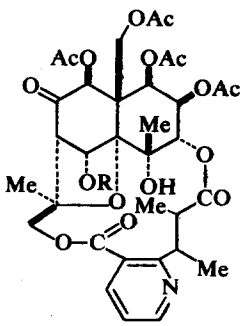
Y. SHIZURI, H. WADA, K. YAMADA,* and Y. HIRATA

Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya, Japan

(*Received in Japan* 5 *July* 1972; *Received in the UK for publication* 11 *December* 1972)

Abstract—The reactions of evonine (1), neoevonine (2), alkaloids of *Euonymus Sieboldiana* Blume, and their derivatives are described. The structural proofs of some derivatives are included.

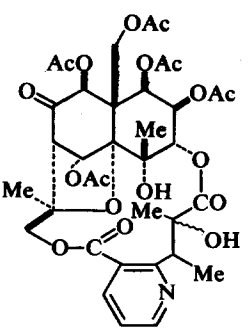
In the course of the structural studies on evonine (1) and neoevonine (2), alkaloids obtained from *Euonymus Sieboldiana* Blume,[1-4] various derivatives were obtained, the structures of which were established. Since many oxygen-functional groups are present in the alkaloids, (1 and 2), some reactions of interest took place.



1: R = Ac: evonine†
2: R = H: neoevonine
3: R = Me

Oxidation

Hydroxyevonine-A (**4a**) *and -B* (**4b**). Oxidation of evonine (1) with CrO_3 afforded two diastereoisomeric products, (**4a** and **4b**). Elemental analysis and mass spectral evidence indicated the increase of one oxygen in the molecular formula of each product. The site of oxidation was disclosed by the NMR spectral data: of the two methine protons (δ 4·67, dq, $J = 1·0$, 7·1 Hz; 2·59, dq, $J = 1·0$, 7·1 Hz) in the evoninic acid part of evonine (1), the signal of the higher field (δ 2·59) disappeared in **4a** and **4b**. Thus the methine hydrogen alpha to the ester CO of the evoninic acid part in **1** was oxidized to an OH. No other types of oxidation in the sesquiterpene part of **1** took place by CrO_3 under a variety of conditions.

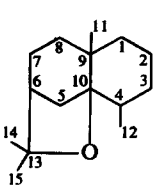


4a and 4b

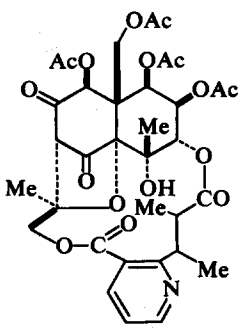
Diacetonide ketone (**7**) *and neoevoninone* (**17**). While pentadesacetyl evonine (**5a**) was converted to the monoacetonide (**8**) as previously reported,[1,4] the diacetonide (**6**) was also formed under somewhat forcing conditions (Chart). The location of the second isopropylidene group at C-1 and C-2 was proved from the fact that the diacetonide (**6**) was inert towards $NaIO_4$ oxidation, whereas the monoacetonide (**8**) consumed one mole of $NaIO_4$. The diacetonide (**6**) on oxidation with CrO_3 was transformed into the diacetonide ketone (**7**). In the NMR spectra, the one proton doublet ($J =$ 1·0 Hz, H-5) at δ 5·19 observed in **6** was missing in **7**, indicating the site of oxidation to be at C-5. In the IR spectrum the C=O band of the newly

*To whom enquiries should be addressed.

†The numbering system shown here is used throughout the present paper.



formed keto group was observed at 1785 cm^{-1} ($CHCl_3$), which was not an unexpected position, considering the special structural environment. Since the product, **7** possessed the non-enolizable β-diketone group in the strained 6-oxabicyclo-[3.2.1]octane system, it was extremely unstable towards bases (e.g. aq NH_3) under mild conditions: various deep-seated structural changes seemed to occur, resulting in the formation of a complex mixture. Another derivative containing this type of β-diketone was also prepared: oxidation of neoevonine (**2**) with CrO_3 afforded neoevoninone (**17**), which showed the characteristic C=O band at 1785 cm^{-1} ($CHCl_3$).



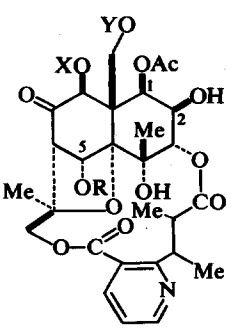
17

Hemiacetal aldehyde (**11**). (Chart). Pentadesacetyl evonine acetonide (**8**) was known to consume one mole of $NaIO_4$ as described.[1,4] Oxidation of **8** with $NaIO_4$ afforded a crystalline product, **11**. Based on the NMR spectral findings, the following structural changes were deduced. The cleavage of a C(1)–C(2) bond by $NaIO_4$ resulted in the formation of two aldehyde groups, one of which formed a hemiacetal with the OH at C-5: a singlet of the aldehyde proton (H-1) appeared at δ 10·38 and the proton (H-2) forming the hemiacetal was observed at δ 6·14 as a doublet ($J = 7·5$ Hz). On treatment of the product (**11**) with Ac_2O-AcONa the diacetate was produced, the structural assignment of which as **12** was based on the following: it showed a band due to an enol acetate (1760 cm^{-1}) in the IR spectrum, and a one proton doublet (δ 6·47, $J = 3·8$ Hz, H-2) due to the hemiacetal acetate part and two acetate Me singlets (δ 2·22 and 2·26) in the NMR spectrum.

Conjugated dienone (**13**). (Chart). Pentadesacetyl evonine (**5a**) was converted into the triacetate (**10**) by three steps.[1,4] Oxidation of the triacetate (**10**) with CrO_3 afforded a product, **13**, which showed properties characteristic of a conjugated dienone group possessing an α-OH [UV (dioxane) λ_{max} 325 nm (ε 20,600); IR (KBr) 3400 (OH), 1748 (ester), 1725 (ester), 1670 (conjugated C=O), 1631 (conjugated C=C), 1578, 1560 cm^{-1}]. Comparison of the molecular formulas of the reactant, **10** and the product, **13** revealed that one mole each of formaldehyde and AcOH was lost together with oxidation of an OH to a ketone. The NMR spectral differences between both compounds are as follows: the signals due to H-2 [δ 5·08 (1H, dd, $J = 3·8$, 3·0 Hz)], H-8 [δ 4·20 (1H, s)], and H-11 [δ 4·10 and 4·48 (2H, ABq, $J = 12·8$ Hz)] in **10** were missing in the product, **13**; and each signal of H-1 and H-3 which appeared as a doublet (H-1, δ 5·81, $J = 3·8$ Hz; H-3, δ 4·73, $J = 3·0$ Hz) in **10** was observed as a singlet (H-1, δ 6·20; H-3, δ 5·93) in **13**. These spectral data unequivocally indicate the structure of the oxidation product to be **13**, which would be formed in the following manner. Oxidation of the α-ketol moiety by CrO_3 led to the formation of the α-diketone group, which underwent acid-catalysed retroaldol reaction with expulsion of C-11 as formaldehyde, followed by acid-catalysed elimination of AcOH and subsequent enolization.

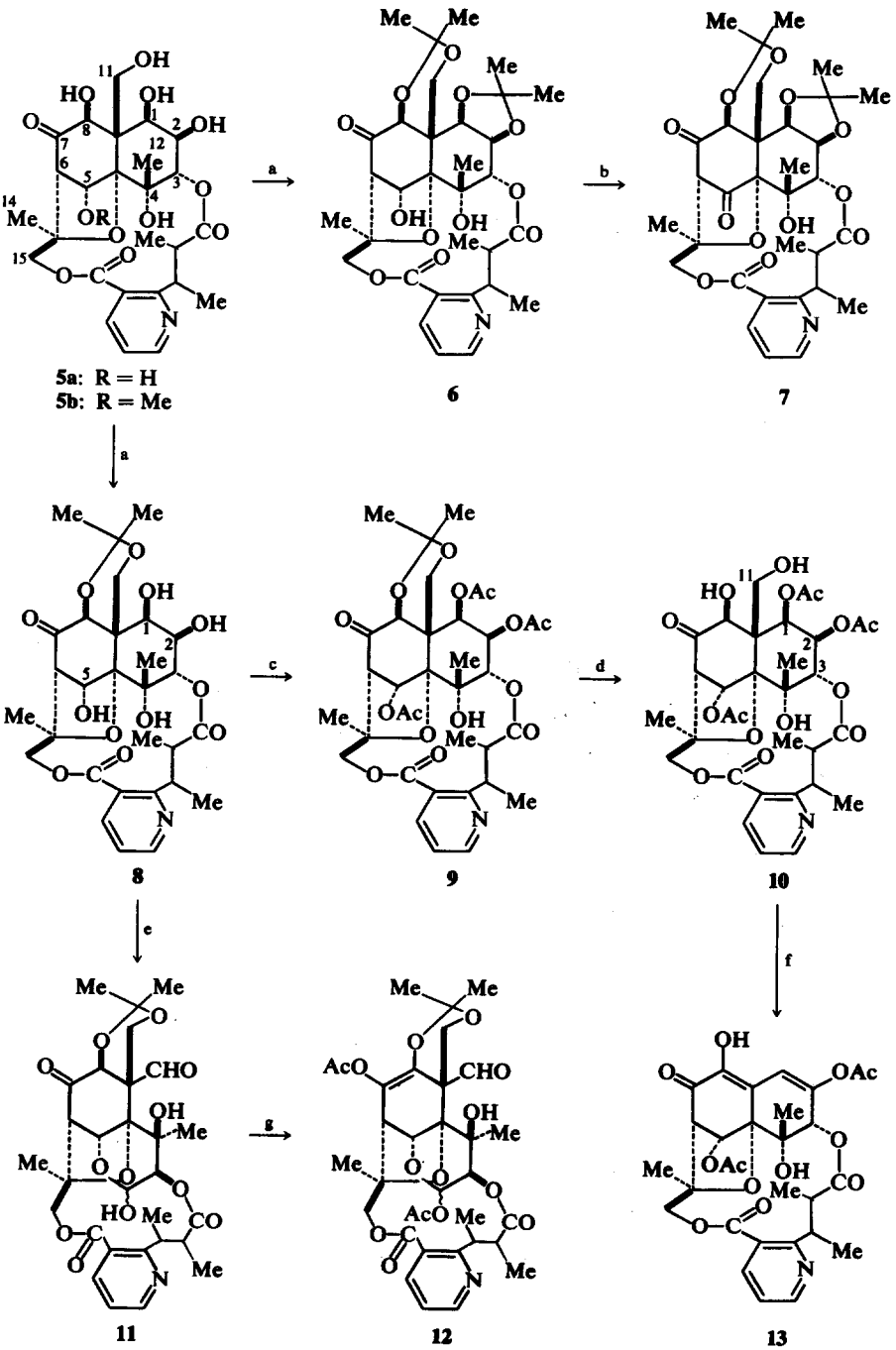
Acetylation of pentadesacetyl evonine acetonide (**8**)

Acetylation of pentadesacetyl evonine acetonide (**8**)[1,4] was examined under a variety of conditions. Formation of the acetonide diacetate (**14**) and the acetonide triacetate (**9**) (Chart), which was previously reported[1,4] revealed that acetylation took place more readily at C(5)-OH than at C(2)-OH. The acetonide monoacetate (**15**) was prepared under slightly different conditions from those employed for the formation of **14** and **9**; pentadesacetyl evonine acetonide (**8**) was treated with Ac_2O to give the acetonide monoacetate (**15**), the NMR spectrum of which indicated the position of acetylation to be at C-1. A signal due to H-1 (δ 4·24, m) in **8** underwent downfield shift (δ 5·63, d, $J = 3·2$ Hz) in **15**, while other spectral patterns were essentially the same in both derivatives. Treatment of **15** with aqueous AcOH afforded pentadesacetyl evonine monoacetate (**16**). Thus, regarding the three secondary hydroxyls in pentadesacetyl evonine acetonide (**8**), the order of acetylation was established as C(1)-OH, C(5)-OH, C(2)-OH.



14: R = Ac; X, Y = isopropylidene
15: R = H; X, Y = isopropylidene
16: R = H; X = Y = H

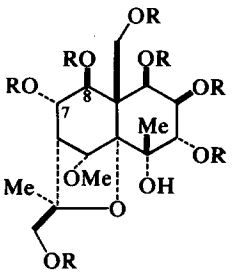
CHART


5a: R = H
5b: R = Me
6
7
8
9
10
11
12
13
Reagents
(a) $(MeO)_2CMe_2/H^+$
(b) CrO_3/Py
(c) Ac_2O/Py
(d) $AcOH/H_2O$
(e) $NaIO_4/EtOH\text{-}H_2O$
(f) $CrO_3/AcOH$
(g) $Ac_2O/AcONa$

Reactions of neoevonine methyl ether (3)

Alkaline hydrolysis of evonine (1) affords deeply coloured, tarry material.[4,5] This instability of 1 towards bases seems partly due to the presence of the β-hydroxyketone moiety, because methanolysis of neoevonine methyl ether (3)[4] with NaOMe proceeded much more cleanly than that of evonine (1) or neoevonine (2), affording the tetradesacetyl derivative, 5b.

Evonine (1) was reduced with LAH to give two possible diastereoisomeric polyhydroxy compounds.[1-4] In contrast, on reduction of neoevonine methyl ether (3) under the same conditions, a single stereoisomer, isoeuonyminol methyl ether (18) was formed. It formed a heptaacetate (19) on acetylation.



18: R = H
19: R = Ac

The configuration of the newly formed OH at C-7 was determined on the basis of the coupling constant of H-7 ($J_{7,8} = 9.5$ Hz) in the NMR spectrum of 19.

EXPERIMENTAL

M.ps were uncorrected. UV spectra were measured on a Perkin-Elmer Model 202 spectrophotometer. IR spectra were recorded with a JASCO Model IRS spectrophotometer and a JASCO DS-402G spectrophotometer. NMR spectra were determined on a JNMC-60H spectrometer; chemical shifts are given in ppm relative to internal TMS (δ). The mass spectra were determined on a Hitachi RMU-6C mass spectrometer equipped with a direct inlet system. For TLC silica gel GF_{254} and PF_{254}, and alumina GF_{254} and PF_{254}-Type T (E. Merck, A. G., Germany) were used. For column chromatography silicic acid (100 mesh, Mallinckrodt, U.S.A.) was used. The organic solns were dried over Na_2SO_4, and evaporated by vacuum rotary evaporator.

Hydroxyevonine-A (4a) *and -B* (4b). A mixture of 1 (400 mg) and CrO_3 (100 mg) in AcOH (20 ml) was kept at 70° for 3 hr, EtOH (*ca* 1 ml) was added, then concentrated, and diluted with H_2O. The resulting mixture was extracted with AcOEt repeatedly and the AcOEt extracts were washed with H_2O, dried, and evaporated. The residue was chromatographed over silicic acid (20 g) with n-hexane-AcOEt: early fractions afforded the unreacted 1; middle fractions gave 4a and from later fractions 4b was obtained.

Compound 4a, (80 mg, recrystallization from EtOH), m.p. 188–190°; IR (KBr) 3480, 1750–1710 (broad band), 1585, 1565 cm^{-1}; NMR ($CDCl_3$) 5·70 (1H, d, $J = 3.0$ Hz, H-1), 5·43 (1H, dd, $J = 3.0$, 3·0 Hz, H-2), 4·85 (1H, d, $J = 3.0$ Hz, H-3), 6·81 (1H, br.s, H-5), 3·11 (1H, br.s, H-6), 5·59 (1H, s, H-8), 4·61 and 4·92 (2H, ABq, $J = 13.0$ Hz, H-11), 1·53 (3H, s, H-12), 1·62 (3H, s, H-14), 3·82 and 5·97 (2H, ABq, $J = 11.5$ Hz, H-15), 1·94, 2·08, 2·14, 2·21, 2·29 (3H each, s, 5 × AcO), 4·59 (1H, q, $J = 7.0$ Hz); Mass 777 (M$^+$). (Found: C, 54·90; H, 5·89; N, 1·72. $C_{36}H_{43}NO_{18}$·EtOH requires: C, 55·45; H, 5·99; N, 1·71%).

Compound 4b, (60 mg, recrystallization from EtOH), m.p. 190°; IR (KBr) 3400, 1750–1710 (broad band), 1585, 1565 cm^{-1}; NMR ($CDCl_3$) 5·84 (1H, d, $J = 3.0$ Hz, H-1), 5·44 (1H, dd, $J = 3.0$, 3·0 Hz, H-2), 4·98 (1H, d, $J = 3.0$ Hz, H-3), 6·90 (1H, br.s, H-5), 3·14 (1H, br.s, H-6), 5·64 (1H, s, H-8), 4·61 and 4·74 (2H, ABq, $J = 10.0$ Hz, H-11), 1·54, 1·65 (3H each, s, H-12 and H-14), 4·60 and 5·05 (2H, ABq, $J = 13.0$ Hz, H-15), 4·90 (1H, q, $J = 7.0$ Hz). Mass 777 (M$^+$). (Found: C, 55·34; H, 5·64; N, 1·86. $C_{36}H_{43}NO_{18}$·EtOH requires: C, 55·64; H, 5·59; N, 1·80%).

Pentadesacetyl evonine diacetonide (6). A mixture of 5a (220 mg), camphorsulphonic acid (100 mg), 2,2-dimethoxypropane (3 ml), and DMF (1 ml) was stirred at 40° for 12 hr and diluted with sat $NaHCO_3$ aq. The mixture was extracted with three 30 ml portions of AcOEt. The AcOEt extracts were washed with sat NaCl aq, dried, and evaporated, giving a residue, which showed two spots on TLC. Separation of the residue by preparative TLC (silica gel) with AcOEt-benzene (2:3) afforded 6 (160 mg, amorphous powder) and 8 (50 mg). 6: IR ($CHCl_3$) 1735 (broad band), 1590, 1570 cm^{-1}; NMR ($CDCl_3$) 5·19 (1H, d, $J = ca$ 1 Hz, H-5), 3·03 (1H, d, $J = ca$ 1 Hz, H-6), 4·99 (1H, s, H-8), 3·75 and 6·00 (2H, ABq, $J = 12.0$ Hz, H-15), 1·62 (3H, s, H-12 or H-14), 1·30–1·55 (18H; 4Me's of two isopropylidenes, H-12 or H-14, and a secondary Me of evoninic acid part), 1·16 (3H, d, $J = 7.2$ Hz, a secondary Me of evoninic acid part).

Pentadesacetyl evonine diacetonide ketone (7). A mixture of 6 (100 mg) and CrO_3 (100 mg) in pyridine (2 ml) was stirred at room temp for 12 hr, concentrated, and AcOEt (30 ml) added. After the mixture had been filtered, the filtrate was washed with sat NaCl aq, dried, and evaporated, affording a residue, which was purified by preparative TLC (silica gel PF_{254}) with AcOEt-benzene (2:3). Recrystallization from n-hexane-benzene gave pure 7 (68 mg), m.p. 193–198°; IR ($CHCl_3$) 1785, 1735, 1590, 1570 cm^{-1}; NMR ($CDCl_3$) 4·84 (1H, d, $J = 2.8$ Hz, H-3), 3·40 (1H, s, H-6), 4·51 (1H, s, H-8), 4·16 and 4·42 (2H, ABq, $J = 11.0$ Hz, H-11), 1·56, 1·66 (3H each, s, H-12 and H-14), 3·84 and 4·49 (2H, ABq, $J = 12.0$ Hz, H-15), 1·30–1·44 (15H; 4Me's of two isopropylidenes and a secondary Me of evoninic acid part), 1·17 (3H, d, $J = 6.8$ Hz, secondary Me of evoninic acid part). Mass 629 (M$^+$). (Found: C, 60·15; H, 6·38; N, 2·24. $C_{32}H_{39}NO_{12}$ requires: C, 60·84; H, 6·54; N, 2·22%).

Neoevoninone (17). A mixture of CrO_3 (196 mg) in pyridine (4 ml) was added to a soln of 2 (216 mg) in pyridine (4 ml) under ice-bath cooling. The mixture was kept at room temp overnight and poured into H_2O (80 ml). The resulting mixture was extracted with ether repeatedly. The ethereal extracts were washed with H_2O and sat NaCl aq, dried, and evaporated, affording an amorphous solid. Recrystallization from EtOH yielded pure 17 (180 mg), m.p. 305–307°; IR ($CHCl_3$) 3500, 1785 (weak), 1755, 1710, 1585, 1565 cm^{-1}; NMR

($CDCl_3$) 5·75 (1H, d, $J = 3·5$ Hz, H-1), 5·37 (1H, dd, $J = 3·5$, 3·0 Hz, H-2), 4·84 (1H, d, $J = 3·0$ Hz, H-3), 3·55 (1H, s, H-6), 5·83 (1H, s, H-8), 4·69 and 4·78 (2H, ABq, $J = 11·5$ Hz, H-11), 2·02 (3H, br.s, H-12), 1·63 (3H, s, H-14), 4·01 and 4·91 (2H, ABq, $J = 12·0$ Hz, H-15). Mass 717 (M^+). (Found: C, 56·95; H, 5·39; N, 1·97. $C_{34}H_{39}NO_{16}$ requires: C, 56·95; H, 5·48; N, 1·95%).

Hemiacetal aldehyde (**11**). A soln of **8** (150 mg) and $NaIO_4$ (75 mg) in EtOH (6 ml)-H_2O (16 ml) was stirred at room temp for 18 hr and concentrated, to give a residue, to which H_2O (10 ml) was added. The mixture was extracted with three 30 ml portions of CH_2Cl_2. The CH_2Cl_2 extracts were washed with sat NaCl aq, dried, and evaporated. Recrystallization of the residue from MeOH gave **11** (80 mg), m.p. 213° (dec); IR (KBr) 3460, 1740, 1710 (shoulder), 1590, 1565 cm^{-1}; NMR (pyridine-d_5) 10·38 (1H, s, H-1), 6·14 (1H, d, $J = 7·5$ Hz, H-2), 5·08 (1H, d, $J = 7·5$ Hz, H-3), 3·50 (1H, d, $J = ca$ 1 Hz, H-6), 4·24 and 6·49 (2H, ABq, $J = 11·0$ Hz); Mass 589 (M^+). (Found: C, 58·98; H, 5·95; N, 2·39. $C_{29}H_{35}NO_{12}$ requires: C, 59·08; H, 5·98; N, 2·38%).

Hemiacetal aldehyde diacetate (**12**). A mixture of **11** (95 mg) and AcONa (200 mg) in Ac_2O (2 ml) was kept at 60° for 20 hr and concentrated. The residue was treated with sat $NaHCO_3$ aq, and the mixture was extracted with three 20 ml portions of AcOEt and the AcOEt extracts were washed with sat NaCl aq. On removal of solvent crude product was obtained, which was purified by preparative TLC (silica gel GF_{254}) with AcOEt-benzene (1:1). Recrystallization from CCl_4 afforded pure **12** (80 mg), m.p. 189° (dec); IR (KBr) 3560, 1760, 1720, 1585, 1565 cm^{-1}; NMR ($CDCl_3$) 9·76 (1H, s, H-1), 6·47 (1H, d, $J = 3·8$ Hz, H-2), 4·81 (1H, d, $J = 3·8$ Hz, H-3), 4·85 (1H, d, $J = 1·0$ Hz, H-5), 2·75 (1H, d, $J = 1·0$ Hz, H-6), 4·23 and 4·71 (2H, ABq, $J = 13·0$ Hz; H-11), 1·16, 1·74 (3H each, s, H-12 and H-14), 3·99 and 6·25 (2H, ABq, $J = 12·0$ Hz, H-15), 2·22, 2·26 (3H each, s, 2 × AcO), 1·37 (6H, s, 2Me's of isopropylidene group). (Found: C, 58·61; H, 5·85; N, 2·06. $C_{33}H_{39}NO_{14}$ requires: C, 58·83; H, 5·84; N, 2·08%).

Conjugated dienone (**13**). A soln of CrO_3 (244 mg) in AcOH (1·3 ml) was added to a soln of **10** (402 mg) in AcOH-dioxane (1:1) (18 ml). The mixture was stirred at room temp overnight, MeOH added, and evaporated, leaving a residue, which was mixed with H_2O. The mixture was extracted with AcOEt repeatedly. The AcOEt extracts were washed with sat NaCl aq, dried, and evaporated. Recrystallization of the residue from EtOH afforded **13** (126 mg), m.p. 240–243° (dec); IR (KBr) 3400, 1748, 1725, 1670, 1631, 1578, 1560 cm^{-1}; UV (dioxane) λ_{max} 325 nm (ϵ 20,600); NMR (pyridine-d_5) 7·19 (1H, s, H-1), 5·93 (1H, s, H-3 or H-5), 6·20 (1H, s, H-3 or H-5), 3·70 (1H, s, H-6), 1·73 (3H, s, H-12), 1·43 (3H, s, H-14), 4·07 and 6·20 (2H, ABq, $J = 11·5$ Hz, H-15). (Found: C, 59·35; H, 5·46; N, 2·28. $C_{29}H_{31}NO_{12}$ requires: C, 59·54; H, 5·34; N, 2·39%).

Pentadesacetyl evonine acetonide monoacetate (**15**). A soln of **8** (86 mg) in Ac_2O (0·5 ml) and pyridine (1 ml) was kept at room temp (*ca* 20°) overnight and poured into sat $NaHCO_3$ aq. The mixture was extracted with three 15 ml portions of AcOEt. The AcOEt extracts were washed with sat NaCl aq, dried, and evaporated, giving crude product, recrystallization of which from MeOH afforded **15** (73 mg), m.p. 247° (dec); NMR ($CDCl_3$) 5·63 (1H, d, $J = 3·2$ Hz, H-1), 3·97 (1H, dd, $J = 3·2$, 3·0 Hz, H-2), 4·77 (1H, d, $J = 3·0$ Hz, H-3), 5·14 (1H, d, $J = ca$ 1 Hz, H-5), 3·08 (1H, d, $J = ca$ 1 Hz, H-6), 4·28 (1H, s, H-8), 4·16 and 4·46 (2H, ABq, $J = 13·0$ Hz, H-11), 1·92 (3H, br.s, H-14), 3·71 and 5·97 (2H, ABq, $J = 12·0$ Hz, H-15), 2·10 (3H, s, AcO), 1·38–1·45 (9H, isopropylidene Me's and H-12); Mass 633 (M^+). (Found: C, 58·68; N, 6·21; N, 2·28. $C_{31}H_{39}NO_{13}$ requires: C, 58·76; H, 6·20; N, 2·21%).

Pentadesacetyl evonine monoacetate (**16**). A soln of **15** (70 mg) in AcOH (1 ml) and H_2O (0·5 ml) was kept at 80° for 4 hr and concentrated. Column chromatography of the residue over silicic acid (2 g) with AcOEt afforded the monoacetate, recrystallization of which from MeOH gave pure **16** (53 mg), m.p. 210° (dec). (Found: C, 56·30; H, 6·03; N, 2·39. $C_{28}H_{35}NO_{13}$ requires: C, 56·66; H, 5·94; N, 2·36%).

Tetradesacetyl neoevonine methyl ether (**5b**). A soln of 0·1 M NaOMe in MeOH (0·2 ml) was added to a soln of **3** (103 mg) in MeOH (10 ml) at 0°. The mixture was stirred at room temp for 12 hr, and concentrated to give a residue, which was taken up in 50% MeOH-H_2O. Ion-exchange resin Amberlite IR-120 (H form, 0·5 ml) was added to the aqueous MeOH soln. After stirring for 10 min, the mixture was filtered and the filtrate was evaporated, giving the product. Recrystallization from acetone-isopropyl ether afforded **5b** (60 mg), m.p. 232°; IR (KBr) 3520, 1730, 1720, 1585, 1570 cm^{-1}. (Found: C, 57·17; H, 6·31; N, 2·46. $C_{27}H_{35}NO_{12}$ requires: C, 57·39; H, 6·24; N, 2·48%).

Isoeuonyminol methyl ether (**18**). A soln of **3** (834 mg) in anhyd THF-ether (1:1) (32 ml) was added to a suspension of LAH (312 mg) in anhyd ether (16 ml). The mixture was stirred at room temp overnight and H_2O (50 ml) was added slowly. The mixture was filtered and the aqueous filtrate was washed with ether. The aqueous soln was neutralized with ion-exchange resin Amberlite IR-120 (H form) and evaporated to give crude product (300 mg). Recrystallization from MeOH afforded **18**, m.p. 250° (dec); IR (KBr) 3370 cm^{-1}; NMR (D_2O) 1·50 (3H, s), 1·63 (3H, s), 3·32(3H, s); Mass 349 (M-31). (Found: C, 50·81; H, 7·51. $C_{16}H_{28}O_{10}$ requires: C, 50·52; H, 7·42%).

Isoeuonyminol methyl ether heptaacetate (**19**). A soln of **18** (105 mg) in Ac_2O (4 ml) and pyridine (10 ml) was kept at 60° for 24 hr, and concentrated. The residue was taken up in AcOEt, and the AcOEt extract was washed with sat $NaHCO_3$ aq and sat NaCl aq, and dried. On removal of the solvent an amorphous residue was obtained, which was chromatographed over silicic acid with $CHCl_3$, giving crude product. Recrystallization from MeOH-isopropyl ether yielded needles, **19**, m.p. 187–188°; IR (KBr) 3500, 1755 cm^{-1}; NMR ($CDCl_3$) 5·58 (1H, d, $J = 3·0$ Hz, H-1), 5·26 (1H, dd, $J = 3·0$, 3·0 Hz, H-2), 4·78 (1H, d, $J = 3·0$ Hz, H-3), 4·63 (1H, s, H-5), 2·65 (1H, d, $J = 3·0$ Hz, H-6), 5·38 (1H, dd, $J = 3·0$, 9·5 Hz, H-7), 5·63 (1H, d, $J = 9·5$ Hz, H-8), 4·48 and 4·85 (2H, ABq, $J = 13·5$ Hz, H-11), 1·67 (3H, s, H-12), 1·58 (3H, s, H-14), 4·06 and 4·70 (2H, ABq, $J = 11·5$ Hz, H-15), 3·38 (3H, s, OMe), 1·87, 1·94, 2·01, 2·07, 2·13, 2·14, 2·21 (3H each, s, 7 × AcO); Mass 614 (M-60). (Found: C, 53·30; H, 6·53. $C_{30}H_{42}O_{17}$ requires: C, 53·46; H, 6·13%).

Acknowledgements—The authors express their deep gratitudes to National Institutes of Health for financial support (Grant No. 5RO1 GM07969) for this project.

REFERENCES

[1]H. Wada, Y. Shizuri, K. Yamada and Y. Hirata, *Tetrahedron Letters* 2655 (1971)
[2]Y. Shizuri, H. Wada, K. Sugiura, K. Yamada and Y. Hirata, *Ibid.* 2659 (1971)
[3]H. Wada, Y. Shizuri, K. Sugiura, K. Yamada and Y. Hirata, *Ibid.* 3131 (1971)
[4]Y. Shizuri, H. Wada, K. Sugiura, K. Yamada and Y. Hirata, *Tetrahedron* **29**, 1773 (1973)
[5]M. Pailer and R. Libiseller, *Monatsh. Chem.* **93**, 403 (1962)