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TRITERPENOIDS—III[1]

THE STRUCTURE OF CYCLAMIGENIN B

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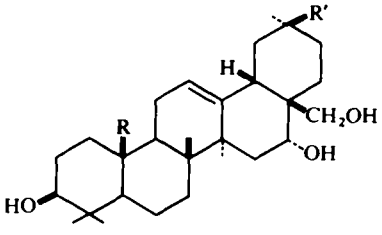
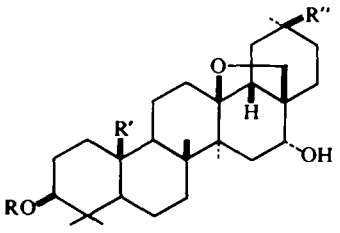
Abstract—Cyclamigenin B is shown to be 13β,28-epoxy-16,30-dioxo-oleanan-3β-ol (VII) by reduction to aegicerin (XII) and by oxidation of cyclamigenin B acetate to the corresponding acid IX acetolysis of which yields 3β,28-diacetoxy-16-keto-olean-12-en-30-oic acid (XVIII). The mass spectra of aegicerin acetate (XI), cyclamigenin B acetate (VIII), and the methyl ester acetate X are discussed.

ACID hydrolysis of cyclamin, a crystalline saponin from the corms of *Cyclamen europaeum* L., has been shown[2] to yield cyclamiretin A and the artifacts the cyclamiretins B, C and D. Acid hydrolysis of the amorphous saponin remaining after removal of cyclamin by crystallization gives, in addition to stigmasterol, a similar mixture of triterpenes, the cylamigenins A, B,[3] C, D and E. Cyclamiretin D was first considered to be the 25-oxo compound I[4] and cyclamiretin A (III), from which the former is obtained on treatment with acid, was formulated analogously.[2] However, since our preliminary communication[3] on the constitution of cyclamigenin B (VII) the structures of the cyclamiretins A (IV) and D (II) have been revised and both are now considered to be 30-oxo compounds.[5] This paper reports details of our work on cyclamigenin B.

Cyclamigenin B (VII) is saturated to tetranitromethane and shows no high-intensity absorption in the UV. The IR spectrum has bands at 2717 (C—H stretch) and 1725 cm^{-1} (C=O stretch), indicative of the presence of a formyl group,[6] and at 3455 (OH), 1701 (cyclohexanone), 1044, and 890 cm^{-1} (ether). This last band suggested that cyclamigenin B contains a tertiary ether function.[7] The presence of the OH and formyl groups was confirmed by the preparation of an acetate (VIII) mild chromic acid oxidation of which furnished an acetoxy acid (IX). The molecular ion in the mass spectrum of the methyl ester X of this acid occurs at *m/e* 542, $C_{33}H_{50}O_6$,

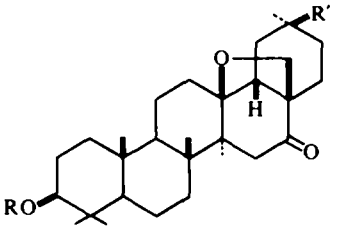


I: R = CHO, R' = Me
II: R = Me, R' = CHO



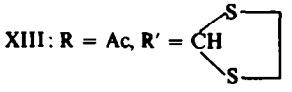
III: R = H, R' = CHO, R'' = Me
IV: R = H, R' = Me, R'' = CHO
V: R = H, R' = R'' = Me
VI: R = Ac, R' = R'' = Me

indicating that cyclamigenin B contains one of each of the functional groups, hydroxyl, ether, ketonic carbonyl, and aldehydic carbonyl, and is pentacarbocyclic with an additional oxide ring. The NMR spectrum of the acetate VIII shows that the formyl group is tertiary (singlet at τ 0·63) and that the ether function is of the type CH_2—O—C (AB quartet with doublets centred at τ 6·12 and 6·66, $J = -8$ Hz).[8]

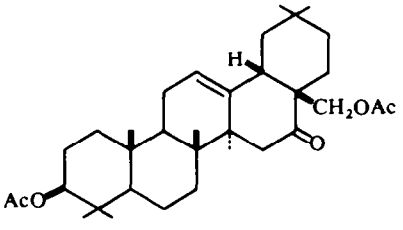


VII: R = R′ = CHO
VIII: R = Ac, R′ = CHO
IX: R = Ac, R′ = CO_2H
X: R = Ac, R′ = CO_2Me

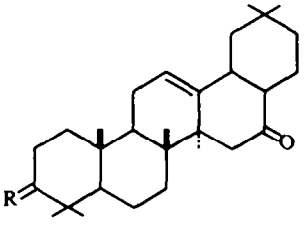
XI: R = Ac, R′ = Me
XII: R = H, R′ = Me



XIII: R = Ac, R′ =



XIV



XV: R = H, β-OH
XVI: R = O

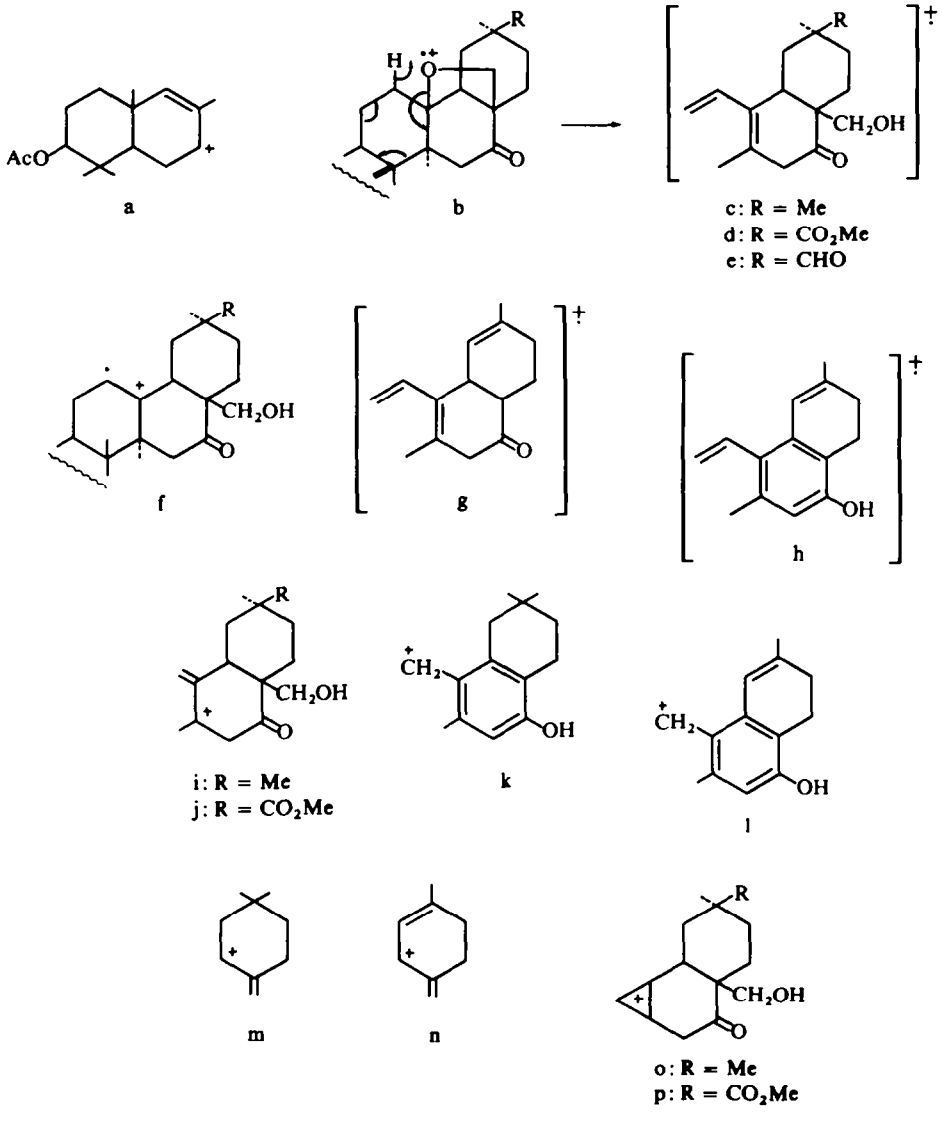
Huang–Minlon reduction of cyclamigenin B (VII) yields the diol (V)[2] the mono-acetate VI of which, when treated with chromium trioxide in pyridine, affords aegicerin acetate (XI).[9] The latter, which was also obtained by desulphurization of the dithioacetal (XIII), was characterized by hydrolysis to aegicerin (XII)[9] and by acetolysis[9] to 3β,28-diacetoxy-16-keto-olean-12-ene (XIV). Alkaline hydrolysis of the keto diacetate XIV yielded norechynocystenolone (XV)[10] oxidation of which furnished norechynocystenedione (XVI).[10] Cyclamigenin B is, therefore, an aldehyde derivative of aegicerin.

The formyl group in cyclamigenin B is not at C-4, C-8 or C-10 since the mass spectra of the acetate VIII and the methyl ester X, and also of aegicerin acetate (XI), show prominent peaks at *m/e* 249 (*a*) and 189 (*a* − AcOH).[11]

As is the case for the cyclamiretins,[5] retro-Diels–Alder fragmentation[11] is an important decomposition mode for the molecular ions of these three substances (VIII, X, XI). The resulting fragments (*c*, *d*, *e*) may be envisaged as arising from the ether molecular ions (*b*) or from the corresponding ether-opened species (*f*) which might be formed either before or after electron impact. Intense peaks at *m/e* 248 (*c*),

218 ($c - CH_2O$), and 217 ($c - CH_2OH$) in the spectrum of aegicerin acetate (XI) are shifted to *m/e* 292 (*d*, base peak), 262 ($d - CH_2O$), and 261 $d - CH_2OH$) for the methyl ester (X). The expected[11] "retro-diene" peaks, at *m/e* 262 (*e*), 232 ($e - CH_2O$), and 231 ($e - CH_2O - H$), in the spectrum of cyclamigenin B acetate (VIII) are weak but fragments resulting from elimination of a second molecule of formaldehyde are abundant, i.e. species of *m/e* 202 (*g*, base peak) (a metastable ion is observed for the formation of this fragment from that of *m/e* 232), 201 ($g - H$) (a metastable ion is observed for the formation of this fragment from that of *m/e* 231), and 200 (*h*). The formation of similar aromatic species from 16-ketones has been noted previously.[11a]

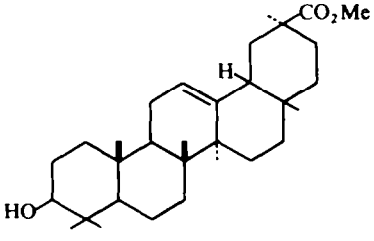
The remaining intense peaks in the spectrum of aegicerin acetate (XI) may be attributed[11a] to the D/E-ring fragment (*i*), *m/e* 235, and its secondary decomposition



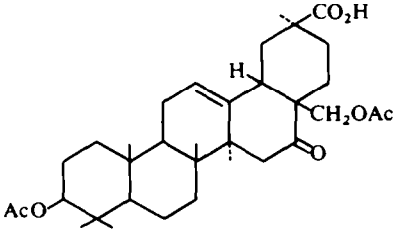
products of *m/e* 205 (*i* − CH_2O), 204 (*i* − CH_2OH), and 203 (*k* or a tropylium ion equivalent, base peak). As expected, these peaks are shifted to *m/e* 279 (*j*), 249 (*j* − CH_2O), 248 (*j* − CH_2OH), and 247 (*j* − CH_3OH) for the methyl ester X. The corresponding fragments from cyclamigenin B acetate (VIII) are of low abundance with the exception of the aromatic species (*l*) of *m/e* 187. A metastable ion is observed for the formation of the latter from a fragment of *m/e* 219 (*l* + CH_3OH).

The peaks at *m/e* 123 and 107, previously[3] noted in the spectra of aegicerin acetate (XI) and cyclamigenin B acetate (VIII) and attributed to species *m* and *n*, respectively, occur, in fact, in the spectra of many triterpenes.[12] Hence, they cannot be used to determine the position of the formyl group in cyclamigenin B. However, a peak at *m/e* 219, which may be assigned to the fragment (*o*), in the spectrum of aegicerin acetate (XI) is shifted to *m/e* 263 (*p*) for the methyl ester X. Since it has been shown that C-27 is eliminated in the formation of this species,[11b] the formyl group in cyclamigenin B must be at C-20.

Some confirmation of the location of the formyl group comes from the rate of saponification of the methyl ester X (Experimental) which is much greater than that for compounds containing angular carbomethoxyl groups but is comparable with the rate of saponification of the 20β-carbomethoxyl function of desoxoglycyrrhetic acid methyl ester (XVII).[13] Furthermore, the IR spectrum of the methyl ester X shows bands at 1151, 1195 and 1225 cm^{-1} indicative[14] of the presence of an axial carbomethoxy group, i.e. cyclamigenin B is 30-oxoaegicerin (VII).



XVII



XVIII

Finally, cleavage of the ether ring on the acid IX with *p*-toluenesulphonic acid in acetic anhydride yields 3β,28-diacetoxy-16-keto-olean-12-en-30-oic acid (XVIII).[5] Cyclamigenin B, therefore, is 13β,28-epoxy-16,30-dioxo-oleanan-3β-ol (VII).

EXPERIMENTAL

Specific rotations were determined for 1% solns in $CHCl_3$ at 18–22°. M.ps were determined in vacuum sealed capillaries in an electrically heated aluminium block and are corrected. NMR spectra were recorded on a Varian A-60 instrument in $CDCl_3$ with TMS as internal standard. Analytical samples were dried for 60 hr at 78°/10^{-2} mm.

Isolation of cyclamin

Minced, air-dried corms (1·4 kg) of *C. europaeum* were extracted (24 hr) with benzene (5 l.). Evaporation of the extract to dryness gave a brown wax (30 g). The dewaxed corms were coarsely ground, extracted (3 × 2 hr) with boiling 90% EtOH (7 l., 6 l., 4 l.), and the extracts stored (2 weeks) at 0° to give yellow crystalline material (115 g, 25 g, trace, respectively). The first extract was concentrated (to 3 l.) and stored (7 days) at 0° to yield more yellow crystals (39 g). The mother liquor was combined with the second extract,

the mixture concentrated (to 1 l.), and stored (7 days) at 0° to give a further crop (9 g) of crystalline material. This last mother liquor and the third extract were combined and concentrated (to 500 ml) to yield a gel on cooling. Crystallization of the combined yellow solids, first from 70% EtOH and then from 80% EtOH furnished colourless needles (75 g) of cyclamin, m.p. 282–283°, $[\alpha]_D$ −22° (pyridine) (lit.[2] m.p. 282–283°, $[\alpha]_D$ −22·6°).

Isolation of the cyclamigenins

The residual gel obtained above was diluted with water (3 l.) and conc HCl (300 ml), the mixture refluxed (3 hr), and left overnight at room temp. The dark ppt was collected, washed well with warm water, sucked dry, and extracted (21 hr) with boiling EtOH (1·8 l.). Removal of the insoluble, soil-like material and dilution of the filtrate with 5% KOH aq (3 l.) gave a yellow ppt which was washed with warm water, dried, and heated (2 hr) on a steam-bath with pyridine (200 ml) and Ac_2O (400 ml). The acetylated material was isolated in the usual way through ether and washed through a column of alumina (1 kg) with benzene–ether (1:1, 10 l.) to yield a pale yellow gum (60 g) a soln of which in hexane (400 ml) was chromatographed on alumina (2 kg). Elution of the column with hexane (2 l.) and hexane–benzene mixtures (9:1, 2 l.; 4:1, 1 l.) gave an oil (100 mg) which was discarded. Elution with hexane–benzene (7:3, 2·5 l.) gave a wax (250 mg) crystallization of which from pentane and then from $CHCl_3$–MeOH furnished waxy plates (53 mg) of stigmasteryl acetate, m.p. 142–143°, $[\alpha]_D$ −54°. (Found: C, 81·5; H, 11·2. Calc. for $C_{31}H_{50}O_2$: C, 81·9; H, 11·1%), identical (mixed m.p. and IR spectrum) with an authentic sample. Saponification of this acetate yielded stigmasterol, m.p. 163–165°, $[\alpha]_D$ −42°. (Found: C, 84·4; H, 11·8. Calc. for $C_{29}H_{48}O$: C, 84·4; H, 11·7%.)

Elution of the column with hexane–benzene (1:1, 1·5 l.) yielded an intractible gum (100 mg). Benzene (3 l.) then eluted a solid froth (A) (7·5 g) that partly crystallized from MeOH. Further elution with benzene (8 l.) gave a crystalline fraction (B) (11 g) and more polar eluants yielded only intractible gums.

Fraction A was dissolved in hexane–benzene (1:1) and chromatographed on alumina (150 g). After removal of traces of oily material with hexane–benzene (1:1, 800 ml) the same eluant (100 ml) gave a crystalline fraction (2·33 g) which was recrystallized from $CHCl_3$–MeOH to yield flakes (1·7 g) of *cyclamigenin A acetate*, m.p. 231–233°, $[\alpha]_D$ +15 ± 1°. (Found: C, 74·3, 74·4; H, 9·8, 9·7. Calc. for $C_{36}H_{56}O_6$: C, 73·9; H, 9·65%.) Further elution of the column with hexane–benzene (1:1, 200 ml) gave crude cyclamigenin A acetate (2 g) which was combined with the corresponding material from fraction B (below).

A soln of fraction B in benzene was chromatographed on alumina (400 g) and the column eluted with the same solvent (1·3 l.) to yield a colourless wax (2·2 g). Continued elution with benzene (4 l.) gave colourless crystals (4·26 g) recrystallization of which from $CHCl_3$–MeOH furnished fine needles (3 g) of *cyclamigenin B acetate*, m.p. 307·5–308·5°, $[\alpha]_D$ −10 ± 1°, ν_{max} (KBr) 2710 (w), 1730 (s), 1706 (s), 1245 (s), 1043 (s), 894 (s) cm^{-1}, ν_{max} (CCl_4) 2710 (w), 1734 (s), 1712 (s), 1238 (s), 1045 (s), 895 (s) cm^{-1}, τ 9·14 (2Me), 9·08 (Me), 8·94 (Me), 8·77 (Me), 9·01 (Me), 7·96 (Ac), 7·25 (doublet, J = −15 Hz) (H-15), 6·66 (doublet, J = −8 Hz) (H-28), 6·12 (doublet, J = −8 Hz) (H-28), 5·5 (multiplet, $W_{\frac{1}{2}}$ = 25 Hz) (H-3), 0·63 (singlet) (CHO), (*m/e*)/% relative abundance 512 (M^+)/ < 1, 262/ < 1, 249/6·5, 232/7, 231/5, 219/7, 202/100, 201/49, 200/80, 189/38, 187/20. (Found: C, 75·2; H, 9·4%. Calc. for $C_{32}H_{48}O_3$: C, 75·0; H, 9·4%.) Tetranitromethane, Zimmermann and Zeisel tests are negative.

Rechromatography of the wax (2·2 g) from fraction B on alumina (100 g) gave crude cyclamigenin A acetate (1·15 g), which was combined with the corresponding material from fraction A to form fraction C (3·35 g), on elution with benzene (600 ml). Continued elution with benzene (400 ml) gave crude cyclamigenin B acetate (D) (960 mg).

A soln of fraction C in hexane–benzene (1:1) was chromatographed on alumina (100 g) and the column eluted with the same solvent mixture (600 ml) to give a fraction (2 g) crystallization of which from $CHCl_3$–MeOH furnished cyclamigenin A acetate (800 mg), m.p. 231–233°, $[\alpha]_D$ +14°. Continued elution with the same mixed eluant (50 ml) gave a fraction (500 mg) which was crystallized successively from $CHCl_3$–MeOH, hexane, CH_2Cl_2–hexane, and $CHCl_3$–MeOH to yield fine needles (80 mg) of *cyclamigenin C acetate*, m.p. 222–223°, $[\alpha]_D$ −125 ± 2°. (Found: C, 74·1, 74·4; H, 9·8; 9·5. Calc. for $C_{36}H_{56}O_6$: C, 73·9; H, 9·65%.) Further elution with hexane–benzene (1:1, 100 ml) yielded crude cyclamigenin B acetate (790 mg).

Fractional crystallization (triagulation) of fraction D gave, from the less soluble fractions, cyclamigenin B acetate (520 mg), m.p. 307–308°, $[\alpha]_D$ −9°, and, from the more soluble fractions, *cyclamigenin D acetate* (35 mg), m.p. 272–274° $[\alpha]_D$ +3 ± 1°. (Found: C, 73·5; H, 9·7%.) The mother liquors from which the latter was obtained yielded crude cyclamigenin E acetate as needles (5 mg), m.p. 315–323° (dec.), $[\alpha]_D$ +4°.

Cyclamigenin B

A soln of cyclamigenin B acetate (600 mg) in dioxan (20 ml) was refluxed (6 hr) with 5% KOH in MeOH (20 ml), the mixture was diluted with water (25 ml), and the ppt crystallized from EtOH to yield *cyclamigenin B* (411 mg), m.p. 295–296°, $[\alpha]_D$ −10°, ν_{max} (KBr) 3491 (s), 2710 (w), 1729 (s), 1710 (s), 1044 (s), 891 (m) cm^{-1}, ν_{max} ($CHCl_3$) 3455 (s), 2717 (w), 1725 (s), 1701 (s), 890 (m) cm^{-1}. (Found: C, 76·3; H, 9·9. Calc. for $C_{30}H_{46}O_4$: C, 76·55; H, 9·85%.) The analytical sample was sublimed at 230–235°/10^{-6} mm. Acetylation of the alcohol regenerated cyclamigenin B acetate.

Oxidation of cyclamigenin B acetate

A solution of CrO_3 (50 mg) in water (0·2 ml) and AcOH (2 ml) was added dropwise, with swirling, to cyclamigenin B acetate (100 mg) in AcOH (4 ml). After 4 hr at room temp the mixture was diluted with water (20 ml), the flocculent ppt was collected, washed with water, and crystallized first from MeOH and then from $CHCl_3$–MeOH to yield blades (63 mg) of the *acid* IX, m.p. 319–320° (dec., sample inserted at 300° and heated at 4°/min), $[\alpha]_D$ −3 ± 2°, ν_{max} (KBr) 3250 (m), 1733 (s, broad), 1705 (s), 1241 (s), 1041 (s), 892 (s) cm^{-1}. (Found: C, 72·4; H, 9·3. Calc. for $C_{32}H_{48}O_6$: C, 72·7; H, 9·15%.)

Treatment of the acid (45 mg) in MeOH (5 ml) with excess diazomethane in ether and crystallization of the product from $CHCl_3$–MeOH furnished the *methyl ester* X, m.p. 289–290° (dec.), $[\alpha]_D$ +5 ± 2°, ν_{max} (KBr) 1740 (s), 1733 (s), 1706 (s), 1242 (s), 1225 (m), 1195 (m), 1151 (s), 1041 (s), 895 (s) cm^{-1}, (*m/e*)/% relative abundance 542 (M^+)/24, 292/100, 279/62, 263/8, 262/25, 261/28, 249/23, 248/15, 247/54, 189/72. (Found: C, 72·8; H, 9·3. Calc. for $C_{33}H_{50}O_6$: C, 73·0; H, 9·3%.)

Saponification of the methyl ester X

A mixture of the methyl ester (16·26 mg) and 10% (w/w) KOH in MeOH (5 ml) was refluxed (8 hr), diluted with water (50 ml), and extracted with ether (3 × 10 ml). The aqueous phase was acidified with dil HCl and also extracted with ether (3 × 10 ml). The washed (water) and dried ($MgSO_4$) ether extracts were evaporated to dryness to give neutral (6·3 mg, 42%) and acid (8·46 mg, 58%) products. The yields of acid product from two similar experiments were 63 and 65%. Under the same conditions the yields of acid from 17β-carbomethoxy and 20β-carbomethoxy triterpenes are 0–20 and 40–47%, respectively.[13]

Acetolysis of the acetoxy acid IX

A soln of the acetoxy acid (50 mg) in Ac_2O (3 ml) was heated (30 min) at 117–120° with *p*-toluenesulphonic acid (30 mg), the mixture poured into ice–water (25 ml), worked up through ether, and the product crystallized from MeOH aq to yield fine needles (14 mg) of 3β,28-diacetoxy-16-keto-olean-12-en-30-oic acid, m.p. 275–277° (dec.), $[\alpha]_D$ +12°, identical (mixed m.p. and IR spectrum) with a sample prepared[5] from cyclamiretin D diacetate.

Huang–Minlon reduction of cyclamigenin B

Cyclamigenin B (279 mg) in EtOH (15 ml) and diethylene glycol (30 ml) was refluxed (30 min) with 100% hydrazine hydrate (0·5 ml), NaOH (3 g) in water (3 ml) was added, and the mixture distilled until the temp of the soln reached 240°. The soln was refluxed (4 hr), cooled, diluted with water (50 ml), and the product isolated through $CHCl_3$. The crude material was heated (1 hr) on a steam-bath with pyridine (5 ml) and Ac_2O (10 ml), the mixture worked up in the usual manner, and the crude acetate chromatographed on alumina (15 g). Elution with hexane–benzene (1:1, 500 ml) gave oily material (180 mg). Elution with benzene (400 ml) afforded a fraction (120 mg) crystallization of which from $CHCl_3$–MeOH yielded matted needles (82 mg) of the *monoacetate* VI, m.p. 281·5–282°, $[\alpha]_D$ +16 ± 1°, ν_{max} (KBr) 3500 (m), 1732 (s), 1245 (s), 1045 (m), 888 (m) cm^{-1}. (Found: C, 76·7; H, 10·5. Calc. for $C_{32}H_{52}O_4$: C, 76·75; H, 10·5%.)

Alkaline hydrolysis of the acetate furnished desoxocyclamiretin D (V), m.p. 254–255° (open capillary), 295·5–296° (vacuum sealed capillary), $[\alpha]_D$ +8° (pyridine), +19° ($CHCl_3$) [lit.[2] m.p. 252–253°, $[\alpha]_D$ +5° (pyridine)]. (Found: C, 78·5; H, 11·1. Calc. for $C_{30}H_{50}O_3$: C, 78·6; H, 11·0%.)

Cyclamigenin B acetate ethylene dithioacetal

Cyclamigenin B acetate (600 mg) was stirred to a homogeneous paste with ethanedithiol (0·6 ml), BF_3-etherate (0·6 ml) was added, and the mixture was stirred (3 min). After dilution with MeOH (10 ml), the product was separated, washed with MeOH (20 ml), and crystallized from $CHCl_3$–MeOH to yield the *dithioacetal* (554 mg), $[\alpha]_D$ +1·5°, which is dimorphous. Slow crystallization gives stout needles, m.p.

315–316°, while rapid crystallization gives fine needles, m.p. 327–328°, which resolidify at ca. 315° to give the material with m.p. 315–316°; ν_{max} (KBr) 1730 (s), 1705 (s), 1247 (s), 1045 (s), 889 (m), 758 (m) cm^{-1}. (Found: C, 69·1; H, 8·8; S, 11·4. Calc. for $C_{34}H_{52}O_4S_2$: C, 69·4; H, 8·9; S, 10·9%.)

A suspension of the dithioacetal acetate (33 mg) in benzene (3 ml) was refluxed (5 hr) with 5% KOH in MeOH (4 ml) and the product crystallized from MeOH to yield the *dithioacetal alcohol* (20 mg), m.p. 267–268°, $[\alpha]_D$ −9 ± 1°, ν_{max} (KBr) 3509 (m), 1705 (s), 1046 (s), 890 (m), 751 (m) cm^{-1}. (Found: C, 69·9; H, 9·1; S, 11·4. Calc. for $C_{32}H_{50}O_3S_2$: C, 70·3; H, 9·2; S, 11·7%.)

Aegicerin acetate

(a) A mixture of VI (23 mg) and CrO_3 (25 mg) in pyridine (1 ml) was stored overnight at room temp, diluted with 5% NaOH aq (20 ml) and MeOH (2 ml), and extracted with ether (3 × 5 ml). The combined extracts were washed with 10% $FeSO_4$ aq, dil. H_2SO_4, and saturated $NaHCO_3$ aq, dried (Na_2SO_4), the ether evaporated, and the residue crystallized from $CHCl_3$–MeOH to yield flakes (20 mg) of aegicerin acetate, m.p. 276–278° (open capillary), 290–290·5° (vacuum sealed capillary), $[\alpha]_D$ −18 ± 2° (lit.[9] m.p. 273–275°, $[\alpha]_D$ −17·7°), ORD a = −130, ν_{max} (KBr) 1733 (s), 1706 (s), 1245 (s), 1046 (s), 897 (m) cm^{-1}, τ 9·14 (3Me), 9·08 (Me), 9·06 (Me), 8·97 (Me), 8·76 (Me), 7·96 (Ac), 7·27 (doublet, J = −16 Hz) (H-15), 6·57 (doublet, J = −8 Hz) (H-28), 6·12 (doublet, J = −8 Hz) (H-28), 5·5 (multiplet, $W_{\frac{1}{2}}$ = 20 Hz) (H-3), (m/e)/% relative abundance 498 (M^+)/21, 294/30, 248/71, 235/83, 219/17, 218/57, 217/59, 205/43, 204/41, 203/100, 189/68. (Found: C, 76·9; H, 10·0. Calc. for $C_{32}H_{50}O_4$: C, 77·1; H, 10·1%.)

(b) A mixture of XIII (101 mg), deactivated Raney Ni (ca. 3 g), and dioxan (30 ml) was refluxed (7 hr), cooled, filtered, the solvent evaporated, and the residue crystallized from $CHCl_3$–MeOH to yield aegicerin acetate (50 mg), m.p. 289–290°, $[\alpha]_D$ −20°, identical with the material prepared above. In a similar experiment using benzene as solvent aegicerin acetate was obtained in 94% yield.

Alkaline hydrolysis of aegicerin acetate furnished aegicerin, m.p. 254–256° (open capillary), 271–272° (vacuum sealed capillary), $[\alpha]_D$ −16 ± 2° (lit.[9] m.p. 254–256°, $[\alpha]_D$ −23·6°). (Found: C, 79·2; H, 10·8. Calc. for $C_{30}H_{48}O_3$: C, 78·9; H, 10·6%.)

Acetolysis of aegicerin acetate

Aegicerin acetate (100 mg) in Ac_2O (5 ml) was heated (30 min) with *p*-toluenesulphonic acid (60 mg) at 115–120°, the mixture was diluted with water (30 ml), the product isolated through ether, and chromatographed on alumina (3 g). Elution with hexane–benzene (2:1, 150 ml) gave a clear gum (98 mg) crystallization of which from hexane furnished XIV (50 mg), m.p. 210–211° (open capillary), 211–212° (vacuum sealed capillary), $[\alpha]_D$ −9° (lit.[9] m.p. 210–211°, $[\alpha]_D$ −7·6°). (Found: C, 75·9; H, 9·5. Calc. for $C_{34}H_{52}O_5$: C, 75·5; H, 9·7%.)

Norechynocystenolone

Hydrolysis of XIV with 5% KOH in refluxing MeOH gave norechynocystenolone as needles from MeOH aq, m.p. 223–224° (open or vacuum sealed capillary), $[\alpha]_D$ −110° ($CHCl_3$), −96° (dioxan) [lit.[10] m.p. 230–233°, $[\alpha]_D$ −86·7° (dioxan)]. (Found: C, 81·3; H, 10·7. Calc. for $C_{29}H_{46}O_2$: C, 81·6; H, 10·9%.)

Norechynocystenedione

Oxidation of the above product with CrO_3 in pyridine yielded norechynocystenedione, m.p. 214–216° (open capillary), 234–235° (vacuum sealed capillary), $[\alpha]_D$ −101° ($CHCl_3$), −97° (dioxan) [lit.[10] m.p. 210–212°, $[\alpha]_D$ −92·7° (dioxan)]. (Found: C, 81·8; H, 10·2. Calc. for $C_{29}H_{44}O_2$: C, 82·0; H, 10·4%.)

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