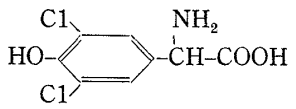
Intensities of 1225 reflections were measured with MoKα radiation on Hilger & Watts' linear diffractometer. Coordinates of the two chlorine atoms were derived from careful analysis of the three dimensional Patterson function. A three dimensional minimum function method and a heavy-atom method were carried out for the elucidation of the positions of light atoms. The structure thus obtained was refined by three dimensional Fourier syntheses and the least squares method. The R factor is 17.5% at the present stage.

In Fig. 1 is given the third three dimensional electron density distribution shown by means of superimposed contour sections projected on (010). The bond lengths and angles (Fig. 2) together with intermolecular contact are reasonable considering the present stage of refinement. The structural formula corresponding to Fig. 1 is thus,



or α-amino-3,5-dichloro-4-hydroxyphenylacetic acid. The existence of this new amino acid in enduracidin would be one of the proofs that the antibiotic has a unique structure.

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Partial Synthesis of Priverogenin B from Camelliagenin A

Recently, in the study of genuine sapogenins of the root of *Bupleurum falcatum* L., Kubota and Hinoh described[1] the synthesis of saikogenin E[1,2] (IIIa) from longispinogenin (Ia) *via* 11-hydroxy-longispinogenin (IIa). In the present communication, we wish to forward our observations of similar line which lead the partial synthesis of priverogenin B[3,4] (IVa) from camelliagenin A[4,5] (Ib) (=dihydropriverogenin A[3,6,7], the former being one of the genuine sapogenins of *Primula veris* L. root, while the latter has been known as one of the common sapogenins of some *Theaceous*[4,5,8,9] and *Primulaceous* plants.[3,6]

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5) *a*) H. Itokawa, N. Sawada, and T. Murakami, *Tetrahedron Letters*, **1967**, 597. *b*) S. Ito, M. Kodama, and M. Konoike, *ibid.*, **1967**, 591.
6) I. Kitagawa, A. Matsuda, T. Nishimura, S. Hirai and I. Yosioka, *Chem. Pharm. Bull.* (Tokyo), **15**, 1435 (1967).
7) M. Kodama and S. Ito, *Chem. Ind.* (London), **1967**, 1647.
8) I. Yosioka, A. Matsuda, and I. Kitagawa, *Chem. Pharm. Bull.* (Tokyo), **15**, 547 (1967).
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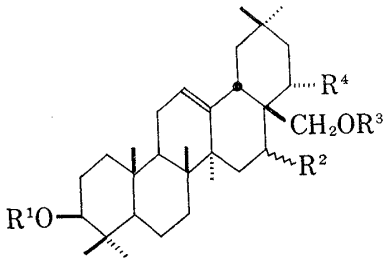
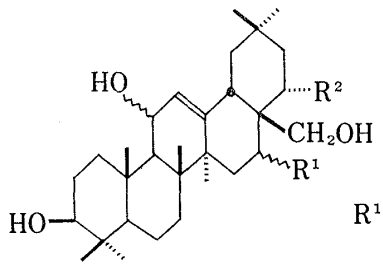
During the course of the study on the photooxidation of erythrodiol (Ic)[10], we have noticed that 11ξ-hydroxy-erythrodiol (IIc)[11], an intermediate of the synthetic route to the photooxidation products, are fairly labile and consequently the previous transformation was performed without further recrystallization.

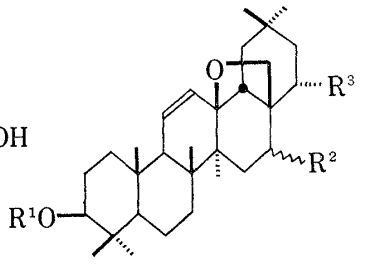
On refluxing the methanolic solution of IIc for 10 min, a crystalline product was separated. Although the crystals exhibited a single spot on TLC, its contamination (less than one per cent) with $\Delta^{11,13,(18)}$-oleanadienic compound (Va) was revealed by the characteristic triplet ultraviolet (UV) absorption bands at 244, 252 and 262 mμ.[12] Repeated recrystallization of the crystals from methanol afforded a pure material (no UV absorption above 210 mμ), $C_{30}H_{48}O_2$,[13] mp 225—226°, $[\alpha]_D$ +115° (c=1.0 in $CHCl_3$), whose constitution is assigned as 3β-hydroxy-13, 28-epoxy-olean-11-ene (IIIc) based on its physical properties: nuclear magnetic resonance (NMR) spectrum (60 Mc in $CDCl_3$, τ): 9.21 (1Me), 9.11 (1Me), 9.09 (1Me), 9.02 (3Me), 8.90 (1Me) (all singlets, totally seven methyls), 6.74, 6.32 (2H, ABq., J=7 cps, -$C_{(28)}\underline{H}_2$-O-$C_{(13)}$-), 6.81 (1H, t.-like, >$C_{(3)}\underline{H}$OH), 4.65 (1H, d.d., J=3 and 11), 4.17 (1H, d. J=11) (as AB quartet), and on the physical properties of its acetate (IIId), $C_{32}H_{50}O_3$, mp 221—223°, $[\alpha]_D$ +127° (c=1.0 in $CHCl_3$), NMR: 9.13 (2Me), 9.05 (2Me), 9.03 (2Me), 8.91 (1Me), 7.98 (1Ac), 6.74, 6.31 (2H, ABq., J=7 cps, $C_{(28)}\underline{H}_2$-O-$C_{(13)}$-), 5.50 (1H, t. -like, >$C_{(3)}\underline{H}$OAc), 4.66 (1H, d.d., J=3 and 11), 4.15 (1H, d., J=11) (as AB quartet). The assignments above are in good agreement with the



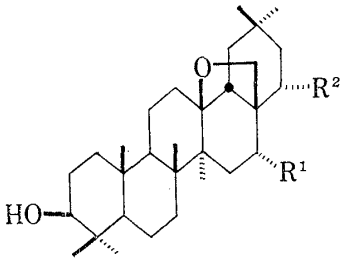
Ia : R^1=R^3=R^4=H, R^2=β-OH
longispinogenin
b : R^1=R^3=H, R^2=α-OH, R^4=OH
camelliagenin A
c : R^1=R^2=R^3=R^4=H
erythrodiol
d : R^1=R^3=Ac, R^2=α-OAc, R^4=OAc



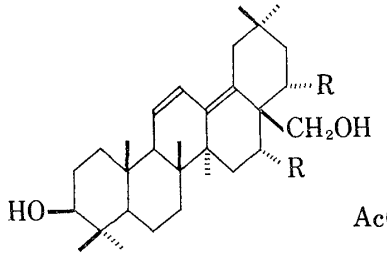
IIa : R^1=β-OH, R^2=H
b : R^1=α-OH, R^2=OH
c : R^1=R^2=H



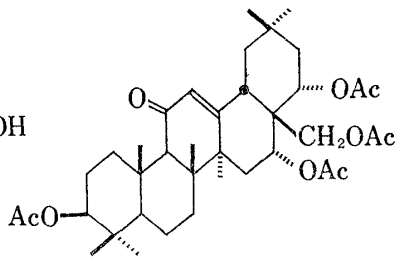
IIIa : R^1=R^3=H, R^2=β-OH
saikogenin E
b : R^1=H, R^2=α-OH, R^3=OH
c : R^1=R^2=R^3=H
d : R^1=Ac, R^2=R^3=H
e : R^1=Ac, R^2=α-OH, R^3=OAc



IVa : R^1=R^2=OH
priverogenin B
b : R^1=R^2=H



Va : R=H
b : R=OH



VI

Chart 1.

10) I. Kitagawa, K. Kitazawa, and I. Yosioka, *Tetrahedron Letters*, **1968**, 2643.
11) A mixture of two epimers at C_{11} as revealed by thin-layer chromatography (TLC).
12) D.H. R. Barton and C.J.W. Brooks, *J. Chem. Soc.*, **1951**, 257.
13) All the compounds given with the chemical formulae gave satisfactory analytical values.

previous investigations of saikogenin E[1,2], and furthermore the acid treatment of IIIc giving smoothly Va substantiates the formulation, thus showing that even the refluxing of the methanolic solution of IIc is satisfactory for converting IIc to IIIc.[14]

Next, our attention was focused to hydrogenate a double bond at $C_{11(12)}$ of IIIc aimed at priverogenin B type compound (as IVb), for it has been mentioned by the previous workers[1] that IIIa suffers hydrogenolysis to yield Ia as a sole product on hydrogenation in acetic acid over Adams' catalyst. On varying the hydrogenation procedure ((i) under atmospheric pressure or 3 atm., (ii) acetic acid, ethanol, dioxane, or ethyl acetate as solvent, (iii) PtO_2, 5% Pd-C or Raney Ni (W-7) as catalyst), it was found that the hydrogenation over Raney Ni in ethanol at room temperature under atmospheric pressure effected the expected conversion of IIIc to IVb, $C_{30}H_{50}O_2$, mp 251—252°, $[\alpha]_D$ +47° (c=1.0 in $CHCl_3$), NMR ($CDCl_3$): 9.22 (1Me), 9.12 (2Me), 9.09 (1Me), 9.01 (2Me), 8.80 (1Me), 6.77 (1H, t.-like, $>C\underline{H}_{(3)}OH$), 6.73, 6.24 (2H, ABq., J=6.9, $-C_{(28)}\underline{H}_2-O-C_{(13)}-$), in addition to the formation of the hydrogenolysis product, Ic (the yield ratio of IVb to Ic was 3:2).

Finally, the foregoing reaction sequence was applied for the derivation of camelliagenin A (Ib) to priverogenin B (IVa) as follows. On *t*-butyl chromate oxidation, tetraacetyl-camelliagenin A (Id) furnished an α,β-unsaturated ketone (VI), $C_{38}H_{56}O_9$, mp 225—227°, $[\alpha]_D$ −2° (c=1.0 in $CHCl_3$), IR (KBr, cm^{-1}): 1652 (enone), 1721 (acetate), which in turn was transformed to a mixture IIb by $LiAlH_4$ treatment. Refluxing of the methanolic solution of IIb for 10 min or keeping IIb in 1% methanolic sulfuric acid at room temperature for 10 min yielded IIIb, $C_{30}H_{48}O_4\cdot\frac{1}{2}H_2O$, mp 255—257°, $[\alpha]_D$ +20° (c=1.0 in pyridine), in an excellent yield. Here again, the contamination with a $\Delta^{11,13,(18)}$-dienic compound (Vb, not isolated) was disclosed by UV in the total product.[15] The formulation of IIIb is corroborated reasonably by the physical properties of its diacetate (IIIe), $C_{34}H_{52}O_6$, mp 259—260°, $[\alpha]_D$ +29° (c=1.0 in $CHCl_3$), NMR: 9.14 (2Me), 9.07 (1Me), 8.99 (2Me), 8.96 (1Me), 8.70 (1Me), 7.95 (2Ac), 6.56 (2H, s., $-C_{(28)}\underline{H}_2-O-C_{(13)}-$), 5.72, (1H., br. s.[16] $>C_{(16)}\underline{H}OH$), 5.50 (1H, t.-like, $>C_{(3)}\underline{H}OAc$), 5.03 (1H, q., J=6 cps, $>C-_{(22)}\underline{H}OAc$), 4.62 (1H, d.d., J=2.6 and 10.6), 4.13 (1H., d., J=10.6) (as AB quartet). Catalytic hydrogenation of IIIb over Raney Ni in ethanol as for IIIc afforded a saturated product (75% yield), mp 268—270° and 280.5—283° (double melting point), which was identified with authentic priverogenin B[3] kindly provided by Prof. Tschesche in all respects (mixed mp, TLC, and IR). It seems worthwhile to mention that, on the contrary to the above mentioned case of IIIc, the hydrogenolysis product was not detected in case of IIIb.

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14) In lit. 1), the mild acid treatment was applied for converting IIa to IIIa. Methanol used here exhibited a doublet at τ 6.64 (3H, J=2.4 cps) and a quartet-like signal at τ 5.16 (1H, J=2.4 cps) in its NMR spectrum.
15) The increasing amount of the dienic compound (Vb) was formed through the acidic treatment.
16) Changes to a doublet, J=5.1 cps by addition of D_2O.