Structures of Chiograsterol A and B

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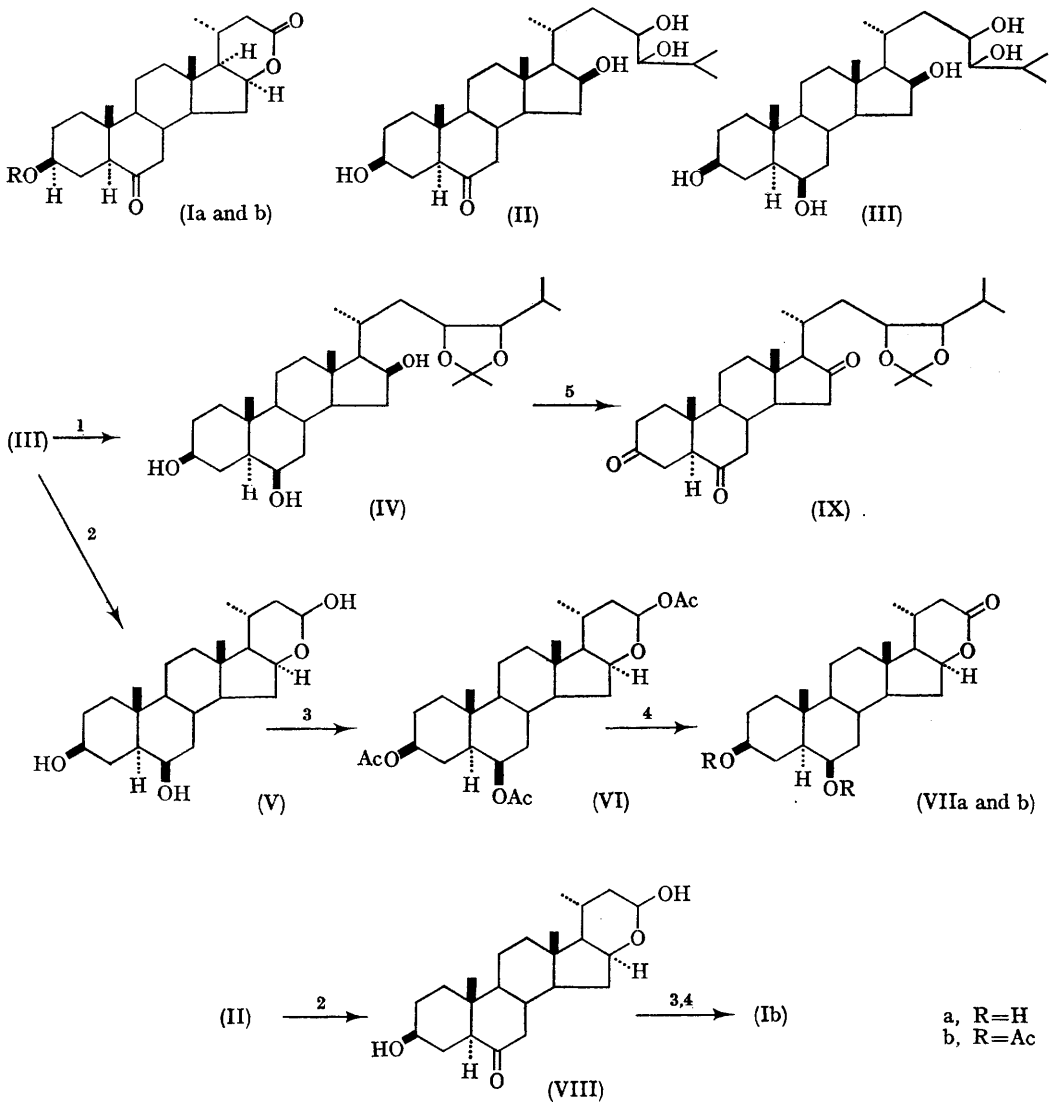
WE have already reported[1] that the steroidal components of *Chionographis japonica* MAXIM. (Shiraitoso in Japanese) were investigated and that chiogralactone,[2,3] a C_{23}-steroidal lactone (Ia), and many poly-oxygenated sterols were isolated. Here we report that the compounds J and K in the previous paper[1] have been named chiograsterol A and B and are represented by structures (II) and (III), respectively.

Chiograsterol B (III), $C_{27}H_{48}O_5$, m.p. 240—243·5°, $[\alpha]_D$ +16·1°, gave a pentabenzoate, m.p. 150—152°, which no longer showed absorption bands due to the hydroxyl group in the infrared spectrum, and a monoacetonide (IV), m.p. 184—185°. Therefore, two hydroxyl groups out of five are vicinal. When chiograsterol B was oxidised with sodium periodate it gave a C_{23}-hemiacetal (V), m.p. 247—248°, the infrared spectra of which showed absorption bands at 1730 cm.$^{-1}$ due to the aldehyde function in chloroform solution and only bands corresponding to the hydroxyl group in a crystalline state. When its triacetate (VI) was oxidised with Jones reagent, it gave a δ-lactone (VIIb), m.p. 190—192°, ν_{max} 1733 and 1723 cm.$^{-1}$, which was hydrolysed to give a diol-lactone (VIIa), m.p. 282—283°. This compound was found to be identical with compound (VIIa),[2] [obtained from chiogralactone (Ia) by the action of sodium borohydride] by mixed melting point determination and comparisons of infrared spectra



Reagents: 1, [OH, OH], H^+; 2, $NaIO_4$; 3, Ac_2O–pyridine; 4, Jones reagent; 5, CrO_3 in pyridine.

and $[\alpha]_D$ values. Therefore, chiograsterol B should be represented by the formula (III), except for the stereochemistry of the side-chain.

Chiograsterol A, (II), $C_{27}H_{46}O_5$, m.p. 125·5—128°/206—210·5°, $[\alpha]_D$ −6·8°, showed an absorption band (c = 0) at 1708 cm.$^{-1}$ in the infrared spectrum and gave a tetra-acetate,m.p. 210—211·5°. It therefore is assumed that chiograsterol A is a compound which is derived by oxidation of one hydroxyl group in chiograsterol B to the carbonyl function. Similarly, chiograsterol A was cleaved with sodium periodate to give a hemiacetal (VIII). On oxidation with Jones reagent, its acetate gave chiogralactone acetate (Ib),[1] m.p. 228—230°, as expected. Moreover, as reduction of chiograsterol A with sodium borohydride afforded chiograsterol B, the former should possess the structure (II).

When the monoacetonide (IV) was oxidised with chromium trioxide in pyridine, it gave a

triketo-acetonide (IX), m.p. 125—128°. The n.m.r. spectrum of (IX) showed signals at τ 6·32 (double-doublet, J = 5.5 and 9·8 c./sec.) and τ 5·83 (double-doublet with unresolved multiplets, J = 5·5 and 11·9 c./sec.) due to the protons at C-24 and C-23, respectively. As the value of 5·5 c./sec. is to the two signals, it is assigned to the coupling between the C-23 and the C-24 protons, and is more consistent with that of the isomer† having these protons in a *cis*-relationship in the acetonide ring.

Chiograsterol A and B have therefore the *erythro*-configuration at C-23 and C-24.

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† The *cis*-values are 5·85 and 6·0 c./sec. and the *trans*-values are 8·35 and 7·3 c./sec. for the acetonide of butan-2,3-diol (ref. 4) and for 1,3-dioxolan (ref. 5), respectively.

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