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ROTATIONAL ISOMERISM IN BISERGOSTATRIENOL (1)

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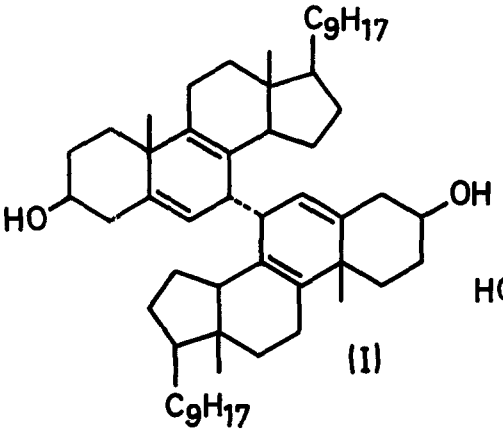
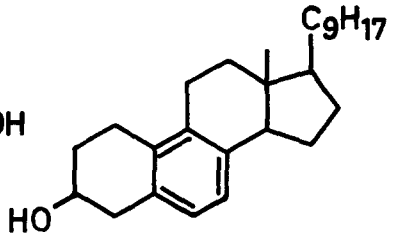
Molecular models suggest that "ergopinakol" (bisergostatrienol) (I) (2,3), the well known irradiation product from ergosterol, should exist in two isomeric forms due to hindrance to rotation about the 7,7' bond. We now wish to report the resolution of the rotamer mixture.

The photodimer (I) is very difficultly soluble in most solvents and is best purified through the diacetate, m.p. (4) 204-205° (decomp.), $[\alpha]_D$ -200 ± 5° (c, 1.2 in $CHCl_3$) [lit. (5) m.p. 205.5-206°, $[\alpha]_D$ -209°], which has normal solubility characteristics. The diacetate is not resolved by fractional crystallisation (triangulation) and shows a single spot on thin-layer chromatography (T.L.C.) (alumina G or silica G Merck with various solvent systems). Hydrolysis of this purified acetate with KOH in refluxing C_6H_6-MeOH gives "pure" "ergopinakol", m.p. 203-204° (decomp.), $[\alpha]_D$ -205 ± 5° (c, 0.8 in pyridine) [lit. m.p. 201-203° (2,3), $[\alpha]_D$ -172° ($CHCl_3$) (3), -209° (pyridine) (2)], which shows two spots (R_f ca. 0.1 and 0.2) on T.L.C. (alumina G-$CHCl_3$). Column chromatography of this difficultly soluble mixture is impracticable but the two components were separated by preparative T.L.C. (6) with repeated development (7) on 1 mm. layers of silica gel G impregnated (8) with Rhodamine 6G. The samples (20 mg. per 200 x 200 mm. plate) were applied as hot, saturated solutions in

tetrahydrofuran and the developing solvent was $CHCl_3$ containing 2% MeOH. The more mobile alcohol, bisergostatrienol-I, m.p. 201.5-202° (decomp.), $[\alpha]_D$ -230 ± 5° (c, 0.75 in pyridine), forms a diacetate, m.p. 193-194° (decomp.), $[\alpha]_D$ -210 ± 5° (c, 1.1 in $CHCl_3$). The less mobile alcohol, bisergostatrienol-II, m.p. 205.5-206.5° (decomp.), $[\alpha]_D$ -155 ± 5° (c, 0.8



(I)



(II)

in pyridine), gives a diacetate, m.p. 210.5-211° (decomp.), $[\alpha]_D$ -180 ± 5° (c, 1.0 in $CHCl_3$). Both acetates have the same R_f value on T.L.C. (alumina G and silica G with various solvent systems). Thermal decomposition (2,9) of either alcohol gives the same mixture of products, viz. neoergosterol (II) and small amounts of a number of other compounds whose structures are now being investigated. The infrared spectra of the alcohols, and also of the acetates, show only minor differences in the fingerprint region. A mixture of approximately equal parts of the two acetaes has m.p. 203-205° (decomp.),

$[\alpha]_D$ -200° (c, 1.2 in $CHCl_3$), and an infrared spectrum identical with that of "ergopinakol" diacetate. A mixture of approximately equal parts of the two alcohols has m.p. 203-204° (decomp.), $[\alpha]_D$ -200° (c, 0.6 in pyridine).

Satisfactory analyses were obtained for all the samples described above; specific rotations were determined at room temperature (18-22°).

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