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THE STRUCTURE OF TORILIN

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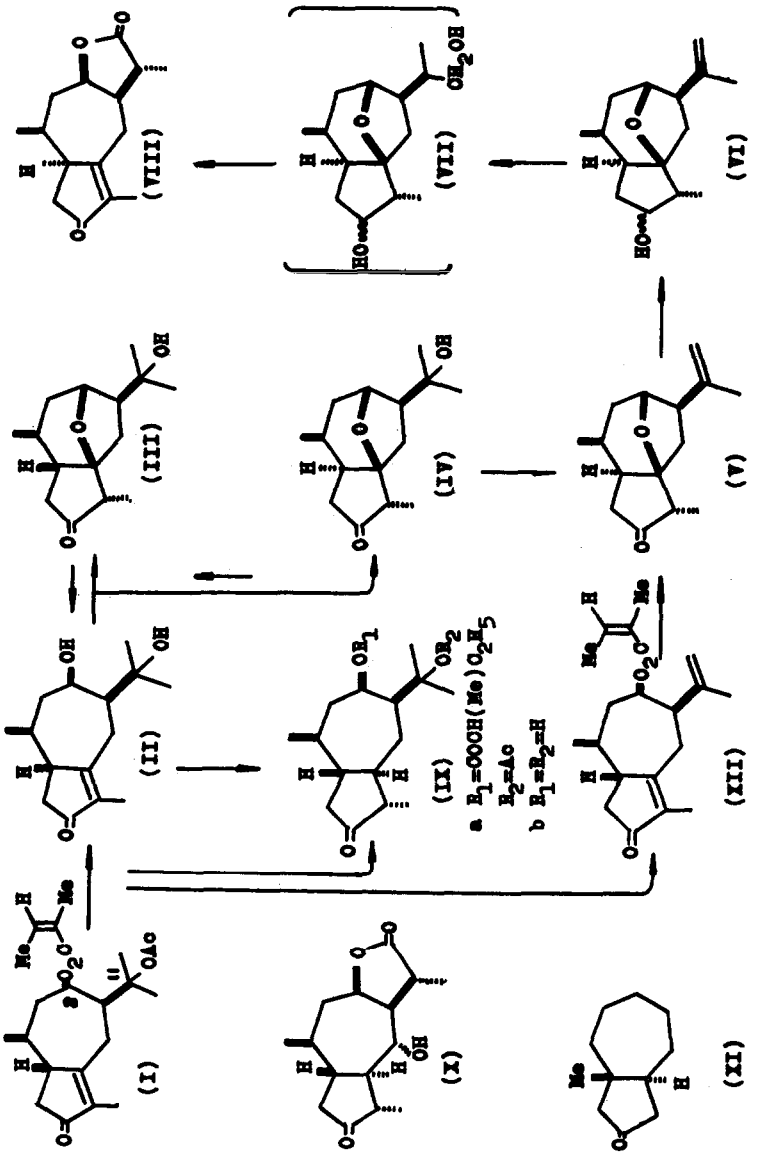
A new sesquiterpenoid ester, torilin (I), $C_{22}H_{32}O_5$, m.p. 77-78°, $[\alpha]_D^{14}$-45.3°(c 0.85 in EtOH) was isolated in a 0.4% yield from the ethanolic extract of the seeds of Torilis japonica DC. Refluxing with 1% methanolic potassium hydroxide for 20 min. hydrolyzed (I) to yield, beside acetic acid and angelic acid, a 7:7:1 mixture of three isomeric alcohols with molecular formula $C_{15}H_{24}O_3$: torilolone (II), m.p.179-180°, $[\alpha]_D^8$-25.7°(c 1.83 in $CHCl_3$), allotorilolone (III), m.p. 151-152°, $[\alpha]_D^{28}$+151.2° (c 0.53 in EtOH), and 1-epiallotorilolone (IV), m.p.135.5-137°, $[\alpha]_D^{14}$-147.5°(c 0.61 in EtOH). Since a more drastic hydrolysis (refluxing with 5% methanolic potassium hydroxide for 2.5 hr.) gave a mixture containing only 17% of (II) and 83% of (IV), allotorilolone (III) appears as a transient existance. This was confirmed by the treatment of (III) with 5% methanolic potassium hydroxide which afforded the same equilibrium mixture of (II) and (IV). Equilibration starting from (II), under basic condition, again yielded the same mixture; reminiscent of the well-known interconversion between geigerin and allogeigeric acid.[1] The structure and stereochemistry of the most stable isomer (IV) was established by its conversion into 1-epideoxygeigerin (VIII).[2]


(I)
(II)
(III)
(IV)
(V)
(VI)
(VII)
(VIII)
(IX)
a R_1=COOH(Me)C_2H_5
R_2=Ac
b R_1=R_2=H
(X)
(XI)
(XII)

Dehydration of (IV) with phosphorus oxychloride and pyridine gave the unsaturated ketone (V), m.p.92-93°, $[\alpha]_D^{24}$-152° (c 0.63 in EtOH) which was reduced with lithium aluminum hydride to yield the unsaturated alcohol (VI). Hydroboration followed by chromic acid oxidation converted (VI), via (VII), into 1-epideoxygeigerin (VIII), m.p.128-129°, $[\alpha]_D^{31}$+130.8°(c 0.47 in EtOH), the identity was established by comparison with an authentic sample.

The spectroscopic data of the second isomer, torilolone (II) indicate a cyclopentenone moiety. Catalytic hydrogenation yielded dihydrotorilolone (IXb), m.p.107-108°, $[\alpha]_D^{20}$+127.4° (c 0.42 in MeOH), which exhibits a positive Cotton curve (Fig. 1) almost superimposable on the curves of dihydrogeigerin (X)[3] and (+)-trans-1β-methylbicyclo[5.3.0]-9-decanone (XI)[4], indicating the configuration at C_1 as the structure (II). Since the increments in $[M]_D$ of p-nitrobenzoate and 3,5-dinitrobenzoate of the secondary hydroxyl group at C_8 to the parent alcohol (IXb) are negative (-288° and -318° respectively), the (R)-configuration was assigned to this asymmetric center according to the "benzoate rule".[5]

The last isomer, allotorilolone (III) shows a strongly positive Cotton curve (Fig.1) which is virtual mirror image of the curve of 1-epiallotorilolone (IV) and very similar to the curve of dihydrotorilolone (IXb). Inspection of the molecular models of (III) and (IV), and application of the octant rule show that these are just the cases to be expected when allotorilolone and 1-epiallotorilolone have the structure (III) and (IV) respectively.[6]

Returning to the structure of torilin itself, there must

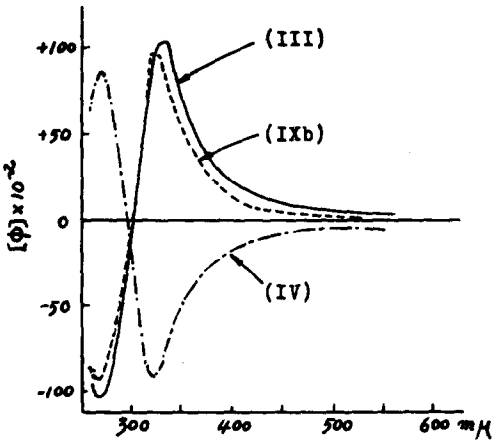


Fig.1

The rotatory dispersion curves of allotorilolone (III), 1-epiallotorilolone (IV) and dihydrotorilolone (IXb).

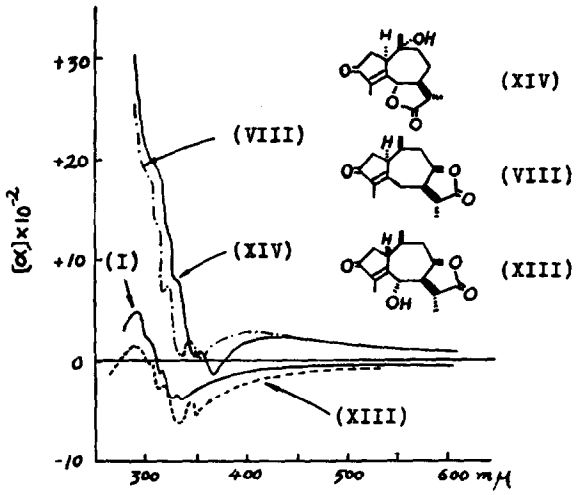


Fig.2

The rotatory dispersion curves of torilin (I), geigerin (XIII), isophotosantonic lactone (XIV) and 1-epideoxygeigerin (VIII).

be decided the locations of the acetate and angelicate groups; C_8-angelicate and C_{11}-acetate or vice versa.

When torilin was distilled at 1 mm, pyrolysis took place to give an oil, $C_{20}H_{28}O_3$, b.p.145-156°/0.02 mm, $[\alpha]_D^{23}$-65.4° (c 0.73 in EtOH) which was shown to be deacetyltorilin (XII). Absence of the peaks due to the acetoxyl group in the infrared spectrum and appearance of a multiplet centered at 5.15 τ (2H) in the n.m.r. spectrum are consistent with the structure (XII). Alkaline hydrolysis afforded the above-mentioned unsaturated ketone (V) and angelic acid. Thus the evidences for the locations of the two ester groups were secured. The stereochemistry at the ring juncture of (I) rests on the following observations. (a) The Cotton curve of (I) (Fig.2) is very close to the curve of geigerin (XIII), but distinctly different from the Cotton curves of isophotosantonic lactone (XIV) and 1-epideoxygeigerin (VIII). (b) Tetrahydrotorilin (IXa) obtained by catalytic hydrogenation of (I) was saponified to yield α-methylbutyric acid and dihydrotorilolone (IXb) whose configuration was discussed above.

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