UDC 581.10 : 582.751.9

Yoshio Hirose*1 : The Structure of Evodol, a Principle of *Evodia rutaecarpa*.

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Evodol (I), m.p. 281~282°, is a non-bitter principle isolated from the fruits of *Evodia rutaecarpa* BENTH. et HOOK (Rutaceae).

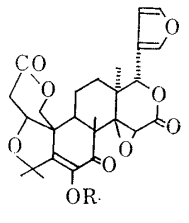
The molecular formula, $C_{29}H_{30(32)}O_{10}$, was first proposed by Maeda[1] for evodol, which was amended to $C_{26}H_{28}O_9$ by Fujita.[2]

On ther other hand, limonin, $C_{26}H_{30}O_8$, which was known as the characteristic bitter principle of *Citrus* spp. has been found in the bark of *E. rutaecarpa*.[3]

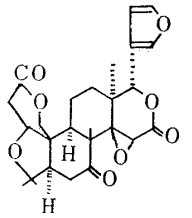
Recently the structure of limonin (II) has been established by the cooperation of several workers.[4~6]

Regarding to the close relation revealed in the molecular formulas of evodol and limonin, and the occurrence of both compounds in the same plant, it would not be so unreasonable to assume that there is a biogenetical relationship between evodol and limonin.

On autoxidation, limonin afforded diosphenol, $C_{26}H_{28}O_9$, whose constitution has been established unequivocally to be presented as in III.



I = III : R = H
IV = V : R = -COCH$_3$



II

The direct comparison of limonin diosphenol and evodol has now been made to give the following results (Table I and II), from which the identity of I and III has been established.

TABLE I.

	Evodol (I)[a]	Limonin diosphenol (III)
IR ν_{max}^{Nujol} cm^{-1}	3450	3450
	3320	3340
	3200	3240
	1748	1745
	1738	1736
	1691	1690
	1664	1665
UV λ_{max}^{EtOH} mμ (ε)	280 (9500)	280 (9800)
UV $\lambda_{max}^{0.1N\text{-}NaOH}$ mμ (ε)	340 (5500)	340 (5950)
$[\alpha]_D$ (c=in solvent)	− 199° (0.58 $(CH_3)_2CO$)	− 200° (1.00 $(CH_3)_2CO$)
m.p. (decomp.) (on Kofler)	280~285°	280~285°
	mixed m.p. 279~283°	

a) Evodol (I), m.p. 282° (decomp.) (H_2SO_4 bath)

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Table II.

	Evodol acetate (IV)[a]	Limonin diosphenol acetate (V)
IR ν_{max}^{Nujol} cm^{-1}	1753	1753
	1739	1739
	1695	1695
	1650	1650
UV λ_{max}^{EtOH} mμ (ε)	246 (12300)	245 (12000)
$[\alpha]_D$ (c. in solvent)	− 97° (0.484 $CHCl_3$)	− 101° (1.20 $CHCl_3$)
m.p. (decomp.) (on Kofler)	300～312°	306～313°
	mixed m.p. 299～311°	

a) Evodol acetate (IV), m.p. 298～299° (decomp.) (H_2SO_4 bath)

Experimental

Evodol (I)——Prepared by means of the method of the literature itself.[1,2] It gave brown coloration with $FeCl_3$ in EtOH. *Anal.* Calcd. for $C_{26}H_{28}O_9$: C, 64.45; H, 5.83. Found: C, 64.47; H, 5.86.

Evodol Acetate (IV)——Prepared by means of the method of the literature itself.[4] *Anal.* Calcd. for $C_{29}H_{30}O_{10}$: C, 63.87; H, 5.74; Ac., 8.75. Found: C, 63.77; H, 5.65; Ac., 8.55.

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Katsumi Tanabe and Yasuhiro Morisawa: Steroid Series. XI.[1] Synthesis of B-Norsteroid.

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Lettré and Jahn described the formation of 6-methoxy-5,6-seco-5ξ-cholestane-3β,5-diol 3-acetate 5,6-peroxide (IIa) in 60% yield by ozonization of cholesterol acetate (Ia) in carbon tetrachloride containing methanol.[2] In the course of our studies on B-norsteroid we found that IIa could be obtained in a higher yield under slightly modified reaction conditions, and it proved to be a useful substance for the preparation of 6β-formyl-B-nor-5β-cholestane-3β,5-diol 3-acetate (IVa), whose synthesis by other procedures and conversion into B-norchlest-5-en-3β-ol acetate have been reported from this laboratory.[3]

When cholesterol acetate (Ia) was treated with an ozonized air in dichloromethane containing 1% of methanol under cooling with dry ice-acetone mixture, there was obtained the peroxidic compound (IIa) of m.p. 151° (decomp.) in 81% yield, which showed a positive potassium iodide test, a negative Criegee test for hydroperoxide with lead tetraacetate, and the presence of a methoxyl group by Zeisel determination. The infrared spectrum in carbon tetrachloride solution exhibiting a band at 3330 cm^{-1} due to a hydroxyl group was superimposable with that described by the German workers.

Reduction of IIa with zinc dust and acetic acid in dichloromethane solution afforded an oily substance, whose infrared spectrum was identical in all regions with that of 3β-hydroxy-5-oxo-5,6-secochlestan-6-al acetate (IIIa) obtained previously.[3]

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