Bulletin of Taipei Medical College
Volume 2, August 10, 1970

The Studies on the new Constituents (Caucalol M) of Torillis scabra DC.

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Torillis scabra DC. (小竊衣) is perennial herbs, which is distributed from Japan to Taiwan. The fluffy seeds are ultilized as astrictive antiphlogistics. Caucalol diacetate, $C_{19}H_{30}O_5$, m.p. 120-121° C (Fig. 1), is isolated from the seeds of Torillis scabra DC. in 0.21% yield. (1),(2)

In this studies, a new minor component, caucalol M, m.p. 129-130°, was isolated from crude caucalol diacetate. The analytical data and MS spectrum show that the formula is $C_{19}H_{30}O_5$ and that is an isomer of caucalol diacetate. This structure is determined by physical and chemical method as Fig. 2.

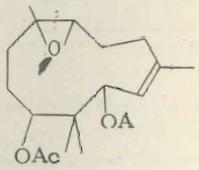


Fig. 1

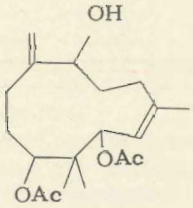


Fig. 2

The IR spectrum of caucalol M indicates the presence of a hydroxyl group (3530 cm^{-1}), acetate (1740, 1720, 1250 cm^{-1}) and a terminal methylene group (1650, 910 cm^{-1}). (Fig. 3)

Comparison of the NMR data of caucalol M(Fig. 4) with that of caucalol diacetate shows that caucalol M has terminal methylene protons at 5.07(s), 5.18(s) ppm and a proton alpha to hydroxyl group at 3.85(m) ppm. But the C_7-Me at 1.38 ppm and C_6-H, which is alpha to the epoxide, appearing at 2.99 ppm in caucalol diacetate is absent. Irradiation of the C_8-Me signal at 1.73 ppm causes the C_2-H signal around 5.1 ppm (q, J 1, 11) to become a doublet (J 11). Conversely, irradiation of the latter signal increases the height of the C_9-Me signal. A weak coupling is also observed between the C_6-H and exocyclic methylene protons. Thus, irradiation of the C_6-H signal at 3.85 (J 3, 10) ppm causes the exo-methylene signal at 5.18 and 5.07(s) to increase in height. Also the coupling constants $J_{9,10}$ and $J_{5,6}$ are very close to those in caucalol diacetate. These results suggest that the moiety incorporating C_{10} to C_1 to C_6 in caucalol diacetate are retained in caucalol M, excepting that the latter is devoid of the influence of the epoxide ring. The oxidation of caucalol M afford caucalol M ketone while the benzoylation of caucalol M gave caucalol M benzoate (Fig. 5). These data permitted one to deduce the structure, as shown in Fig. 2.

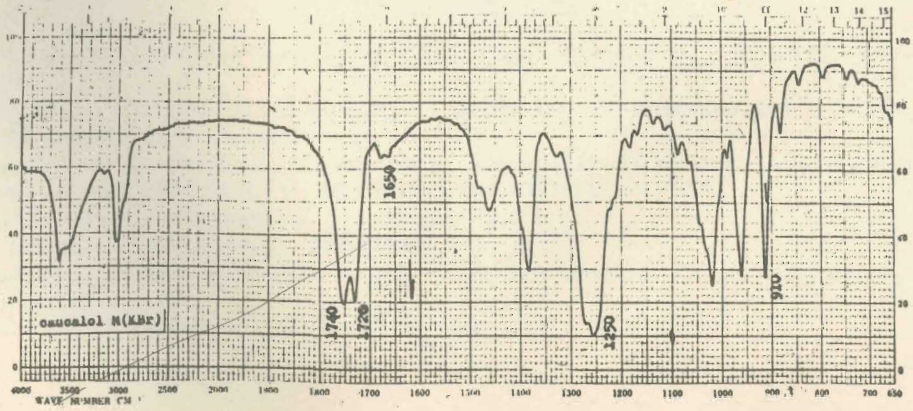


Fig. 3. IR spectrum of caucalol M

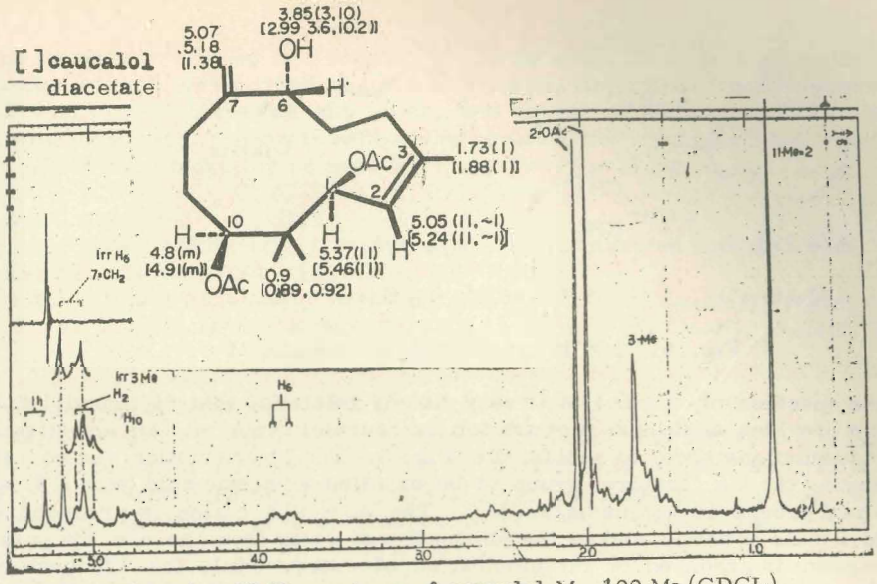


Fig. 4. NMR spectrum of caucalol M, 100 Mc ($CDCl_3$) numbers in [ ] are chemical shifts (ppm) of cancalol diacetate

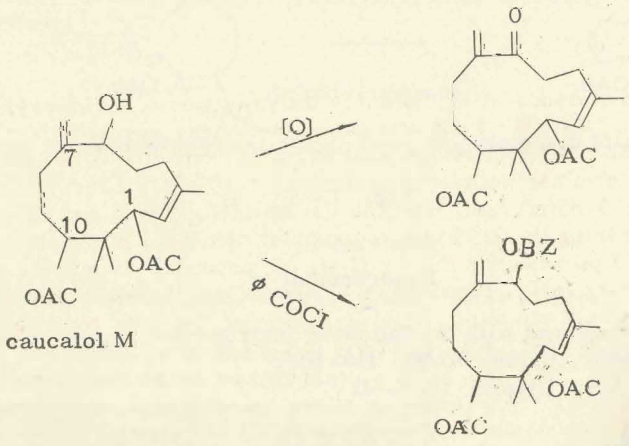
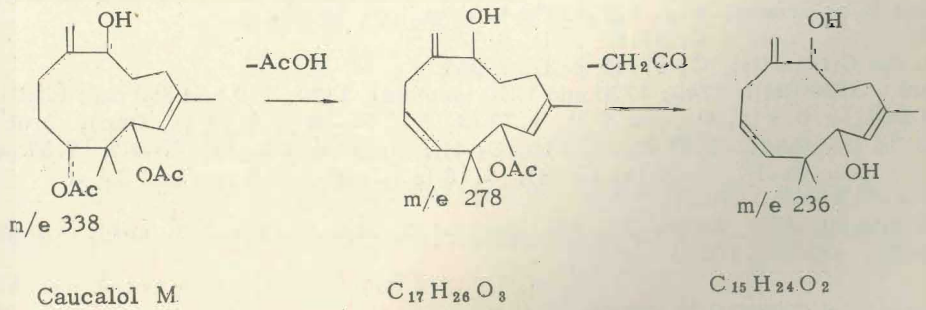


Fig. 5.



Caucalol M $C_{17}H_{26}O_3$ $C_{15}H_{24}O_2$

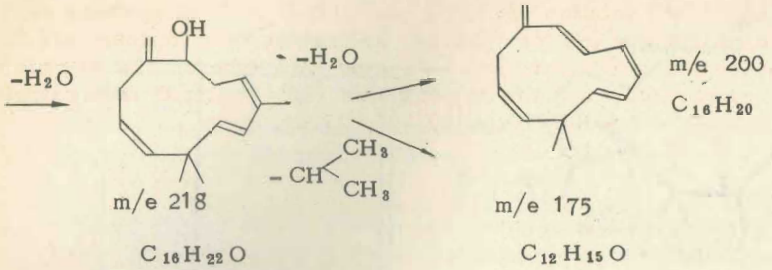


Fig. 6. MS fragmentation of caucalol M

The mass spectrum of caucalol M is very closely related to that of caucalol diacetate (2), and this provides additional support for the caucalol skeleton. An investigation of the main fragmentations occur as indicated in Fig. 6. The fragmentation can be rationalized by assuming the C_{10} acetoxyl group to be expelled as acetic acid (m/e 278) and the allylic acetoxyl groups as ketone (m/e 236). The m/e 218 cation is produced by the expulsion of 2 mole of acetic acid or the elimination of water from the m/e 236 peak. The m/e 200 fragment is produced by the elimination of water, while the 175 peak can be accounted for by the loss of an isopropyl radical from the m/e 218 ion (Fig. 6).

Biogenetically, caucalol M may be obtained by the cleavage of the epoxide ring of caucalol diacetate as shown in Fig. 7.

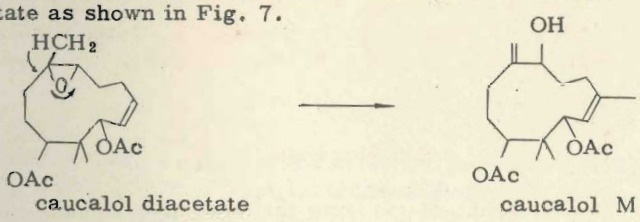


Fig. 7

Experimental

The spectra were measured with the following instruments:
IR, Hitachi EPI-S2; NMR, Varian A-60, HA-100;
UV, Beckman DK-2; MS, Hitachi RMV-6D

Isolation of Caucalol M

Crude caucalol diacetate (1) (6 g) was chromatographed on silica gel (300 g, Merck) and eluted with choloroform/ether(1:1). The eluate from the first band afforded caucalol diacetate(5.6g). The second eluate was recrystallized from n-hexane/ether(1:1) to afford caucalol M as prisms, m.p. 129-130°, 120 mg.

Found: C, 67.69 ; H, 8.92%
Calcd. for $C_{19}H_{30}O_5$: C, 67.43 ; H, 9.34%
IR(KBr) : 3530(OH), 1740, 1720 and 1250 (acetate), 1670, 910 and 850 cm^{-1} (C=C)
NMR($CDCl_3$) : 0.9 (s, C_{11}-Me X 2), 1.73 (d, J 1, C_8-Me), 1.93 (s, OAc), 2.07 (s, OAc), 3,85 (q, J 3, 10, C_6-H), 5.05 (q, J 1, 11, C_2-H), 5.35 (d, J 11, C_1-H), 5.07 (s, C_7-H), 5.18 (s, C_7-H), 4.8 ppm (m, C_{10}-H)
$[\alpha]_D$ + 21.3 (c=1, $CHCl_3$)
MS 278(M-60, 2%), 236(M-102, 3%), 218(M-120, 23%), 175(M-163, 28%), 107 (M-231, 68%), 43(CO , 100%)

Preparation of Caucalol M ketone

A chromium pyridine complex solution prepared from 2 ml of pyridine and 30 mg of

chromium trioxide was added to a solution of 50 mg caucalol M in 1 ml pyridine at 0°C. The reaction mixture was stirred at 0°C for 5 hours, and left at room temperature for 2 days. The mixture was treated with water, and extracted with ether. The extract was washed with water and evaporated, and the residue was recrystallized from petroleum ether to afford the monoketone as needles, m.p. 89-90°, 25 mg.

Found: C, 67.74 ; H, 8.13%
Calcd. for $C_{19}H_{28}O_5$: C, 67.83 ; H, 8.39%
IR(KBr): 1730 and 1245(acetate), 1670 cm^{-1} (α,β-unsaturated ketone)
UV(methanol): 220(ε, 6700), 310 mμ(ε, 60)
NMR($CDCl_3$): 0.83(s, C_{11}-Me), 0.89(s, C_{11}-Me), 1.82(s, C_8-Me), 1.98(s, OAc), 2.05(s, OAc), 4.7(m, C_{10}-H), 5.02(s, J 11, C_2-H), 5.24(d, J11, C_1-H), 5.79(s, C_7=CH), 5.82(s, C_7-CH)

Preparation of Caucalol M benzoate

A solution of benzoyl chloride(50 mg) in pyridine(1 ml) was added to a chilled solution of caucalol M(40 mg) in pyridine(2 ml) and the solution was allowed to stand at room temperature for 24 hours. After working in the usual way, the product was recrystallized from ethanol/water(1:1) to gave needles, m.p. 117-118°, yield 31 mg.

Found: C, 70.62 ; H, 8.04%
Calcd. for $C_{26}H_{34}O_6$: C, 70.54 ; H, 7.74%
IR(KBr): 1735 and 1245(acetate), 1715 and 1285(benzoate), 715 cm^{-1} (phenyl)
NMR($CDCl_3$): 0.90(s, C_{11}-Me X 2), 1.77(s, C_8-Me), 2.02(s, OAc), 2.05(s, OAc), 4.84(m, C_{10}-H), 5.10(q, J 1, 11, C_2-H), 5.20(m, C_6-H), 5.40(d, J 11, C_1-H), 5.23(s, C_7=CH), 5.38(s, C_7=CH), 7.30-8.13 ppm(m, phenyl)

Acknowlegement

This work was supported by grant-in-aid from the National Council of science to which thanks are due.

References

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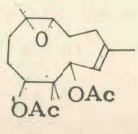
(2) S. Sasaki, Y. Itagaki, H. Moriyama, K. Nakanishi, E. Watanabe and T. Aoyama; Tetrahedron Letters, 623(1966)

中文摘要

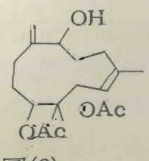
小竊衣果實之新成分(Caucalol M)之研究

中西香爾 Columbia 大學化學系
姜 宏 哲 台北醫學院藥學系

由小竊衣(Torillis scarbrs DC.)果實，分離微量之新成分，Caucalol M，$C_{19}H_{30}O_5$，m.p. 129—130°c 該成分之紅外線吸收光譜，核磁共鳴光譜，質量分析光譜等之資料與小竊衣之主成分Caucalol diacetate，$C_{19}H_{30}O_5$，m.p. 120—121°（圖(1)），詳細比較研究可推得Caucalol M之構造如圖(2)。



圖(1)



圖(2)