Tetrahedron Letters No. 29, pp 2501 - 2502, 1976. Pergamon Press. Printed in Great Britain.

# ISOLATION AND STRUCTURE OF TWO DITERPENE QUINONES FROM SALVIA BALLOTAEFLORA BENTH (LABIATAE)

William H. Watson* and Zenei Taira

FASTBIOS Laboratory, Department of Chemistry

Texas Christian University, Fort Worth, Texas 76129

Xorge A. Dominguez, Humberto Gonzales, Marcos Guiterrez and Raul Aragon

Department of Chemistry, Monterrey Institute of Technology

Monterrey, N. L., Mexico

(Received in USA 12 December 1975; received in UK for publication 10 June 1976)

Salvia Ballotaeflora Benth (Labiatae) was collected around Monterrey Mexico in July 1973. 3.2 Kg of aereal parts were extracted with petroleum ether yielding 30 grams of a resinous colored material. The extract was chromatographed on a silica gel column and elution with petroelum ether-benzene yielded 285 mg. of a yellow crystalline solid, conacytone (I), and 310 mg. of an orange crystalline solid, icetexone (II).

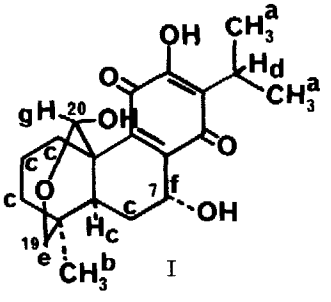
Conacytone (I): $C_{20}H_{26}O_6$, yellow crystals, m.p. 240° (closed capillary), $[\alpha]_{589}$ -36.5°, $[\alpha]_{578}$ -49.8°, $[\alpha]_{546}$ -108.3° (10 mg/ml in $CHCl_3$, 25°C); UV $\lambda_m$(EtOH) 204 ($\epsilon$,24000), 272($\epsilon$,12600), 380($\epsilon$,579); IR, $\nu_m$ 3550, 3320 (broad), 2970, 2940, 2880, 1660, 1625, 1610, 1460, 1395, 1370, 1330, 1250 $cm^{-1}$; m/e, 362 ($M^+$), 344 ($M^+$-18), 316, 298, 283, 269, 255, 244, 230; NMR($CDCl_3$), 1.17d(6Ha, J = 7), 1.26s(3Hb), 1.5-2.3m(9Hc), 3.00m(1Hd), 3.98(2$H_e$), 4.85m(1Hf), 5.62s(1Hg), 7.24 and 7.30(2H,OH). The third OH proton was not observed. Found: C, 66.40%, H, 7.13%. Calcd: C, 66.28%, H, 7.23%.

Icetexone (II): $C_{20}H_{22}O_5$, orange crystals, m.p. 226-227°, $[\alpha]_{589}$ +33.3° $[\alpha]_{578}$ +37.8°, $[\alpha]_{546}$ +50° (10 mg/ml in $CHCl_3$, 26°C); UV, $\lambda_m$(EtOH) 213 ($\epsilon$,13900), 260 (sh), 315 ($\epsilon$,7900), 430 ($\epsilon$,750); IR, $\lambda_m$ 3360(OH), 1770($\gamma$-lactone), 1640, 1620, 1600, 1450, 1420, 1380 and 1370 (isopropyl group), 1320, 1240, 1195, 1145, 1105, 990, 800, 730 $cm^{-1}$; m/e, 342 ($M^+$,99), 314(73), 289(53), 274(60), 261(33), 246(40), 227(12), 205(30), 95(67), 82(57), 78(53), 55(50), 43(100).

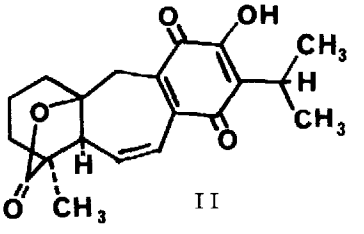
The structures and relative stereochemistries were elucidated by single crystal X-ray diffraction techniques. Both compounds crystallize in the orthorhombic space group $P2_12_12_1$. Conacytone: a = 13.620(3), b = 12.666(3), c = 10.948(3) Å, U = 1888.7 Å$^3$, $D_m$ = 1.274 g.$cm^{-3}$, Z = 4, $D_c$ = 1.274 g.$cm^{-3}$. Icetexone: a = 20.991(7), b = 10.354(7), c = 7.738(4) Å, U = 1682.6 Å$^3$, Z = 4, $D_c$ = 1.351 g.$cm^{-3}$.

Data were collected on the Philips PAILRED and Syntex $P2_1$ diffractometer systems using the $\omega$-scan technique. The structures were solved by application

of the direct methods program MULTAN[1]. Anisotropic least-squares refinement of conacytone reduced R to 0.047 for the 1381 reflections with intensities greater than 3σ(I). The R factor for icetexone was reduced to 0.037 for the 1331 reflections with intensities greater than 3σ(I).




I




II

Conacytone is an abietane diterpene quinone where oxidation of the C19 and C20 methyl groups has led to the formation of a 6-membered hemiacetal. Symbolically, icetexone can be derived from conacytone by insertion of the C20 methyl group into the B ring to form a 7-membered ring. The bridging hemiacetal is replaced by a γ-lactone. The C7 hydroxyl group has been lost giving rise to a double bond conjugated with the benzoquinone moiety and shifting the visible spectrum to the red. Nemorone, isolated from Salvia Nemorosa[2], is an abietane type diterpene quinone with a C20 aldehyde group. Through an oxidative pathway conacytone can be related to nemorone. The royleanones[3], isolated from Inula royleanone, are similar to conacytone but without the oxidation of the C20 and C19 methyl groups. 6,7-Dehydroroyleanone has a 6-membered B ring, but the chromophoric group is identical to that of icetexone. The spectral parameters are similar, $\lambda_m$(EtOH) 213, 245(sh), 329, 455 nm; IR, $\nu_m$ 3340, 1660, 1635, 1615(sh) $cm^{-1}$. Icetexone appears to be an example of a new diterpene ring system.

We would like to acknowledge the financial support of the Robert A. Welch Foundation (P-074) and CONACYT of Mexico (Grant No. 0.5). We thank Syntex Analytical Instruments Inc. (Dr. A. T. Christensen) for collecting the data on icetexone.

## References

1. G. Germain, P. Main and M. M. Woolfson, Acta Cryst., A27, 368 (1971).
2. A. S. Romanova, G. F. Pribylova, P. J. Zakharov, V. I. Sheichenko and A. I. Ban'kovskii, Khim. Prirod Soedineii, 7, 199 (1971).
3. O. E. Edwards, G. Feniak and M. Los, Can. J. Chem., 40, 1540 (1962).