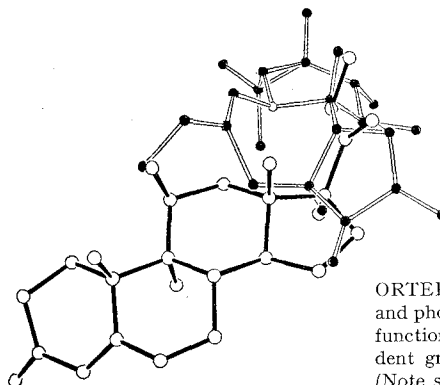
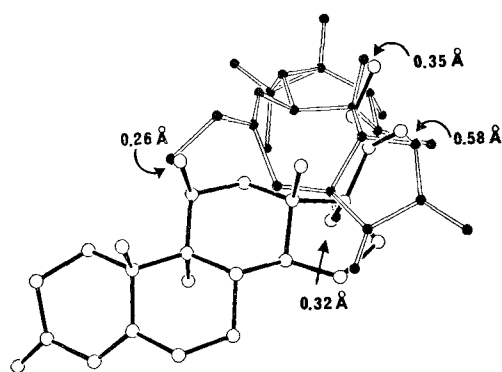


O(20) carbonyl oxygen would readily add to the reactive C(1) atom of phorbol in a 'Micheal-type' addition reaction. Such a mechanism has been suggested for the anti-tumor action of α -methylene lactones¹⁹.



ORTEP Stereopair of 9 α -fluoro-cortisol \circ and phorbol \bullet showing overlap of crucial functional groups. Arrows indicate coincident groups with distance in angstroms. (Note superposition of cortisol O(20) and phorbol C(1).)

The molecular similarity of 9 α -fluoro-cortisol **1** and phorbol **2**

	Cortisol atom ¹⁴	Phorbol atom ¹⁵	Delta (Å)
Least squares fit of these atoms	O(17)	O(4)	0.322
	O(21)	O(9)	0.348
	O(20)	C(1)	0.577
	O(11)	O(20)	0.263
Unmatched atoms	C(13)	C(5)	0.533
	C(17)	C(4)	0.472
	C(20)	C(10)	0.346
	C(16)	C(3)	0.498
	C(12)	C(6)	1.546
	C(21)	C(9)	0.239
	C(11)	C(20)	2.309

¹⁶ C. M. WEEKS, D. C. ROHRER and W. L. DUAX, *Science* **190**, 1096 (1975).

¹⁷ E. A. HAM, H. G. OIEN, E. H. ULM and F. A. KUEHL, *Prostaglandins* **10**, 217 (1975). Random reaction of phorbol with sulfhydryl groups seems unlikely, since the number of free thiols increases on treatment with croton oil¹⁸.

¹⁸ G. CALCUTT, *Br. J. Cancer* **15**, 390 and 855 (1961).

¹⁹ S. M. KUPCHAN, D. C. FESSLER, M. A. EAKIN and T. J. GIACOBBE, *Science* **168**, 376 (1970).

²⁰ *Gammacoat*¹²⁵I Cortisol Radioimmunoassay (Clinical Assays, Inc., 237 Binney Street, Cambridge, Massachusetts, USA).

²¹ Note added: Since the submission of this manuscript a report on co-carcinogen receptors has appeared: J. R. SYMTHIES, F. BENINGTON and R. D. MORIN, *Psychoneuroendocrinology* **1**, 123 (1975); *Chem. Abs.* **84**, 159826c (1976).

Dehydroacetic Acid in Anthers of *Solandra nitida* (Solanaceae)

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Summary. The chloroform extract of anthers of *Solandra nitida* contains 3-acethyl-6-methyl-1,2-pyran-2,4(3H)dione (dehydroacetic acid) as one of the main products.

The size of certain tropical flowers allow the isolating of chemical compounds from the different parts of the flower. We have collected and extracted a quantity of anthers of *Solandra nitida* (solanaceae) called 'golden cup'. The first compound that was found was saccharose from the methanolic extract¹ besides hexaeicosanol, 8-pentaeicosanol and nonaeicosane². Now we report the presence of dehydroacetic acid.

1 kg of anthers were extracted with hexane and then with chloroform. By TLC the chloroform extract showed 14 spots in toluene-ethyl formate-formic acid (5/5/1). By column chromatography in the same eluent, we got 13 different fractions. The 8th fraction was crystallized from toluene-AcOEt (5/5) and gave yellow needles, m.p. 100–104°C, recrystallization in AcOEt-MeOH (1/5) gave amber needles m.p. 109–110°C. The MS showed that the compound has 8 carbon atoms ($M+1=8.5\%$)³, molecular weight 168 and formula $C_8H_8O_4$. The IR-spectrum showed the following bands; 3065 cm^{-1} (w) $CH=C$, 1720 (s) $C=O$ lactone and diketone, 1450 (m) $C=CH$, 1375 (m) CH_3 , 1255 $CH_3-C=O$ $O=C-O-C$, 1000 (s) $C=CH$ out of plane, 860 (m) $-O-C-CH_3$, 780 (m) and 712 (w) $C=CH$ st. UV-spectrum showed 2 bands at λ 223 nm (log E = 3.9) and

λ_{max} at 308 nm (log E = 1.2). The NMR-spectrum showed 3 signals at δ in ppm 2.33 (s) (3H) CH_3-CO , 2.66 (s) (4H) $CH_3C=C$ and $-C-C=O$, 5.95 (m) (1 H) vinylic proton. All

these data suggest that the compound is 2,6-dioxo-2-methyl-5-acethyl-dihydropyran (dehydroacetic acid). The mass spectrum confirms this structure because we observe the following fragments; m/e 168, 153, 125, 110, 69, 56, 43 (base peak).

To our knowledge it is the first time that dehydroacetic acid is found in nature, but it is well known as the dimerization product of ethyl acetoacetate. The fact that it was found in the masculine sexual organ of the flower (anthers) suggests a metabolic activity related to the reproduction, e.g. a way for anabolism different to the well-known one through mevalonic acid.

¹ F. GIRAL and T. REGUERO, *Ciencia, Méx.*, in press.

² C. RIVERA, J. REYES and F. GIRAL, 10th Panamerican Congress of Biochemistry and Pharmacy, Punta del Este, Uruguay, Dic 1975.

³ J. SEIBL, *Massenspektrometrie* (Akademische Verlagsgesellschaft, Frankfurt, Main 1970).