and 5.5 ppm 10 olefinic protons of the acid residue. The preceding spectral data and those given in tables 1 and 2 prove that $Ti_7$ is 13-O-acetyl-12-O-(2,4,6,8,10-tetradecapentaenoyl)phorbol.

$Ti_8$: MS: (m/e) 608 ($M^+$), 548 ($M^+$-60), 389 ($M^+$-219); IR (KBr): $\nu_{max}$: 3430, 1715, 1625, 1605, 1000 $cm^{-1}$; UV ($CH_3OH$): $\lambda$ ($\varepsilon$): 193.5 nm (17680); $\lambda_{max}$ ($\varepsilon_{max}$): 203.5 (16200), 231 (10530), 336 nm (35000); $^1$H-NMR ($\delta$, $CDCl_3$): differences as compared to $Ti_5$: between 7.4 and 5.5 ppm 8 olefinic protons of the acid residue. In accordance with the preceding data and those given in tables 1 and 2 $Ti_8$ is 13-O-acetyl-12-O-(2,4,6,8-tetradecatetraenoyl)phorbol.

$Ti_9$: MS: (m/e) 606 ($M^+$), 546 ($M^+$-60), 389 ($M^+$-217); UV (MeOH): $\lambda_{max}$ ($\varepsilon_{max}$): 260 (9000), 394 nm (29000); $^1$H-NMR ($\delta$, $CDCl_3$): differences as compared to $Ti_5$: slight downfield shifts of 12-H at 5.55 ppm and OH-9 at 5.67 ppm; between 7.5 and 5.5 ppm 10 olefinic protons of the acid residue. The combination of these data with those given in tables 1 and 2 proves that $Ti_9$ is 12-O-acetyl-13-O-(2,4,6,8,10-tetradecapentaenoyl)phorbol.

A common feature of the euphorbia factors $Ti_5$-$Ti_9$ is their marked instability with respect to autoxidation yielding biologically inactive material insoluble in all solvents. From such materials the parent alcohol may still be obtained by mild hydrolytic procedures.

Factor group Ia (see formula) was separated in 2 subfractions $M_{23}$ and $M_{24}$. $M_{23}$: MS (m/e) 522/496 ($M^+$), 330 ($M^+$-192/166), 192, 166; $^1$H-NMR ($\delta$, $CDCl_3$): 7.8-5.7 ppm (7 olefinic protons), all other signals are identical with those of the euphorbia factor $I_6$ from E. ingens[12]. $M_{24}$: MS (m/e): 548/522 ($M^+$), 330 ($M^+$-218/192), 218, 192; $^1$H-NMR ($\delta$, $CDCl_3$): differences to the spectrum of $M_{23}$: 7.8-5.7 ppm (9 olefinic protons of the acid residue). Factor group Ib was separated in 2 subfractions $M_{25}$ and $M_{26}$, containing 3 further ingenol esters. $M_{25}$: MS (m/e) 524/498 ($M^+$), 330 ($M^+$-194/168), 194, 168; $^1$H-NMR ($\delta$, $CDCl_3$): differences to the spectrum of $M_{23}$: 7.8–5.7 ppm (5–6 olefinic protons of the acyl residue). $M_{26}$: MS (m/e): 550/524 ($M^+$), 330 ($M^+$-220/194), 220, 194; $^1$H-NMR ($\delta$, $CDCl_3$): differences to the spectrum of $M_{25}$: 7.8–5.7 ppm (7–8 olefinic protons of the acid residue).

Evidence for the ester positions results from NMR-data and from treatment of the 2 factor groups with acetone/$HClO_4$ followed by base catalyzed transesterification in methanol yielding 5,20-O-isopropylideneingenol (**6**)[13]. The chemical structure of the fatty acids follows from the spectral data (MS and UV) of the fatty acid methyl esters obtained by transesterification and from GLC-analysis of the homologous saturated methyl esters, obtained by catalytic hydrogenation.

Thus factor group Ia comprises 3 homologous 3-O-acylingenols, each of which is esterified with a highly unsaturated fatty acid of the type $CH_3$–$(CH_2)_2$–$(CH=CH)_n$–COOH (n = 3,4,5).3-O-(2,4,6-decatrienoyl)ingenol (n = 3) was isolated already from Euphorbia ingens (euphorbia factor $I_6$)[12] and 3-O-(2,4,6,8,10-tetradecapentaenoyl)ingenol (n = 5) from latex of E. lathyris (euphorbia factor $L_6$)[14] and from roots of E. jolkinii Boiss[15]. Factor group Ib comprises 3 homologous 3-O-acylingenols, esterified with highly unsaturated fatty acids of the type $CH_3$–$(CH_2)_4$–$(CH=CH)_n$–COOH (n = 2,3,4). They were unknown as yet. Again the factor groups Ia and Ib are highly susceptible to autoxidation leading to highly insoluble and biologically inert materials, from which, by hydrolytic procedures, the diterpene parent alcohol may be obtained. The biological data of the new euphorbia factors and factor groups will be published elsewhere.

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## β-(p-hydroxyphenyl) ethanol in the chest gland secretion of a galago (Galago crassicaudatus)

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*12 July 1976*

*Summary.* β-(p-hydroxyphenyl)ethanol is present in the chest gland secretion of the galago Galago crassicaudatus.

Although pheromones have been demonstrated to be of major importance in the social biology of primates[2], the chemistry of these exocrine products still constitutes relative terra *incognita*. Indeed, except for the identification of short chain fatty acids as sexual releasers for Macaca mulatta[3], no primate pheromones have been identified. It has been established, however, that similar acids are produced by other monkeys, baboons, and humans[4]. The purpose of the present note is to report the identification of β-(p-hydroxyphenyl)ethanol in the chest gland secretion of the galago Galago crassicaudatus. This compound releases an unusual behavior response in this primate and may constitute one of its marking pheromones.

*Material and methods.* The secretion was obtained by wiping the chest gland located on the midline about the base of the throat over the clavick with absorbent tissue. The tissues were immediately extracted with chromatoquality methylene chloride and these extracts were used for all subsequent analyses. Analyses were performed on an LKB-9000 gas chromatograph-mass spectrometer (GC-MS)[5] using a 1% OV-17 column and a 10% SP-1000 column both on Supelcoport 80–100 mesh (Supelco, Bellefont, Pa.). The columns were programmed from 50 °C to 300 °C and 200 °C, respectively.

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*Results.* GC-MS analysis on 1% OV-17 showed only one peak which exhibited m/e 138(18) as the molecular ion with a base peak at m/e 107 and other large peaks at m/e 77(16), 53(5), 51(5) and 39(5). Comparison of retention times (isothermal, 150 °C) and mass spectra of the unknown material with those of synthetic β-(o, m, and p-hydroxyphenyl)ethanol prepared by lithium aluminum hydride reduction of the corresponding methyl esters, p-methoxymethyl phenol and 2-phenoxyethanol indicated that the natural material was β-(p-hydroxyphenyl)ethanol. The base peaks of all 3 hydroxyphenyl ethanol isomers and the p-methoxymethyl phenol were identical while that of 2-phenoxyethanol was m/e 94. The methoxymethyl phenol elutes significantly earlier than the hydroxyphenyl ethanols and the isomers of the latter can be distinguished from both their isothermal gas chromatograms and their mass spectra. Both the m and o isomers have significantly higher m/e 77(35) and m/e 108(67,22). When β-(p-hydroxyphenyl)ethanol was placed on the perch of a galago, the animals responded to it in a way which was never observed with any other odorants (including its isomers). The galago, slowly and deliberately, placed its open mouth over the treated spot. This response appeared to place either the inside of the mouth or the back of the tongue in contact with the perch, and thus constituted a highly distinctive type of biting behavior.

*Discussion.* Scent marking is important in the social biology of many primates, and the chest gland of G. crassicaudatus is frequently utilized as a marking gland. Field observations of G. senagalensis indicate that galagos frequently mark their territories[6] and the chest gland secretion may possess an important pheromonal role for these animals. However, we are unable to interpret the paticular significance of the oral presentation to sites marked with β-(p-hydroxyphenyl)ethanol and the exact function of this compound remains to be determined. Nevertheless, with the identification of this first aromatic compound in the exocrine secretion of a primate, it may be possible now to explore scent marking in primates in terms of defined chemical releasers of behavior.

## (–)-(R)-1-O-Geranylgeranylglycerol from the brown alga Dilophus fasciola[1]

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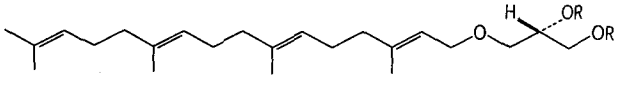
*Summary.* A novel ether lipid, (–)-(R)-1-O-geranylgeranylglycerol (**1**), has been isolated from the brown alga Dilophus fasciola and its structure proved by spectroscopic methods and chemical degradation.

Among the brown algae, members of the family Dictyotaceae are a particularly rich source of new natural compounds[2]. During the course of our search for novel metabolites of Mediterranean macroalgae, we have now investigated a further species, Dilophus fasciola (Roth) Howe, belonging to the same family.

*Material and methods.* Chloroform extraction of the freeze-dried alga gave a green oil which was chromatographed on silica gel using increasing concentrations of ether in light petroleum as the eluent. Repeated chromatography of the more polar fractions eventually resulted in the isolation of (–)-(R)-1-O-geranylgeranylglycerol (**1**) (0.15% yield, dry weight of alga) as a colourless, viscous liquid, $[\alpha]_D$ –2.1° (c 1.5 in $CHCl_3$).




**1** R = H **2** R = Ac

*Results and discussion.* Compound **1**, $\nu_{max}$ (liquid film) 3300 $cm^{-1}$ (OH), had molecular formula $C_{23}H_{40}O_3$ (high resolution mass spectrometry m/e 364.2972; calculated for $C_{23}H_{40}O_3$ 364.2977). The IR- and UV-spectra of **1** indicated the absence of carbonyl and conjugated system in the molecule. On acetylation with acetic anhydride in pyridine, **1** afforded the diacetate **2** ($M^+$ m/e 448), oily, $[\alpha]_D$ –8.4° (c 1.5 in $CHCl_3$), $\nu_{max}$ 1750 $cm^{-1}$, which showed no hydroxyl IR absorption. Thus 2 of the oxygen functions of **1** were assigned to 2 hydroxyls (which must be vicinal, since **1** gives a positive periodate test), the remaining oxygen being probably involved in an ether link ($\nu_{max}$ 1150 $cm^{-1}$). These results and the mass spectrum which indicated cleavage of the molecular ion with loss of 92 amu ($C_3H_8O_3$) suggested that **1** must be a $C_{20}$ 1-ether of glycerol. Indeed, the PMR spectrum of **2** in $CCl_4$ contains all the required proton signals[3]: a) singlets for 2 acetyl protons at δ 1.98 and 2.01, b) an ABX system (AB-part, 4.20 δ, $J_{AB}$ 14 Hz; X-part, 4.98 δ, obscured by overlapping with the signal of vinyl protons) which could be assigned to the $-CH(OAc)CH_2OAc$ group and c) a doublet at δ 3.43 assigned to $-CH_2O-$. Irradiation at δ 4.98 simplified the AB-part into an AB system and at the same time collapsed the doublet at δ 3.43 to a singlet. The structure of the additional $C_{20}$-moiety could be deduced from the remaining PMR signals [δ 1.60 (9H, s, 3 vinyl Me's), 1.67 (6H, s, 2 vinyl Me's), 2.03 (12H, m, 6 $>C=CHCH_2-$), 3.94 (2H, d, J 7 Hz, $>C=CHCH_2O-$), 5.10 (3H, b, $>C=CHCH_2-$) and 5.29 (1H, bt, $>C=CHCH_2O-$)], which closely paralleled those reported[4] for all-trans-geranylgeraniol.

At this juncture it became apparent that the new compound must be represented by the formula **1**, which is also supported by the fragmentation pattern in the MS

1 This work was supported by CNR, Rome, Italy.

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