had mp 86–87°, $[\alpha]_D$ −2° (*c* = 1); (Found: C, 76.96; H, 10.06. $C_{32}H_{52}O_4$ requires: C, 76.75; H, 10.47%); IR ν_{max} cm^{-1}: 1720, 1710, 1250; PMR: δ 5.98 (*t*, 1H), 4.45 (*m*, 1H), 3.70, 2.10, 1.88 (three 3H, *ss*). Pure **2b**, by hydrolysis with 10% hydromethanolic KOH and esterification with excess ethereal CH_2N_2, was quantitatively converted into methyl 3-epiisomasticadienolate mp and mmp 140–141°, $[\alpha]_D$ −16°, identical with an authentic specimen [5]. Further elution with petrol–C_6H_6 (1:1; 0.8 l.) gave the crude **1b** (1400 mg) which after crystallization from MeOH had mp 129–130°, $[\alpha]_D$ −26° (*c* = 0.9); (Found: C, 76.12; H, 10.96. $C_{32}H_{52}O_4$ requires: C, 76.75; H, 10.47%); IR ν_{max} cm^{-1}: 1720, 1710, 1250; PMR: δ 5.88 (*t*, 1H), 5.20 (*m*, 1H), 4.45 (*m*, 1H), 3.70, 2.10, 1.88 (three 3H *ss*). Pure **1b**, under the conditions reported above for **2b**, afforded quantitatively methyl 3-epimasticadienolate (**1d**) mp and mmp 100–101°, $[\alpha]_D$ −44°, identical with the natural **1d**.

Masticadienonic aldehyde (**1f**). Evapn of the mother liquors (280 mg) of crystallization of oleanonic aldehyde afforded a semicrystalline solid which was recrystallized from MeOH to give crude **1f**. Further purification of **1f** was not possible since the substance was very prone to undergo visible alterations. IR ν_{max} cm^{-1}: 1675; PMR: δ 9.45 (*s*, 1H, —CHO), 6.50 (*m*, 1H, C-24 vinyl H), 5.20 (*m*, 1H, C-7 vinyl H), 1.75 (*s*, 3H, Me on double bond). LAH reduction of crude **1f** (100 mg) led to a crystalline product which after two crystallizations gave pure masticadienediol (**1e**) mp and mmp 186–187°, $[\alpha]_D$ −50°, identical with an authentic specimen.

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ON THE OCCURRENCE OF FILICAN-3-ONE IN *STRYCHNOS DOLICHOTHYRSA*

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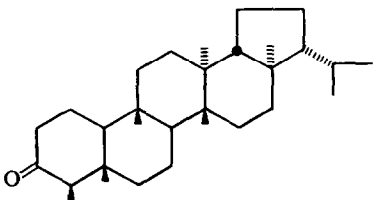
Key Word Index—*Strychnos*; Loganiaceae; filican-3-one; triterpene.

Plant material of *Strychnos dolichothyrsa* Gilg ex Onochie et Hepper (Loganiaceae) was collected by Dr A. J. M. Leeuwenberg and Prof. F. Sandberg in the vicinity of Kribi, Cameroun (collection number Lg 7870) [1, 2]. A voucher specimen is kept in the herbarium at Wageningen, The Netherlands. The stem bark of this species was investigated for its muscle relaxant alkaloids [3, 4]. Prior to the alkaloid extraction the ground stem bark was extracted with hexane. Upon evaporation of the hexane, a crystalline compound was formed. The isolated compound proved to be a saturated pentacyclic triterpene, filican-3-one (**1**) (D: A. Friedo-B': A'-neogammaceran-3-one), its structure and its stereochemistry having been established by X-ray crystallography [5]. Filican-3-one has been described previously in connection with the structure elucidation of triterpenes with the filicane skeleton [6, 7]. However, to our knowledge its natural occurrence has not been reported before.

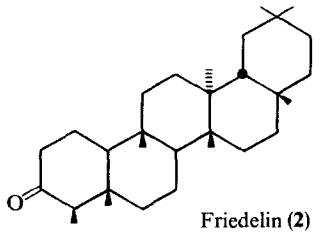


Filican-3-one (**1**)

Filican-3-one (recrystallized ×2 ether) mp 248–249° (some sublimation was observed). $[\alpha]_D^{25°}$ −25.4, no depression of the mmp with an authentic sample of filican-3-one (kindly provided by Prof. A. Marsili, Pisa, Italy). High resolution mass spectrometry (direct inlet, 240°, 70 eV) *m/e* M^+ ($C_{30}H_{50}O$) 426 (32), 411 (36), 383 (4) M^+-isopropyl, 341 (44) $C_{24}H_{37}O^+$, 274 (18) $C_{19}H_{30}O^+$, 273 (20) $C_{20}H_{33}^+$ and $C_{19}H_{29}O^+$ (1:3), 259 (20) $C_{18}H_{27}O^+$, 257 (20) $C_{18}H_{25}O^+$, 234 (56) $C_{16}H_{26}O^+$ and $C_{17}H_{19}^+$ (1:10), 233 (32) $C_{16}H_{25}O^+$ and $C_{17}H_{29}^+$ (1:1), 231 (16) $C_{16}H_{23}O,^+$ 219 (20) $C_{15}H_{23}O,^+$ 206 (36)

$C_{14}H_{22}O^+$ and $C_{15}H_{26}^+$ (1:5), 205 (40) $C_{14}H_{21}O,^+$ 191 (76) $C_{13}H_{19}O^+$ and $C_{14}H_{23}^+$ (1:10), 179 (44) $C_{12}H_{19}O^+$ and $C_{13}H_{23}^+$ (1:2), 178 (28), 177 (24), 149 (34), 137 (48) $C_9H_{13}O^+$ and $C_{10}H_{17}^+$ (1:8), 135 (40), 123 (60) $C_8H_{11}O^+$ and $C_9H_{15}^+$ (1:7), 121 (74), 109 (100) and 107 (48).

The peaks at *m/e* 302, 246 and 218, present in the MS of friedelin, (**2**) are not observed in that of filican-3-one. Other fragments as 341 (loss of E-ring) and 205 contain oxygen, unlike the fragments *m/e* 341 and 205 in friedelin. The fragments 341, 234 and 191 are more abundant in the mass spectrum of filican-3-one than in the spectrum of friedelin; the opposite is true for the 232 and 125 fragments [8–10]. These differences distinguish filican-3-one clearly from friedelin.



Friedelin (**2**)

IR spectrum ν_{max} (KBr-disc): 3400, 2900, 1705, 1455, 1380, 1260, 1200, 1070, 1005 and 800 cm^{-1}. NMR spectrum (100 MHz in $CDCl_3$): the most upfield signal is at δ0.71 ppm, like in friedelin it is assigned to 5-Me [11, 12]. Based on the integration, stereochemical considerations and the shifts observed for the Me groups upon increasing concentration of the shift reagent Eu $(FOD)_3$, the following assignments are made for the methyl signals: δ in ppm 0.71 (5-Me), 0.80 (17-Me), 0.83 (*d*, J = 6.5 Hz, 22-Me), 0.875 (*d*, J = 6.5 Hz, 4-Me), 0.89 (*d*, J = 6.5 Hz, 22-Me), 0.915 (6 H, 13-Me and 9-Me) and 0.99 (14-Me). In deuterobenzene the NMR spectrum showed the following shift for the methyl groups: δ in ppm, 0.68 (5-Me), 0.75 (17-Me), 0.835 (9-Me), 0.87 (13-Me), 0.901 (*d*, J = 6.5 Hz, 22-Me), 0.96 (*d*, J = 6.5 Hz, 22-Me), 0.975 (*d*, J = 6.5 Hz, 4-Me), and 1.01 (14-Me). This means that the 4-Me signal is shifted 0.10 ppm to the lower field, which is in accordance with the shift observed for friedelin, under the same circumstances [12]. This confirms the β-configuration of the 4-Me (= equatorial).

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CAROTENOID SYNTHESIS IN TURKISH LEMONS AND ORANGES AS INFLUENCED BY TRIETHYLAMINE DERIVATIVES

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Key Word Index—*Citrus*; Rutaceae; lemons; oranges; carotenoids; triethylamines; lycopene.

Abstract—Two triethylamines, 2-(4-chloro-phenylthio)-triethylamine (CPTA) and 4-chloro[β-(diethylamino)-ethyl]-benzoate (CDEB), were used to investigate C_{30} carotenoid biosynthesis in Turkish oranges and lemons. It was not possible to determine the pathway, since not all the intermediates from phytoene to the C_{30} compounds were observed. Lycopene and ζ-carotene, absent in controls, were identified in large amounts in certain CPTA- and CDEB-treated lemons and oranges. Furthermore there were varietal differences, since CDEB-treated Turkish oranges did not produce the increases in α- and β-carotene earlier observed in Californian *Citrus* fruits.

INTRODUCTION

Yokoyama *et al.* [1–3] have shown that CPTA affected carotenoid biosynthesis by increasing lycopene production whilst CDEB increased β-carotene over a certain period [4]. Since it is known that varietal differences played an important role in response to these compounds