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STEROIDS FROM *GRANGEA MADERASPATANA*

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Key Word Index—*Grangea maderaspatana*; Compositae; steroids; chondrillasterol; chondrillasterone.

We report the isolation and identification of the steroids chondrillasterol (**1**) and chondrillasterone (**2**) from *Grangea maderaspatana*. This is the first reported isolation of chondrillasterone.

EXPERIMENTAL

The residue from the petrol extract of the plant was separated into neutral and acidic fractions. The neutral fraction was chromatographed over a Si gel column when the following fractions were eluted: (i) Petrol, (ii) Petrol–C_6H_6 (1:1) and (iii) C_6H_6.

Fraction (iii) on rechromatography over Al_2O_3 and elution with C_6H_6–$CHCl_3$ (9:1) gave an alcohol (**1**), identified as chondrillasterol. Fraction (ii) on rechromatography over Al_2O_3 and elution with C_6H_6 gave a ketone (**2**).

Compound (**1**). Needles from Me_2CO, mp 163–165° [1]. It gave a positive Liebermann–Burchard and Salkowski reactions and a yellow colour with tetranitromethane. The IR spectrum (Nujol) had ν_{max}: 3350 (—OH), 1665, 840 (trisubstituted double bond) and 970 (*trans* disubstituted double bond) cm^{-1}. The NMR spectrum (60 MHz) $CDCl_3$, TMS ($\delta = 0.00$) showed signals at δ 0.58–1.10 (Me protons), δ 3.6 ($>\underline{C}H$—OH) and δ 5.18 (3H, *m*, vinylic). The MS showed the molecular ion peak at *m/e* 412 (M^+, $C_{29}H_{48}O$). The other major peaks occur at *m/e* 394 ($M - H_2O$), 369 ($M - CHMe_2$, 19.8%), 351 ($M - H_2O + CHMe_2$, 12%), 300 M – ring A and Me, 19.8%), 273 (M – side chain, 21%), 271 (M – side chain + 2H, 100%), 255 (M – side chain + H_2O, 52.6%) and 229 (M – side chain + 42 mass units forming ring D fragment, 21%).

The acetate prepared by the Ac_2O/Py method, crystallized from Me_2CO as flakes, mp 179–81° [1], M^+ 454. The fact that the mp of the acetate is higher than that of the parent alcohol suggested the absence of a $\Delta^{5,6}$ and the presence of a $\Delta^{7,8}$ double bond [2]. Compound (**1**) on hydrogenation over PtO_2 formed a dihydro compound mp 110–112°, $[\alpha]_D^{25}$ + 19° (*c* 3.4 in $CHCl_3$). The IR spectrum (Nujol) lacked the absorption bands at 1665, 840 and 970 cm^{-1}. The NMR spectrum did not show signals due to vinylic protons indicating migration of the trisubstituted double bond from the 7,8 position to a hindered tetrasubstituted double bond which is not easily hydrogenated. The methyl resonances at C_{10} and C_{13} (δ 0.72 and 0.86) indicated $\Delta^{8,(14)}$ position (δ 0 72 and 0.84) [3].

By comparison (mp, mmp, IR and MS) with an authentic sample, (**1**) has been identified as chondrillasterol.

Compound (**2**). Needles from (Me_2CO, mp 168–70°, $[\alpha]_D^{24}$ + 17° (*c* 3.1 in $CHCl_3$), TLC (Si gel, eluent, Petrol–EtOAc (9.5:0.5), R_f 0.42. (Found: C, 84.40; H, 11.59. $C_{29}H_{46}O$ requires: C, 84.87; H, 11.21%). **2** gave positive Liebermann–Burchard and Salkowski reactions and a yellow colour with tetranitromethane. The IR spectrum (Nujol) had ν_{max}: 1720 ($>C = 0$ on a 6 membered ring), 1670, 845 (trisubstituted double bond) and 970 (*trans* di-substituted double bond) cm^{-1} The NMR spectrum (60 MHz), $CDCl_3$, TMS ($\delta = 0.00$), showed signals at: δ 0.6–1.15 (Me protons), δ 2.3 (4H, *m*, $C\underline{H}_2$—CO—$C\underline{H}_2$), δ 5.23 (3H, *m*, vinylic). The MS showed molecular ion peak at *m/e* 410 (M^+, $C_{29}H_{46}O$). The mass spectral fragmentation agrees well with that reported for stigmastane skeleton [4]. The molecular ion peak appearing at *m/e* 410 (M^+) undergoes loss of 139 mass units to give the peak at *m/e* 271 (M – side chain, 68.1%). The other peaks are at *m/e* 367 (M—$CHMe_2$, 17.54%), 298 (M – ring A and Me, 27.6%) and 229 (M-side chain + 42 mass units forming ring D fragment, 41.98%). The peak at *m/e* 269 was the base peak (100%) [5]. **2** on refluxing with NH_2OH–HCl and EtOH for 1 hr, formed an oxime which crystallized from Me_2CO as needles mp 239–41° (Found: N, 2.9, $C_{29}H_{47}NO$, requires: N, 3.27%). Reduction of **2** with $NaBH_4$ gave an alcohol identical with (**1**) (mmp, IR, NMR and MS). Ketone **2** is thus chondrillasterone.

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STRUCTURE OF THE CAROTENOID PHYSOXANTHIN*

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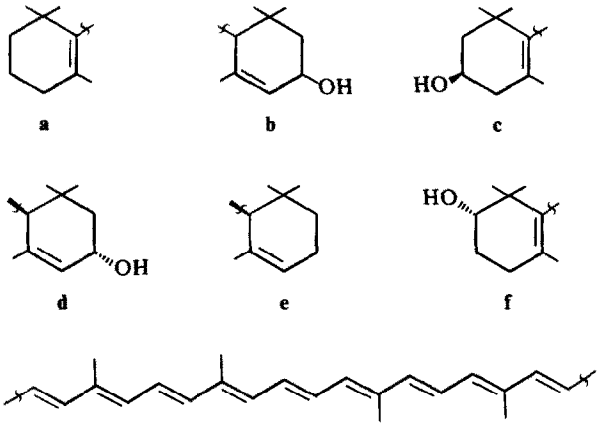
Key Word Index—*Physalis alkekengi*; Solanaceae: physoxanthin identity with 3*R*,6′*R*-β,ε-caroten-3-ol (α-cryptoxanthin).

Physoxanthin from *Physalis alkekengi* was assigned structure **1** by Bodea and Nicoara [1] on the basis of its electronic spectrum, polarity similar to cryptoxanthin (**2**) and ester formation. Location of the hydroxy function was based on the identification of a $KMnO_4$-oxidation product as an α-citraurin derivative on the basis of its electronic spectrum.

A small sample (0.1 mg) of physoxanthin was available for stereochemical studies. The absorption spectrum with λ_{max} (acetone) 423, 447 and 477, % III/II [2] 68 and λ_{max} (EPA = diethyl ether–isopentane–ethanol, 5:5:2) at 421, 445 and 478 nm, % III/II = 60, was consistent with the previously assigned β,ε-chromophore. MS confirmed the molecular weight: *m/e* 552, M − 92, M − 106. The CD spectrum (Fig. 1) gave a further clue to the structure of physoxanthin. It is now known that chiral centres at C-2 [3] or C-3 [4] in ε-rings do not contribute to the CD spectrum of carotenoids containing such end groups, e.g. decaprenoxanthin [3] and lutein (**3**) [4]. If physoxanthin were β,ε-caroten-3′(or 2′)-ol, its CD-spectrum should correspond to that of 6′*R*-β,ε-carotene (**4**) [5] or its enantiomer. On the other hand, provided physoxanthin were 3*R*,6′*R*-β,ε-caroten-3-ol (**5**) its CD spectrum should be very similar to that of lutein (**3**). Comparison of the CD spectra of physoxanthin, 6′*R*-β,ε-carotene (**4**) and lutein (**3**) in Fig. 1 reveals a clear agreement with the latter. This rules out C-3′ or C-2′ substitution of physoxanthin and is consistent with the formulation of physoxanthin as **5**. It should be noted that the CD contribution of end group **f** is equivalent to that of end group **c** [5], hence structure **6** cannot be ruled out. Compound **6** is the C-2 epimer of 2*R*,6′*R*-β,ε-caroten-2-ol present in the green alga *Trentepohlia iolithus* [5].

PMR data or kinetic acetylation studies on physoxanthin could clearly differentiate between structures **5** and **6**, and 4-substitution could be ruled by allylic oxidation. Attempts to reisolate physoxanthin in recent years have, however, failed because of poor growing conditions.



1 a—R—b
2 c—R—a
3 c—R—d
4 a—R—e
5 c—R—e
6 f—R—e
7 c—R—c

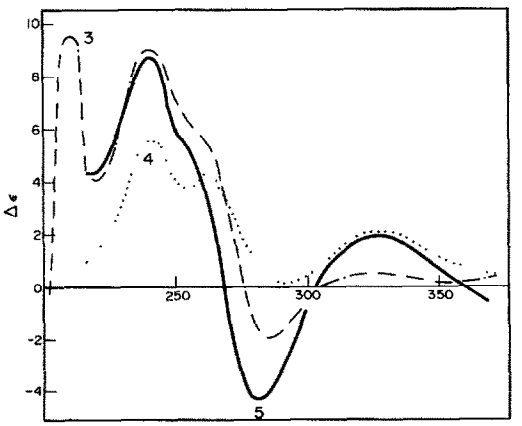


Fig. 1. CD spectra in EPA solution of physoxanthin (**5**), 6′*R*-β,ε-carotene (**4**) and lutein (**3**).

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