The Δδi values for H-2 and H-4 of β-CD and H-6′ aromatic proton of RAH need special attention. Normally the signal for all the β-CD protons show upfield shifts (if any) while all the guest protons show downfield shifts. The downfield shifts of H-2 and H-4 of β-CD and upfield shift of H-6′ of RAH may be attributed to their interaction through solvent. The ratios Δδi(H-5)/Δδi(H-3) were calculated for all the samples. The relatively smaller values (1.01–1.05) for Δδi(H-5)/Δδi(H-3) ratios compared to those reported for other complexes (1.2–3.0) suggest that the penetration of the aromatic ring in the β-CD cavity is not deep which is expected due to the presence of two bulky groups in the meta position of aromatic ring.

Finally, the ^{1}H NMR spectroscopic study of RAH in the presence of β-CD shows that a 1 : 1 RAH-β-CD complex is formed in solution which is in rapid equilibrium with free β-CD and RAH since the spectra consisted of mainly one set of resonances. Moreover, the aromatic ring of the RAH selectively penetrates into the β-CD cavity driven by hydrophobic interactions

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A new triterpenoid: taraxerol-3-β-*O*-tridecyl ether from *Derris triofoliata*

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Received January 12, 2004, accepted February 20, 2004

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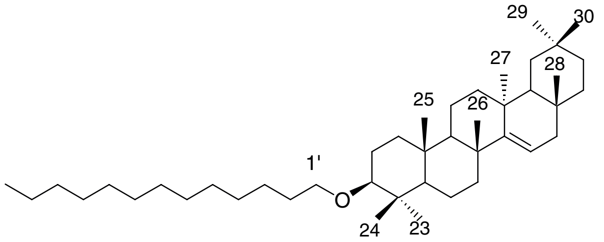
Pharmazie 59: 655–656 (2004)

The new triterpenoid taraxerol-3-β-*O*-tridecyl ether was isolated from the aerial part of *Derris triofoliata*. The structure was established on the basis of spectral data.

The genus *Derris* (Leguminous family) is widely spread in southeast Asia. It is employed for pest control in horticulture, agriculture and in poultry (Gupta et al. 1999). Some species are also used in folk medicine (Sekine et al. 1999; Mahidol et al. 1997). *D. triofoliata*, a woody climber growing in the coastal forest throughout south east Asia, is used for poisoning fish by local people. The whole plant is also used as a stimulant, antispasmodic, and counter-irritant (Ramachandran et al. 1986). Previous investigations of leaves of *Derris trifoliata* have yielded hydrocarbons, wax esters (Misra et al. 1987), sterols, amyrin, lupeol (Ghosh et al. 1985), and two flavonol glycosides: rhamnetin-3-*O*-β-neohesperidoside and quercetin-3-*O*-β-neohesperidoside (Ramachandran et al. 1986). We have investigated the chemical constituents of the aerial parts of *D. triofoliata*, and report here the isolation and characterization of a new etherified triterpenoid.

Compound **1**, prismy crystalline ($CHCl_3{-}CH_3OH$), was formulated as $C_{43}H_{76}O$ from ESI-MS (m/z 647 $[M + k]^+$, 631 $[M + Na]^+$). Its ^{1}H and ^{13}C NMR spectra showed great similarity to that of taraxerol (Sakurai et al. 1987). In ^{1}H NMR, eight tertiary methyls at δ 1.09 (3 H, s), 0.98 (3 H, s), 0.95 (3 H, s), 0.93 (3 H, s), 0.91 (6 H, s), 0.82 (3 H, s) and 0.80 (3 H, s) were typical for triterpene; an oxymethine proton at δ 3.20 (1 H, dd, J = 11.0, 4.6 Hz, H-3) was observed; a downfield one proton double doublet centered at δ 5.53 (J = 11.3, 3.2 Hz, H-15) indicated the presence of an olefinic bond, and was assigned to the olefinic proton at C-15 of the taraxerane skeleton (Talapatra et al. 1981); Two geminal methylene protons at δ 1.92 (1 H, dd, J = 14.7, 2.9 Hz, H-16a) and 2.03 (1 H, m, H-16b) could be discerned in the ^{1}H NMR spectra; Chemical shifts for one oxymethine carbon at δ 79.08 (C-3), olefinic carbons at δ 158.10 (C-14) and 116.88 (C-15) were all observed. Thus, the carbocyclic nucleus of compound **1** proved to be that of a typical taraxerol. Additional signals as one oxymethylene carbon at δ 63.11, one terminal methyl carbon at δ 14.11, multiple methylene carbon signals at δ 29.34 ~ 29.70 indicated that the hydroxyl of taraxol was substituted by a long alkane. And all these was evidenced by DEPT experiments. The ESIMS of **1** exhibited a molecular peak at m/z $647[M+K]^+$, indicating 13 carbon atoms in the alkane compared with the molecular weight of taraxerol. In NOE difference spectra, irradiation of H-3 showed both the enhancement of H-1′ which proved the location of the tridecyl alkane, and H-23 which indicated a β-configuration. Furthermore, a proton double doublet at δ 3.20 (1 H, dd, J = 11.0, 4.6 Hz, H-3) was typical of the axial proton associated with a 3β-configuration taraxerol (Corbett et al. 1972).

The structure of compound **1** was finally elucidated as shown, named taraxerol-3-β-*O*-tridecyl ether. Combined with HMQC, HMBC and data from literature, the spectral data was assigned.



Compound **1**

Experimental

1. Apparatus

The NMR were obtained on a Bruker ARX-400 spectrometer (400 MHz for ^1H NMR, 100 MHz for ^{13}C NMR. ESI-MS spectra was recorded on a Bruker Esquire-LC ion trap mass spectrometer operated in positive ion mode.

2. Plant material

The material investigated were aerial parts of *D. triofoliata* collected in October 2002 from Hainan Province, southern China. The material was identified by Prof. Yongshui Lin, Laboratory of Marine Biology, South China Sea Institute Of Oceanology, Chinese Academy of Sciences. A voucher specimen is deposited at the herbarium of the South China Sea Institute of Oceanology (No. GKLMMM003).

3. Extraction

The dry powdered aerial parts (10 kg) of *D. triofoliata* were extracted with 95% EtOH at 80 °C three times. After evaporation of the solvents under reduced pressure, the residue (1.2 kg) was suspended in H_2O and defatted with petroleum ether. The aqueous layer was further extracted with ethyl acetate and *n*-butanol successively.

4. Isolation and characterization of 1

The ethyl acetate extract (150 g) was subjected to silica gel CC with elution of $CHCl_3-CH_3OH$ system, the first fraction (99 : 1) was chromatographed repeatedly on silica gel CC eluted with *n*-hexane-ethyl acetate, in order of increasing polarity to afford a prismy crystalline 35 mg (*n*-hexane: ethyl acetate – 20 : 1). Compound **1**: ^1H NMR (400 MHz, $CDCl_3$): 3.20 (1 H, dd, J = 11.0, 4.6 Hz, H-3), 5.53 (1 H, dd, J = 11.3, 3.2 Hz, H-15), 1.92 (1 H, dd, J = 14.7, 2.9 Hz, H-16a), 2.04 (1 H, m, H-16b), 0.98 (3 H, s, H-23), 0.80 (3 H, s, H-24), 0.93 (3 H, s, H-25), 0.91 (6 H, s, H-26, H-30), 1.09 (3 H, s, H-27), 0.82 (3 H, s, H-28), 0.95 (3 H, s, H-29), 3.64 (2 H, t, J = 6.6, H-1′) ; ^{13}C NMR (100 MHz, $CDCl_3$): 37.75 (C-1), 27.15 (C-2), 79.08 (C-3), 38.99 (C-4), 55.55 (C-5), 18.80 (C-6), 35.13 (C-7), 38.77 (C-8), 48.78 (C-9), 37.57 (C-10), 17.50 (C-11), 35.78 (C-12), 37.57 (C-13), 158.10 (C-14), 116.88 (C-15), 36.69 (C-16), 38.01 (C-17), 49.29 (C-18), 41.34 (C-19), 28.80 (C-20), 33.71 (C-21), 33.10 (C-22), 28.00 (C-23), 15.45 (C-24), 15.42 (C-25), 29.92 (C-26), 25.90 (C-27), 29.83 (C-28), 33.35 (C-29), 21.31 (C-30), 63.11 (C-1′), 29.34 ~ 29.70 (C-2′ ~ C12’), 14.11 (C-13′).

Acknowledgements: The authers are grateful to the financial support by the National Key Program for Base Research (grant: 2001CCA04700) and Knowledge Innovation Program of Chinese Academy of Sciences (grant: KZCX3-SW-216).

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