

TARAXERYL *cis-p*-HYDROXYCINNAMATE, A NOVEL TARAXERYL FROM *RHIZOPHORA APICULATA*

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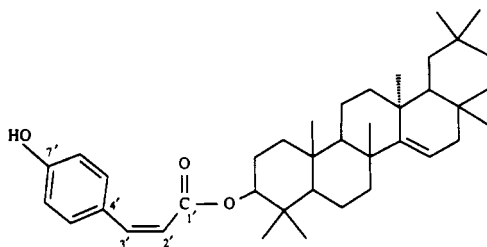
ABSTRACT.—Taraxerol, careaborin (taraxeryl *trans-p*-hydroxycinnamate), and the novel triterpenoid taraxeryl *cis-p*-hydroxycinnamate were isolated from the leaves of *Rhizophora apiculata*.

The Thai mangrove tree, *Rhizophora apiculata* Bl. (Rhizophoraceae), was used by the local Thai people as a folkloric medicine (1). Following primitive beliefs, the bark when boiled in water was used as an astringent for diarrhea, nausea, and vomiting, and as an antiseptic. This extract was also used to stop bleeding in fresh wounds and for the treatment of chronic typhoid fever. This plant has been exported from the Philippines to various parts of the world for utilization in the textile industry (2). The only previous chemical investigation resulted in the isolation of β -amyirin, β -amyrone, taraxerol, β -sitosterol, and triacantanol (3). In this paper, the isolation of taraxerol, careaborin (4–6), and taraxeryl *cis-p*-hydroxycinnamate (**1**) from the leaves of *R. apiculata* is presented. Because they are known compounds, the data for taraxerol and careaborin are presented in the Experimental section only. However, the structure

proof for the new compound **1** is discussed below.

Compound **1** was recrystallized from a CHCl_3 /hexane mixture as a white amorphous solid, mp 275° (dec). The molecular formula $\text{C}_{39}\text{H}_{56}\text{O}_3$ was deduced by hreims. This formula indicated twelve degrees of unsaturation. Fragmentations at m/z 408, 204, and 189 indicated the possibility of a triterpenoid compound (7). The presence of a triterpenoid structure was also suggested by the violet color using Liebermann-Burchard's reagent. Compound **1** showed ^1H -nmr absorptions at δ 0.8–2.0 (typical for triterpenoids), 5.50 (vinylic protons), and 5.42 (α proton attached to oxygen) and was identified as taraxerol by ir, ^1H nmr, ^{13}C nmr, and hreims comparison with data reported previously for taraxerol (4–9).

After acid hydrolysis of **1**, one of the products was identified as a phenol due to bands at 3600 and 1605 cm^{-1} in the



ir spectrum and a positive response to the FeCl_3 color test. The presence of a double bond was indicated by an ir band at 1630 cm^{-1} while an acid was indicated by a broad signal from 3600 to 2500 and a carbonyl signal at 1715 cm^{-1} . The presence of a cis double bond was confirmed by ^1H -nmr signals at δ 7.61 and 6.75 with a coupling constant of $J = 8.55\text{ Hz}$. This coupling constant value is typical for a cis double bond (10). The presence of an aromatic ring was confirmed by signals at δ 6.83 (2H, d, $J = 11.69$) and 5.82 (2H, d, $J = 11.69$). These data suggested that this hydrolysis product was *p*-coumaric acid. This structure assignment was further confirmed (11, 12) by uv (0.1 M NaOH) absorptions at 312 nm ($\log \epsilon = 5.64$), 208 nm ($\log \epsilon = 6.89$), 225 nm ($\log \epsilon = 4.14$), 312 nm ($\log \epsilon = 5.64$), and 368 nm ($\log \epsilon = 4.11$) and by the ms (13, 14), which gave signals at m/z 164 ($\text{C}_9\text{H}_8\text{O}_3$), 147, and 119.

All ^{13}C -nmr signals coincided with those previously reported for taraxerol (8, 9) except for an ester carbonyl signal at 166.53 ppm, aromatic carbon signals at 115.07, 117.02, 118.10, 132.23, 142.91, and 156.67, and olefinic carbon signals at 115.07 and 158.19 ppm. These signals are in agreement with a cinnamate ester moiety (13).

Talapatra and co-workers (6) have previously reported the isolation of the esters careaborin and taraxeryl *trans-p*-hydroxycinnamate from the leaves of *Careya arborea*; however, there is no report of taraxeryl *cis-p*-hydroxycinnamate [1] in the chemical literature. Therefore, 1 is a novel ester of the known natural product taraxerol. The occurrence of cis cinnamates in nature is rare.

EXPERIMENTAL

PLANT MATERIAL.—Leaves of *R. apiculata* were collected from the Klong Wat Mai district, Samutsongkarm Province, Thailand, during October 1985. The plant identification was made by Amorn Uboncholaker and Pipat Patanaponpaiboon, Department of Botany, Chulalongkorn

University. An herbarium specimen (voucher no. 6821) is filed at the Department of Botany, Chulalongkorn University.

EXTRACTION.—Dried leaves of *R. apiculata* were extracted with CH_2Cl_2 by soaking at room temperature. The CH_2Cl_2 solution was evaporated in vacuo, and the residue was chromatographed on an open column on Si gel eluted with hexane/ CHCl_3 /MeOH solvent systems. Taraxeryl (5.67 g), careaborin (210 mg), and compound 1 (50 mg) were isolated. The known compounds were identified by mp, ir, ms, ^1H nmr, and ^{13}C nmr.

TARAXEROL *cis-p*-HYDROXYCINNAMATE [1].—White amorphous solid, mp 275° (dec); ir (KBr) ν max 3600–3570, 3050, 2950, 2865, 1715, 1630, 1605, 1520, 1445, 1390, 1340, 1270, 1190, 845, 820 cm^{-1} ; ms m/z 572 (13.02), 408 (20.33), 284 (31.34), 269 (33.36), 204 (94.90), 164 (30.86), 147 (100.08); uv λ max 208 nm ($\log \epsilon = 6.89$), 225 nm ($\log \epsilon = 4.14$), 312 nm ($\log \epsilon = 5.64$), 368 nm ($\log \epsilon = 4.21$); ^1H nmr (CDCl_3), 0.84 (s, 3H, H-25), 0.87 (s, 3H, H-28), 0.91 (s, 6H, H-29 and H-30), 0.93 (s, 3H, H-27), 0.95 (s, 6H, H-23 and H-24), 1.09 (s, 3H, H-26), 4.52 (t, 1H, $J = 5.88\text{ Hz}$, H-3), 5.50 (dd, 1H, $J = 2.56, 7.05\text{ Hz}$, vinylic H-15), 5.82 (d, 2H, $J = 11.69\text{ Hz}$, Ar, H-5' and H-9'), 6.75 (d, 1H, $J = 8.55\text{ Hz}$, olefinic, H-2'), 6.83 (d, 2H, $J = 11.69\text{ Hz}$, Ar, H-6' and H-8'), 7.61 (d, 1H, $J = 8.55\text{ Hz}$, olefinic, H-3'); ^{13}C nmr 15.55 (C-25), 16.63 (C-24), 17.61 (C-11), 18.80 (C-6), 21.34 (C-30), 23.56 (C-2), 25.95 (C-26), 28.12 (C-23), 28.88 (C-20), 29.96 (C-27 and C-28), 33.26 (C-7), 33.42 (C-29), 33.86 (C-16), 35.27 (C-21), 35.86 (C-17), 36.84 (C-12), 37.60 (C-10), 37.69 (C-1), 37.87 (C-13 and C-22), 38.08 (C-4), 39.11 (C-8), 41.44 (C-19), 49.08 (C-18), 49.35 (C-9), 55.85 (C-5), 81.21 (C-3), 115.07 (C-2'), 115.07 (C-6' and C-8'), 117.02 (C-15), 118.10 (C-4'), 132.23 (C-5' and C-9'), 142.91 (C-3'), 156.67 (C-7'), 158.19 (C-14), 166.53 (C-1'). Compound 1 showed a violet color with Liebermann-Burchard's reagent, a deep green color with 5% FeCl_3 , and decolorized Br_2/CCl_4 .

ACKNOWLEDGMENTS

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