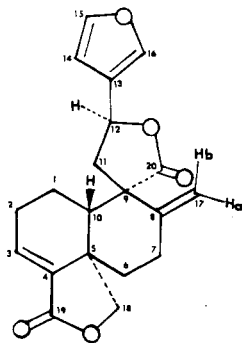


STRUCTURE OF SWASSIN, A NEW FURANOID DITERPENE

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It has been reported that some species, such as *Croton tiglium*, in the genus *Croton* has cocarcinogenic properties (2). As part of our work on the chemical investigation of plants of the genus *Croton*, family Euphorbiaceae, which are available in Thailand, we found, from *Croton joufra* Roxb (1), a novel furanoid diterpene whose structure was shown to be swassin (1) by spectral evidence.



(1)

RESULTS AND DISCUSSION

Swassin (1) is a white solid, mp 169–170°. The molecular formula, $C_{20}H_{20}O_5$, was determined by high resolution ms [M^+ , abs. 340.1266 calc. 340.1305]. The ir spectrum revealed the presence of two γ -lactone (1770, 1760 cm^{-1}), a furan ring (1505, 870 cm^{-1}) and a double bond (1640 cm^{-1})^{3,4}. The 1H -nmr ($CDCl_3$) shows a β -monosubstituted furan (6.37, 1H, H-14; 7.42, 2H, H-15, H-16) which concurs with ^{13}C -nmr absorption at 124.7 (s, C-13), 108.3 (d, C-14), 143.9 (d, C-15) and 139.9 (d, C-16) and also ms at m/e 95, 94 and 81^{3,4}.

From the spectral data, it is plausible that this compound possesses a clerodane-type diterpene structure.

The absence of the methyl signal

in the 1H -nmr spectrum and the quartet pattern in the off-resonance ^{13}C experiment both indicate that this clerodane-type diterpene does not have a free methyl group at C-4, C-5, C-8 or C-9, as is the case for the clerodane skeleton. One methyl group was clearly substituted by an exocyclic methylene, which was shown by ir at 1640 cm^{-1} and 1H -nmr absorption at 4.80 ppm (1H, s) and 5.05 ppm (1H, s) (3). The rest of the methyl group in the clerodane skeleton were present as carbonyls in the lactone moieties, which was shown by ^{13}C -nmr absorption at 176.6 (s, C-20) and 169.3 (s, C-19), and 73.4 (t, C-18). An absorption at 5.53 ppm (1H, t, $J=8$ Hz) is a resonance of H-12 (4). The proton at C-3 appeared as a double-doublet at 6.70 ppm (1H, $J=4, 7$ Hz) (5). The singlet at 4.27 (2H) is found to be C-18 protons.

The structure proposed for swassin (1) was confirmed by ^{13}C -nmr analysis (table 1) and compared to those

TABLE 1. ^{13}C -nmr spectral data of swassin (1), with δ values in ppm, $CDCl_3$, and TMS as the internal standard.

Carbon	^{13}C -nmr (22.5 MHz)
1*	21.4 (t)
2*	26.4 (t)
3	133.5 (d)
4	137.0 (s)
5	43.7 (s)
6*	27.8 (t)
7*	32.5 (t)
8	147.3 (s)
9	53.4 (s)
10	48.8 (d)
11	44.0 (t)
12	71.4 (d)
13	124.7 (s)
14	108.3 (d)
15	143.9 (d)
16	139.9 (d)
17	113.2 (t)
18	73.4 (t)
19	169.3 (s)
20	176.6 (s)

*Assignments may be interchanged.

previously reported for other furanoid diterpenes with a clerodane skeleton (4, 5). Stereochemistry at C-5, C-9, C-10 and C-12 has been shown to be 5S, 9S, 10S and 12S by X-ray analysis (6).

EXPERIMENTAL¹

ISOLATION OF SWASSIN (1).—The dried stem of *C. joufra* (5 kg) was extracted with ethanol and the crude extract was separated into the neutral and acidic fractions in the usual manner. The neutral fraction was chromatographed on alumina with toluene-hexane (1:1 v/v); colorless needles of swassin (1, 2.1 g) were obtained.

Swassin (1) mp 169–170°; $[\alpha]^{20}_D +49.37$ ($c = 0.48$, CH_3OH); ν max (KBr) cm^{-1} : 2890, 2880, 1770, 1760, 1660, 1640, 1610, 1340, 1315, 1268, 1234, 1210, 1175, 1160, 1000, 980, 940, 875, 870, 820 and 720; λ max (MeOH) 225 nm ($\epsilon = 3250$); ms m/e (rel. int.): 340(27.5), 310(100), 292(10), 264(17.5), 229(50), 211(10.5), 198(7.5), 129(40), 128(40), 115(45), 95(42.5), 94(32.5), 91(87), 81(32), 77(52), 44(82). The ^1H -nmr (CDCl_3) δ : 1.13–2.8 (11H, m, H-1,

H-2, H-6, H-7, H-10 and H-11), 4.27 (2H, s, H-18), 4.80 (1H, s, H-17b), 5.05 (1H, s, H-17a), 5.53 (1H, t, $J = 8$ Hz, H-12), 6.37 (1H, deformed t, $J = 1$ Hz, H-14), 6.63, 6.75 (1H, dd, $J = 4, 7$ Hz, H-3) and 7.2 (2H, deformed d, $J = 1$ Hz, H-15, H-16).

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¹ ^1H and ^{13}C -nmr spectra were recorded at 90 and 22.5 MHz, respectively, on the JEOL FX-90Q spectrometer, and the chemical shifts (δ , ppm) were measured from TMS as internal standard.