

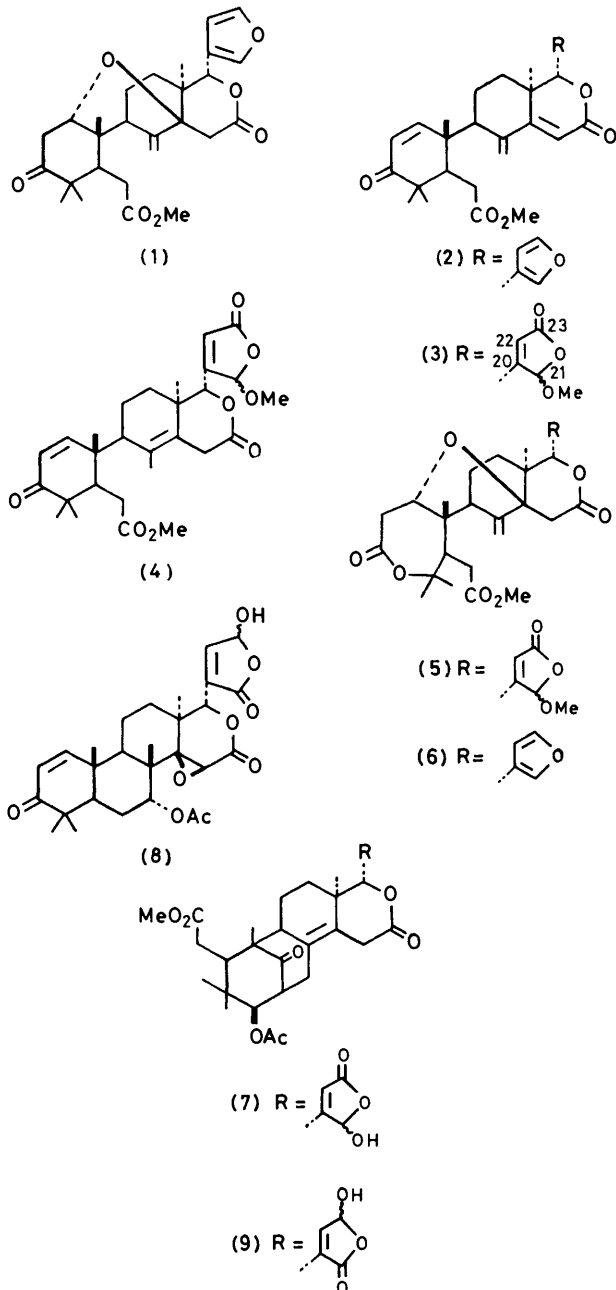
Tetranortriterpenoids and Related Substances. Part 18.¹ Two New Tetranortriterpenoids with a Modified Furan Ring from the Bark of *Soymida febrifuga* A. Juss (Meliaceae)

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Two new tetranortriterpenoids from the bark of *Soymida febrifuga* A. Juss (Meliaceae) have been assigned structures (3) and (5). Both compounds have a β -substituted γ -methoxybutenolide in place of the usual β -substituted furan system.

PREVIOUS work² on the extract of the bark of *Soymida febrifuga* resulted in the identification of methyl angolen-



sate (1) and deoxyandirobin (2) as the major tetranortriterpenoid constituents. We have examined the

minor components of this extract and have isolated two new tetranortriterpenoids (A and B); these lack the β -substituted furan system which normally characterises^{3,4} members of this series. We now present spectroscopic evidence which leads to the assignment of structures (3) and (5) respectively to these compounds.

The ¹H and ¹³C n.m.r. spectra (see Tables 1 and 2) of compound A (3), C₂₈H₃₄O₈, had resonances for a methoxycarbonyl, an exocyclic methylene, and four tertiary methyl groups. These data, in conjunction with the observation of only three fully substituted carbon resonances (δ 46.1, 42.7, and 39.9), suggested a ring-B-cleaved skeleton. The i.r. [ν_{\max} (CCl₄) 1686 (cyclohexenone), 1742 (unsaturated δ -lactone and CO₂Me), and 1776 and 1801 cm⁻¹ (γ -methoxybutenolide)] and u.v. [λ_{\max} 227 (ϵ 17 700) and 266sh (7 000) nm] spectra indicated the presence of conjugated chromophores, two of which were readily identified as a cyclohexenone and a *cisoid* diene-lactone by reference to the ¹H and ¹³C n.m.r. data. These are the same structural features as are present in deoxyandirobin (2),^{2,5} and comparison of the ¹H spectra of compounds (2) and (3) confirmed that they have the same overall structure with the exception of the furan ring. The modified furan ring contains a β -substituted $\alpha\beta$ -unsaturated carbonyl system [δ_C 168.7 (C-23), 163.3 (C-20), and 123.3 (C-22); δ_H 6.39 (dd, *J* 1.0 and 1.5 Hz, H-22)], a secondary carbon attached to two oxygen atoms [δ_C 103.6 (C-21); δ_H 5.74 (d, *J* 1.0 Hz, H-21)] and a methoxy-group (δ_C 57.6, δ_H 3.60). These data are readily accommodated in a β -substituted γ -methoxybutenolide system. In addition, H-17 [δ_H 5.05 (d, *J* 1.5 Hz)] shows the expected small allylic coupling with H-22. The configuration at C-21 remains undefined.

Hydrogenation of compound A resulted in the uptake of 1 mol. equiv. of hydrogen with 1,4-addition to the diene-lactone system to give compound (4). This was apparent from the loss of the u.v. maximum at 266 nm, the appearance of a new carbonyl i.r. band at 1756 cm⁻¹, and new ¹H resonances at δ 1.87br (s, vinylic methyl) and 3.44br (s, H₂-15).

¹ Part 17, G. Ferguson, P. A. Gunn, W. C. Marsh, R. McCrindle, R. Restivo, J. D. Connolly, J. W. B. Fulke, and M. S. Henderson, *J.C.S. Perkin I*, 1975, 491.

² K. K. Purushothaman and S. Chandrasekharan, *Indian J. Chem.*, 1974, **12**, 207.

³ D. L. Dreyer, *Fortschr. Chem. org. Naturstoffe*, 1968, **26**, 190.

⁴ J. D. Connolly, K. H. Overton, and J. Polonsky, *Progr. Phytochem.*, 1970, **2**, 385.

⁵ W. D. Ollis, A. D. Ward, H. Meirelles De Oliveira, and R. Zelnik, *Tetrahedron*, 1970, **26**, 1637.

TABLE 1
¹H N.m.r. spectra ^a of compounds A and B and related compounds

	A(3)	Deoxyandi- robin (2) ^b	Dihydro-A (4)	B(5)	Methyl ivorensate (6)
C-Me	1.12 (9 H) 1.14	1.03 1.13 (6 H) 1.15	1.08 1.17 1.20 1.33 1.87br (s)	0.92 1.05 1.49 1.64	0.88 1.01 1.37 1.59
O-Me	3.60 3.74	3.75	3.59 3.74	3.70 3.72	3.72
H-1	6.63 (d, <i>J</i> 10.5)	6.72 (d)	6.54 (d, <i>J</i> 10.5)	3.55 (m)	3.37 (dd, <i>J</i> 2.2 and 5.8)
H-2	5.93 (d, <i>J</i> 10.5)	5.98 (d)	5.89 (d, <i>J</i> 10.5)	2.4 (2 H, m)	2.86 (dd, <i>J</i> 5.8 and 15) 3.13 (dd, <i>J</i> 2.2 and 15)
>C=CH ₂	5.15 (d, <i>J</i> 1.0) 5.61 (d, <i>J</i> 1.0)	5.18 5.23		4.94 (s) 5.25 (s)	4.92 (s) 5.16 (s)
H-15	6.08 (s)	6.10 (s)	3.44br (2 H, s)	2.84 (2 H, s)	2.53 (d, <i>J</i> 18) 2.95 (d, <i>J</i> 18) 5.70 (s)
H-17	5.05 (d, <i>J</i> 1.5)	5.58 (s)	4.87 (d, <i>J</i> 1.5)	5.48 (d, <i>J</i> 1.6)	
H-9	2.92 (dd, <i>J</i> 3.8 and 6.1)			2.59 (m)	
H-5				2.25 (dd, <i>J</i> 4.5 and 10.5)	
H ₂ -6				2.95 (dd, <i>J</i> 10.5 and 18.8)	
H-21	5.74 (d, <i>J</i> 1.0)	7.52	5.65 (d, <i>J</i> 1.0 Hz)	5.70 (d, <i>J</i> 1.0)	7.47
H-22	6.39 (dd, <i>J</i> 1.0 and 1.5)	6.47	6.34 (dd, <i>J</i> 1.0 and 1.5)	6.28 (dd, <i>J</i> 1.0 and 1.6)	6.40
H-23		7.52			7.37

^a Solvent CDCl₃; Me₄Si standard. Shifts (in p.p.m. downfield from Me₄Si) and coupling constants (Hz) are derived by first-order analysis. ^b From ref. 5.

TABLE 2
¹³C N.m.r. spectra ^a of compounds A and B

Carbon no.	A(3)	B(5)
1	153.4	78.5
2	125.5	32.5 *
3	202.9	168.4
4	39.9	87.4
5	49.0	50.6
6	30.9	33.7 *
7	174.0	175.5
8	142.1	145.7
9	41.8	48.3
10	46.1	48.6
11	21.7	26.2
12	29.4	30.2
13	42.7	41.9
14	160.2	81.8
15	112.8	34.7 *
16	165.9	171.1
17	80.1	79.6
20	163.3	162.3
21	103.6	103.9
22	123.3	122.3
23	168.7	169.1
30	122.9	112.4
C-Me	23.1 22.3 20.5 18.7	33.2 26.8 24.9 15.2
CO ₂ Me	52.1	52.3
OMe	57.6	58.4

^a Pulse FT spectra with 1.25 Hz per data point were obtained at 25.2 MHz from solutions in CDCl₃ at room temperature (ca. 25 °C). Shifts are given as positive downfield from internal Me₄Si. Assignments are based on chemical shift rules, multiplicities in off-resonance-decoupled spectra, correlation with ¹H chemical shifts using two off-resonance-decoupled spectra, and comparison with published data for similar compounds (D. A. H. Taylor, *J.C.S. Perkin I*, 1974, 437).

* These assignments may be interchanged.

The spectroscopic properties of compound B (5), C₂₈H₃₆O₁₀, showed that the γ -methoxybutenolide system

⁶ E. K. Adesogan and D. A. H. Taylor, *J. Chem. Soc. (C)*, 1970, 1710.

⁷ D. L. Dreyer, *Tetrahedron*, 1965, **21**, 75.

⁸ J. D. Connolly, K. L. Handa, and R. McCrindle, *Tetrahedron Letters*, 1968, 437.

was again present (see Tables 1 and 2). The i.r. spectrum showed the same unusually high frequency bands at 1 803 and 1 779 cm⁻¹ in addition to ester and lactone absorption at 1 760 and 1 745sh cm⁻¹. The nature of the carbon skeleton was revealed by the ¹H and ¹³C n.m.r. spectra, which showed signals for four tertiary methyl groups, two at lower field (δ_{H} 1.49 and 1.64), an exocyclic methylene, a methoxycarbonyl group, and four fully substituted carbon atoms, two bearing oxygen. This indicated that both rings A and B were cleaved with an ϵ -lactone system in ring A. The remaining oxygen was present as a 1,14-ether of the methyl angolensate (1) type [δ_{H} 3.55 (m, H-1), δ_{C} 78.5 (C-1) and 81.8 (C-14)]. The structure of compound B is the same as that of methyl ivorensate (6) ⁶ with the exception of the furan ring; the similarity of their ¹H spectra supported this (see Table 1).

Several reports of tetranortriterpenoids with modified furan rings have already appeared.⁷⁻¹⁰ Isocabralin (7) ¹⁰ has a γ -hydroxybutenolide system with the same orientation as compounds A and B whereas photogedunin (8) ⁹ and cabralin (9) ¹⁰ have the alternative arrangement.

EXPERIMENTAL

For general experimental details see ref. 11. N.m.r. spectra (¹H and ¹³C) were run on a Varian XL-100 spectrometer with VFT-100 accessory, for solutions in deuteriochloroform with tetramethylsilane as internal reference.

Extraction.—Powdered bark (15 kg) of *S. febrifuga* A. Juss was extracted with benzene in the cold. Concentration of the extract and addition of ether afforded a crude solid (2.5 g) which was crystallised from ethyl acetate-ether to give methyl angolensate (1) (1.5 g), m.p. 199–204°. The

⁹ B. A. Burke, W. R. Chan, K. E. Magnus, and D. R. Taylor, *Tetrahedron*, 1969, **25**, 5007.

¹⁰ M. M. Rao, H. Meshulam, R. Zelnik, and D. Lavie, *Phytochemistry*, 1975, **14**, 1071.

¹¹ J. D. Connolly, R. Henderson, R. McCrindle, K. H. Overton, and N. S. Bhacca, *J. Chem. Soc.*, 1965, 6935.

residual extract was chromatographed over silica gel. Elution with benzene-chloroform (3:1) yielded more methyl angolensate (0.7 g). The fractions eluted with chloroform and chloroform-methanol (2%) were combined and crystallised from benzene-ether to give deoxyandirobin (2)^{1,5} (0.25 g), m.p. 170—172°. Elution with chloroform-methanol (9:1) and crystallisation from methanol-ether afforded *compound A* (3), (80 mg), m.p. 186°, $[\alpha]_D +480^\circ$ (CHCl₃) (Found: *m/e*, 498.225 15. C₂₈H₃₄O₈ requires *M*, 498.225 3). Preparative t.l.c. of the mother liquors and crystallisation from chloroform-ether yielded *compound B* (5) (30 mg), m.p. 248—252° (Found: C, 62.95; H, 6.8. C₂₈H₃₆O₁₀ requires C, 63.15; H, 6.8%).

Dihydro-A (4).—Compound A (3) (60 mg) in methanol was hydrogenated over 5% palladium-charcoal at room temperature. After the usual work-up the product was crystallised from chloroform-ether to yield dihydro-A (4) (50 mg) as fine needles, m.p. 198°, *m/e* 500.

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