

SHORT COMMUNICATIONS

CONSTITUENTS OF THE ROOTS OF *PILIOSTIGMA THONNINGII* (LEGUMINOSAE)

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ABSTRACT. The isolation of 5α -stigmasta-7,22-dien- 3β -ol and four labdane-derivatives from *Piliostigma thonningii* is reported.

INTRODUCTION

The roots of *P. thonningii* (Schumach.) Milne-Redh. had been reported to have contraceptive properties. In Malawi an infusion of it is used, together with that of *Vigna phaseoloides* Baker (Leguminosae) (1).

In search of biologically active constituents the roots of *P. thonningii* collected from western Ethiopia have been studied. In this communication we report the isolation and characterization of a stigmastadienol (1) and four labdane-derivatives: lambertianic acid (2a), lambertianol (2c), the hitherto unknown 2d, and trans-communic acid (3a), obtained from the petroleum ether extract.

RESULTS AND DISCUSSION

The chemical structures of these compounds were identified by spectral analysis. The ^{13}C -NMR data of 2a-2d and 3a are reported here for the first time.

1 (2), 2a (3-8), and 3a (9-14) are known compounds. Although because of insufficient amount of material the acids 2a and 3a could not be purified completely they nevertheless were unequivocally identified by their spectra. They have also been transformed into their methyl esters 2b and 3b, respectively. These spectral data also agree with those from the literature. According to the ^1H -NMR spectrum of 3b (cf. lit. (9)) the configuration in the side chain is 2'-E.

The dextrorotatory alcohol 2c has not yet been found in nature, but its enantiomer daniellol is known (15). We cannot exclude that 2c is an artifact arising from saponification of 2d during isolation. Compound 2d was found in very small amounts, and no parent peak was detectable in its mass spectrum, but from IR-spectra and especially from several different NMR-experiments its structure could also be deduced unequivocally.

EXPERIMENTAL

^1H -NMR and ^{13}C -NMR spectra were recorded on an AM 400 (Bruker) using CDCl_3 as solvent; IR spectra were measured in CHCl_3 with a Perkin Elmer 1310; mass spectra on a Varian CH-5; column chromatography was carried out

Table 1. ^{13}C -NMR chemical shifts

| Carbon | 2a | 2b(20) | 2c | 2d | 3a | 3b(10) |
|--------|-------|--------|-------|-------|-------|--------|
| 1 | 44.2 | 44.2 | 38.8 | 37.3 | 44.2 | 44.3 |
| 2 | 38.6 | 38.2 | 35.3 | 36.2 | 37.8 | 38.2 |
| 3 | 19.8 | 19.9 | 18.9 | 18.9 | 19.9 | 20.0 |
| 4 | 39.0 | 39.0 | 38.9 | 38.8 | 39.2 | 39.3 |
| 4a | 40.1 | 40.1 | 39.4 | 39.4 | 40.3 | 40.1 |
| 5 | 56.2 | 56.2 | 56.0 | 56.0 | 56.2 | 56.2 |
| 6 | 147.8 | 147.9 | 147.9 | 147.7 | 147.7 | 148.0 |
| 7 | 37.8 | 38.7 | 38.5 | 38.5 | 38.4 | 38.5 |
| 8 | 26.0 | 26.2 | 24.4 | 24.4 | 25.8 | 26.0 |
| 8a | 55.2 | 55.2 | 56.1 | 56.1 | 56.2 | 56.4 |
| 9 | 106.5 | 106.3 | 106.5 | 106.7 | 107.7 | 107.6 |
| 10 | 12.8 | 12.6 | 15.3 | 15.3 | 12.8 | 12.6 |
| 11 | 29.0 | 28.8 | 27.0 | 27.6 | 29.0 | 28.8 |
| 12 | 184.6 | 177.7 | 64.9 | 66.5 | 184.7 | 177.7 |
| 13 | - | 51.1 | - | 174.1 | - | 51.2 |
| 1' | 24.2 | 24.2 | 24.1 | 24.1 | 23.2 | 23.3 |
| 2' | 23.5 | 23.5 | 23.5 | 23.5 | 133.9 | 133.9 |
| 3' | 125.4 | 125.4 | 125.5 | 125.5 | 133.4 | 133.4 |
| 4' | 110.9 | 110.9 | 110.9 | 110.9 | 141.5 | 141.6 |
| 5' | 142.6 | 142.6 | 142.6 | 142.7 | 109.9 | 109.9 |
| 6' | 138.7 | 138.6 | 138.6 | 138.7 | 11.8 | 11.8 |
| 14 | | | | 34.5 | | |
| 15 | | | | 25.0 | | |
| 28 | | | | 31.9 | | |
| 29 | | | | 22.7 | | |
| 30 | | | | 14.1 | | |

Table 2. ^1H -NMR chemical shifts

| Prot. | 2a(8,18) | 2b(8) | 2c(8) | 3a | 3b(9) |
|-------|----------------------|----------------------|------------------------|----------------------|----------------------|
| 7 | | 2.40(m) & 1.96(m) | 2.38(m) & 1.92(td) | 2.4(m) & 1.95(m) | 2.38(m) & 1.95(m) |
| 9 | 4.57(s) & 4.87(s) | 4.55(s) & 4.87(s) | 4.54(s) & 4.84(dd) | 4.90(s) & 4.45(s) | 4.45(s) & 4.85(s) |
| 10 | 0.6(s) | 0.49(s) | 0.63(s) | 0.69(s) | 0.53(s) |
| 11 | 1.25(s) | 1.15(s) | 0.95(s) | 1.27(s) | 1.17(s) |
| 12 | | | 3.36(d,d) & 3.73(d) | | |
| 13 | | 3.6(s) | | | 3.6(s) |
| 1' | | | | 2.4 & 2.15 | 2.38(m) & 2.15(m) |
| 2' | 2.55(m) & 2.25(m) | 2.55(m) & 2.22(m) | 2.53(m) & 2.21(m) | 5.4(t) | 5.37(t) |
| 4' | 6.25(t) | 6.23(dd) | 6.24(dd) | 6.32(dd) | 6.32(dd) |
| 5' | 7.35(t) | 7.35(t) | 7.34(t) | 5.05(d) & 4.9(d) | 5.05(d) & 4.85(d) |
| 6' | 7.19(s) | 7.17(m) | 7.17(m) | 1.75 | 1.73(s) |

s = singlet; d = doublet; t = triplet; m = multiplet; dd = double doublet

using silica gel Grace Type 254 (20-45 mesh).

Plant material. The plant material was collected in February 1986, 364 km west of Addis Ababa in the Wollega-region, 29 km along the Nekemt-Ghimbi road at a height of 1520 m. The plant was authenticated by Dr. Sebsibe Demissew, a voucher specimen is deposited in the National Herbarium in Addis Ababa (Nr Sebsibe 1731).

Extraction and isolation. Air dried, powdered roots (400 g) and powdered root

bark (400 g) were macerated separately with cold petroleum ether for three weeks. Comparison of both extracts (3.62 g (0.9%) and 1.9 g (0.47%), resp.) by TLC showed that they contain identical compounds in comparable amounts. Chromatography on silica gel with petroleum ether/acetone (30:1) afforded 0.07 g of **2d** and 0.61 g of **2c**. Elution with ethyl acetate afforded 0.525 g of a mixture of **2a** and **3a**, and then 0.09 g of **1**. The acids **2a** and **3a** were esterified with CH_2N_2 and the methyl esters separated by column chromatography on silica gel with petroleum ether/ethyl acetate (100:1) to yield pure **2b** and **3b**.

5 α -Stigmasta-7,22-dien-3 β -ol (1) (16,17): Mp 156-160°C; MS m/z (rel. int.) 412 (M^+ , $\text{C}_{29}\text{H}_{48}\text{O}$, 60%), 271 (100); $^1\text{H-NMR}$ (400 MHz): δ 0.58 (s, 3H, $\text{H}_3\text{C-18}$); 0.77 (t, 3H, $\text{H}_3\text{C-29}$); 0.78 (s, 3H, $\text{H}_3\text{C-19}$); 0.80 (d, 3H) and 0.83 (d, 3H, $\text{H}_3\text{C-26}$ and $\text{H}_3\text{C-27}$); 1.04 (d, 3H, $\text{H}_3\text{C-21}$); 3.57 (m, 1H, HC-3); 5.00 (dd, 1H, HC-23); 5.14 (dd, 1H, HC-22); 5.14 (1H, HC-7).

5 β -[2-(3-Furanyl)ethyl]-decahydro-1 α ,4 α β -dimethyl-6-methylene-1-naphthalene carboxylic acid (2a). (8,18): IR (cm^{-1}): 2400-3400(m), 1690(s), 1640(m), 890(s).

Methyl 5 β -[2-(3-furanyl)ethyl]-decahydro-1 α ,4 α β -dimethyl-6-methylene-1-naphthalene carboxylate (2b). (8,19): Oil; $[\alpha]_{\text{D}} = +95.6$ (c = 0.7, CHCl_3); MS m/z (rel. int.) 330 (M^+ , $\text{C}_{21}\text{H}_{30}\text{O}_3$, 50%), 121 (100), 81 (80), 189 (35), 271 (10).

5 β -[2-(3-Furanyl)ethyl]-decahydro-1 α ,4 α β -dimethyl-6-methylene-1-naphthalene methanol (2c). (8): Oil; $[\alpha]_{\text{D}} = +33.8$ (c = 0.7, CHCl_3); IR (cm^{-1}): 3400(m), 1640(m), 895(m); MS m/z (rel. int.) 302 (M^+ , $\text{C}_{20}\text{H}_{30}\text{O}_2$, 30%), 81 (100), 95 (62), 271 (30).

5 β -[2-(3-Furanyl)ethyl]-decahydro-1 α ,4 α β -dimethyl-6-methylene-1-naphthalene methyl stearate (2d): Oil; IR (cm^{-1}): 1720(s), 1640(m), 895(m).

5 β -(2E-3-Methyl-2,4-pentadienyl)-decahydro-1 α ,4 α β -dimethyl-6-methylene-1-naphthalene carboxylic acid (3a): IR (cm^{-1}): 3400-2400(m), 1690(s), 1640(m), 890(s).

Methyl 5 β -(2E-3-methyl-2,4-pentadienyl)-decahydro-1 α ,4 α β -dimethyl-6-methylene-1-naphthalene carboxylate (3b) (11,12): Mp: 103-105°C; $[\alpha]_{\text{D}} = +45.3$ (c = 2.6, CHCl_3) (10); IR (cm^{-1}): 1715(s), 1645(m), 1615(m), 990(m), 895(m); Ms m/z (rel. int.) 316 (M^+ , $\text{C}_{21}\text{H}_{32}\text{O}_2$, 60%), 121 (100), 81 (99), 175 (90), 257 (40).

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