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FURTHER OLEANANE TRITERPENOIDS FROM *VICOA INDICA*[1]

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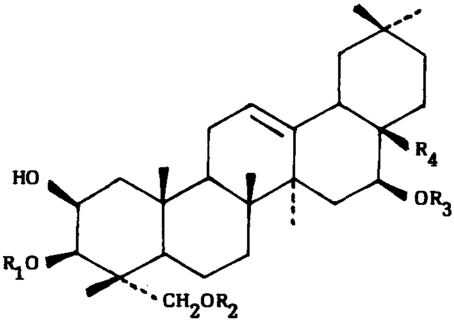
ABSTRACT.—Vicosigenin [**1**], a new 28-nortriterpenoid, and vicoside B [**4**], a new triterpenoid glucoside, were isolated from *Vicoa indica*. Their structures were elucidated by spectral methods.

Previous investigations on *Vicoa indica* DC. (Asteraceae), a tribal female antifertility drug in India, led to the isolation of four sesquiterpenoid lactones (1,2), a monoterpene diol (3), and a 28-noroleanane glucoside, vicoside A [**2**] (4). The present work describes the isolation and characterization of a new 28-nortriterpenoid, vicosigenin [**1**], and a new triterpenoid glucoside, vicoside B [**4**], from the same plant.

Chromatography of the $CHCl_3$ extract of the aerial parts of *V. indica* afforded vicosigenin [**1**]. Compound **1** was assumed to have molecular formula $C_{30}H_{48}O_6$ from its DEPT spectrum. Its ir spectrum showed hydroxyl and ester bands at 3425 and 1735 cm^{-1}, respectively. The ^1H- and ^{13}C-nmr spectra of **1** exhibited signals for six tertiary methyl groups, a trisubstituted double bond, three secondary and one primary hydroxyl groups, and a formate group (see Experimental). The mass spectrum of **1** did not exhibit the molecular ion peak and gave the highest mass peak at *m/z* 458 $[M-HCO_2H]^+$. The facile loss of formic acid from the molecule suggested that the formate group in **1** must be at C-17, as it is well known that substituents at C-17 are readily lost (5). Furthermore, fragment peaks at *m/z* 239 and 218 (base peak) were due to retro-Diels-Alder cleavage from *m/z* 458. This indicated that three hydroxyl groups were in the rings A/B and one hydroxyl group was in the D/E portion of a 28-norolean-12-ene skeleton (4). The presence of a singlet at δ 73.5 (C-17) coupled with the absence of a singlet at δ 28.0 for the Me-28 agreed with mass spectral data and confirmed placement of the -OCHO at C-17. With the exception of the glucose residue, the ^1H- and ^{13}C-nmr spectra of **1** exhibited resonances closely similar to vicoside A [**2**] previously isolated from the same plant (4). ^1H-nmr signals for H-23, H-2, and H-16 observed at δ 3.32, 4.25 (m), and 4.00 (dd, $J=11.5$ and 5 Hz), respectively, were in conformity with those of the aglycone part of the saponified product of vicoside A hexacetate [**3**] (4). The ^{13}C-nmr data also confirmed the above assignments. Thus, the structure of vico-



1 $R_1=R_2=R_3=H$, $R_4=OCHO$
2 $R_1=\beta$-D-Glc, $R_2=R_3=H$, $R_4=OCHO$
3 $R_1=\beta$-D-Glc$(Ac)_4$, $R_2=R_3=Ac$, $R_4=OCHO$
4 $R_1=\beta$-D-Glc, $R_2=R_3=H$, $R_4=CHO$
5 $R_1=\beta$-D-Glc$(Ac)_4$, $R_2=R_3=Ac$, $R_4=CHO$

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sigenin [**1**] was deduced to be 17β-formyloxy-28-norolean-12-ene-2β,3β,16β-23-tetraol.

The EtOAc-soluble portion of the MeOH extract of the plant was chromatographed to afford an inseparable mixture of vicosides A [**2**] and B [**4**] which was acetylated with pyridine and Ac_2O to give pure vicoside B hexacetate [**5**] as an amorphous solid. The molecular formula $C_{48}H_{68}O_{16}$ for **5** was suggested by DEPT ^{13}C-nmr analysis. The ir spectrum of **5** exhibited hydroxyl absorption at 3400 cm^{-1}. An aldehyde group attached to a tertiary carbon was revealed as a singlet at δ 9.85 in its ^1H nmr and by a doublet at δ 204.1 in ^{13}C nmr. Inspection of the ^1H- and ^{13}C-nmr spectra of **5** (see Experimental) showed similarity with those of **3** except for a -CHO group instead of a -OCHO. The absence of a peak at δ 28.0 for C-28 and the presence of a doublet at δ 204.1 required the placement of -CHO at this position.

The placement of the aldehyde group at C-17 was further supported in **5** by the downfield shift of H-18 occurring as a dd at δ 2.90 ($J=$ 12 and 5 Hz) as compared to δ 2.50 (br d) in compound **3**. The remaining resonances and coupling constants were consistent with structure **5** for vicoside B hexacetate, and therefore the structure of vicoside B [**4**] was deduced to be 2β,3β,16β,23-tetrahydroxyolean-12-ene-28-al-3-*O*-β-D-glucopyranoside.

Vicoside B [**4**] is an important biogenetic intermediate in the formation of vicoside A [**2**], the latter arising by the Bayer-Villiger oxidation of the former. So far, oleanolic aldehyde has been reported from *Mangifera indica* (6), from the cactus *Heliabrove chende* (7) and its 3-acetate, and from the wood of *Machaerium scleroxylon* (8), but this is the first report of isolation and of an oleanane glucoside with a C-17 aldehyde function from natural sources.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's were uncorrected. Ir spectra were obtained on a Perkin-Elmer 337 grating spectrophotometer in KBr pellets, and ^1H-nmr and ^{13}C-nmr spectra (at 300.13 and 75.15 MHz respectively) were recorded on a Bruker instrument with TMS as the internal standard.

PLANT MATERIAL.—*V. indica* (whole plant) was collected from Tambaram, Tamil Nadu, India during February 1987. A voucher specimen (No. 39/147) is deposited at the Department of Botany of Captain Srinivasa Murti Drug Research Institute for Ayurveda.

EXTRACTION AND ISOLATION OF VICOSIGENIN [**1**] AND OF VICOSIDE B [**4**] AS ITS HEXAACETATE **5**.—Shade-dried and coarsely powdered plant material (5 kg) was extracted with $CHCl_3$ (30 liters). The $CHCl_3$ solution was concentrated in vacuo to give 100 g of extract. The marc was then extracted with MeOH.

The $CHCl_3$ extract was subjected to cc over Si gel and eluted with C_6H_6 and increasing proportions of EtOAc in C_6H_6. Elution with C_6H_6-EtOAc (3:1) gave a gum which, after repeated chromatography and crystallization from Et_2O, gave crystals of vicosigenin [**1**] (50 mg).

The MeOH extract was concentrated in vacuo to yield a syrupy mass. It was then partitioned between EtOAc and H_2O, and the EtOAc layer was dried with Na_2SO_4 and concentrated to give a residue (5 g). The residue was chromatographed over a column of Si gel in C_6H_6 and eluted with EtOAc with increasing proportions of MeOH. Elution with EtOAc-MeOH (9:1) yielded a solid which was filtered, washed with EtOAc, and dried. The resulting solid (2 g) was acetylated with Ac_2O/pyridine at room temperature. Chromatography of the acetylated product over Si gel and elution with C_6H_6-EtOAc (4:1) yielded vicoside B hexaacetate [**5**] as a minor product (50 mg) which was slightly less polar than vicoside A hexaacetate [**3**]. Compound **5** was washed with hexane to yield an amorphous powder.

Vicosigenin [**1**].—Mp 252–254°; ir ν max 3425, 1735 cm^{-1}; eims (probe) 70 eV *m/z* $[M-HCO_2H]^+$ 458, 440, 239, 221, 218 (base peak), 203, 200, 189; ^1H nmr (MeOH-d_4) δ 0.86–1.25 (6 × Me), 3.32 (m, H-23), 3.50 (d, $J=3.0$ Hz, H-3), 4.25 (m, H-2), 4.00 (dd, $J=11.5$ and 5 Hz, H-16), 5.25 (br s, H-12), 8.25 (s, OCHO); ^{13}C nmr (MeOH-d_4) δ 44.8 (C-1), 71.8 (C-2), 73.4 (C-3), 42.9 (C-4), 50.5 (C-5), 18.9 (C-6), 32.2 (C-7), 40.8 (C-8), 48.9 (C-9), 37.6 (C-10), 24.5 (C-11), 124.1 (C-12), 142.1 (C-13), 42.3 (C-14), 35.9 (C-15), 66.3 (C-16), 73.5 (C-17), 50.2 (C-18), 49.3 (C-19), 31.4 (C-20), 36.8 (C-21), 31.8 (C-22), 67.2 (C-23), 14.5 (C-24), 18.1 (C-25), 17.5 (C-26), 27.1 (C-27), 33.1 (C-29), 24.6 (C-30), 161.2 (-OCHO).

Vicoside B hexacetate [**5**].—Ir ν max 3400, 1720 cm^{-1}; ^{1}H nmr (CDCl$_3$), δ 0.93–1.25 (6 × Me), 2.90 (dd, J = 12.0 and 5 Hz, H-18), 3.50 (br s, W½ = 5 Hz, H-3), 3.85 (ABq, J = 11.5 Hz, H-23), 4.20 (br s, W$_{1/2}$ = 9 Hz, H-2), 5.50 (br t, H-13), 5.40 (m, H-16), 9.85 (s, CHO); sugar acetate protons δ 4.60 (d, J = 8.0 Hz, H-1′), 5.08 (m, H-2′ and -4′), 5.24 (t, J = 9 Hz, H-3′), 3.70 (m, H-5′), 4.12 (d, J = 12 Hz, H-6′); ^{13}C nmr (CDCl$_3$), δ 42.7 (C-1), 69.2 (C-2), 84.0 (C-3), 43.7 (C-4), 47.6 (C-5), 17.6 (C-6), 29.7 (C-7), 39.6 (C-8), 47.5 (C-9), 36.1 (C-10), 23.6 (C-11), 123.6 (C-12), 142.1 (C-13), 40.7 (C-14), 31.4 (C-15), 71.2 (C-16), 47.3 (C-17), 51.8 (C-18), 45.8 (C-19), 30.4 (C-20), 33.8 (C-21), 30.4 (C-22), 66.0 (C-23), 14.2 (C-24), 16.2 (C-25), 17.6 (C-26), 26.2 (C-27), 204.1 (C-28), 32.4 (C-29), 25.1 (C-30), 101.7 (C-1′), 71.4 (C-2′), 72.5 (C-3′), 68.5 (C-4′), 71.8 (C-5′), 61.8 (C-6′).

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