work-up and column chromatography, eluting with *n*-hexane–EtOAc (2:3), 650 mg of **2b** + **3b**; mp 118–121° (EtOH); IR ν_{max}^{KBr} cm^{-1}: 3520, 2960, 1750, 1720, 1710, 1660, 1650, 1380, 1260, 1230, 1150, 1075, 1040, 1020, 960; ^{1}H NMR (90 MHz, $CDCl_3$): δ6.30 (1H, *d*, *J* = 6 Hz, H-3), 5.10 (1H, *d*, *J* = 7.8 Hz, H-1), 5.25–4.90 (6H, H-4, H-6, H-1′, H-2′, H-3′, H-4′), 4.20 (2H, *br s*, H-6′), 3.76 (1H, *m*, H-5′), 3 53 (1H, *t*, *J* = 2 Hz, H-7), 3.16 (1H, *d*, *J* = 3 Hz, OH), 2 46 (1H, *br d*, *J* = 7.8 Hz, H-9), 2.06–1.96 (12H, *s*, 4 × OAc), 1.50 (3H, *s*, Me-10); the senecioyl and angeloyl resonances appear as above; ^{13}C NMR (25.2 MHz, $CDCl_3$): δ141.22 (*d*, C-2), 107.22 (*d*, C-4), 96.37 (*d*, C-1′), 94.51 (*d*, C-1), 77 56 and 78.05 (*d*, C-6), 73.27 (*s*, C-5), 72.52 (*d*, C-3′), 72.37 (*d*, C-5′), 71.04 (*d*, C-2′), 68.59 (*d*, C-4′), 62.97 (*d*, C-7), 62.83 (*s*, C-8), 61.67 (*t*, C-6′), 52.44 (*d*, C-9), 17 03 (*q*, C-10); additional signals for acetyl, senecioyl and angeloyl groups at δ170.24–169.27, 20.46; 169 27, 158.06, 115.61, 27.35, 20.46 and 165.92, 138.95, 127.59, 20 40, 15 93, respectively. (Found: C, 54.51; H, 5.99. $C_{28}H_{36}O_{15}$ requires. C, 54.90; H, 5.88%.)

Acid hydrolysis of **2a** + **3a** in the usual manner yielded glucose, identified by conventional methods [1]. Alkaline hydrolysis according to ref. [3] afforded, in addition to senecioic and angelic acids, antirrinoside (**1a**) $[\alpha]_D^{24}$ −68.10° (dioxane; *c* 0.54), identical in all respects with an authentic sample.

Antirride [mp 152–153°; $[\alpha]_D^{24}$ −93.7° (dioxane; *c* 1 55)] and *antirrinoside* were fully characterized by analytical, physical and spectroscopic data and preparation of some derivatives. In every cases the reported values are in agreement with those obtained by us.

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REFERENCES

1. Scarpati, M. L and Guiso, M. (1969) *Gazz. Chim. Ital.* **99**, 807.
2. Scarpati, M. L., Guiso, M. and Esposito, P. (1968) *Gazz. Chim. Ital.* **98**, 177.
3. Kitagawa, I., Hino, K., Nishimura, T., Iwata, E. and Yosioka, I. (1971) *Chem. Pharm. Bull.* **19**, 2534.

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OCCURRENCE OF 24-EPIMERS OF CYCLOART-25-ENE-3β,24-DIOLS IN THE STEMS OF *EUPHORBIA TRIGONA*

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Key Word Index—*Euphorbia trigona*; Euphorbiaceae; mortenol, 24-epimeric cycloart-25-ene-3β,24-diols; betulin.

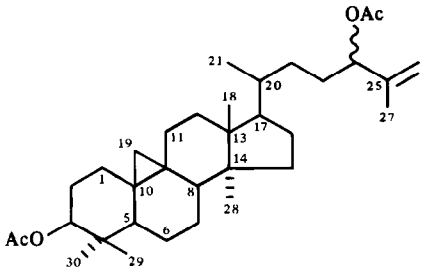
Abstract—^{13}C NMR spectroscopy has demonstrated that the cycloart-25-ene-3β,24-diol isolated from the stems of *Euphorbia trigona* is a 1:1 mixture of the 24-epimers. This seems to be the first instance of the detection of the natural occurrence of 24-epimeric cycloart-25-ene-3β,24-diols.

INTRODUCTION

In our previous communication [1] we reported the isolation of taraxeryl acetate, friedelin, friedelan-3β- and 3α-ols, taraxerol, cycloartenol, 24-methylenecycloartanol, α- and β-amyrins, lupeol, sitosterol and an unidentified triterpene alcohol from the stems of *Euphorbia trigona* Haw. We now report the characterization of the unidentified triterpenoid as mortenol together with the isolation of the 24-epimeric cycloart-25-ene-3β,24-diols and betulin.

RESULTS AND DISCUSSION

The *n*-hexane extract of *E. trigona* stems on CC gave a gummy material after separation of the monohydroxytriterpenoids [1]. This gummy material resisted crystallization and was, therefore, acetylated. Repeated CC gave compounds **1** and **2**. Compound **1** crystallized from chloroform–methanol as colourless needles, mp 122° and showed a single spot on TLC. The ^{1}H NMR spectrum of compound **1** exhibited two doublets (*J* = 4 Hz) at δ0.3 and 0.55, characteristic of cyclopropane protons in 9,19-cyclotriterpenoids, five methyls between δ0.8 and 0.95, a singlet at δ1.7 for a vinyl methyl, two acetoxyls at δ2.0, a doublet of doublets at δ4.5 assignable to an H-3α over an acetoxyl with axial–axial and axial–equitorial couplings (*J* = 10, 5 Hz), two broad singlets at δ4.9 and 4.95 due to a vinyl methylene and a triplet at δ5.1 which can be attributed to a proton α- to an acetoxyl. From the above ^{1}H NMR data it was assumed that compound A is a 9,19-cyclotriterpenoid with two acetoxyls and a side chain terminating in an isopropenyl group. The mass spectral



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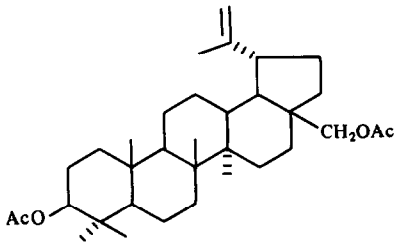

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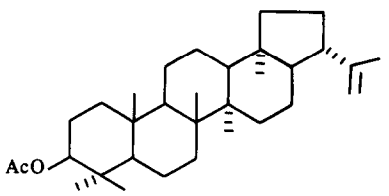

3

Table 1. ^{13}C NMR chemical shifts (δ) compound 1

C No.	Cycloartanyl acetate	1
1	31.5	31.6 (*t*)
2	26.7	26.8 (*t*)
3	80.3	80.7 (*d*)
4	39.4	39.5 (*s*)
5	47.0	47.2 (*d*)
6	20.8	20.9 (*t*)
7	28.0	28.0 (*t*)
8	47.6	47.8 (*t*)
9	20.1	20.1 (*s*)
10	26.0	26.0 (*s*)
11	25.8	25.8 (*t*)
12	35.4	35.5 (*t*)
13	45.1	45.3 (*s*)
14	48.6	48.8 (*s*)
15	32.8	32.8 (*t*)
16	26.5	26.5 (*t*)
17	52.2	52.1 (*d*)
18	17.9*	18.0† (*q*)
19	29.6	29.8 (*t*)
20	36.0	35.8 (*d*)
21	18.3*	18.2† (*q*)
22	36.4	31.6 (*t*)
23	24.1	29.2 (29.4) (*t*)
24	37.4	78.1 (77.3) (*d*)
25	28.0	143.1 (143.4) (*s*)
26	22.5	113.2 (112.5) (*t*)
27	22.7	*ca* 18
28	19.2*	19.3† (*q*)
29	25.3	25.4 (*q*)
30	15.1	15.1 (*q*)
OCOMe	170.0	171.0, 170.4 (*s*)
OCOMe	21.2	21.3, 21.3 (*q*)

*,†Assignments with the same sign may be interchanged.

fragmentation suggested [2–4] the presence of one acetoxyl at C-3 (*m/z* 397 and 337) and the second acetoxyl in the side chain (*m/z* 344 and 175). The lowfield shift (δ5.1) of the side chain secondary acetoxyl proton suggested that it was allylic. This can be rationalized by placing the acetoxyl at C-24 in a cycloart-25-ene system. Thus, compound **1** was assigned the structure of cycloart-25-ene-3β,24-diol diacetate.

The ^{13}C NMR spectrum (Table 1) of compound **1** (deuterochloroform) showed doubling of certain resonances. Analysis by GC indicated the presence of two compounds with R_ts 10.87 and 11.02 min. Comparison of the ^{13}C NMR shifts with those of cycloartanyl acetate [5] revealed doubling of the resonances of C-24 and its adjacent carbons C-23, C-25 and C-26. The doubling of the signals for these four carbons is consistent with the presence of a mixture of C-24 epimers in compound **1**. The signal for the Me-27 of compound **1** was not resolved. It should be doubled and one of the components can be seen as a shoulder on the methyl resonance at δ18.0. This is a reasonable shift for the Me-27 which could be shifted upfield by γ-interaction with the O-24 substituent.

One of the 24-epimers of cycloart-25-ene-3β,24-diol has been reported to occur naturally [6–8] and this on oxidation [6] gave cycloart-25-ene-3,24-dione, mp 126–130°. Oxidation of the diol mp 150°, $[\alpha]_D^{30}$ +42° obtained from compound **1** gave the same diketone, mp 128–130° whose IR spectrum showed two carbonyl absorptions at 1705 and 1680 cm^{-1}.

Compound **2** mp 222–225°, $[\alpha]_D$ +25° was identified as betulin diacetate by direct comparison with an authentic sample.

EXPERIMENTAL

Mps are uncorr. Chromatography: silica gel (100–200 mesh). The extraction procedure was described in ref. [1]. Elution of the column with *n*-hexane–C_6H_6 (1:1) afforded a mixture of triterpenoids [1] which, on acetylation and fractional crystallization, furnished colourless needles, mp 260–262° This solid, upon

repeated crystallization, gave colourless needles, mp 282–285°, $[\alpha]_D$ +22°, identified as mortenyl acetate (3) by comparison of the spectral data [9]. Further elution of the column with C_6H_6 gave a gummy material, which, on acetylation (Ac_2O–C_5H_5N, room temp, 24 hr) and repeated CC, afforded compounds 1 and 2

24-Epimeric cycloart-25-ene-3β,24-diol diacetate (1). Compound 1 crystallized from $CHCl_3$–MeOH as long needles: mp 122°, $[\alpha]_D^{30}$ +28° ($CHCl_3$; *c* 0.8); ^{1}H NMR (100 MHz, $CDCl_3$): δ0.3, 0.55 (AB*q*, *J* = 4 Hz, 2 × H-19), 2.0 (2 × OAc), 4.5 (*dd*, *J* = 10, 5 Hz, H-3α), 4.95, 4.9 (*br s*, CH_2), 5.1 (*t*, *J* = 6 Hz, H-24). MS *m/z* (rel. int.): 526 $[M]^+$ (7), 511 (3), 480 (7), 466 (100), 451 (50), 423 (35), 406 (25), 397 (3), 391 (1), 357 (17), 354 (25), 344 (30), 337 (20), 297 (55), 287 (32), 269 (32), 255 (25), 251 (17), 203 (37), 187 (25), 178 (42), 175 (42)

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REFERENCES

1 Anjaneyulu, V., Sambasiva Rao, G. and Prasad, K. H. (1983) *Indian J. Pharm. Sci.* **44**, 91.
2. Audier, H. E., Beugelmans, R. and Das, B. C. (1966) *Tetrahedron Letters* 4341.
3. Aplin, R. and Harnby, G. M. (1966) *J. Chem. Soc.* 1078.
4. Wyllie, S. G. and Djerassi, C. (1968) *J. Org. Chem.* **33**, 305.
5 Khuong-Huu, F., Sangare, M., Chari, V. M., Bekaert, A., Devys, M., Barbier, M. and Lukacs, G. (1975) *Tetrahedron Letters* 1789.
6. Djerassi, C. and McCrindle, R. (1962) *J. Chem. Soc.* 4034.
7 Kikuchi, T., Toyoda, T., Arimoto, M., Takayama, M. and Yamano, M. (1969) *Yakugaku Zasshi* **89**, 1358.
8 Altman, L J and Zito, S. W. (1976) *Phytochemistry* **15**, 829.
9. Galbraith, M. N., Miller, C. J., Rawson, J. W. L., Ritchie, E., Shaunon, J. S and Taylor, W. C. (1965) *Aust. J. Chem* **18**, 266.

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NEOLIGNANS FROM *VIROLA ELONGATA*

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Key Word Index—*Virola elongata*; Myristicaceae; neolignans, 4-hydroxy-2,3-dimethyl-6,7-dimethoxy-4-piperonyl-1-tetralone, 4-hydroxy-2,3-dimethyl-5,6-methylenedioxy-4-piperonyl-1-tetralone; 1-(3,4-dimethoxyphenyl)-2,3-dimethyl-4-piperonylbutan-1-one.

Abstract—The bark of *Virola elongata* contains the new 8.8′-neolignan, 1-(3,4-dimethoxyphenyl)-2,3-dimethyl-4-piperonylbutan-1-one besides the known 8.8′, 2.7′-neolignans, 4-hydroxy-2,3-dimethyl-6,7-dimethoxy-4-piperonyl-1-tetralone and 4-hydroxy-2,3-dimethyl-5,6-methylenedioxy-4-piperonyl-1-tetralone.

Continuing our studies of Colombian Myristicaceae [1], we have identified two 8.8′,2.7′-neolignans [2]‡ [(1) and (2)] and a new 8.8′-neolignan (3) in the benzene extract of the bark of *Virola elongata* (Benth.) Warburg. This is a plant native to the Colombian Amazonic region and its use by Amazonian Indians as a constituent of hallucinogenic snuff has been reported [3]. Previous studies of the wood of *V. elongata* by Gottlieb and his coworkers [4] demonstrated the presence of virolanol A, virolanol B, virolanol C and (−)-fisetinidol.

The structures of compounds 1 and 2 were deduced from their spectroscopic data (see Experimental). Both compounds have been reported [5] as constituents of the fruits of *V. sebifera*, and comparison with the published data showed agreement, with one exception. Whereas our mp for 1 agrees with that published [5], the value we found for neolignan (2) [mp 86–87°] is different from that reported (mp 115–117°) [5]. This is possibly due to different crystalline forms being obtained from different solvents (acetone in our work, methanol in ref. [5]).

The structure of 3, without regard to stereochemistry, followed from analysis of its NMR spectra and electron impact mass spectrum. The ^{1}H NMR spectrum showed doublets at δ0.85 (*J* = 7 Hz) and 1.15 (*J* = 7 Hz) assigned to C-methyl groups (H-9′ and H-9, respectively). Methoxy resonances were observed at δ3.90 and 3.95, and the methylenedioxy group gave a singlet at δ5.94. The protons H-8 and H-8′ resonated at δ3.38 (*dq*, *J* = 7 and 7 Hz) and 2.25 (*dddq*, all *J* ≈ 7 Hz). The diastereotopic protons at C-7′ gave signals (*dd*) at δ2.43 (J_{gem} 14.4 Hz, J_{vic} 7.8 Hz) and

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‡The system of nomenclature devised by Gottlieb [2] is used in the discussion of NMR spectral assignments.