

**Compound II.** Golden-yellow needles (*n*-hexane), m.p. 137–139°,  $C_{16}H_{18}O_3$ ,  $\lambda_{\max}^{EtOH}$  (log  $\epsilon$ ): 223 (4.12), 239sh (3.94), 243sh (4.05), 249 (4.21), 255 (4.35), 261 (4.41) 419 (2.99) nm;  $\lambda_{\max}^{EtOH-NaOH}$  (log  $\epsilon$ ) 233 (4.16) 243 (4.10), 249 (4.21), 254.5 (4.34), 260.5 (4.39), 327 (5.94), 470 (3.36) nm;  $\nu_{\max}$  (KBr) 3230 (OH), 2800, 2700, 1660 (CHO), 1610, 1585, 1525, 1455 (arom. ring), 1355, 1375 ( $CH(CH_3)_2$ )  $cm^{-1}$ ; NMR: similar to that of compound I, but the signal of AB quartet centered at  $\delta$  7.29 of compound I shifted to  $\delta$  7.27 (1H, s) and a new singlet appeared at  $\delta$  3.95 (3H, Ar- $CH_3$ ). **3,5-Dinitrobenzoate:** pale brown crystals, m.p. 214–216°. From the data presented above the compound II appeared to be 3-methoxy-7-hydroxycadalenal which was confirmed by comparison with an authentic sample (TLC, IR, and m.m.p.).

**Compound III.** Orange-red needles, m.p. 138–139°,  $C_{15}H_{16}O_2$  ( $M^+$   $m/e$  228);  $\nu_{\max}$  (KBr) 1660, 1648 (*o*-quinone CO)  $cm^{-1}$ , absence of OH;  $\lambda_{\max}^{MeOH}$  (log  $\epsilon$ ) 210 (3.68), 259 (3.78) nm; NMR:  $\delta$  2.63 (3H, s, Me in peri position), 2.10 (3H, s, Me on double bond), 1.35 (6H, d,  $J = 7$  Hz) and 3.33 (1H, m,  $J = 7$  Hz) indicated  $CH(CH_3)_2$  on arom. ring, centered at  $\delta$  7.35 (ABq,  $J = 9$  Hz, two arom. H), 7.70 (1H, s, olefinic H); MS:  $m/e$  230 ( $M + 2$ , 2.2%), 229 ( $M + 1$ , 1.1), 228 ( $M^+$ , 1.4), 200 ( $M-CO$ , 74.8), 185 (200-Me, 100), 157 (185-CO, 11.6), 142 (185- $C_3H_7$ , 33.3), 115 (157- $C_3H_6$ , 17.2). This feature of the spectrum, the relative intensities of  $M + 1$  and  $M + 2$  peaks were 1.1 and 2.2 respectively, bigger than the calculated values and the  $M + 2$  peak (2.2) was bigger than the  $M^+$  peak (1.4), suggested the presence of *o*-quinone. Further, treatment with *o*-phenyldiamine a quinoxaline derivative, yellow needles, m.p. 105–106°, was obtained which also indicated the presence of *o*-quinone structure. From the above data, it is clear that the compound III must be mansonone C which was confirmed by comparison with an authentic sample (TLC, IR, and m.m.p.).

**Compound IV.** Colourless plates, m.p. 138–140°, identical (TLC and IR) with authentic sitosterol; the monoacetate: m.p. 120°.

**Compound V.** Orange needles, m.p. 218–219° (benzene),  $C_{15}H_{16}O_3$  ( $M^+$   $m/e$  244);  $\nu_{\max}$  (KBr) 3280 (OH), 1658, 1645 (*o*-quinone CO)  $cm^{-1}$ ;  $\lambda_{\max}^{MeOH}$  (log  $\epsilon$ ) 221 (4.34), 239 (4.16), 275 (4.27), 410 (3.93) nm;  $\lambda_{\max}^{MeOH-NaOH}$  (log  $\epsilon$ ) 232 (4.36), 304 (4.09), 435 (3.63) nm; NMR spectrum was very similar to that of compound III, but the signal of  $\delta$  7.35 (AB q,  $J = 9$  Hz) displaced to 6.72 (1H, s) indicated this compound to be a *o*-quinone with OH group;  $m/e$  246 ( $M + 2$ , 1.9%), 245 ( $M + 1$ , 1.5), 244 ( $M^+$ , 4.2), 229 ( $M-Me$ , 7.3), 216 ( $M-CO$ , 52.9), 201 (216-Me, 100), 173 (201-CO, 5.9), 158 (173-Me, 7.4), 115 (158- $C_3H_7$ , 10.1). Treatment with *o*-phenyldiamine afforded a quinoxaline derivative, yellow needles, m.p. 197° (soften), 218–219°.

**The monoacetate.** Red crystals, m.p. 95–97°, NMR spectrum showed the protons of the acetoxyl group as a singlet at  $\delta$  2.40 (3H).

The above feature of the spectrum suggested that the compound V must be mansonone G which was confirmed by comparison with an authentic sample (TLC, IR, and m.m.p.).

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**Key Word Index**—*Ulmus parvifolia*; Ulmaceae; sesquiterpenes; cadalenals; mansonones; sitosterol.

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## MONOCOTYLEDONAE

### AMARYLLIDACEAE

#### STEROIDAL SAPOGENINS FROM *AGAVE COCUI*

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**Plant.** *Agave cocui*. **Source.** Between Ejido-Las González. Edo. Mérida. Venezuela.

*Uses.* Fabrication of drinks and fibers. *Previous work.* One unidentified saponine isolated.<sup>1</sup>

*Present work.* The fresh plants were cut and the expressed juice (15 l.) boiled with HCl (3 N) for 4 hr and then allowed to stand at room temp. overnight. A powdery precipitate formed which was filtered off, dried and continuously extracted with benzene. Evaporation of the solvent afforded a brown mass which was chromatographed on a column of silica gel. Elution with benzene yielded intractable resins while subsequent elution with benzene-EtOAc (98:2) gave a white solid (1.5 g yielded 0.075%). Recrystallization several times from EtOH (95%) gave fine needles which were shown (IR, NMR) to be identical with tigogenin m.p. 207–208°,  $[\alpha]_D^{20} - 48^\circ$  (C = 1.53%, CHCl<sub>3</sub>), acetate m.p. 203–204°,  $[\alpha]_D^{20} - 80^\circ$  (C = 1.72%, CHCl<sub>3</sub>).

Further elution with benzene-EtOAc (95:5) afforded a second white solid (0.6 g yielded 0.03%) m.p. 265–267°,  $[\alpha]_D^{20} + 7^\circ$  (C = 1.64%, CHCl<sub>3</sub>), acetate m.p. 203–204°,  $[\alpha]_D^{20} - 3.2^\circ$  (C = 1.5%, CHCl<sub>3</sub>), 2,4-dinitrophenylhydrazone m.p. 247–248°. Comparison of these properties with those reported for hecogenin<sup>2</sup> suggested identity which was confirmed by comparison (m. m.p., IR, NMR) with an authentic sample.

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<sup>1</sup> F. PÉREZ BARRÉ, *Rev. Fac. Farm. Universidad de Los Andes* 7, 68 (1964).

<sup>2</sup> R. FERNÁNDEZ DÍAZ, R. FREIRE BARRERA and A. GONZÁLEZ GONZÁLEZ, *An. R. Soc. Españ. Fis. y Quím.* 53B, 927 (1967).

*Key Word Index*—*Agave cacui*; Amaryllidaceae; sapogenins; tigogenin; hecogenin.

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## GRAMINEAE

### FATTY ACIDS FROM CERTAIN ANDROPOGONEAE

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Caryopsis from the taxa described in Table 1 were found to contain varying amounts of palmitic, stearic, oleic, linoleic and linolenic acids. Separation of methyl esters of these acids was achieved by GLC. Identifications were based upon comparisons to known samples. All percentages were based on data from a Varian Aerograph electronic integrator.

Hilditch and Williams<sup>1</sup> list other grass taxa that have been investigated for fatty acids. The data presented here contrasts wild, weed, and crop forms of *Coix*, *Sorghum*, *Tripsacum* and *Zea*.

<sup>1</sup> T. P. HILDITCH and P. N. WILLIAMS, *The Chemical Constitution of Natural Fats*, Wiley, New York (1964).