

and linoleic acid. These were characterized in the same manner as described above. *n-Alkanes*: GLC indicated the alkanes to be composed of almost equal amounts of *n*-C<sub>16</sub>H<sub>34</sub> to *n*-C<sub>31</sub>H<sub>64</sub>. *Phytol*: C<sub>20</sub>H<sub>40</sub>O,  $n_D^{25}$  1.4637,  $[\alpha]_D^{25} + 0.98^\circ$  (c 1.708, CHCl<sub>3</sub>), *m/e* 296 (M<sup>+</sup>), 71 (base),  $v_{max}$ (liquid) 3300 (O-H), 1670 (C=C) 790 cm<sup>-1</sup> (>C=CH-),  $\delta_{ppm}$  1.65 (s, 3H, >C-CH<sub>3</sub>-), 4.12 (d, J 7Hz, 2H, =CH-CH<sub>2</sub>-O-), 5.38 (t, J 7Hz, 1H, -CH-CH<sub>2</sub>-O-), direct comparison (co-TLC, IR, NMR and MS) with a known sample *Stigmasteryl* C<sub>26</sub>H<sub>48</sub>O, mp 168.8-170°,  $[\alpha]_D^{25} - 52.9^\circ$  (c 0.846, CHCl<sub>3</sub>), *m/e* 412 (M<sup>+</sup>), 55 (base),  $v_{max}$  (KBr) 3350 (O-H), 1640 (C=C), 970 (trans, -CH=CH-), 840 cm<sup>-1</sup> (>C=CH-),  $\delta_{ppm}$  5.09 (t, J 3Hz, 2H), 5.37 (broad s, 1H), direct comparison (m.m.p., co-TLC, IR, NMR and MS). *Fatty acids*: The acidic fraction (0.28 g) was methylated with CH<sub>2</sub>N<sub>2</sub>. The methylated acids were then subjected to co-GLC with authentic samples. The acidic fraction was thus found to be composed of palmitic acid (33.2%), stearic acid (18.6%), linoleic acid (13.6%), linolenic acid (20.4%) and other acids (14.2%).

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## TWO PENTAMETHOXYLATED FLAVONOIDS FROM *GYMNOSPERMA GLUTINOSUM*

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**Key Word Index**—*Gymnosperma glutinosum*, Compositae, essential oil, phellandrene, camphene  $\alpha$ -pinene, 5,7-dihydroxy-6,8,3',4',5'-pentamethoxyflavone (luiselzondin), 5-hydroxy-3,6,7,8,3'-pentamethoxyflavone, emmaosunin.

*Plant*: *Gymnosperma glutinosum* (Spreng) (Syn. *Selloa glutinosum*, (Spreng)) Tatalencho, xonoquilitl (Voucher specimen No. 7268). Collected in San Luis Potosí in February 1972. Is a monotypic genus. *Uses*: The flower heads as a cure of rheumatic illness.<sup>1</sup>

*Previous work*: None.

*Steam distillation*: The semidried aerial part was steam distilled, a colorless, odiferous oil was obtained (yield 0.7%), sp. gr. 0.92,  $n_D^{25}$  1.4725,  $[\alpha]_D^{25} + 17^\circ$ . IR and NMR did not show aromatic or carbonyl compounds. TLC and VPC showed phellandrene, camphene and  $\alpha$ -pinene as main components.

*Extraction*: The pulverized dried aerial part was extracted with EtOH, the extract was evaporated and the residue was taken in CHCl<sub>3</sub>. This solution was chromatographed on silica gel. On elution with CHCl<sub>3</sub>-MeOH, two new flavonoids were successively percolated. *Luiselzondin*, as yellow crystals, mp 178-179°, C<sub>20</sub>H<sub>20</sub>O<sub>9</sub>. Zeisel number gave 5CH<sub>3</sub>O. IR, 1650, 1620, 1585 and 1518 cm<sup>-1</sup>. NMR singlet at 7.4 $\delta$  (2H), another at 6.2 (s, 1H), four singlets at 4.12 (3H), 4.08 (3H), 4.0 (6H) and 3.9 (3H), corresponding at five CH<sub>3</sub>O groups, at down field 400 Hz there was a signal (1H). The UV in MeOH gave a spectrum typical of a flavone.<sup>2</sup> The addition of AlCl<sub>3</sub>, AlCl<sub>3</sub>-HCl and NaOAc-H<sub>3</sub>BO<sub>3</sub> gave the expected displacements for a 5-hydroxyflavone. The MS gave a molecular ion at *m/e* 404 (C<sub>20</sub>H<sub>20</sub>O<sub>9</sub>). The fragmentation pattern was as expected for a 5,7-dihydroxy-6,8,3',4',5'-pentamethoxyflavone,<sup>3</sup> a microfusion with KOH gave the expected 3,4,5-trimethoxyben-

<sup>1</sup> MARTÍNEZ, M. (1959). *Las Plantas Medicinales de México* 4a. Ed. Botas, México, p. 299.

<sup>2</sup> MABRY, T. J., MARKHAM, K. R. and THOMAS, M. B. (1970). *The Systematic Identification of Flavonoids*. Springer, New York.

<sup>3</sup> AL-DIER, H. (1966). *Bull. Soc. Chim. Et.* 2893.

zoic acid. The gossipetone test for *p*-dihydroxyflavonoid and the ammonium vanadate test<sup>4</sup> for an *o*-dihydroxyflavone were negative, confirming the assigned structure to luiselizonidine *Emmaosunin*, as yellow crystals, m.p. 150–152°.  $C_{20}H_{20}O_8$ , Zeisel number gave 5  $CH_3O$ . IR, 1650, 1610, 1570, 1500, 1040, 998  $cm^{-1}$ . The NMR and UV spectra were typical of a 3-methoxy-5-hydroxyflavone.<sup>3</sup> And the addition of  $AlCl_3$ ,  $AlCl_3-HCl$  or  $NaOAc-H_3BO_3$  gave the expected shifts in the UV. The NMR exhibited a multiplet centered at  $7.5\delta$  (4H) for singlets at 4.10 (CH), 4.00 (3H), 3.95 (3H) and 3.90 (6H) at down field a multiplet was observed corresponding to the 5-OH proton. The MS gave a molecular ion at  $m/e$  384 and the fragmentation pattern of a 3-methoxyflavone. Wilson and  $FeCl_3$  tests were positive. On fusion of emmaosunine with KOH, 3-methoxy-benzoic acid was detected by TLC and PC comparison, confirming the structure as 5-hydroxy-3,6,7,8,3'-pentamethoxyflavone.

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<sup>4</sup> VENKATARAMAN, K. (1962) In *The Chemistry of flavonoid Compounds* (GEISSMAN, T. A., ed.), p. 75, Macmillan, New York.

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## IDENTIFICATION DU L-(+)-BORNESITOL DANS LE GENRE *GENTIANA*\*

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**Key Word Index**—*Gentiana* sp., Gentianaceae, cyclitols, L-(+)-bornésitol, chemotaxonomy.

Dans une précédente communication,<sup>1</sup> nous avons décrit l'identification du L-(+)-bornésitol dans les feuilles de *Gentiana lutea* L. Dans le cadre de nos études phytochimiques du genre *Gentiana*, nous avons isolé ce cyclitol peu répandu dans la nature à partir des autres espèces de gentianes géantes, formant avec *G. lutea* L. la section Coelanthé.<sup>2</sup>

*Plantes et provenance*, *G. purpurea* L., Valais, Suisse; *G. punctata* L., Grisons, Suisse; *G. pannonica* Scop., Churfirsten, Suisse; *G. villarsii* Ronn., Dpt Hautes-Alpes, France; *G. burseri* Lapeyr., Dpt Pyrénées orientales, France. La poudre de feuilles séchées est extraite à chaud, successivement par la ligroïne,  $Et_2O$ ,  $EtOAc$  et  $MeOH$ . L'extrait méthanolique est adsorbé sur une colonne de polyamide; l'élution est effectuée avec  $MeOH$  à 90% et les fractions analysées par CCM; les fractions de tête sont riches en L-(+)-bornésitol, les autres sont utilisées pour la recherche des glycosides flavoniques.<sup>3</sup> Après traitement par

\* Partie IV de la série "Contribution à la phytochimie du genre *Gentiana*".

<sup>1</sup> BELLMANN, G. et JACOT-GUILLARMOD, A. (1973) *Helv.* **56**, 773.

<sup>2</sup> SCHARFETTER, R. (1953) *Biographien von Pflanzensippen*, pp. 315–331, Springer, Wien.

<sup>3</sup> HOSTETTMANN, K. et JACOT-GUILLARMOD, A. (1974) *Phytochemistry*, en préparation.