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SHORT COMMUNICATION

THE XANTHONES OF A *HALENIA* SPECIES[1]

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Abstract—Extracts of a Colombian species of *Halenia* (Gentianaceae) yielded three xanthones, 1-hydroxy-2,3,4,7-tetramethoxy-, 1-hydroxy-2,3,4,5-tetramethoxy-, and 1-hydroxy-2,3,5-tetramethoxyxanthone, which have also been found to be the major xanthones of *Frasera caroliniensis*

AS PART of our study of the xanthonic constituents of the various genera of the Gentianaceae, we have examined a species of *Halenia*, collected in flower on the Páramo de Guasca, near Bogotá, Colombia. This material has been tentatively identified as *H. asclepidea* (HBK) G. Don., but in view of the several very similar species described from this area,[2] the taxonomy is not entirely secure.

The entire plants were air-dried, ground, and extracted with hexane. Extraction of the hexane with Claisen's alkali removed the phenolic components and left behind a purely aliphatic (NMR) residue. The basic extract yielded, by preparative TLC, two major and one minor yellow crystalline compounds, all showing u.v. spectra characteristic of xanthones.

The least polar of the three products, m.p. 118·3–119·3°, was present in very small amounts (0·27% of the base-soluble material), but was identical in its u.v., NMR, and mass spectrum with 1-hydroxy-2,3,4,7-tetramethoxyxanthone (I), a compound previously obtained from the roots of *Frasera caroliniensis* Walt. (Gentianaceae).[3] The identification was confirmed by a mixed m.p. with an authentic sample.

The second product, m.p. 154–156°, 17% of the alkali soluble fraction, was identified by u.v., NMR, mass spectra, and mixed m.p. with 1-hydroxy-2,3,4,5-tetramethoxyxanthone (II).[3] The most polar, m.p. 191–193°, 9% of the alkali extract, was similarly shown to be 1-hydroxy-2,3,5-trimethoxyxanthone (III).[3] Both II and III are among the major xanthonic constituents of *F. caroliniensis*[3] as well as other *Frasera* species.[4]

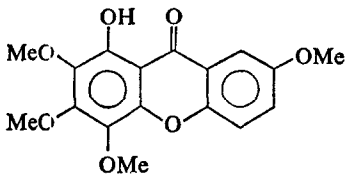
Further extraction of the ground plants with acetone–CH_2Cl_2 yielded considerable amounts of dark-green viscous gum. Hydrolysis with dilute HCl afforded a yellow precipitate which proved by TLC to be a mixture of the same three xanthones, indicating that the bulk of this material occurs in the plant as glycosides.

[1] Paper V in the series *Xanthones of the Gentianaceae*. G. H. STOUT, B. J. REID and G. D. BRECK, *Phytochem.* **8**, 2417 (1969).

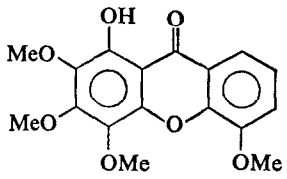
[2] C. K. ALLEN, *Ann. Mo. Bot. Gard.* **20**, 119 (1933); also annotated specimens in the Herbarium of the Instituto de Ciencias Naturales, Bogotá.

[3] G. H. STOUT and W. J. BALKENHOL, *Tetrahedron* **25**, 1947 (1969).

[4] G. H. STOUT, E. N. CHRISTENSEN, W. J. BALKENHOL and K. L. STEVENS, *Tetrahedron* **25**, 1961 (1969).



(I)



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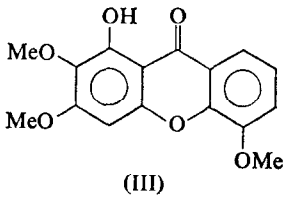

(III)

The close agreement between the xanthones of this *Halenia* and those of the various *Frasera* species we have studied is striking, especially since both genera were initially identified with *Swertia*.[2, 5] Although *Swertia* has been regarded as the nearest genus to *Halenia*,[2] our results suggest a closer phytochemical relationship between *Halenia* and *Frasera* than between either and *Swertia*, since the latter produces xanthones of quite different substitution pattern.[3] Clearly, further studies are required, however, and should be combined with additional morphological and cytological investigations.

EXPERIMENTAL

Whole plants, including roots, of *Halenia asclepidea* (HBK) Don (?) were collected in flower in January 1968 on the Páramo de Guasca, Cundinamarca, Colombia. Voucher specimens have been deposited as *Garcia-Barriga* 18839 at the herbarium of the Instituto de Ciencias Naturales, Bogotá, and in the Oaks Ames Herbarium of Useful Plants, Harvard.

Isolation

Air-dried plants (422 g) were ground and extracted in a Soxhlet with hexane. After removal of hexane, the residue, 15·5 g, was dissolved in CH_2Cl_2 (100 ml), filtered, and extracted with Claisen's alkali (4 × 75 ml). The extracts were diluted with H_2O, acidified, and extracted with CH_2Cl_2 which was dried ($MgSO_4$) and evaporated to leave 2·55 g of yellow solid residue. Preparative TLC of 0·222 g base soluble material using continuous elution on Merck silica gel HF_{254} with petroleum ether:EtOAc (8:1) gave three u.v.-absorbing yellow bands, which were collected and purified separately.

The least polar band was rechromatographed in the same manner, sublimed at 100°, 10^{-4} Torr, and recrystallized from MeOH to give 0·6 mg (0·27%) of I in the form of bright yellow needles, m.p. 118·3–119·3°; mixed m.p. with authentic I, 119–120°. The intermediate yellow band was collected from the silica gel and recrystallized from methanol, giving 38·1 mg (17·1%) of II, m.p. 154–156°; mixed m.p. with authentic II, 154–156·5°. The most polar yellow band, after recrystallization from methanol, yielded 20·3 mg (9·1%) of pale yellow needles, m.p. 191–193°, mixed m.p. with authentic III, 190–191°.

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[5] C. LINNAEUS, *Amoen. Acad.* **2**, 344 (1751).