

# A NEW AGERATONE DERIVATIVE FROM *ISOCARPHA OPPOSITIFOLIA*

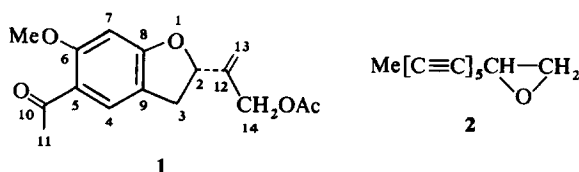
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(Received 31 January 1977)

**Key Word Index**—*Isocarpha oppositifolia*; Compositae; dihydroageratone-O-methyl ether.

The taxonomic position of the genus *Isocarpha* is unsettled. Normally it is placed in the tribe Heliantheae, subtribe Galinsoginae. Though only small amounts of plant material were available, the isolation of a new ageratone derivative supports a position for this genus in the tribe Eupatorieae. The roots as well as the aereal parts of *I. oppositifolia* (L.) R.Br. contain the acetate 1, identified by its NMR spectrum (see Table 1). The root also contain very small amounts of a pentayne, most probably 2 [1].



Benzofuran derivatives of type 1 are very widespread in members of the tribe Eupatorieae. Up to now they have been isolated from species of *Ageratina* [2], *Ayapana* [3], *Ageratum* [4], *Brickellia* [5], *Radlkoferotoma* [6], *Condylis* [7], *Cronquistiandium* [8], *Eupatorium* [9], *Heterocondylus* [7], *Liatris* [10] and *Praxelis* [11]. Together with other compounds, they are also found in other tribes, though not in the subtribe Galinsoginae, where *Isocarpha* is placed by Stuessy [12]. *Isocarthusia* has no close relatives in the Heliantheae, although it has some in the Eupatorieae. Thus, there is one species of *Ayapana*, which has the same form of style appendage as *Isocarpha*. *Ayapana* is, in turn, related by carpopodium structure and the usually capillary pappus to other members of the Eupatorieae with larger style branches. The anthers of *Isocarpha* are entirely Eupatorian. The cells of the anther collar have prominent annular thickenings, the exothecial cells have nodular thickenings on both transverse and vertical walls, the anther appendages are flat with only two layers of cells, and the pollen is only 18–20  $\mu\text{m}$  in diameter, all these features being common in the Eupatorieae but unknown in the Heliantheae [13]. The style bases of some species of *Isocarpha* are papillose to hirsute, a feature almost completely restricted to the Eupatorieae though recently seen in a species of *Arnica* in the Heliantheae [13]. Perhaps, further chemical investigations will further clarify these relationships.

Table 1.  $^1\text{H-NMR}$ -data of 1 ( $\delta$ -values, 270 MHz,  $\text{CDCl}_3$ , TMS as internal standard)

2-H	<i>dd</i> ( <i>br</i> ) 5.37	13-H	<i>s</i> ( <i>br</i> ) 5.33
3-H	<i>dd</i> ( <i>br</i> ) 3.37	13'-H	<i>s</i> ( <i>br</i> ) 5.27
3'-H	<i>dd</i> ( <i>br</i> ) 3.09	14-H	<i>ABq</i> 4.68
4-H	<i>s</i> ( <i>br</i> ) 7.70	OAc	<i>s</i> 2.05
7-H	<i>s</i> 6.43	OMe	<i>s</i> 3.89
11-H	<i>s</i> 2.57		

$J(\text{Hz})$ : 2, 3 = 9; 2, 3' = 7.5; 3, 3' = 15.

## EXPERIMENTAL

$^1\text{H-NMR}$ : Bruker WH270; IR: in  $\text{CCl}_4$ . The air dried plant material (collected in Mexico, voucher RMK 6859) was extracted with  $\text{Et}_2\text{O}$  and the resulting extracts separated by TLC (Si gel, GF 254). 3 g roots yielded 1 mg 1 (E–P 1:1) and traces of a pentayne (UV: 267, 253, 240 nm), polarity of 2 (TLC). 20 g aereal parts afford 1 mg 1.

*Dihydroageratone O-methyl ether* (1). Colourless oil, IR  $\nu_{\text{max}}$ : OAc 1745, 1230; PhCO 1668, 1615, 1590; OMe 2850, 1482, 1135  $\text{cm}^{-1}$ . MS:  $\text{M}^+$   $m/e$  290.115 (36% calc. for  $\text{C}_{16}\text{H}_{18}\text{O}_5$ , 290.115); –Me 275 (29); –AcOH 230 (30); 230 – Me 215 (34); 215 – (34); 215 – CO 187 (48);  $\text{MeCO}^+$  43 (100).

**Acknowledgment**—We thank the Deutschen Forschungsgemeinschaft for supporting this investigation.

## REFERENCES

- Bohlmann, F., Burkhardt, T. and Zdero, C. (1973) *Naturally Occurring Acetylenes*. Academic Press, London.
- Bohlmann, F., Jakupovic, J. and Lonitz, M. (1977) *Chem. Ber.* **110** in press.
- Bohlmann, F., Zdero, C. and Grenz, M. (1977) *Chem. Ber.* **110** in press.
- Anthonson, T. and Chanthazarakul, S. (1970) *Acta Chem. Scand.* **24**, 721.
- Bohlmann, F. and Zdero, C. (1976) *Chem. Ber.* **109**, 1436.
- Bohlmann, F. and Zdero, C. (1971) *Chem. Ber.* **107**, 964.
- Bohlmann, F. and Grenz, M. (1977) *Chem. Ber.* **110**, in press.
- Christensen, W. L. (1965) *Econ. Botany* **19**, 293.
- Nakaoki, T., Morita, N. and Nishino, S. (1958) *Yakugaku Zasshi* **78**, 557.
- Herz, W. and Wahlberg, I. (1973) *Phytochemistry* **12**, 429; Herz, W., Paplawski, J. and Sharma, R. (1975) *J. Org. Chem.* **40**, 199.
- Bormer, W. A. (1961) *Tetrahedron Letters* 417.
- Stuessy, T. F. (1977) in *Biology and Chemistry of Compositae*, (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds.) in press. Academic Press, London.
- King, R. M. and Robinson, H. (1975) *Annals of the Missouri Gardens* **62**, 888.