

Note on a Possible Dihydro-furofuran-(3,2-b) from *Chrysanthemum vulgare* Bernh.

ERLING GUDDAL*

Institutt for organisk kjemi, Norges tekniske høgskole, Trondheim, Norway

The recent appearance of a communication¹ concerning polyacetylenic compounds contained in the roots of *Chrysanthemum vulgare* Bernh. (= *Tanacetum vulgare* L.) prompts us to report preliminary data on a new compound isolated from the same plant some time ago², thereby extending our earlier reports on investigations in the same field³⁻⁵.

The compound was isolated as colourless crystals from acetone extracts of the roots of *Chrysanthemum vulgare* Bernh. upon chromatography and subsequent countercurrent distribution. From deactivated alumina it is eluted by benzene:light petroleum (1:5), together with a complex mixture of polyacetylenes, the properties of which have been extensively investigated by Bohlmann *et al.*¹ When this fraction is distributed between light petroleum and 90% aqueous alcohol over 50 cells in a Craig apparatus with a mobile upper phase, the compound is found in the cells Nos. 9-15, as

* Present address: Leo Pharmaceutical Products, Ballerup, Denmark.

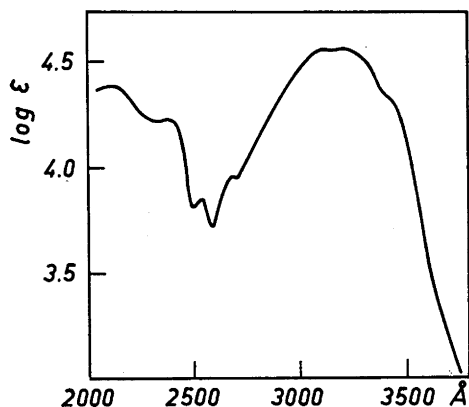


Fig. 1. Ultraviolet spectrum in hexane of compound from *Chrysanthemum vulgare* Bernh.

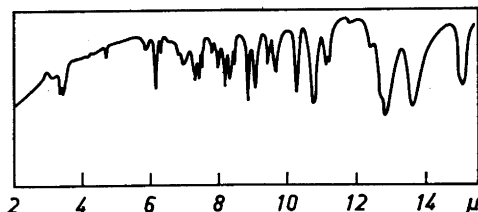


Fig. 2. Infrared spectrum in KBr of compound from *Chrysanthemum vulgare* Bernh.

indicated by the ultraviolet spectra. These fractions are combined, evaporated to dryness, and the residue dissolved in hexane. Upon cooling to -70°C , a complex mixture of polyacetylenes of the tri-yn-ene- and triyne-diene type is precipitated. The supernatant, upon concentration to a small volume and prolonged cooling to -10°C , deposits colourless crystals, which after two crystallisations from hexane melt at $64.5-66^{\circ}\text{C}$ in an evacuated capillary. When heated in air the m.p. is $80-84^{\circ}\text{C}$ (decomp). From 15 kg of fresh roots 32 mg of the new compound was obtained, the elementary analysis of which agrees with the formula $\text{C}_{14}\text{H}_{14}\text{O}_2$. The ultraviolet spectrum is shown in Fig. 1, and the infrared spectrum in Fig. 2. The spectrum contains no hydroxyl or carbonyl bands, but a band at 2138 cm^{-1} indicates the presence of a triple bond. The double bond-stretching band at 1637 cm^{-1} corresponds to a band reported to occur in vinyl ethers⁶⁻⁸. The two high-frequency bands in the C-H-stretching region — appearing at 3057 cm^{-1} and 3101 cm^{-1} — would indicate the presence of two different olefinic hydrogen atoms, one aliphatic and one in an unsaturated five-membered ring, respectively.

The infrared spectrum is very complex, but throughout the spectral region there is a strong resemblance to that of 2,2,5,5-tetramethyldihydrofurofuran (3,2-b), the remarkable isomerization product of 2,7-dimethyl-2,7-dihydroxy-octa-3,5-diyne described by Audier⁹. This compound absorbs at 2400 Å ($\epsilon = 6900$) and 3030 Å ($\epsilon = 14820$), while the main absorption band of the compound isolated from *Chrysanthemum vulgare* Bernh. occurs at 3225 Å ($\epsilon = 37500$). In this region, a red-shift of about 200 Å would be the normal effect of one double bond added to a poly-ene chromophore.

The isolated compound is optically active, $[\alpha]_{\text{D}}^{20} = -15.3^{\circ}$ (0.2%, CHCl_3). As all acetylenic compounds previously isolated from natural

Table 1.

| | Pine Wood Test ¹⁰ | Ehrlich's Test ¹⁰ | Vanillin-HCl Test ⁹ |
|--|---|------------------------------|--|
| Isolated cpd. Perhydro cpd. Octahydro cpd. | Light green No reaction Deep purple | Light yellow No reaction | Light orange No reaction Deep orange, turning brown on heating |

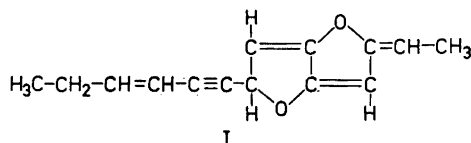
sources may be derived from straight-chain compounds, the presence of an asymmetric carbon atom suggests that one of the ether oxygens is bound to a saturated carbon atom bearing two alkyl groups and one hydrogen. When hydrogenated over a Pd/BaSO₄-catalyst, the compound absorbs six moles of hydrogen, giving an oil which is transparent in the ultraviolet down to 2 200 Å, and in the infrared shows two ether bands at 1 115 cm⁻¹ and 1 015 cm⁻¹. In addition to these two bands, the infrared spectrum shows only the normal CH, CH₂, and CH₃ absorption bands.

When hydrogenated over a deactivated Pd-catalyst ⁹, only four moles of hydrogen are absorbed. The octahydro-compound also shows un-specific absorption down to 2 200 Å, step-off beginning at 2 700 Å. Its infrared spectrum is quite complex, showing double-bond absorption and a strong band at 1 710 cm⁻¹, indicative of a saturated ketone. The formation of this grouping might be explained as the hydrogenolytic cleavage of a vinyl ether. This is in accordance with the formation of ketones upon catalytic hydrogenation of tetramethyldihydrofurofuran (3,2-b) ⁸. Lack of substance prevented the isolation of the two hydrogenation products in a pure state, but the hydrogenation data together with the elementary analysis of the isolated compound suggests the presence of two rings in the molecule. Since the presence or absence of a furanoic structure could not be unequivocally stated from spectral studies, some colour tests ^{9,10} were made. The results are presented in Table 1.

According to Reichstein ¹⁰, a purple colour in the Pine Wood Test suggests the presence of a furan nucleus with at least two substituents. The isolated compound does not react with H₃CMgI at room temperature, but upon 5 min interaction in boiling benzene, followed by hydrolysis and chromatography on deactivated alumina, a compound with absorption maxima at 2 900 Å, 2 730 Å, and 2 590 Å is eluted by 10 % alcohol in ether. Seen in relation to the ultraviolet spectrum of 5-phenyl-pent-2-ene-4-yne-1-ol ¹¹ — with absorption maxima at 2 890

Å, 2 720 Å, and 2 590 Å — this spectrum might well originate from the hitherto unknown chromophoric system furyl-yne-ene. Its infrared spectrum shows double bond and triple bond absorption, and indicates the presence of a saturated ketone group. With only one triple bond in the molecule, this must have a central position in the chromophoric system to produce acetylenic fine structure ¹².

Based on these data — especially the similarities between the IR-spectra of the new compound and 2,2,5,5-tetramethyl-dihydrofurofuran (3,2-b) ⁸ — the compound from *Chrysanthemum vulgare* Bernh. is supposed to be a dihydrofurofuran with an exocyclic double bond and an isolated ene-yne chromophore. With the assumption that one oxygen atom is bound to carbon atom three as in *n*-tetradeca-6-ene-8,10,12-tri-yne-3-one, a compound which occurs in the same plant, the tentative structure would be: 2(1-hex-1-yne-3-enyl)-5-ethylidene-dihydrofurofuran-(3,2-b) (I).



This work was carried out under the tenure of a research grant from *Norges tekniske høgskole*. Professor Dr. N. A. Sørensen is greatly acknowledged for his kind interest and helpful suggestions.

1. Bohlmann, F., Arndt, Chr. and Bornowski, H. *Chem. Ber.* **93** (1960) 1937.
2. Guddal, E. *Thesis, Norges tekniske høgskole*, May 1958.
3. Sørensen, J. S. and Sørensen, N. A. *Acta Chem. Scand.* **12** (1958) 771.
4. Guddal, E. and Sørensen, N. A. *Acta Chem. Scand.* **13** (1959) 1185.

5. Guddal, E. *Acta Chem. Scand.* **13** (1959) 834.
6. Bohlmann, F. and Viehe, H. G. *Chem. Ber.* **88** (1955) 1017.
7. Christensen, P. K. *Norge Tekniske Vitenskapsakademi, Serie 2 Nr. 7* (1959) 74. *Chem. Abstr.* **54** (1960) 6531.
8. Audier, L. *Ann. chim. (Paris)* **13** (1957) 105.
9. Quilico, A., Piozzi, F. and Pavan, M. *Tetrahedron* **1** (1957) 177.
10. Reichstein, A. *Helv. Chim. Acta* **15** (1932) 1110; **16** (1933) 28, 37.
11. Haynes, L. J., Heilbron, I., Jones, E. R. H. and Sondheimer, F. *J. Chem. Soc.* **1947** 1585.
12. Dale, J. *Acta Chem. Scand.* **11** (1957) 265.

Received February 21, 1961.

Studies Related to Naturally Occurring Acetylene Compounds

XXVIII. A Note on the Occurrence of Pontica Epoxide in the Genus *Achillea* L.

E. HEMMER, E. TUXEN BORLAUG and
NILS ANDREAS SÖRENSEN

Institut for Organisk Kjemi, Norges Tekniske Høgskole, Trondheim, Norway

In a recent paper Bohlmann, Arndt and Boronowski¹ have described the isolation of the polyacetylenic epoxide C₁₃H₁₀O (I) from four different *Artemisia* species. After the first isolation from *A. pontica* L. the substance has been named "pontica epoxide". Some 100 members of the tribus *Anthemideae* of the *Compositae* are stated to have been investigated. Outside the genus *Artemisia* pontica epoxide was iso-

lated only from three members of the genus *Chrysanthemum* (*viz. serotinum* L., *boreale* L. and *vulgare* Bernh.) and *Cladanthus arabicus* Cars.

A substance with the same properties as I had been isolated in our laboratory some years ago^{2,3} from some members of the genus *Achillea*, also a member of the tribus *Anthemideae*. The m.p. and U.V. maxima are given below together with those of pontica epoxide.

| | m.p. | | | | | |
|------------------------------------|-------------|-------|-------|-------|---------|--|
| Pontica epoxide | 66° | | | | | |
| <i>Achillea ptarmica</i> | 60–63° | | | | | |
| <i>A. atrata</i> * <i>clusiana</i> | 62–62.5° | | | | | |
| | U.V.-maxima | | | | | |
| 3 335 | 3 115 | 2 920 | 2 755 | 2 505 | (2 435) | |
| 3 335 | 3 112 | 2 928 | 2 756 | 2 510 | (2 415) | |
| 3 345 | 3 130 | 2 930 | 2 765 | 2 500 | 2 400 | |

The U.V. absorption curves are conform in height of all the 6 maxima and the 5 minima.

Bohlmann *et al.* have reported the infrared spectrum of pontica epoxide in carbon tetrachloride solution. Our measurements on the compound from the above mentioned *Achillea* species are in chloroform and in carbon disulfide. The small differences between the three spectra may be due to the effect of the solvents.

In five other *Achillea* species no I could be demonstrated. Besides some unknown polyacetylenes some members of this genus contained *cis*- and *trans*-dehydromatricaria-ester.

Details of our investigations will be presented in another contribution to this journal.

1. Bohlmann, F., Arndt, Chr. and Boronowski, H. *Chem. Ber.* **93** (1960) 1937.
2. Borlaug, E. Tuxen, *Graduation work*, N.T.H. 1953.
3. Hemmer, E. (née Vorvik), *Graduation work*, N.T.H. 1955.

Received February 9, 1961.

