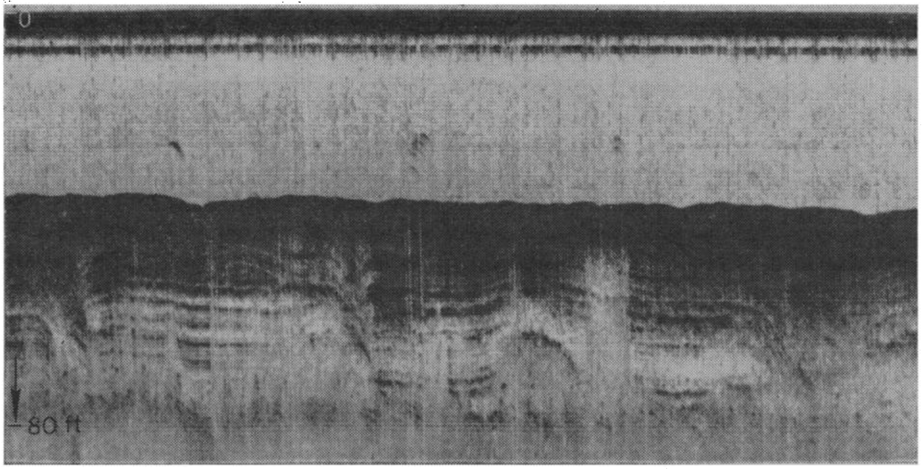


Fig. 4. Pinger record made just south of the Quonset Point Naval Air Station showing nonuniform distribution and peculiar slumping of the layers in the sub-bottom sediment.

min, was carried in the *R/V Billie* from the University of Rhode Island, Narragansett Marine Laboratory. Figure 1 shows tracings of successive east-west runs across an area south of Quonset Point Naval Air Station (Figs. 2 and 3).

The pinger probe is a 12-kc, short-pulse, high peak-power sonar (0.1 msec, 108 db) which has been adapted for bottom penetration in shallow water. It can detect sedimentary layers and objects in the sub-bottom. Its components consist of a sonar transdriver which contains a power supply, storage capacitors, and a two-stage preamplifier, a marking amplifier, a high-resolution recorder (Alden), and a submersible transducer (EG&G type 228 transducer with type 226 transformer). The sonar transducer is supported by the electrical driving cable from the side of the ship. No mounting on the hull is required. The ship is required to operate at a slow speed, about 5 km per hour.

Figure 1 is a north-south sequential compilation of east-west runs, each about 300 meters in length and spaced about 100 meters apart, with the northernmost record on top. The solid black band at the top of each strip is the recorded surface signal. The bottom profile and sub-bottom rock bedding is clearly shown beneath a water depth of about 6 meters. The irregular rocky surface is post-glacial land surface which has been largely covered by marine sediments. The sediment in this area probably is sandy silt (25 to 50 percent sand, 10 to 20 percent clay) (*3*).

Beginning at the top, or north end, a rock layer is shown, first submerged; then outcropping through the bottom sediment (strips 2 to 5); submerging again (strips 6 to 11); outcropping briefly again (strip 12); and finally disappearing beneath the bottom (strips 13 to 14). Some of the strips are printed in reverse, in order to correlate the east-west edges. A "second" bottom echo, due to the sound traversing the bottom to surface path a second time, is visible in several of the strips, for example, in the second, third, and fourth strips measured from the top. Scouring of sediment to a depth of about 0.3 meter from around the outcropping rocks is evident, which indicates that tidal flow or hurricane-induced flow has left its mark.

The horizontal alignment of the several sonar records of Fig. 1 is probably inaccurate. The main outcrop of rock may not be uniform in a north-south direction.

Another area, just south of the Quonset Point Naval Air Station (Fig. 4), shows sediments about 13 meters deep with nonuniform distribution and peculiar slumping of the layers. Similar profiles obtained on other runs across this area ruled out the possibility of electronic vagaries.

HAROLD E. EDGERTON
HAROLD PAYSON
JOHN YULES
*Massachusetts Institute of Technology, Cambridge*
WILLIAM DILLON
*University of Rhode Island, Kingston*

### References

1. H. E. Edgerton, *Electronics* **33**, 93 (24 June 1960).
2. ———, *J. Geophys. Res.* **68**, 2753 (1963).
3. R. L. McMaster, *J. Sediment Petrol.* **30**, 249 (1960).

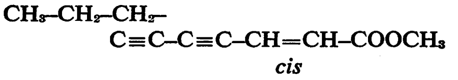
20 October 1964

---

# Acetylene Ester from Aster spinosus

Abstract. *A polyacetylene compound,* cis-*lachnophyllum ester, has been isolated from* Aster spinosus *Benth. The presence of this compound in this genus is of taxonomic interest.*

We have isolated an acetylene compound, *cis*-lachnophyllum ester (I) from an Arizona desert plant, *Aster spinosus* Benth.



$$CH_3\text{–}CH_2\text{–}CH_2\text{–}C{\equiv}C\text{–}C{\equiv}C\text{–}\underset{cis}{CH{=}CH}\text{–}COOCH_3$$

I

Although polyacetylenes have been isolated from numerous members of the *Compositae* (*1*), *cis*-lachnophyllum ester (I) has been previously isolated only from the genera *Lachnophyllum* (*2*) and *Erigeron* (*3*). This is the first report of its occurrence in the genus *Aster* and appears to have some chemotaxonomic significance; all acetylene esters previously isolated from *Aster* species have *trans* configurations (*1*).

A recent survey of desert plants (*4*) showed that species with steam-distillable terpene constituents lacked thorns and that thorny species commonly lacked terpenes or other oils. Subsequently we examined a spiny aster (*Aster spinosus* Benth.), which grows beside the San Pedro River in southern Arizona. Unexpectedly, steam distillation of the wet plant material yielded an oil which became a waxy solid at room temperature. An unexpected strong band in the 2200-$cm^{-1}$ region of the infrared spectrum of this compound indicated that it was not a terpene but an unusual acetylene compound. The acetylene, after separation from olefinic contaminants, was characterized as *cis*-lachnophyllum ester (I) by procedures outlined below.

Fresh samples of unground *A. spinosus* (1.0 kg) were steam-distilled, yielding 1.0 g of a yellow, waxy solid which melted at room temperature. Thin-layer chromatography of the solid on silica gel G with chloroform revealed seven compounds. The major constituent ($R_F$ 0.86) crystallized easily in the form of long white needles (mp 32.6° to 32.8°C) from light petroleum. It was positive in permanganate, tetranitromethane, and hydroxamate tests.

The infrared spectrum ($CCl_4$) contained bands at 2235 and 2140 $cm^{-1}$ (acetylenic groups), 1729 $cm^{-1}$ (conjugated ester), and 1610 $cm^{-1}$ (double bond). The ultraviolet spectrum (hexane) contained maxima at 225.3 $m\mu$ [log $\epsilon$ (extinction) $= 4.57$], 276 $m\mu$ (log $\epsilon = 4.08$), 292 $m\mu$ (log $\epsilon = 4.31$), and 310.5 $m\mu$ (log $\epsilon = 4.30$) and closely resembled that of *cis*-lachnophyllum ester (*3*).

The nuclear magnetic resonance also was in agreement with the structure of *cis*-lachnophyllum ester. Absorption occurred at $\tau$ 8.97 (triplet, 3H), 8.44 (multiplet, 2H), 7.66 (triplet, 2H), 6.27 (singlet, 3H), and 3.90 (singlet, 2 vinyl hydrogens).

To completely identify the ester, we secured a small quantity of authentic *cis*-lachnophyllum ester (*5*). The melting point of our compound mixed with the authentic sample was undepressed.

Sorensen (*1*) has argued that knowledge of the structures of naturally-occurring acetylenes may aid taxonomists in resolving difficult classification problems in the *Compositae*. Morphologically similar species from different genera can be divided according to the type of $C_{10}$ acetylene present. For this reason we feel that an extensive survey of the desert aster and related species for polyacetylene content may reveal interesting taxonomic relationships.

JEFFREY C. SPITZER
CORNELIUS STEELINK*

*Department of Chemistry,*
*University of Arizona, Tucson*

### References and Notes

1. N. A. Sorensen, in *Chemistry of Natural Products*, Intern. symp., Australia, 1960 (Butterworths, London, 1961), p. 569.
2. V. V. Viljams, V. S. Smirnov, V. P. Goljmov, *Khim. Zhur. Ser. A.* (*Zhur. Obshschei Khim.*) **5**, 1195 (1935).
3. N. A. Sorensen and K. Stavholt, *Acta Chem. Scand.* **4**, 1575 (1950).
4. P. S. Martin and C. Steelink, *Bull. Ecol. Soc. Amer.* **41**, 129 (1960).
5. We thank Prof. N. A. Sorensen, Norges Tekniske Hogskole, Trondheim, Norway, for providing a sample of *cis*-lachnophyllum ester.

* On sabbatical leave at the Forest Products Laboratory, Madison, Wis.

24 September 1964

■

## Thermodynamic Equilibria in Prebiological Atmospheres

Abstract. *The concentrations of a large number of compounds of biological interest which would be present in the atmosphere at thermodynamic equilibrium were computed under many combinations of temperature, pressure, and elemental composition. These computations revealed a possible mechanism for the abiological formation of asphaltic tar and an oxidative threshold at which all but the simplest compounds disappear.*

One of the principal problems in understanding prebiological conditions on the earth and extraterrestrial atmospheres concerns the nature of the complex chemical species to be encountered. Certain complex compounds must have been necessary for the origin, structure, and nutrition of the first living things. These compounds must have been produced by nonliving processes in suitable quantities and proportions. The elucidation of these concentrations is one essential for a detailed rational theory of the evolution of chemical reactions and the origin of life.

Experiments have been performed in which biologically interesting compounds, such as amino acids, were generated in an atmosphere of small molecules (*1*). Electrical discharge, ultraviolet or other radiation, or heat was applied to the gaseous mixtures.

Computations of the equilibrium concentrations of major constitutents in particular reactions have been made previously. The most important of these are summarized by Miller and Urey (*2*) and by Oparin (*3*). Suess (*4*) has considered the equilibrium of five major chemical species in the system C, H, O. He has calculated the compositions at which solid carbon would appear. No unified study including a great many organic compounds in the equilibrium has been undertaken heretofore.

We have computed the thermodynamic equilibrium concentrations of all major constituents and a representative group of over 100 minor compounds containing O, N, H, and C, considering all elemental compositions and a large range of temperatures and pressures. To include many regions of interest to models of the primitive atmosphere, temperatures between 300° and 1000°K and pressures between $10^{-6}$ and 300 atm were used.

The distribution of molecular species at chemical equilibrium is independent of the specific reactions by which that equilibrium was reached. It requires only that there be at least one reversible reaction path from the major constituents that will produce each compound, and depends only on pressure, temperature, and elemental composition. The equilibrium constants for all possible reactions are then simultaneously satisfied. Many of the conditions which might have arisen naturally can be approximated by thermodynamic equilibria (*5*). These approximations are particularly good at elevated temperatures where reactions proceed rapidly in both directions, as for example in the atmosphere of Venus or in volcanic areas of the earth, or in other regions where catalysts are available. In regions where special mechanisms operate to favor the production of certain compounds, there will be also a tendency to form the products required by thermodynamic equilibrium. Compounds which can be formed at equilibrium need no such special mechanism to explain their presence. However, such special mechanisms would have to be sought for those compounds which could not be so produced but which would have been required for the structure and nutrition of the first living things.

The difficulties previously limiting the computation of concentrations of many organic compounds were overcome by using a high-speed computer. Our program for the IBM 7090 computer minimizes the free energy of the system and yields equilibrium compositions of the compounds by means of the very general method developed by White, Johnson, and Dantzig (*6*). The solution is approached by an iterative process. At each step, $M + 1$ linear equations are solved, where $M$ is the number of elements in the system. The atmosphere was assumed to be a mixture of perfect gases. Twenty-five elements and over 500 compounds can be handled by the program.

The standard free energies of formation for the compounds were obtained from National Bureau of Standards tables (*7*) or computed by summing the free energies of their component groups by Van Krevelen's method (*8*). Values for the major constituents such as $CO_2$, $CH_4$, $H_2O$, and CO are known accurately. For the biologically interesting compounds, the free energies are known to an accuracy of about 2 kcal/mole, although differences within a series of homologous compounds are less. If the free energy used for a compound is too high by 1 kcal, the concentration calculated will be too small by a factor of 0.36 at 500°K and 0.60 at 1000°K.

Only compounds having molecular weights less than 300 were included in this initial study. The free energies of an extended list of biologically inter-