(M^+-CHO); acetate, m.p. 123–124° (EtOH), methyl ether, m.p. 56–58° (MeOH); benzoate, m.p. 196–198° (EtOH); m.m.p., co-PC.

EtOAc *fraction.* Scutellarin as before.[3] *Comment.* This is the first record of the isolation, from the Bignoniaceae, of hydroquinone, the only C_6 phenol of systematic interest, which is common[4] in the Ericaceae, Rosaceae, Proteaceae and Compositae. The recent isolation of hydroquinone from *Majorana hortensis*,[5] Labiatae and the present report justifies the two families in the Tubiflorae.

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COMPOSITAE

CYNAROPICRIN: A SESQUITERPENE LACTONE FROM *CENTAUREA AMERICANA*

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Key Word Index—*Centaurea americana*; Compositae; sesquiterpene lactone; cynaropicrin; guaianolide.

A chloroform extract of *Centaurea americana* collected in Mexico yielded after chromatography a polar sesquiterpene lactone as major constituent. IR and NMR spectral properties of the lactone were very similar to those of cynaropicrin which was first isolated from *Cynara scolymus* L.[1] and whose spectral data were given by the Czechoslovakia group[2] and the structure has been recently revised to I[3] with the described stereochemistry at C_3 and C_8 which were deduced by the Horeau's method and the empirical NMR rule.[4]

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[2] Z. SAMEK, M. HOLUB, B. DROZDZ, G. IOMMI, A. CORBELLA and P. GARIBOLDI, *Tetrahedron Letters* 4775 (1971).
[3] A. CORBELLA, P. GARIBOLDI, G. IOMME, Z. SAMEK and M. HOLUB, *Chem. Commun.* 386 (1972).
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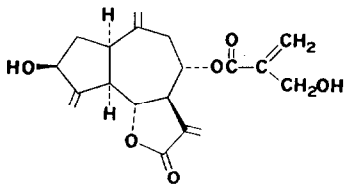
The identity of the *Centaurea* lactone with cynaropicrin was well established by comparison of NMR spectra of deacylated cynaropicrin.[5]



(I)

A crystalline di(trimethylsilyl)ether and a C_3-*O*-*p*-bromobenzoate IV[6] were prepared from deacylcynaropicrin upon standard procedures. The *p*-bromobenzoate is being submitted to X-ray analysis for confirmation of the absolute structure I and the possible conformation proposed in the NMR rule.[4]

EXPERIMENTAL

All m.ps are uncorrected. NMR spectra were recorded in δ-scale on a Hitachi R-20B (60 MHz) spectrometer unless otherwise stated.

Isolation of cynaropicrin (I) *from* Centaurea americana. Dried and ground plant material (500 g) of *Centaurea americana* collected in June 1971 on Highway Las Torres, Monterrey, Nuevo Leon, Mexico was extracted at room temp. with three 2-l. portions of $CHCl_3$. The $CHCl_3$ extract was concentrated *in vacuo*; yield of crude syrup: 19·2 g. The crude syrup was chromatographed over silica gel eluted with $CHCl_3$, then with $CHCl_3$–acetone (3:1). The $CHCl_3$–acetone fraction yielded cynaropicrin (I) as colorless viscous oil (2·96 g). IR (Nujol) and NMR (DMSO-d_6) spectra of the substance were nearly identical with those of the authentic specimen.[5]

Desacylcynaropicrin (II) *from cynaropicrin* (I). Cynaropicrin (I) was heated at 100° with 1·0 N Na_2CO_3 for 2 hr. The acidified solution was extracted with *n*-BuOH and the residue from the washed (NaCl soln) extract purified by TLC on silica gel with acetone–EtOAc (1:1) (R_f 0·8). NMR spectrum (recorded on a Varian HA-100 spectrometer) of (II) was identical with that of deacylcynaropicrin.[5]

Deacylcynaropicrin-di-(trimethylsilyl) ether (III) *from* (II). Deacylcynaropicrin (II) was silated in anh. pyridine with trimethylchlorosilane and hexamethylsilazane and after evaporation extracted with CCl_4 to give the crude silyl-ether; 69 mg, m.p. 115–117° (from cyclohexane). IR bands (Nujol): 1768, 1665, 1640, 1250, 1080, 900, 880, 842 cm^{-1}. NMR signals ($CDCl_3$): 0·15 and 0·20 (*s*, 9H) for Si–Me groups, 3·5–4·5 (*m*, 3H) for –OC$\underline{H}<$ *s* at C_3, C_6 and C_8, 4·90, 5·06, 5·20 and 5·31 (*b s*, 1H for each) for two C=C$\underline{H}_2$ groups 5·95 and 6·23 (*dd*, *J* 3, 1 Hz, 1H for each) C=CH_2 at C_{13}.

Desacylcynaropicrin C_3-O-p-*Bromobenzoate* (IV) from (II). Deacylcynaropicrin (II) was acylated with *p*-bromobenzoyl chloride and anh. pyridine at room temp. The $CHCl_3$ soluble material from the basified mixture was purified by TLC on dried silica gel with benzene–acetone (4:1) (R_f 0·45) giving the bromobenzoate: 40 mg. m.p. 163–165° (from EtOAc). ($C_{22}H_{21}O_5Br$ requires: C, 59·33; H, 4·75; Br, 17·97. Found: C, 59·28; H, 4·70; Br, 17·97%.) IR bands (Nujol): 3420, 1745, 1725, 1645, 1590, 1265, 1102, 755 cm^{-1}. NMR signals ($CDCl_3$): 1·5–3·2 (*c*, 7H), 3·8–4·3 (overlapped *m*, 2H) for O–$C_8\underline{H}$ and O–$C_6\underline{H}$, 5·05, 5·15, 5·40 and 5·60 (*b s*, 1H for each) for two C=C$\underline{H}_2$ groups, 5·75 (*b d*, *J* 7 Hz, 1H) for C_3–$\underline{H}$, 6·21 (two overlapped *d d*, 2H) for C=C$\underline{H}_2$ at C_{13}, 7·57 and 7·90 (two *AB d*, *J* 9 Hz, 2H for each) for aromatic protons.

[5] We are thankful to Dr. Z. SAMEK for the authentic specimen and NMR spectra of cynaropicrin and the deacyl derivative. Due to quick deterioriation of the sent natural lactone and minor impurities results of direct comparison at the natural lactone were not quite satisfactory. We are also indebted to Dr. K. TORI for NMR analysis (100 MHz).

[6] The position to which *p*-bromobenzoyl group was introduced was deduced from the NMR data given in the Experimental.