Constituents of *Casimiroa Edulis Llave et Lex.* V.[1] Identity of Casimirolid and Obacunone

FRANZ SONDHEIMER, ALEX MEISELS, AND FRED A. KINCL[2]

Received December 15, 1958

The isolation of the lactone casimirolid (m.p. 229–231°, $[\alpha]_D$ −49°) from the seeds of *Casimiroa edulis Llave et Lex* was described in 1911 by Power and Callan[3] and recently by our group.[4] The lactone obacunone (m.p. 229–230°, $[\alpha]_D$ −51°) was first isolated by Kaku and Ri[5] from the bark of *Phellodendron amurense;* it was later obtained from citrus oil by Emerson,[6] who suspected it to be identical with casimirolid. We have now carried out a direct comparison between casimirolid and obacunone. The complete identity of the characteristic infrared spectra, as well as the fact that no melting point depression was observed on admixture, conclusively proves the two substances to be identical.

Casimirolid had been assigned the formula $C_{24}H_{28}O_6$ by Power and Callan[3] and $C_{28}H_{32}O_8$ by ourselves,[4] whereas obacunone undoubtedly possesses the formula $C_{26}H_{30}O_7$.[6,7] A series of new analyses of casimirolid has now shown the previously proposed formulas to be incorrect and favors the $C_{26}H_{30}O_7$ formulation also for this substance.

Although the name casimirolid has priority,[3] the structural investigations by Emerson[6] and especially by Dean and Geissman[7] have been carried out with obacunone, yielding degradation products the names of which have been derived from this substance. We propose therefore that the name obacunone be retained and casimirolid be abandoned.

EXPERIMENTAL

Comparison of casimirolid with obacunone. A sample of casimirolid[4] was crystallized repeatedly from ethanol and was then dried for 24 hr. at 120° (0.1 mm.). It showed m.p. 230–231°, $[\alpha]_D$ −49.6° ($CHCl_3$).

Anal. Calcd. for $C_{26}H_{30}O_7$: C, 68.70; H, 6.65; O, 24.64; Calcd. for $C_{28}H_{32}O_8$: C, 67.73; H, 6.50; O, 25.78. Found: C, 68.90, 68.79; H, 6.76, 6.83; O, 24.57, 24.33.

The infrared spectrum (potassium bromide pellet, determined on a Baird double-beam spectrophotometer) showed more than 20 well defined bands, the main ones being at 2.87, 3.31, 5.78, 5.88, 6.68, 6.85, 7.20, 7.45, 7.63, 7.83, 8.17, 8.62, 8.95, 9.35, 9.40, 9.75, 10.16, 10.24, 10.92, 11.46, 12.17, and 12.48μ.

An authentic sample of obacunone showed m.p. 229–231°, $[\alpha]_D$ −49.8° ($CHCl_3$). There was no depression in m.p. on admixture with a sample of casimirolid. The infrared spectrum was completely identical with that of casimirolid.

Acknowledgment. We are indebted to Dr. O. H. Emerson and to Drs. F. M. Dean and T. A. Geissman for their courtesy in providing us with samples of obacunone.

THE DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL

---

[1] Part IV, F. Sondheimer and A. Meisels, *J. Org. Chem.*, **23**, 762 (1958).

[2] Syntex S.A., Apart. Post. 2679, Mexico D.F., Mexico.

[3] F. B. Power and T. Callan, *J. Chem. Soc.*, 1993 (1911).

[4] F. A. Kincl, J. Romo, G. Rosenkranz, and F. Sondheimer, *J. Chem. Soc.*, 4163 (1956).

[5] T. Kaku and H. Ri, *J. Pharm. Soc. Japan*, **55**, 222 (1935) [*Chem. Abstr.*, **31**, 6643 (1937)].

[6] O. H. Emerson, *J. Am. Chem. Soc.*, **73**, 2621 (1951).

[7] F. M. Dean and T. A. Geissman, *J. Org. Chem.*, **23**, 596 (1958).

Beckmann Rearrangement of 4-Trimethylsilylacetophenone Oxime

ROY G. NEVILLE[1]

Received December 17, 1958

Few reports of aminoaryltrialkylsilanes occur in the literature[2] as these compounds readily undergo fission of the aromatic carbon-silicon bond, particularly in acidic media. Those amines which have been reported were prepared by hydrogenation of the corresponding nitro compounds over a Raney nickel catalyst.[3–5]

Since 4-trimethylsilylacetophenone oxime (I) has recently become available[6] an attempt has been made to prepare 4-trimethylsilylacetanilide (II), by a Beckmann rearrangement, and then to hydrolyze this compound to 4-trimethylsilylaniline. Treatment of an ethereal solution of I with thionyl chloride or phosphorus pentachloride gave good yields of II. With sulfuric acid the yields of II were lower. The anticipated cleavage of the aromatic carbon-silicon bond of I did not occur under the conditions employed.[7] Analysis for nitrogen and silicon, and the infrared spectrum, confirmed the structure of II.

On heating the anilide under reflux with 40 or 70% aqueous-alcoholic potassium hydroxide for 30 minutes, then neutralizing, unreacted II was quantitatively recovered. The anilide is thus extremely difficult to cleave under basic conditions.

Heating II under reflux for 15 minutes with 10% aqueous-alcoholic sulfuric acid liberated a dark-brown oil (III). On distilling this oil and examining

---

[1] For reprints: 783 Cereza Drive, Palo Alto, Calif.

[2] F. S. Kipping and N. W. Cusa, *J. Chem. Soc.*, 1088 (1935); F. S. Kipping and J. C. Blackburn, *J. Chem. Soc.*, 1085 (1935).

[3] R. F. Fleming, U.S. Patent **2,386,452** (1945).

[4] B. N. Dolgov and O. K. Panina, *J. Gen. Chem. U.S.S.R.*, **18**, 1129 (1948).

[5] R. A. Benkeser and P. E. Brumfield, *J. Am. Chem. Soc.*, **73**, 4770 (1951); **74**, 253 (1952).

[6] R. G. Neville, *J. Org. Chem.*, **24**, 111 (1959).

[7] N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Oxford; Clarendon Press, 1950, vol. 1, p. 561.