

ether (IV) was obtained by condensing the stearyl *p*-toluenesulfonate (I) with the potassium salt of 1,3-benzylideneglycerol (III) in benzene; in the second stage, 1,3-benzylideneglycerol 2-stearyl ether (IV) was hydrolyzed with dilute hydrochloric acid.

Five hundred ml. of dry benzene and 6.8 g. (0.17 mole) of freshly cut (0.5 cm.) pieces of potassium were placed in a dry 1-liter three-necked round bottom flask fitted with a sealed mechanical stirrer and a reflux condenser. A calcium chloride tube was connected to the reflux condenser to protect the reaction from moisture. The third neck was closed by a glass stopper. The flask was heated carefully to allow the benzene to reflux, until the potassium melted (1–1.5 hr.) and then stirring was started slowly. The potassium was first distributed in fine particles. A part of it on continuous refluxing and stirring disappeared, forming a light blue solution, leaving the remaining in suspension. To this solution, 31.5 g. (0.17 mole) of 1,3-benzylideneglycerol (II) was added very slowly. The stirring and refluxing was continued for 2–3 hr. until a clear light brown solution was obtained, then 70.1 g. (0.16 mole) of stearyl *p*-toluenesulfonate (I) in 250 ml. of benzene was added slowly through a dropping funnel. The solution in the flask was heated to allow it to reflux and was stirred during the addition of stearyl *p*-toluenesulfonate (I). The stirring and heating was continued for another 12–16 hr. to complete the reaction, a brownish precipitate, potassium *p*-toluenesulfonate, appeared. Approximately 400 ml. of benzene was removed from the condensation product by distillation and traces of potassium in the neck of the flask decomposed cautiously with moist ether. The residue in the flask was extracted with ether, the extract was washed with water and dried over anhydrous potassium carbonate. The ether was removed by distillation and the last traces of solvent removed under vacuum. The 1,3-benzylideneglycerol 2-stearyl ether (IV) was obtained in 100.2% yield, saponification value 0.00. It was recrystallized from petroleum ether (40–60°), yield 98.7%, m.p. 59–60°.

Anal. Calcd. for $C_{28}H_{48}O_3$: C, 77.72; H, 11.18. Found: C, 77.57; H, 11.24.

Hydrolysis of 1,3-benzylideneglycerol 2-stearyl ether (IV). Fifty and one-tenth g. of 1,3-benzylideneglycerol 2-stearyl ether (IV) was placed in a 250-ml. round bottom flask. About 20 ml. of 0.5*N* hydrochloric acid was added and the flask was heated on a steam bath for 1 hr. The resultant product was cooled, filtered, and washed with cold water. The crude 2-stearyl glycerol ether (V) was dried under vacuum, yield 98.3%. It was recrystallized from petroleum ether (40–60°), yield 86.6%; acetyl value 261.6 (calcd. 261.7) and m.p. 70–71°.

Anal. Calcd. for $C_{21}H_{42}O_3$: C, 73.25; H, 12.79. Found: C, 73.27; H, 13.19.

1-Stearyl glycerol ether (IX). This ether was prepared under conditions similar to those described for 2-stearyl glycerol ether (V). Approximately 4.5 g. (0.11 mole) of potassium was used in 500 ml. of benzene and 15.8 g. (0.12 mole) of 1,2-isopropylideneglycerol (VI) was substituted for 1,3-benzylideneglycerol (III). Forty-seven and five-tenths g. (0.11 mole) of stearyl *p*-toluenesulfonate (I) was added. The crude 1,2-isopropylideneglycerol 3-stearyl ether (VIII) was obtained in 100.1% yield, saponification value 0.00. It was recrystallized from petroleum ether, yield 97.2% m.p. 60–61°.

Anal. Calcd. for $C_{24}H_{48}O_3$: C, 74.94; H, 12.48. Found: C, 75.2; H, 12.56.

Crude 1-stearyl glycerol ether (IX) was obtained on the hydrolysis of 35.5 g. of 1,2-isopropylideneglycerol 3-stearyl ether (VIII) with 15 ml. of 0.5*N* hydrochloric acid, yield 92.4%. It was recrystallized from petroleum ether, yield 90.0%, acetyl value 261.4 (calcd. 261.7); m.p. 69–70°.

Anal. Calcd. for $C_{21}H_{42}O_3$: C, 73.25; H, 12.79. Found: C, 72.89; H, 12.91.

DEPARTMENT OF FOOD TECHNOLOGY
UNIVERSITY OF ILLINOIS
URBANA, ILL.

Isolation of Cycloeucaenol from West Indian Mahogany Wood¹

LUIS AMORÓS-MARÍN, WANDA I. TORRES, AND CONRADO F. ASENJO

Received July 7, 1958

We wish to report the isolation of cycloeucaenol from the unsaponifiable fraction of the oil from West Indian mahogany wood (*Swietenia mahagoni* Jacq.).

EXPERIMENTAL

Finely shredded mahogany hardwood was extracted exhaustively with petroleum ether (b.p. 35–60°). The petroleum ether was removed by distillation. The remaining viscous reddish oil (0.75% of wood), on standing at ice box temperature, deposited a waxy white precipitate, insoluble in petroleum ether. This waxy material was removed. Its composition and properties have been studied and reported elsewhere.² The supernatant oil was filtered and 100 g. saponified with 150 ml. of 5*N* alcoholic KOH. Extraction of the alkaline saponified solution with petroleum ether removed 18 g. of a white crystalline material, which after several recrystallizations from the above solvent, yielded a product with a constant melting point. The crystals thus obtained (compound I) had the following properties: m.p. 135–136°, $[\alpha]_D^{25} +42^\circ$ (in chloroform). The purified crystals gave a positive digitonin and a reversed Salkowski test. The conventional Tortelli-Jaffe and Lieberman-Burchard tests were negative. With the latter test, however, compound I gave a brown solution with a green fluorescence.

Anal. Calcd. for $C_{30}H_{50}O$: C, 84.4; H, 11.8. Found: C, 84.4; H, 11.7.⁴

A mixed melting point with authentic cycloeucaenol^{5–8} (4- β -demethyl-24-methylenecycloartanol), did not show any depression.

Several derivatives were prepared. Their melting points, analysis, and other characteristics are compared in Table I, with those reported for cycloeucaenol by Cox *et al.*⁶

In Fig. 1 are shown the superimposed infrared spectra curves⁹ of compound I from West Indian mahogany and

(1) Aided by a grant from the Agricultural Experiment Station of the University of Puerto Rico.

(2) C. F. Asenjo, L. Amorós-Marín, W. Torres, and A. del Campillo, *J. Agric. Univ. of Puerto Rico*, **42**, 185 (1958).

(3) All melting points are uncorrected.

(4) Elemental analysis done by Geller Laboratories, West Englewood, N. J.

(5) We are indebted to Dr. Roland E. Kremers and collaborators, Institute of Paper Chemistry, Appleton, Wis. for suggesting to one of us (C.F.A.) the possible identity of our compound with cycloeucaenol.

(6) J. S. G. Cox, F. E. King, and T. J. King, *J. Chem. Soc.*, 1384 (1956).

(7) J. S. G. Cox, F. E. King, and T. J. King, *Proc. Chem. Soc.*, 290 (1957).

(8) We wish to thank Prof. T. J. King, Nottingham University, England, for the gift of some cycloeucaenol for our comparison.

(9) We are indebted to Mr. J. S. Ard, Eastern Utilization Research and Development Division (EURDD), Philadelphia, Pa., for the infrared spectra of compound I and the cycloeucaenol supplied to us by Professor T. J. King. Our thanks to Dr. C. F. Krewson, Head, Biochemical Investigations, Plant Products Laboratory (EURDD), for making this cooperation possible.

TABLE I
DERIVATIVES PREPARED FROM CYCLOEUCALENOL, ISOLATED FROM
WEST INDIAN MAHOGANY AND EUCALYPTUS, RESPECTIVELY

Derivative	<i>Swietenia mahagoni</i> Jack	<i>Eucalyptus microcorys</i>	Calculated for Derivatives of C ₂₀ H ₃₀ O
Cycloeucaenol 3,5-dinitrobenzoate			
M.P.	204-205°	205°	
Analyses	C = 71.6% H = 8.5% N = 4.4%	C = 71.9% H = 8.3% N = 4.5%	C = 71.6% H = 8.4% N = 4.5%
Cycloeucaenol benzoate			
M.p.	127-128°	130°	
Analyses	C = 83.9% H = 10.3%	C = 83.7% H = 10.5%	C = 83.7% H = 10.3%
Cycloeucaenyl acetate			
M.p.	105-106°	110°	
[α] _D ²⁵	+63.0°	+63.0°	
Analyses	C = 81.8% H = 11.2%	C = 81.9% H = 11.5%	C = 82.0% H = 11.2%
Hydrogenated cycloeucaenol (cycloeucaenol)			
M.p.	144-145°	149-150°	
[α] _D ²⁵	+46.4°	+52.0°	
Analyses	C = 83.9% H = 12.1%	C = 84.2% H = 12.1%	C = 84.0% H = 12.2%
Hydrogenated cycloeucaenol acetate (cycloeucaenyl acetate)			
M.p.	105-106°	112-113°	
[α] _D ²⁵	+61.3°	+62.0°	
Analyses	C = 81.9% H = 11.5%	C = 82.0% H = 11.9%	C = 81.6% H = 11.6%
Oxidized cycloeucaenol (cycloeucaenone)			
M.p.	82-83°	84°	
2,4-Dinitrophenylhydrazone of cycloeucaenone			
M.p.	236°	246°	
Light absorption in CHCl ₃	λ _{max} at 368- 370 mμ	λ _{max} at 368 mμ	
ε	23,700	24,000	
Analyses	C = 70.2% H = 8.3% N = 9.6%	C = 71.9% H = 8.7% N = 9.4%	C = 71.5% H = 8.7% N = 9.3%
Cycloeucaenol <i>p</i> -nitrobenzoate ^a			
M.p.	178°	—	
Analyses	C = 77.0% H = 9.3% N = 2.3%	—	C = 77.2% H = 9.3% N = 2.4%
Cycloeucaenol dibromo acetate ^a			
M.p.	159-160°	—	
Analyses	C = 61.4% H = 8.3% Br = 25.0%	—	C = 61.1% H = 8.3% Br = 25.4%

^a These derivatives have not been reported before, as far as we know.

cycloeucaenol from Eucalyptus. The spectral lines of each coincide within instrumental error limits, except for negligible impurity effects in compound I just detectable at 1713 and 855 cm.⁻¹ Otherwise these two curves are identical.

The occurrence of this 4-monomethylated sterol in West Indian mahogany wood furnishes additional evidence of its wide distribution in nature, since it has been isolated before

from the woods of the *Eucalyptus microcorys*⁸ and *Erythrophloeum guineense*.⁵

DEPARTMENT OF BIOCHEMISTRY AND NUTRITION
SCHOOL OF MEDICINE
SCHOOL OF TROPICAL MEDICINE
UNIVERSITY OF PUERTO RICO
SAN JUAN 22, PUERTO RICO