at a dose of 16.1 mg./kg., reduced the volume of secretions and total acid content by approximately 35%.

The screening results indicate that acridine derivatives of the I, II, III, and/or IV types possess biological activity similar to 9-aminoacridine, especially in the areas of antibacterial action and parasitology. The antisecretory action of Compound Ia is a new potential use of acridine derivatives which has not been reported previously.

EXPERIMENTAL[5]

9-Acridinecarbamic Acid Esters (Ic and Id)—9-Aminoacridine (0.02 mole) and 0.02 mole of the necessary chloroformate ester were refluxed for 1 hr. in 300 ml. of acetone in the presence of 4 g. of sodium bicarbonate. The hot suspension was filtered, followed by evaporation of the acetone to yield a residue. The residue was recrystallized from ethanol or ethanol–water to give a solid, 80% yield.

The melting point for Ic was 210–213°.

Anal.—Calc. for $C_{21}H_{16}N_2O_2$: C, 76.81; H, 4.91; N, 8.53. Found: C, 76.91; H, 4.95; N, 8.46.

The melting point for Id was 152–154°.

Anal.—Calc. for $C_{18}H_{18}N_2O_2$: C, 73.44; H, 6.16; N, 9.51. Found: C, 73.29; H, 6.13; N, 9.59.

1-(9-Acridinyl)-3-benzyl-2-thiourea (IIIb)—*Method A*—9-Aminoacridine (0.02 mole) and 0.02 mole of benzyl isothiocyanate were refluxed for 1 hr. in 300 ml. of acetone.The acetone was evaporated, and the residue was recrystallized from ethanol–water to give a yellow solid, m.p. 178–180°, in 90% yield.

Method B—9-Isothiocyanatoacridine (0.02 mole) and 0.02 mole of benzylamine in 100 ml. of ethanol were heated on a water bath for 30 min. When the reaction mixture cooled to room temperature, the precipitate was collected and dried. Two recrystallizations from 25% ethanol–water gave a yellow powder, m.p. 178–180°, in 80% yield.

Anal.—Calc. for $C_{17}H_{17}N_3S$: C, 73.44; H, 4.99; N, 12.23. Found: C, 73.15; H, 5.15; N, 12.05.

Ethyl-N-(9-acridinyl)thiocarbamate (IV)—9-Isothiocyanatoacridine (0.02 mole) and 50 ml. of absolute ethanol were refluxed for 10 hr. The ethanol was evaporated to yield a residue, which was recrystallized from ethanol–water to give an orange solid, m.p. 160–162°, in 90% yield.

Anal.—Calc. for $C_{16}H_{14}N_2OS$: C, 68.06; H, 4.99; N, 9.92. Found: C, 68.16; H, 5.02; N, 10.04.

[5] Melting points were taken in capillary tubes on a Thomas-Hoover apparatus and are uncorrected. Elemental analyses were obtained from Atlantic Microlabs, Atlanta, Ga. IR spectra were recorded on a Perkin-Elmer model 237B spectrophotometer and were as expected. 9-Isothiocyanatoacridine was obtained from Eastman Organic Chemicals.

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Isolation of β-Amyrin and Ellagic Acid from *Couroupita amazonica*

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Abstract □ A phytochemical examination of *Couroupita amazonica* (Lecythidaceae) led to the isolation of β-amyrin and ellagic acid.

Keyphrases □ *Couroupita amazonica* (Lecythidaceae)—isolation, identification of β-amyrin and ellagic acid □ β-Amyrin—isolated and identified from *Couroupita amazonica* □ Ellagic acid—isolated and identified from *Couroupita amazonica*

The Amazonian plant *Couroupita amazonica* was selected for investigation because no phytochemical studies have as yet been reported on this genus of plants. These studies resulted in the isolation of β-amyrin and ellagic acid, which are commonly encountered plant principles.

EXPERIMENTAL

Plant Material[1]—The trunk bark of *Couroupita amazonica* Kunth. (Lecythidaceae) was collected during July 1969 in the vicinity of Iquitos, Perú.

Extraction—The coarsely milled plant material (1.1 kg.) was extracted continuously for 24 hr. in a soxhlet apparatus with petroleum ether (b.p. 30–60°). The petroleum ether extract yielded 6 g. of a semicrystalline residue. The defatted plant material was then air dried and extracted with 95% ethanol, which afforded 67 g. of residue following evaporation of the solvent. This residue was partitioned between equal volumes of chloroform and water, and the aqueous fraction was extracted four times with ethyl acetate.

[1] Voucher specimens (2331 and 2342) were identified by Dr. J. Wurdack, Smithsonian Institution, Washington, D. C., and are deposited at this address.

Isolation and Identification of β-Amyrin—The semicrystalline precipitate from petroleum ether was crystallized from methanol to yield 0.592 g. of colorless needles, m.p. 197–199° [lit. (1) m.p. 194–200°]. The UV spectrum showed only end-absorption at λ_{max}^{MeOH} 206 nm. (log ε 3.48) and $[\alpha]_D^{25}$ + 89.4° (0.5, $CHCl_3$) [lit. (1) $[\alpha]_D^{25}$ + 87°]. An IR spectrum (KBr) was superimposable with that of an authentic sample of β-amyrin. An acetate derivative was prepared in the usual manner and exhibited m.p. 237–238° [lit. (1) m.p. 237–242°]. The identity of the isolate as β-amyrin was confirmed by a direct comparison with an authentic sample (mixed melting point, TLC, and IR).

Isolation and Identification of Ellagic Acid—On standing, a yellow compound (180 mg.) precipitated from the ethyl acetate fraction. This compound was insoluble in all common organic solvents; it was slightly soluble in hot pyridine but would not crystallize from this solvent. It did not melt below 350°, and it gave a green color with ferric chloride (phenolic). The compound was soluble in alkaline solution, giving a yellow color after the addition of alkali. It gave a positive Greissmayer test, indicating the presence of the 4,4′-dihydroxydiphenyl moiety (2). The UV spectrum of an impure sample showed absorption bands at λ_{max}^{MeOH} 366 and 255 nm. In the presence of sodium acetate, a new band appeared at 280 nm., with a corresponding weakening of the band at 255 nm. These UV data are in agreement with those published for ellagic acid (2). The IR spectrum (KBr) showed absorption bands at 3520 (OH), 1720 (unsaturated lactone), and 1601 (aromatic character) cm.$^{-1}$. An NMR spectrum in dimethyl sulfoxide showed only two aromatic protons in symmetric position at δ 7.5. A comparison by paper chromatography showed the isolate and a reference sample of ellagic acid to be identical.

A 30-mg. sample of the impure ellagic acid was heated under reflux with an excess of acetic anhydride for 15 hr. The resulting product was crystallized from dioxane to obtain colorless crystals, which began to sinter at 331° and melted at 338–341° [lit. (3) m.p. 343–346°]. A second 30-mg. sample was methylated in the usual manner with diazomethane. The product was crystallized from dioxane to yield pale-yellow crystals, m.p. 338–340° [lit. (4) m.p. 342–344°]. The IR spectrum (KBr) corresponded with published data for the tetramethyl ether of ellagic acid (4).

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Isolation of Daphnetin-8-β-glucoside from *Daphne papyracea*

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Abstract □ Daphnetin occurs free and bound as β-glucoside in the roots of *Daphne papyracea* Wall. ex Steud. The bound form, however, is not in the form of daphnin, as found in several Thymelaceae, but in the form of daphnetin-8-β-glucoside.

Keyphrases □ Daphnetin-8-β-glucoside—isolated from *Daphne papyracea* □ *Daphne papyracea*—isolation of daphnetin-8-β-glucoside

The isolation of three flavone glycosides was reported by Basu and Nasipuri (1) in their preliminary investigation of the roots of *Daphne papyracea* Wall. ex Steud., collected from Ranikshet, India. Later, Sharma *et al.* (2) reported the isolation of daphnin from the roots of the same plant. The present authors found that daphnetin occurs free and bound as 8-β-glucoside in the roots of the same plant[1] collected in Nepal.

[1] The plant was identified by Mr. P. Joshi, Pharmaceutical Expert to the Government of U.P., India, and the late Prof. N. K. Basu of Banaras Hindu University, Banaras, India. A specimen of the plant was deposited in the Department of Pharmaceutics, Banaras Hindu University, Banaras, India.

DISCUSSION

Two crystalline compounds were isolated: A, m.p. 255–256° dec.; and B, m.p. 229–230°, $[\alpha]_D^{25}$ −92° (solvent: 50% alcohol).

Acid hydrolysis of Compound B provided A_1, identical to Compound A, as shown by its chromatographic behavior, no depression of melting point by admixture with Compound A, and identical UV and IR spectra. The hydrolysate of B contains glucose, identified by chromatography and chromogenic tests. Emulsin hydrolyzed B into A and glucose, showing B to be a β-glucoside of A.

Compound A, giving color reactions for phenols, has the elementary composition of $C_9H_6O_4$ (mol. wt. 178.0282; theoretical 178.0266), and the UV spectral characteristics of a coumarin: λ_{max}^{EtOH} 224 (log ε 4.2), 262 (log ε 3.9), and 326 nm. (log ε 4.05) [literature (3) data for 7,8-dihydroxycoumarin: λ_{max}^{EtOH} 260 (log ε 3.8) and 327 nm. (log ε 4.1)].

Compound A was identified as 7,8-dihydroxycoumarin (daphnetin) from the mass spectrometry, IR, and NMR data.

Mass spectral findings can be rationalized as follows (Scheme I). The fragmentation pattern and relative mass peak abundance are very similar to those of umbelliferone (4), each corresponding *m/e* having an additional value of 16 (for the added oxygen).

The IR spectrum shows absorptions at 3360 (OH), 1665 (lactone), 1580, and 1490 (aromatic) cm.$^{-1}$.

A comparison of the chemical shifts and splitting pattern of the