extracts put at our disposal. S.C. is grateful to NORAD for a fellowship.

1. Henrick, C. A. and Jefferies, P. R. *Aust. J. Chem.* **17** (1964) 578, 915.
2. Cavell, B. D. and Mac Millan, J. *Phytochemistry* **6** (1967) 1107.
3. Shibata, S., Mihashi, S. and Tanaka, O. *Tetrahedron Letters* **1967** 5241.
4. Petridis, C., Verbeck, R. and Massart, L. *Naturwiss.* **53** (1966) 331.
5. Katsumi, M., Phinney, B. O., Jefferies, P. R. and Henrick, C. A. *Science* **144** (1964) 849.
6. Galt, R. H. B. *J. Chem. Soc.* **1965** 3143.
7. Verbiscar, A. J., Cragg, C., Geissman, T. A. and Phinney, B. O. *Phytochemistry* **6** (1967) 807.
8. Sitton, D., Richmond, A. and Vaadia, Y. *Phytochemistry* **6** (1967) 1101.
9. Graebe, J. A., Dennis, D. T., Upper, C. D. and West, C. A. *J. Biol. Chem.* **240** (1965) 1847.
10. Dennis, D. T. and West, C. A. *J. Biol. Chem.* **242** (1967) 3293.
11. Kamthong, B. and Robertson, A. *J. Chem. Soc.* **1939** 925.
12. De Graw, J. I. and Bonner, W. A. *J. Org. Chem.* **27** (1962) 3917.

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Synthesis of an α-Bromo-β-lactam, 7-Bromo-8-oxo-1-azabicyclo-[4.2.0]octane, by Carbene Insertion*

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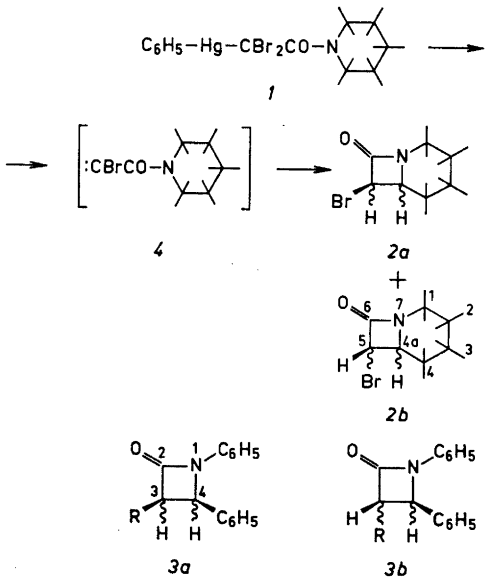
For some time we have been searching for methods of synthesizing β-lactams, containing in the α-position an atom or group capable of undergoing transformation under conditions not affecting the β-lactam system. Our attention was directed to the discovery of Seyferth and co-workers, that halomethylphenylmercury compounds readily decompose giving phenylmercury halides and halocarbenes,[1] and we have found that on thermal decomposition (*N*-dibromoacetylpiperidine)phenylmercury (*1*) gives a mixture consisting of two bromo-β-lactams, A and B, and phenylmercury bromide.

For the β-lactams we propose the structures *2a* and *2b*, respectively. These structures would explain the lability of the β-lactams in acidic and alkaline media and are in agreement with their elemental analysis and spectroscopic properties. The NMR spectra indicated that the coupling constant for the C-4a and C-5 protons of the bromo-β-lactam A was larger than that of the isomer B and the resonance of the C-5 proton of A occurs at lower field than that of B. It has been shown that in 2-azetidinones (*e.g. 3*) the coupling constant is larger for the *cis* protons (*3a*) than for the *trans* protons (*3b*) and that the C-3 and C-4 protons of the *cis* isomer absorb at lower field than those of the *trans* isomer.[2-4] Hence A must have the *cis* configuration (*2a*) and B the *trans* configuration (*2b*).

These conclusions were supported by the mass spectra of the bromo-β-lactams. The

* Synthesis of Strained Heterocyclic Rings, Part 2. Publication delayed by request of the authors. Part 1. Åkermark, B., Johansson, N. G. and Sjöberg, B. *Tetrahedron Lett.* **1969** 371.



relative intensities of the peaks corresponding to loss of bromine and to cleavage of the azetidinone ring were higher for *2a* than for *2b* which is in accordance with earlier results for similar compounds.[5,6]

In several reports α-haloorganometallic compounds have been assumed to form carbenes on thermal decomposition.[7,8] Thus in our case the analogous carbene *4* from the thermal cleavage of *1* could be the intermediate.

We are now exploring the scope of this novel β-lactam synthesis.

Experimental. *N-Dibromoacetylpiperidine.* Dibromoacetic acid (34.0 g) was added to an excess of refluxing thionyl chloride (30 ml) over a period of 1 h. The solution was heated under reflux for an additional 3 h period, the thionyl chloride was removed, and the product distilled at reduced pressure to give dibromoacetyl chloride, b.p. 58°/12 mm (31.5 g, 86 %). The acid chloride was slowly added to an ice cooled solution of piperidine (25 g) in ether (500 ml); the precipitated piperidine hydrochloride was filtered off, the ether solution washed, dried, and the ether evaporated. The residue was recrystallised from ether, giving *N*-dibromoacetylpiperidine (28.8 g, 75 %), m.p. 70–71°. (Found: C 29.0; H 3.8; Br 58.9. Calc. for $C_7H_{11}Br_2NO$: C 29.5; H 3.9; Br 56.1.)

(N-Dibromoacetylpiperidine)phenylmercury (1). A mixture of *N*-dibromoacetylpiperidine (55.0 g) and phenylmercury chloride (17.2 g) in dry benzene (500 ml), under an atmosphere of purified nitrogen, was stirred with a high speed stirrer and cooled to 0–5°C. Freshly sublimed potassium *t*-butoxide (13.0 g) was added during 1.5 h. After an additional 3 h period, the mixture was poured into ice water (500 ml). After filtration and work up in the usual manner,[1] the product was chromatographed on silica gel (Grace Chemical, Copenhagen, 0.15–0.30 mm) giving (*N*-dibromoacetylpiperidine)phenylmercury (*1*) (15.0 g, 50 %), m.p. 126–128°. (Found: Br 28.2; Hg 35.4. Calc. for $C_{13}H_{15}Br_2HgNO$: Br 28.45; Hg 35.7.) NMR ($CDCl_3$, δ-units relative to TMS as internal standard): 1.65 (s. CH_2), 3.73 (s. $N-CH_2$), 7.27 (s. aromatic protons). IR: CO 1605 cm^{-1}. Substantial amounts of *N*-dibromoacetylpiperidine (35.5 g) were recovered.

Thermal decomposition of (N-dibromoacetylpiperidine)phenylmercury. (*N*-Dibromoacetylpiperidine)phenylmercury (2.05 g) was decomposed by heating for 1.7 h in refluxing bromobenzene (dried over sodium hydride and distilled). The solvent was removed *in vacuo*, ether was added, and the insoluble phenylmercury bromide (1.27 g, 98 %) was filtered off. The other components of the product were then separated by preparative thin layer chromatography on silica (Merck, PF_{254}, using ether as developer) giving the two isomeric β-lactams (*2a*) and (*2b*) and a small amount of *N*-dibromoacetylpiperidine (0.10 g, 14 %).

cis-5-Bromo-6-oxoazetidino[1,2-a]piperidine (*2a*, 0.10 g, 14 %). (Found: C 42.7; H 5.0; Br 38.0. Calc. for $C_7H_{10}BrNO$: C 41.2; H 4.9; Br 39.2.) NMR: 1.2–2.2 (m, H-2, H-3, and H-4) 2.5–4.0 (m, H-1, H-4a), 4.98 (two d, *J* 1.4 and 4.4 cps, H-5). IR: CO 1760 cm^{-1}. Mass spectrum: 205, 203 (M, 2), 124 (M–Br, 100), 82 (M–C_2H_2BrO, 22), and *trans*-5-bromo-6-oxoazetidino[1,2-a]piperidine (2b, 0.34 g, 47%), m.p. 72–74°. (Found: C 40.9; H 4.9; Br 39.1. Calc. for $C_7H_{10}BrNO$: C 41.2; H 4.9; Br 39.2.) NMR 1.2–2.3 (m H-2, H-3, and H-4), 2.5–4.0 (m, H-1 and H-4a), 4.4 (d, *J* 1.3 cps, H-5). IR: CO 1760 cm^{-1}. Mass spectrum: 205, 203 (M, 4), 124 (M-Br, 100), 82 (M–C_2H_2BrO, 14).

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1. Seyferth, D., Burlitch, J. M., Dertouzos, H. and Simmons, Jr., H. D. *J. Organomet. Chem.* **7** (1967) 405.
2. Kagan, H. B., Basselier, J.-J. and Luche, J.-L. *Tetrahedron Letters* **1964** 941.
3. Barrow, K. D. and Spotswood, T. M. *Tetrahedron Letters* **1965** 3325.
4. McMillan, I. and Stoodley, R. J. *Tetrahedron Letters* **1966** 1205.
5. Audier, H. E., Fétizon, M., Kagan, H. B. and Luche, J. L. *Bull. Soc. Chim. France* **1967** 2297.
6. Imbach, J.-L., Doomes, E., Cromwell, N. H., Baumgarten, H. E. and Parker, R. G. *J. Org. Chem.* **32** (1967) 3123.
7. Seyferth, D., Mui, J. Y.-P. and Burlitch, J. M. *J. Am. Chem. Soc.* **89** (1967) 4953.
8. Bevan, W. J., Haszeldine, R. N. and Young, J. C. *Chem. Ind. (London)* **1961** 789.

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Some Unusual Flavonoids from *Myrica gale* L.

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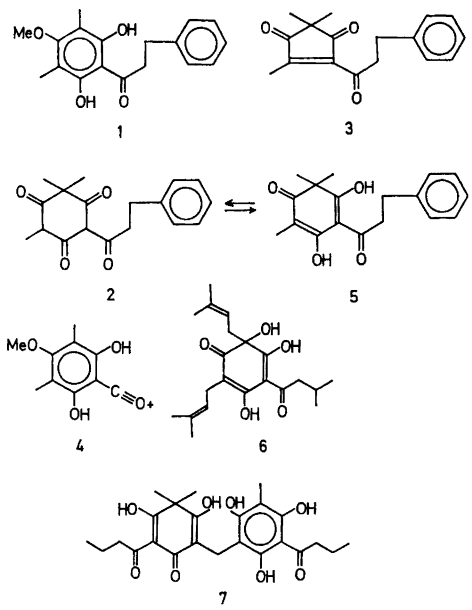
A small bush with a strong aromatic scent, *Myrica gale* L. (bog myrtle) which is very common on moist ground and on peat land in this country, has for ages been utilized as a moth repellant and as a hop substitute in the brewing of beer. A number of terpenoids and flavonoids are known to be present in the plant.[1]

We now wish to report the isolation of three new aromatic compounds *1*, *2*, and *3* from an acetone extract of fruits from this bush. *1* was isolated by column and thin-layer chromatography as yellow needles and recrystallized from ether-petroleum ether (m.p. 116–117°C) [λ_{max} (EtOH) 224 (14 200), 280 (17 400), and 350 (4200) nm; IR: 3600, 1620, 1500, and 1455 cm^{-1}]. The molecular composition of this compound was established as $C_{18}H_{20}O_4$ by accurate measurement of the molecular ion peak (calc. 300.1362, found 300.1365). The NMR spectrum shows two aromatic methyl groups (7.92, 6H *s*) and one methoxy methyl group (6.32, 3H *s*). An A_2B_2 system (τ_A 6.60, τ_B 7.00) and a five proton singlet at 2.80 suggest that the compound might be a dihydrochalcon. Finally a two proton singlet at 0.45 due to two identical hydrogen-bonded hydroxy protons is in good agreement with the constitution *1*.



Additional evidence can be found in the mass spectrum where the base peak at *m/e* 195 ($C_{10}H_{11}O_4^+$) is due to a favoured cleavage leading to the oxonium ion *4*. The relative positions of the methoxy and methyl groups were assigned on the basis of symmetry considerations.

2 was isolated from a more polar fraction from the column and proved to be an isomer of *1* (calc. for $C_{18}H_{20}O_4$ 300.1362, found 300.1365) (m.p. 138–139°C) [λ_{max} (EtOH) 350 (19 900) nm].

The NMR spectrum in deuteriochloroform solution shows that *2* is a mixture of