NOTES

9-*n*-Propyl- and 9-*n*-Butyl-phenanthrene

By G. B. Bachman and R. I. Hoaglin

Bradsher and Amore[1] have reported that samples of 9-*n*-propyl- and 9-*n*-butylphenanthrene prepared by them have different melting points than the same material prepared by Miller and Bachman.[2] It was their suggestion that our samples had somehow become interchanged and that the melting point of 9-*n*-butylphenanthrene as given was actually that of 9-*n*-propylphenanthrene and *vice versa.*

Having available small samples of the original preparations we have re-examined them and have found the Bradsher and Amore suggestion to be correct. The latter authors very kindly supplied us with samples of their own preparations for mixed melting point determinations.

Results with our recrystallized materials indicate the following melting points to be correct:

9-*n*-Propylphenanthrene, m. p. 59°, mixed m. p. 59°
9-*n*-Butylphenanthrene, m. p. 78.5–79°, mixed m. p. 79°
9-*n*-Propylphenanthrene picrate, m. p. 99°

We agree with these authors that 9-*n*-butylphenanthrene does not form a picrate.

It is greatly regretted that this mistake appeared.

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(1) Bradsher and Amore, This Journal, **63**, 493 (1941).

(2) Miller and Bachman, *ibid.*, **57**, 769 (1935).

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Saponins and Sapogenins. XVI. Some Properties of Echinocystic Acid and the Diketomethyl Ester Derived from It

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In their recent paper on quillaic acid Elliott, Kon and Soper[1] have reported that they were unable to dissolve anhydrous echinocystic acid in alcohol and that the diketomethyl ester derived from it "gave no methane under the conditions of the Zerewitinow test." These observations are contrary to that of Bergsteinsson and Noller,[2] who determined the rotation of echinocystic acid in 95% ethyl alcohol in a concentration of 0.25 g. per 50 cc., and that of White and Noller[3] who obtained from the diketomethyl ester a volume of methane corresponding to 3.45 and 3.50% hydroxyl compared with the calculated value of 3.52% for one hydroxyl group per molecule.

We have repeated this work and confirmed both of the original observations.

Echinocystic acid which had been purified by crystallization from isopropyl alcohol was heated at 160° (boiling cyclohexanol) under the vacuum of an oil pump to remove solvent of crystallization. A preliminary determination showed the solubility to be approximately 1 g. per 100 g. of 95% ethyl alcohol. One and one-half grams was then dissolved in ethyl alcohol by heating, the flask stoppered, allowed to cool, shaken mechanically for forty-eight hours at room temperature and then allowed to stand over the week-end. A sample of the clear supernatant solution at 23° was pipetted into a tared weighing bottle and weighed. The solvent was removed in a current of air on the steam-bath and the residue allowed to stand overnight in a vacuum desiccator. The weight of the residue showed a solubility of 1.28 g. (including solvent of crystallization) per 100 g. of solvent.

A redetermination of the optical rotation gave $[\alpha]^{26}_{D} + 27.7 \pm 1°$. $[\alpha]^{26}_{546} + 34.7 \pm 1°$ in 95% ethyl alcohol.

The determination of active hydrogen in the diketomethyl ester which had been dried to constant weight at 140° and 30 mm. pressure, was carried out essentially by the procedure described by Weygand.[4] The methylmagnesium iodide was prepared in isoamyl ether and the compound dissolved in dry xylene. The average blank determination on 2 cc. of the solvent was 0.31 cc. S. T. P. Samples weighing 0.04905, 0.05085 and 0.04870 g. gave corrected volumes of methane of 2.44, 2.28 and 2.34 cc. These corresponded to 3.80, 3.43 and 3.67% hydroxyl compared with the calculated value of 3.52% for one hydroxyl per molecule. Check runs on cholesterol gave 4.29 and 4.15% hydroxyl while the calculated value is 4.45%.

In order to be certain that the diketomethyl ester did not contain alcohol or water of crystallization, the same sample was analyzed for carbon and hydrogen.[5]

Anal. Calcd. for $C_{31}H_{46}O_4$: C, 77.13; H, 9.61. Calcd. for $C_{31}H_{46}O_4 \cdot CH_3OH$: C, 74.67; H, 9.79. Calcd. for $C_{31}H_{46}O_4 \cdot H_2O$: C, 74.35; H, 9.67. Found: C, 76.82; H, 9.44.

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(1) Elliott, Kon and Soper, *J. Chem. Soc.*, 612 (1940).

(2) Bergsteinsson and Noller, This Journal, **56**, 1403 (1934); Bergsteinsson, Doctor's Dissertation, p. 66, Stanford University, 1934.

(3) White and Noller, *ibid.*, **61**, 983 (1939).

(4) Weygand, "Quantitative Analytische Mikromethoden," Leipzig, 1931, p. 209.

(5) Microanalysis by Dr. Carl Tiedcke, New York.