Chemistry

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Structural formulas I, II, and III

Figure 1: Structural formulas I, II, and III

Abstract

Full Text

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Synthesis of Edpetiline

For the synthesis of edpetiline (1), *d*-glucose is acetylated and brominated. The tetraacetylbromoglucose I obtained is condensed in benzene solution, in the presence of dry silver carbonate and with heating, with imperialine II. The water formed in the interaction of hydrobromic acid with silver carbonate is continuously removed by distillation with benzene. From the reaction products a crystalline base with m.p. 224-226° is isolated, identical with tetraacetyledpetiline (1), obtained from natural edpetiline.

The tetraacetyl derivative, upon saponification with alcoholic alkali, gives a crystalline base with m.p. 272-276°, identical with edpetiline III, which is also confirmed by comparison of the IR and UV spectra (Fig. 1) and by the R_f values on the chromatogram.

Experimental Part

Into a three-necked round-bottom flask, with a weak stream of nitrogen constantly being passed through, are placed 2 g of imperialine in 400 ml of absolute benzene and 2.9 g of freshly prepared silver carbonate. To the boiling mixture, dropwise over one hour, are added 100 ml of a benzene solution of 6% tetraacetylbromoglucose. To remove water from the reaction mixture, benzene is continuously distilled off. The amount of benzene in the flask is maintained by adding fresh portions of dry benzene. Boiling of the reaction mixture and distillation of benzene are continued for 4 hours. The benzene solution is then separated from the silver salt by filtration and concentrated in vacuo.

The residue is dissolved, with cooling, in 100 ml of 2% H_2SO_4, washed with ether, alkalized with soda solution, and extracted with ether. On concentration of the ether, imperialine (0.99 g) precipitates. The ether mother liquor after concentration gives crystals with m.p. 220-222°, which after recrystallization from a mixture of acetone and ether (1:5) have m.p. 224-226° (A). A mixed

Fig. 1. IR absorption spectra of natural (1) and synthetic (2) edpetiline

Figure 2: Fig. 1. IR absorption spectra of natural (1) and synthetic (2) edpetiline

sample of these crystals with tetraacetyledpetiline melts at 224-226°. Yield 0.2 g.

Preparation of edpetiline. 0.12 g of (A) in 20 ml of a 10% methanolic solution of caustic potash is heated for 2 hours. After removal of the methanol in vacuo, the residue is dissolved, with cooling, in 5% H_2SO_4. The acidic solution is sub —

alkalinized with ammonia, and the base is extracted with chloroform. The residue after distilling off the chloroform and treating with methanol gives crystals which, after recrystallization from methanol, have m.p. 272-276°, $[\alpha]_D = -56.03$ (c 0.464; methanol), $R_f = 0.86$ (butanol—acetic acid—water 4 : 1 : 5). A mixed sample with natural edpetiline melts

Fig. 1. IR absorption spectra of natural (1) and synthetic (2) edpetiline

at 272-276°. This substance in alcoholic solution has an absorption maximum in the UV region at $\lambda_{\max}290$, $\lg\varepsilon = 1.7$.

Found, %: C 66.2; H 9.06; N 2.35
$C_{33}H_{53}O_8N$. Calculated, %: C 66.9; H 9.2; N 2.36

Saponification of the mother liquor (A). 1.05 g of the mother liquor is saponified analogously to (A). The saponified products are extracted from the alkaline solution with ether and chloroform. From the residue of the ethereal solution, after treatment with acetone, 0.35 g of imperialine is isolated, while the chloroform solution, upon treatment with methanol, gives crystals which, after purification from methyl alcohol, have m.p. 272-276°. A mixed sample of these crystals with natural edpetiline has m.p. 272-276°. Yield 0.25 g.

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REFERENCES

1. R. Shakirov, N. R. Nuriddinov, S. Yu. Yunusov, *Dokl. AN UzSSR*, No. 9, 23 (1963).
2. R. N. Nuriddinov, S. Yu. Yunusov, *Dokl. AN UzSSR*, No. 4, 33 (1961); No. 5, 47 (1962).