243. 4-*Methoxycinnamylidenepyruvic Acid.*

By E. FRIEDMANN.

ALIPHATIC–AROMATIC unsaturated α-ketonic acids, injected into spayed mice, cause the appearance of cornified cells in the vaginal smears (Friedmann, *Nature*, 1935, **135**, 622). It was therefore of interest to investigate whether a similar œstrogenic effect could be obtained with such acids having a pair of conjugated double bonds vicinal to the α-ketonic group.

Cinnamylidenepyruvic acid, which fulfils these conditions, has already been prepared (Friedmann and Mai, *Helv. Chim. Acta*, 1931, **14**, 1213), and its 4-*methoxy*-derivative has now been readily obtained by Erlenmeyer's method for the preparation of unsaturated α-ketonic acids (*Ber.*, 1903, **36**, 2527).

4-*Methoxycinnamaldehyde*.—The yield of this aldehyde, prepared according to Scholz and Wiedemann (*Ber.*, 1903, **36**, 853), was 6·5%, calculated on the anisaldehyde; it was rectified three times, b. p. 166—171°/11 mm.

Sodium 4-*Methoxycinnamylidenepyruvate*.—The foregoing aldehyde (3·1 g.) and pyruvic acid (1·8 g.) in alcohol (5 c.c.) were dropped into an ice-cooled solution of sodium hydroxide (1·5 g.) in dilute alcohol (15 c.c. of 50%); on addition of a few drops of alcohol, the *sodium* salt separated as yellow crystals. After standing over-night, it was triturated with 90% alcohol and collected (yield 74%). When recrystallised repeatedly from hot water (15 vols.), it formed yellow needles, containing water of crystallisation, partly volatile at room temperature (Found : H_2O, 8·3. $C_{13}H_{11}O_4Na,1\frac{1}{2}H_2O$ requires $1\frac{1}{2}H_2O$, 9·6%. Found in dried salt : Na, 9·0. $C_{13}H_{11}O_4Na$ requires Na, 9·0%).

On addition of dilute mineral acids to the salt, a turbid solution resulted which crystallised rapidly. The *acid* was collected after 2 hours, dried, and repeatedly recrystallised from benzene (18 vols.), forming rosettes of orange needles, m. p. 137—138° (decomp.) (Found : C, 67·2; H, 5·2. $C_{13}H_{12}O_4$ requires C, 67·1; H, 5·2%). The acid is easily soluble in cold acetone and methyl and ethyl alcohols, sparingly soluble in water and ether, insoluble in light petroleum. It can be recrystallised from hot glacial acetic acid (10 vols.), chloroform, or benzene. Heated with concentrated sulphuric acid, it gives an intense, dark cherry-red solution. The colour is stable on standing and on gentle heating. By heating with concentrated hydrochloric acid, a pale orange-coloured solution is obtained.

The 2 : 4-*dinitrophenylhydrazone* separates when the acid (0·23 g.) and 2 : 4-dinitrophenylhydrazine (0·2 g.), each in 5 c.c. of glacial acetic acid, are heated together for 1 hr. It forms dark red curved needles, surrounded by a light red jelly. Crystallisation from ethylene glycol monoethyl ether (30 vols.) gives a homogeneous product of dark red granules of rosettes of needles, m. p. 201° (decomp.) (Found : N, 13·7. $C_{19}H_{16}O_7N_4$ requires N, 13·6%).

I am indebted to the British Drug Houses for the supply of material. My best thanks are due to Professor Sir F. G. Hopkins, P.R.S., for the interest he has taken in this work.

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244. *The Alkaloids of* Anagyris Foetida. *Part II.*

By H. RAYMOND ING.

IN Part I (J., 1933, 504), a method of isolating cytisine and anagyrine, the two chief alkaloids present in the seeds of *Anagyris foetida*, was described, but no account was given of other alkaloids present. Subsequent working up of the mother-liquors from these two alkaloids has revealed the presence in small amounts of *N*-methylcytisine and *d*-sparteine. The former (caulophylline) had previously been found to occur in *Caulophyllum thalictroides* by Power and Salway (J., 1913, **103**, 194). *d*-Sparteine has recently been isolated from *Sophora pachycarpa* and from *Thermopsis lanceolata* (Oréchov *et al.*, *Ber.*, 1933, **66**, *B*, 621, 625). The latter species also contains anagyrine and *N*-methylcytisine (Oréchov, Norkina, and Gurevitsch, *Ber.*, 1934, **67**, *B*, 1394).

Since *d*-sparteine was shown in Part I to be identical with hexahydrodeoxyanagyrine, it is not surprising to find it accompanying anagyrine in *Anagyris foetida*, but the amount present is very small and certainly not sufficient to make the seeds of this species a useful source of the alkaloid. No *l*-lupanine (tetrahydroanygyrine) was detected in the mother-liquors from cytisine or anagyrine.

Experimental.

Isolation of N-*Methylcytisine*.—The ethyl acetate mother-liquors from the crystallisation of cytisine were evaporated, and the gummy residue dissolved in water and treated with benzenesulphonyl chloride and alkali. The cytisine still present was precipitated as *benzenesulphonylcytisine*, which is sparingly soluble even in hot water but crystallises from alcohol in diamond-shaped plates, m. p. **263—264°** (Found: N, 8·6. $C_{17}H_{18}O_3N_2S$ requires N, 8·5%). The aqueous filtrate was made strongly alkaline, and extracted first with benzene and then with chloroform. The first extract left on evaporation a non-crystallisable base, which was proved to be anagyrine by comparison of its perchlorate (Found: N, 8·1. Calc. for $C_{15}H_{21}ON_2ClO_4$: N, 8·1%) and picrate, m. p. **244—245°**, with genuine specimens of these anagyrine salts. The second extract left on evaporation a base which slowly solidified; this was crystallised by solution in benzene and addition of light petroleum, forming prisms, m. p. **136—137°**, and was proved to be *N*-methylcytisine (Found: C, 70·9; H, 7·8; N, 13·6. Calc. for $C_{12}H_{16}ON_2$: C, 70·6; H, 7·8; N, 13·7%) by comparison with a genuine specimen prepared from cytisine and also by comparison of its picrate, m. p. **228°**, with *N*-methylcytisine picrate (Power and Salway, *loc. cit.*).

Isolation of d-*Sparteine*.—The acid mother-liquors from anagyrine perchlorate, after treatment with charcoal, were basified with ammonia and extracted with chloroform. Evaporation of the solvent left a residue which solidified on treatment with hot light petroleum. The solid after several crystallisations from ethyl acetate or alcohol melted at **171—172°**, and proved to be identical with hexahydrodeoxyanagyrine (*d*-sparteine) monoperchlorate (Found: C, 53·9; H, 8·0; N, 8·2; Cl, 10·8. Calc. for $C_{15}H_{27}N_2ClO_4$: C, 53·8; H, 8·1; N, 8·2; Cl, 10·6%). A mixture of the monoperchlorate with that of *l*-sparteine melted at **135—140°**, but there was no depression of m. p. on admixture with hexahydrodeoxyanagyrine monoperchlorate. It had been found in Part I that sparteine monoperchlorate was readily soluble in chloroform, but its extraction from an ammoniacal solution was unexpected.

The free base was liberated by alkali and extracted with ether. The amount available was too small for extensive purification, but it distilled at **130—135°/1** mm., and had $[\alpha]_D^{19°}$ + **13·8°** (*c* = **2** in alcohol) (Oréchov *et al.* record $[\alpha]_D$ + **16·3°** for *d*-sparteine). The monohydriodide, m. p. **232—233°**, and the dipicrate, m. p. **204—205°** (Oréchov *et al.* give m. p.'s **234—235°** and **199—200°** respectively for the corresponding salts of *d*-sparteine), gave no depression of m. p. with the corresponding salts of hexahydrodeoxyanagyrine (Ing, *loc. cit.*; m. p.'s **230—231°** and **205—206°** respectively) and of Clemo, Raper, and Tenniswood's *d*-sparteine (J., 1931, 429; m. p.'s **229°** and **205—206°** respectively).

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