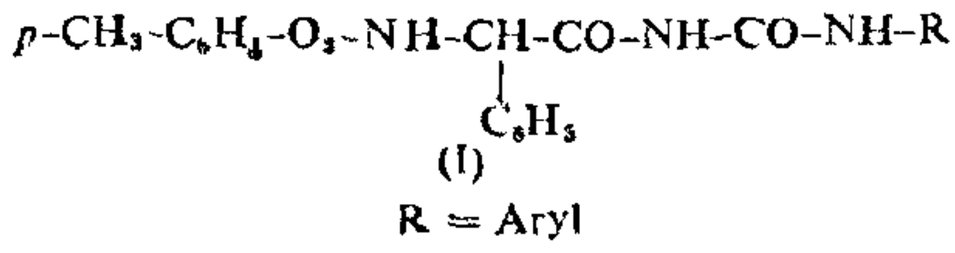


(I)

R = Aryl

EXPERIMENTAL

1. *Preparation of D (−)-α-p-toluenesulphonamidophenylacetyl chloride*:

D (−)-α-*p*-toluenesulphonamidophenylacetic acid was prepared by condensing D (−)-α-aminophenylacetic acid with *p*-toluene sulphonyl chloride[8] % yield 66, m.p. 120–22°, $[\alpha]_D^{30}$ −101 (c, 0·5, 1, 1 in dioxane). The acid was then converted to acid chloride by the action of PCl_5[10], % yield 72, m.p. 155–57°, $[\alpha]_D^{30}$ −88 (c, 1, 1, 1 in dioxan). It gave correct N analysis.

2. *Preparation of D (−)-α-p-toluenesulphonamidophenylacetyl arylureas*:

A mixture of D (−)-α-*p*-toluenesulphonamidophenylacetyl chloride (0·002 mole), different phenyl ureas (0·002 mole) and benzene (15 ml.) was heated under reflux at 60–70° C. for 4 hours. The product was isolated after removal of solvent and crystallised from alcohol. The substituent R, yield in %, m.p. and optical rotation (c, 1, 1, 1 in dioxan) are as under. Phenyl, 92, 90–92°, −71; *o*-Tolyl, 89, 138–40°, −68; *m*-Tolyl 88, 82–84°, −55; *p*-Tolyl 93, 105–07°, −72; *o*-Anisyl 82, 85–87°, −76; *p*-Anisyl 70, 87–89°, −56; *o*-Chlorophenyl 88, 80–82°, −75; *m*-Chlorophenyl 91, 104–06°, −62; *p*-Chlorophenyl 93, 106–08°, −81; α-Naphthyl 84, 70–72°, −61. All compounds gave correct N analysis.

Authors are thankful to Saurashtra University for providing research facilities. They are also thankful to C.S.I.R. (New Delhi) for J.R.F. to V.N.K.

Department of Chemistry, V. N. KHUNT.
Saurashtra University, A. R. PARIKH.
Bhavnagar. *December* 13, 1976.

1. Spiceman, M. A., Ceiszler, A. O. and Clase, W. J., *J. Am. Chem. Soc.*, 1948, **70**, 4189.
2. Mishra, V. S. and Prakash, S., *J. Ind. Chem. Soc.*, 1974, **51**, 969.
3. Clayson, D. B., Pringle, J. A. S. and Ronser, G. M., *Biochem. Pharmacol.*, 1967, **16** (4), 614.
4. Bossche, W. V. D., *Pharm. Tijdschr. Belg.*, 1965, **42** (8), 156; *Chem. Abstr.*, 1966, **64**, 6408*h*.
5. Horstamann, H., Pluemple, H. and Schroeder, *S. African Patent*, 1969, 6904136; *Chem. Abstr.*, 1970, **73**, 25497*n*.
6. Beeslay, W. N., Peters, W. and Mangen, K., *Ann. Trop. Med. Parasitol.*, 1968, **62** (3), 288.
7. Tarbini, G., *Inst. Congr. Chemother. Proc.*, 1967, **5th 2** (2), 909.
8. Goores, E. and Lange, B., *Acta Biol. Med.*, 1968, **21** (2), 193.
9. Vogel, A. I., *A Textbook of Practical Organic Chemistry*, p. 437.
10. Beechamp, A. R., *J. Am. Chem. Soc.*, 1957, **79**, 3257.

FLAVONE FROM *ARTEMISIA HERBA-ALBA* A SYNTHETIC STUDY

A NEW flavone isolated from *Artemisia herba-alba* was assigned its constitution by Segal *et al.*[1] as 5, 4′-dihydroxy-6, 7, 3′-trimethoxyflavone had m.p. 147° whereas Morita *et al.*[3], who isolated its 4′-monoglucoside from *Cirsium lineare*, reported that 5, 4′-dihydroxy-6, 7, 3′-trimethoxyflavone had m.p. 208–10°. However, Krishnamurti *et al.*[2] made this compound in some other connection and recorded its m.p. 200–01°. In view of the different melting points reported for the three different samples of the same flavone, its synthesis by another method was considered desirable to settle this discrepancy. For this purpose, 5, 6, 7, 3′-tetramethoxy-4′-benzyloxyflavone obtained by selenium dioxide oxidation of 2′-hydroxy-3, 4′, 5′, 6′-tetramethoxy-4-benzyloxychalkone[4] when subjected to the catalytic debenzylation and then subsequent selective demethylation yielded 5, 4′-dihydroxy-6, 7, 3′-trimethoxyflavone. This dihydroxytrimethoxyflavone was identical with the sample made by the procedure described by Krishnamurti *et al.*[2].

The natural sample kindly provided by Dr. R. Segal was insufficient for the melting point or mixed melting point determinations which could have settled this discrepancy. Hence the constitution assigned to the flavone isolated[1] from *A. herba-alba* needs revision.

Experimental

5, 6, 7, 3′-Tetramethoxy-4′-benzyloxyflavone.—A mixture of 2′-hydroxy-3, 4′, 5′, 6′-tetramethoxy-4-benzyloxy chalkone[4] (1·0 g), selenium dioxide (1·7 g), and amyl alcohol (40 ml) was refluxed for 24 hrs and then worked out. The flavone crystallised from benzene-acetone as colourless needles, m.p. 178–79°. Mixed melting point with the sample made by the other method* was unchanged.

5, 6, 7, 3′-Tetramethoxy-4′-hydroxyflavone.—The above benzyloxytetramethoxyflavone (0·5 g) in ethyl acetate (50 ml) and Pd–C (0·3 g) were stirred in an atmosphere of hydrogen till debenzylation completed. 5, 6, 7, 3′-Tetramethoxy-4′-hydroxyflavone crystallised from benzene as colourless needles, m.p. 208–10° (Found : C, 63·3; H, 4·8. $C_{19}H_{18}O_7$ requires : C, 63·68; H, 5·02%).

5, 4′-Dihydroxy-6, 7, 3′-trimethoxyflavone.—The above monohydroxytetramethoxyflavone (0·3 g) in acetonitrile (5 ml) and aluminium chloride (0·3 g) were refluxed for 4 hrs., and then worked out. The demethylation product crystallised from alcohol as pale yellow needles, m.p. 200–201°. Mixed melting point with the sample obtained by the other method[2] was unchanged.

Authors thank U.G.C. and C.S.I.R. for the financial assistances.

Department of Chemistry,
University of Delhi,
Delhi 110 007,
December 29, 1976.

D. K. BHARDWAJ.
S. C. JAIN.
C. K. MEHTA.
G. C. SHARMA.

* Krishnamurti *et al.*[2] had reported the m.p. 144–46°. However this flavone, when made by their method, was found to have m.p. 178–79°.

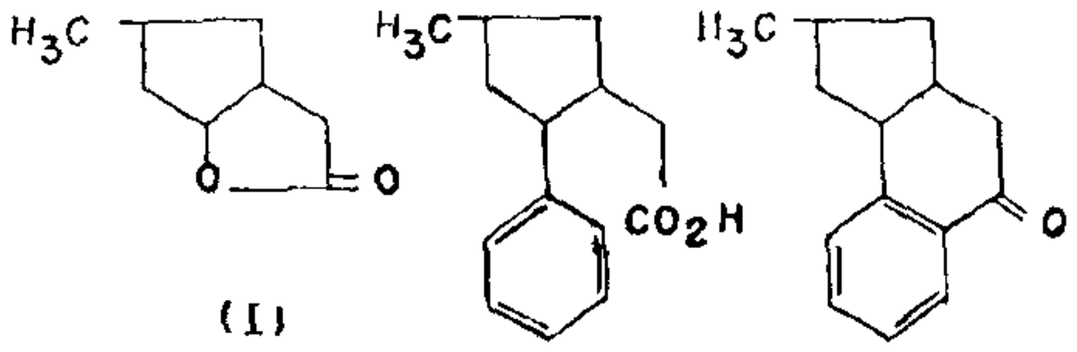
1. Segal, R., Cohen, D., Sokoloff, S. and Zaitschek, D. V., *Lloydia*, 1973, 36, 103.
2. Krishnamurti, M., Seshadri, T. R. and Sharma, N. D., *Indian J. Chem.*, 1973, 11, 201.
3. Morita, N., Shimizu, M. and Arisawa, M., *Phytochemistry*, 1973, 12, 421.
4. Horhammer, L., Wagner, H., Graf, E. and Farkas, L., *Ber. dt. chem. Ges.*, 1965, 98, 548.

FRIEDEL-CRAFTS ALKYLATION OF AROMATIC HYDROCARBONS WITH SUBSTITUTED ALICYCLIC LACTONES

THE aluminium chloride-catalysed condensation of aromatic hydrocarbons with simple substituted alicyclic lactones like the lactone of 4-methyl-2-hydroxycyclohexaneacetic acid was found by Chatterjee and Bhattacharya[1] to afford a mixture of secondary alkylates consisting of 2-aryl and 3-aryl-4-methylcyclohexaneacetic acid to the exclusion of the tertiary alkylate, *e.g.*, the 4-aryl isomer. The facile rearrangement in the cyclopentane system has also been observed by Chatterjee and coworkers[2] who studied the catalysed alkylation of aromatic hydrocarbons with the lactone of cyclopentanol-2-acetic acid. We now report the synthesis of lactone of 4-methyl-2-hydroxycyclopentaneacetic acid (I) and the Lewis acid catalysed alkylation of aromatics with it.

The lactone (I) was prepared from β-methyl adipic acid, m.p. 93° obtained from 4-methylcyclohexanol by oxidation with 50% nitric acid in the presence of V_2O_5. The diethyl ester, b.p. 130–32°/14 mm, on *Dieckmann cyclisation furnished* 4-methyl-2-carbethoxycyclopentanone, b.p. 90–92°/1 mm., which on alkylation by ethyl chloroacetate in the presence of sodium ethoxide afforded ethyl 4-methyl-2-carbethoxy-2-acetate, b.p. 132–35°/0·5 mm. This on hydrolysis by 1:1 HCl yielded 4-methylcyclopentane-2-one-1-acetic acid, b.p. 155–60°/2 mm., semicarbazone, m.p. 210°, which on $NaBH_4$ reduction gave a stereoisomeric mixture of the desired lactone (I), b.p. 95–100°/1 mm n_D^{30} 1·4650, containing a major amount of the trans variety[3].

The Friedel-Crafts condensation of the lactone (I) with benzene in the presence of $AlCl_3$ gave as expected a secondary alkylate consisting of a stereoisomeric mixture of 4-methyl-2-phenylcyclopentaneacetic acids (II), b.p. 155–57°/0·6 mm as the exclusive product, isolated through the ethyl ester, b.p. 140–41°/0·6 mm in 78% yield together with a small amount of 3 methylcyclopentaneacetic acid formed by hydride transfer and consequent reduction of the



(I) (II) (III)

lactone (I). The acid (II) on PPA cyclisation afforded 2-methyl-6-keto 6, 7, 8, 9-tetrahydro-4, 5-benzindane (III), b.p. 137–38°/1 mm. semicarbazone m.p. 206°. DNP derivative m.p. 209° as a stereoisomeric mixture. The structure of the ketone was confirmed by its reduction and dehydrogenation to 2-methyl-4, 5-benzindane, picrate m.p. 91° TNB complex m.p. 103° as well as by its unequivocal synthesis starting from ethyl 4-methylcyclopentane-2-ene-1-acetate and phenyl lithium followed by Paar reduction of the resulting lactone and cyclisation.

A research grant by the Govt. of West Bengal is gratefully acknowledged.

Department of Chemistry,
Presidency College,
Calcutta–73, *January* 3, 1977.

D. N. CHATTERJEE.
(MISS) MALATI SARKAR.

1. Chatterjee, D. N. and Bhattacharya, S. P., *Tetrahedron*, 1971, 27, 4153.
2. —, — and Sarkar, M., *Curr. Sci.*, 1977, 46, 74.
3. House, H. O., Babad, H., Toothill, R. B. and Noltes, A. W., *J. Org. Chem.*, 1962, 27, 4141.

ISOLATION OF α-AMYRIN STEARATE, β-AMYRIN AND LUPEOL PALMITATES FROM THE COSTUS LEAVES

THE isolation of taraxasterol and its acetate from the hexane extract of the leaves (and stalks) of the costus plant, *Saussurea Lappa* clarke, has been reported.[1] By chromatography of the hexane extract over alumina and silver nitrate impregnated silicic acid, followed by cyrstallisation of some of the fractions, three low melting esters A, B, C have been isolated in the pure state. These have been identified as α-amyrin stearate, β-amyrin palmitate and lupeol palmitate respectively, by chemical reactions and comparison of physical constants and spectral data with those reported in literature.[2a,b,c] Ester A, $C_{48}H_{84}O_2$ m.p. 46–48° (EtOH + Me_2CO; 1:4) $(\alpha)_D$ + 61° (benzene, c, 1·84). On saponification, yields stearic acid, $C_{18}H_{36}O_2$, M⁺ 284, m.p. 69° (EtOH) and α-amyrin (I), $C_{30}H_{50}O$, M⁺ 426, m.p. 181 183 (hexane + 10%