Tetrahedron Letters No.15, pp. 985-990, 1965 Pergamon Press Ltd.
Printed in Great Britain.

# SYNTHESIS OF CIS-NORBERGAMOTINIC ACID*

C.S. Narayanan, S.S. Welankiwar, S.N.Kulkarni
and S.C. Bhattacharyya
National Chemical Laboratory, Poona, India.

(Received 14 January 1965)

From Indian valerian root oil, we have recently isolated β-bergamotene[1] which possesses the structure (I) as determined by chemical degradation and spectral characteristics. Its α-isomer, α-bergamotene (II) has been previously examined by Sorm *etal* and also by others.[2] We now report the synthesis of *cis*-norbergamotinic acid, an intermediate required for the synthesis of I & II. The synthesis is patterned in the lines used for the synthesis of *cis*-norpinic acid.[3] Methylhept enone on condensation with ethyl cyanoacetate in the presence of ethanolic ammonia gave the Guareschi's imide (III) which was crystallised from ethanol or isopropyl alcohol, m.p. 190°. The cyclobutane ring was introduced by refluxing the sodium salt of III in methanolic solution with methylene iodide. Acidification then gave IV (crude m.p. 152°) which on two crystallisations showed a constant m.p. 178°. The presence of the cyclobutane ring was confirmed from its NMR+ spectrum (in pyridine) which gives a typical quartet at 5.98, 6.15, 6.44 and 6.62 which is almost identical with a similar quartet (6.0, 6.18, 6.5, 6.68 )observed in the case of IV ($R=CH_3$). A strong IR band is also indicated at $8.8\ \mu$.

Complete hydrolysis of IV by gentle refluxing with aqueous potassium hydroxide (10%, 10 mole, 120 hr) and working up as usual gave the tetracarboxylic acid (V), along with products of partial decarboxylation, as revealed by the analysis of the cyclohexylamine salt. Hence, decarboxylation was completed by heating at 180-185° for 30 minutes to yield a mixture of *cis*- and *trans*- dicarboxylic acids in the form of a gum. Attempt to get an isomerically pure dicarboxylic acid via the crystalline cyclohexylamine salt (m.p. 168°) did not give the desired result. For the preparation of the pure *cis*-dicarboxylic acid, the mixture of the dicarboxylic acids was heated with acetic anhydride (3 ml for 1 g.) at 180-200° for 5 hrs. in a sealed tube. The anhydride (VII) thus obtained was distilled, b.p.175° (bath)/0.5 mm. On hydrolysis with water it gave the pure *cis*-norbergamotinic acid (VIII), which was crystallised from ether-pet.ether as a colourless product, m.p. 165°. The NMR spectrum (in $CCl_4$) of the dimethyl ester is shown in the Figure 1.

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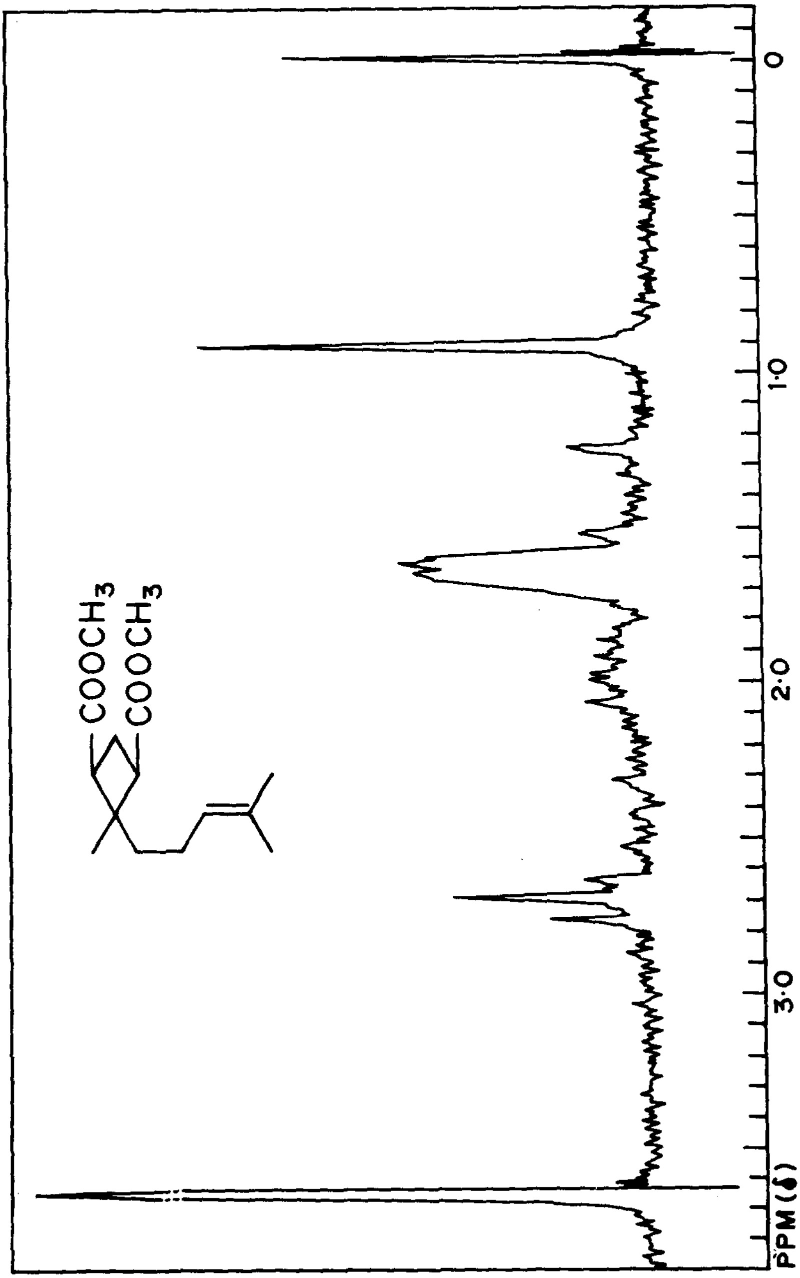
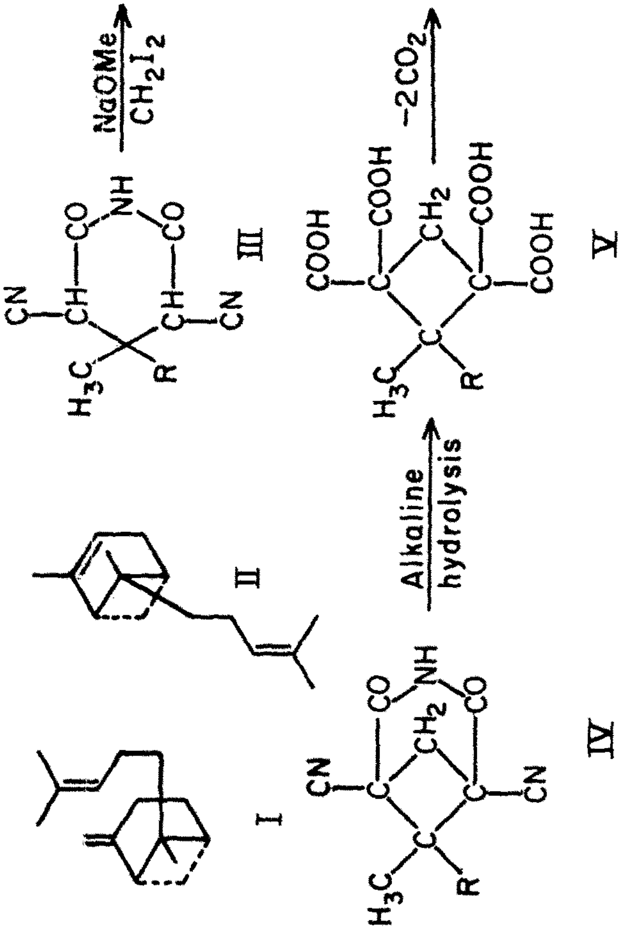
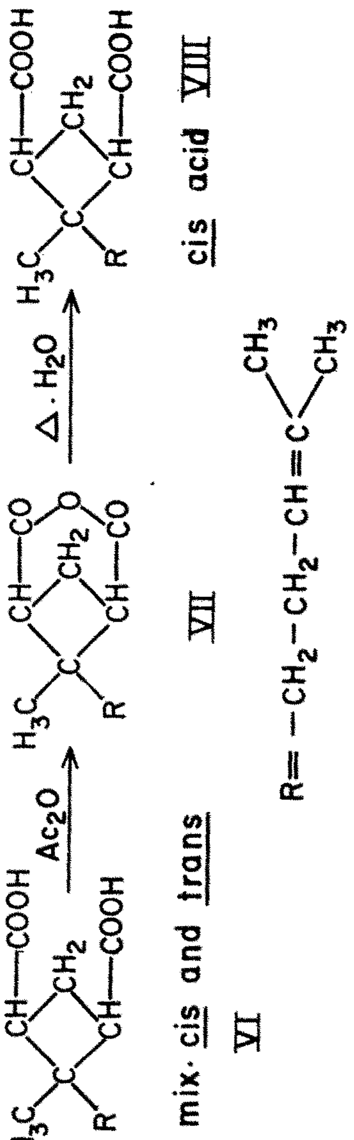
* Communication No.          from the National Chemical Laboratory, Poona-8, India.

\+ NMR spectra were determined by Dr. P.M.Nair and colleagues on a Varian A-60 instrument with TMS as internal standard.

≠ All compounds reported here gave correct elemental analysis which were carried out by Mr. Pansare and colleagues.


COOCH3
COOCH3
0
1·0
2·0
3·0
PPM (δ)


I
II
III
IV
V
NaOMe
CH2I2
Alkaline hydrolysis
-2CO2
H3C
R
CN
CH
CO
NH
CH2
COOH



mix. cis and trans
VI

VII

cis acid VIII

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