A NEW ANTIBACTERIAL POLYISOPRENE BENZOATE FROM GARCINIA KOLA HECKEL FRUITS

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ABSTRACT

From Garcinia Kola Heckel (Guttiferae) fruits a Polyisoprene benzoate (0.9%) was isolated for the first time. The spectral data for the given compound is described. The compound showed antibacterial activity.

INTRODUCTION

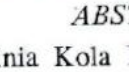
Garcinia Kola Heckel popularly known as bitter cola is a member of Guttiferae and is a native to West Africa (1). It is found under cultivation in Southern part of Nigeria and the native name (Esan) for it is "Adu". The young trees provide chew-stick and the yellow pulp of the fruit and seeds are eaten (1).

EXPERIMENTAL

Plant Material:

The fruits of bitter cola were purchased locally. The botanical origin was established with the authenticated specimens bearing similar anatomical data in the Herbarium of Nigerian Medicinal plants and West African Flora in the Nigerian Institute for Oil Plam Research.

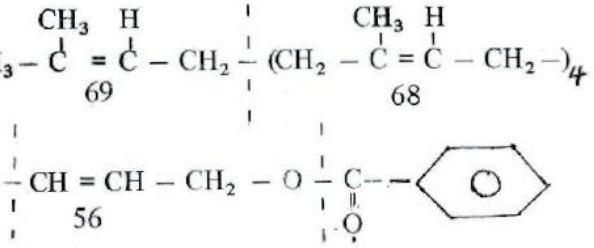
Extraction and Isolation Procedure:

Three hundred and thirty-two grams of the dried and powdered pulp of the fruit of Garcinia Kola Heckel was extracted with 1 litre of petroleum other (40–60°) in a soxhlet apparatus. The extract was concentrated to a low volume at 50° under vacuo. The concentrate on standing in a cool environment yield a brown yellow precipitate (3g). The chloroform solution of the product was spotted on TLC plates. The adsorbent was Kieslger G (type 6) and solvent system was ethyl acetate: chloroform (1:9) and 1:4 (Gradient elution). The TLC plates when developed indicated five spots which were designated as A, B, C, D and E, whose Rf values were A = 0.92, B = 0.85, C = 0.8, D = 0.45 and E = 0.35. The preparative TLC was also performed with the same absorbent and solvent system. On extraction of the bands in methanol only component B gave appreciable amounts of crystalline product. The product was recrystallised from a mixture of ethanol in water (7:3) to give pale yellow needles, m.p. 107–109°; U.V. λmax ETOH 255 and 357mm; I. R. Vmax KBr 3120( ) 2960, 2920, 1650, 1590, 1450, 1420, 1375, 1320, 1270, 1230, 1210, 1180, 1155, 1100, 1080 980, 920, 800, 790, 770, 730, 690, 655cm^{-1}; NMR signals at 1.6 (dimethyl allyl) 2.1 () 2.6 (= C – CH_2) 3.2 (CH_2–CH_2) 5.0 (CH-O-COAr), 7.2 and 7.48 δ (aromatic); M.S. m/e 502, 434, 433, 378, 377, 365, 309, 298, 297, 135, 105, 93, 81, 79, 77, 69, 55, 53, 41, 29. (Found: C, 80.73; H, 8.82; Calc. for $C_{35}H_{50}O_2$: C, 81.27; H, 9,16).

RESULTS AND DISCUSSION

After some initial uncertainty we are now fairly confident that the compound isolated from the pulp of the bitter cola fruits is a polyisoprene benzoate. The chain length of the compound was settled by mass spectroscopy and the nature of the isoprene residue was determined by nuclear magnetic resonance spectroscopy. The precise position of all the cis and trans residue is not yet known but is tempting to speculate that the residues are trans from infra-red absorption peaks.

The mass spectrum of the compound shows that the molecular weight is 502 and also the cracking pattern confirms structure of the compound to be farnesyl geranyl propenyl benzoate shown in Scheme I.



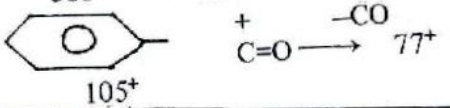
Scheme I

The major fragmentation pattern of I is pictured in Scheme II which account for the important peaks in mass spectrum.

502	→	434^+	+	68	H Transfer
502	→	433^+	+	69	
433^+	→	377^+	+	56	
434^+	→	365^+	+	69	
or 433^+	→	365^+	+	68	

Repeated pattern:

377^+	→	309^+	+	68	
365^+	→	297^+	+	68	



Scheme II

In a molecule of this type one would expect the molecular ion to lose C_3H_4O and also fracture at bonds between adjacent methylene groups (2). This is in fact what happens. The major peaks below m/e = 135 are at 41, 55, 69. This 69 peak corresponds to the ω-terminal residue coming as a charged fragment.

In the nmr spectrum the resonance in the region at δ 1.6 is due to dimethyl allyl group. The peaks of δ 7.2 and 7.4 respectively must be due to 5 protons on the aromatic ring. The absorption band at δ 5.0 is a sort of a multiplet showing the presence of grouping HC-O-CO-Ay. The infra-red spectrum shows the presence of unsaturated linkage at 1650cm^{-1} overlapping with aryl carbonyl group. Two other bands at about 980 and 920cm^{-1} arise from out of plane bending motions on vinyl group. The aromatic and the aliphatic C–H stretching frequencies respectively are apparent on the higher frequency and lower frequency side of 3000cm^{-1}. Bands at 1590 and 1450cm^{-1} are associated with the presence of phenyl group. The methylene bending occurs 1420cm^{-1}. Shown with good resolution the absorption bands at 2960 and 2920cm^{-1} are assignable to C–H stretchings in methyl and methylene groups respectively. The absorption band at 1375cm^{-1} is from a symmetrical deformation of the terminal methyl groups. The bands at 1270 and 1230cm^{-1} are due to C–O stretching vibrations. The absorption bands at 790, 770, 690 and 655cm^{-1} show the presence of five adjacent protons in the phenyl group.

Quantitative determination of isoprepylidene groups (3) in the compound indicated that the molecule contained only one isopropylidene group in agreement with structure I.

Structure I required one terminal methyl in each isoprene unit. A determination showed 0.72–0.73 terminal methyl group for each isoprene unit (4). Since the terminal methyl analysis usually show 0.8 or less for each group, our results are consistent with structure I.

Antibacterial Screening:

The compound isolated from the petroleum ether extract was subjected for investigation of antibacterial activity. The sample and the solvent (Absolute ethanol) system sterilized previously and 1% W/v were placed especially in bores made in nutrient agar seeded with test organisms. The petridishes were examined for bacterial growth after twenty-four hours incubation at 37°C and then compared The highest zones of inhibition were produced by the sample.

Microbiological Screening:

Organism	Gram type	Strain	Zone of inhibition for the compound (mm)	Zone of inhibition for the control (mm)
Pseudomonas acruginosa		isolated locally	15±0.2	1.5
Staphylococcus Aureus	+	ATCH 10081	14.4±0.1	1.5
Bacillus subtilis	+	isolated locally	14.2±0.2	1.5
Streptococcus Pheumoniae	+	isolated locally	14.0±0.1	1.5
Candida Albicans	+	isolated locally	14.1±0.1	1.5
Staphylococcus Aureus			15±0.2 14.4	1.5

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