THE SYNTHESIS AND THE ANALYSIS OF THE CURCUMINE AND OF SOME DERIVATIVES

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Abstract
The curcumin and its derivates are obtained by condensing the carbonyl components. In this condensation vanillin and substitute benzaldehids used in synthesis react as carbonyl components and acetyl acetone react as metylene component through its two metylenic lateral groupings. The problem that appears consists in the fact that acetyl acetone contains also a median metylene grouping the reactivity of which is bigger than that of the lateral ones. Because of this, during the synthesis it is necessary to block the median metylene grouping following that at the end of the synthesis this one is liberated.
The present work aims to synthesise and analyze the curcumin and some of its derivatives using the experimental data regarding the spectrums H-RMN and the electronic spectrums of these components. It was used as primary matter the vanillin for the synthesis of curcumine and of the substituted benzadehids such as : 4 nitro-benzaldehide, N'-dimetilamino-benzaldehide and 4-hidroxi-benzaldehide, for the synthesis of the derivatives of curcumine.

Keywords: derivates of curcumin, chemical synthesis, spectral analysis;

1. INTRODUCTION

The colour is an attribute of the sensorial quality of a food product which together with the form, the size, the structure and the general aspect of the product is determined in the visual reception.
The colorants are organic combinations, natural or synthetic, themselves coloured which intensively absorb the light in the visible domain of the spectrum, but which have the property to colour different materials. In order that an organic combination be coloured material as well, it has to fulfil certain conditions linked to solubility, stability at light or at other physical agents, at adherence on the support it colours.
The necessity to use colorants results from the Directive 94/36 EC from 3-6 June 1994 of the "European Parliament and Council Directive" which specifies the fact that in the category of the colorants it is included those substances that are introduced in the food products in order to establish the colour of the food product which was affected by production, depositing, packaging, and distribution or which are introduced in the food products so that the person who consumes them identifies better the flavour (there is an association between colour and flavour) and to colour respectively o product that lacks colour.
The colour of the food products is not important itself but because it gives a psychic disposition of the subject in order to feed themselves , by unleashing a series of organic reactions that induce ingestion and digestion. This thing is possible because the colour was previously associated to a tasty and nourishing food product and it is very possible that this process permitted and still permits people to chose the best and most convenient food products.
Usually the product becomes the prisoner of a colouring with which the consumers are used. A defined colour is associated to a food product and any modification is appreciated by the consumer as an alteration and from here reclaims to the producer and drop of sales.[1]
If the colour is suppressed or replaced, the consumer thinks it was a change in quality and flavour, even if these do not modify. It is known that the sensorials afferent to the taste, hearing, sight and touch receiver converge to certain superior centres where the sensorial

associations are realized and retained.
The attraction to certain food products is determined to a great extent by colour and is the result of habits and of a real tradition.
The colorants are used in food products only from organoleptic considerations usually to re-establish the colour that degraded during the production process , to fortify the natural colour or even to confer to the products the colorants they never had but which are in direct report with the taste, the flavour , the composition and the aspect.[2]

2. MATERIALS AND METHODES

From the wide number of colorants we will take into study the curcumin using for its synthesis as primary matter the vanillin and derivatives of curcumin using substituted benzadehids such as: 4 nitro-benzaldehide, N'-dimetilamino-benzaldehide and 4-hidroxi-benzaldehide. [4,5] Thus we succeeded to extend the tinctorial palette of the colorants analogues to curcumin by introducing the vanillin and other aromatic substituted aldehides

2.1. Synthesis 1, 5 bis (4 – hidroxi, 3-metoxi phenyl, pentane, 2, 4 diona (curcumin) (la)

In a balloon with a mechanical agitation device it is introduced at room temperature 15,2 g (0,1 mol) vanillin and 50 ml ethyl acetate. The ethyl acetate does not have to contain water in order not to inactivate boric anhydride.
To the obtained solution it is added 50 ml of tributile borate . Separately we put to react in a mortar 2,5g (0,035 mol) boric anhydride well mortared and 5 g (0,05 mol) acetyl acetone. By mortaring ahead after a few minutes it is formed a paste that solidifies. The reaction is considered closed after another 15 minutes.
The obtained solid (ester boro complex of acetyl acetone) is introduced in the reaction bowl prevailed with magnetic device. It is agitated for 5 minutes after which it is added under agitation 1 g of N- dodecilamine during 15-20 minutes.
We continue to agitate for four hours while the boric complex of acetyl acetone passes in the solution. If the boric complex did not dissolve completely we continue to agitate until it dissolves totally. The homogenous solution obtained is let to stay for 20 hours at room temperature for perfecting the reaction.
After this time passed it is added under agitation a solution of HC1 prepared from 50 ml solution HCl 6N with 70 ml warm water (50^0C).
The mixture is stirred (2 liquid phases) for about 30 min. The watery stratum is separated , we add on top of it 100 ml ethyl acetate, it is agitated, the organic stratum is separated after which we add it on top of the ethyl acetate separated initially. The organic phase is washed with water for removing the free acid. It is dried with Na_2SO_4 anhydride and is distilled a part of the solvent under reduced pressure up to a volume of 37 – 38 ml.
It is added 25 ml of methanol and the obtained solution is let at cold 3-4 hours. The formed precipitate is filtered and washed with cold methanol and is dried. It is re-christalled from a mixture the ethyl acetate: methanol at a report of 3:2 (in volume), solvent report : curcumin (masse) being of 7:1;
We obtain 13 g powder of a yellow-orange colour (return of 77,6%)

2.2. Synthesis 1, 5 bis (4-nitrofenil) pentan 2,4-diona (curcumin) (1b)

Instead of vanillin 15,1 g (0,1 mol) p-nitro benzaldehide. It is obtained 14 g powder yellow straw (return of 77%)

2.3. Synthesis 1, 5 (4N, N-dimeti lamino phenil) pentan 2, 4diona (curcumin) (1c)

Instead of vanillin it is used 15 g (0,1 mol) 4 N, N'- dimeti lamino- benzaldehide. It is obtained 14 g powder ywllow –green (return of 65,3%)

2.4. Synthesis 1, 5 bis (4 - hidroxifenil) pentan 2, 4 - diona (curcumin) (1d)

Instead of vanillin it is used 15 g (0,1 mol) 4-hidroxi benzaldehide. It is obtained 13 g powder dark red (return of 66%)

The manner of dealing with the synthesis of these derivates of the curcumin is the same as in the case of synthesis of the curcumin.[6]

3. RESULTS AND DISCUSSION

The Spectre ^{1}H-RMN (in deuterated chlorofor) for the synthetized structures has lead to obtaining the data presented in table 1 and those regarding the electronic spectres , realized in ethanol in table 2.

As we may establish from the data presented I table 2, the structures attributed to synthesized compound are correct. [3]

Table 1. – Experimental data regarding the spectres ^{1}H-RMN of the synthesized curcumin derivates (δ, ppm);

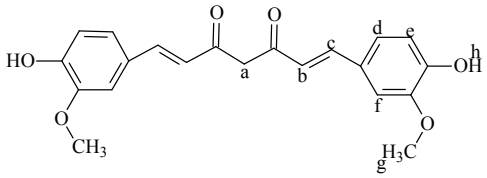
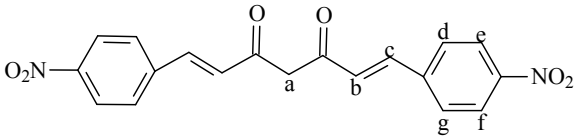
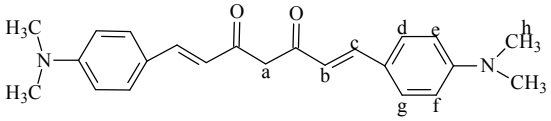
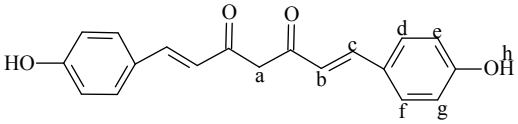
Chemical movement δ (ppm) –$CDCl_3$								
H^a	H^b	H^c	H^d	H^e	H^f	H^g	H^h	H^i
 **51a**								
4.75	6.25	7.91	6.78	6.58	6.75	4.27	5.83	-
 **51b**								
4.75	6.25	7.91	7.59	8.19	7.59	8.19	-	-
 **51c**								
4.75	6.25	7.91	7.08	6.44	7.08	6.44	2.49	-
 **51d**								
4.75	6.25	7.91	7.21	6.68	7.21	6.68	5.83	-

Table 2. – Experimental data regarding the electronic spectres of the synthesized curcumin derivates;

Compound	Maximum of absortion (nm) (EtOH)	ε
51a	490	24900
51b	375.5	26400
51c	498.3	22400
51d	510	22100

In all cases the values δ for atoms of hydrogen engrafted at the carbon placed between the two carbonylic groupings present small values δ situated between 4 and5.
The closeness to marginal flavouring cycles leads to un-screening significantly these ones.
The registered δ values are bigger being situated between 6 and 8 for the H atoms linked to C atoms b and c.
In the case of 1d compound we notice the significant un-screening that the group OH induces to the H atoms linked to the C c and g atom , a more powerful un-screening in the case of the compound 1b (hydrogen atoms from carbon c and f because of the effect – an increased E of the grouping NO_2) . To the compounds 1a and 1c we could notice the groupings CH_3-with H atoms more powerfully evidenced in case of the grouping OH than in the grouping $(CH_3)_2N$-.

4. CONCLUSIONS

- We have synthesized the curcumin and a number of 4 derivates of analogue curcumin type that are not included in the literature of specialty.
- This synthesis has at its basis the formation of the boric mixt ester of acetyl acetone; the enolic form is stabilized by etherification with boric anhydride. After the condensation of the two lateral metilens with two molecules of vanillin or of substituted benzaldehids , the ester is hydrolyzed in acid catalysis obtaining curcumin in free stade respectively derivatives of curcumin that correspond.
- The products obtained were characterized through electronic spectrums IR and ^{1}H-RMN.
- The analyses made acknowledge the mentioned structures for the synthesised components.
- Their utilization as food colorants will be possible only after a preliminary testing of their toxicity by standard biological determinations

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