[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENTS OF THE UNIVERSITY OF BRISTOL AND THE IMPERIAL COLLEGE OF TROPICAL AGRICULTURE]

THE CATECHIN OF THE CACAO BEAN

BY W. B. ADAM, F. HARDY AND M. NIERENSTEIN

RECEIVED NOVEMBER 20, 1930 PUBLISHED FEBRUARY 9, 1931

The presence of a catechin-like substance in the cacao bean was first definitely established by Ultée and van Dorssen,[1] although it appears fairly certain that previously to them Trojanowsky,[2] Hilger[3] and Schweizer,[4] seem to have observed such a substance in the cacao bean. Cacao-ole, the name adopted by Ultée and van Dorssen for the catechin, was shown by them to have the empirical formula $C_{16}H_{16}O_6$, to melt at 220° and to yield an acetyl derivative which melted at 153–154°. The empirical formula of Ultée and van Dorssen thus showed cacao-ole, $C_{16}H_{16}O_6$, to be a methyl derivative of catechin, $C_{15}H_{14}O_6$. The existence of such a methylated catechin in nature seemed to us of great interest, as so far no derivative of catechin has been recorded in the literature to be present in the plant. We have therefore investigated the West African cacao bean. The catechin thus obtained had the empirical formula $C_{15}H_{14}O_6$, melted at 229° and gave a pentaacetyl derivative melting at 151°. The same catechin was also obtained by us from the cacao bean grown in Trinidad. Since both catechins thus derived from Forostero beans,[5] and Ultée and van Dorssen had obtained their cacao-ole from the cacao bean grown in Java, which belongs to the Criollo class, we also investigated the catechin present in the Java cacao bean. Here again a catechin having the empirical formula $C_{15}H_{14}O_6$ was obtained, and a direct comparison of the three catechins proved them to be identical in every respect. In view of this we wrote to Dr. Ultée, who kindly sent us some of his original cacao-ole. On purification, the latter proved also to have the empirical formula $C_{15}H_{14}O_6$, to melt at 229° and to yield a pentaacetyl derivative which melted at 151°. We thus find that the catechin present in the cacao bean is not a methyl derivative of catechin but catechin itself, namely, *l*-acacatechin, one of the catechins present in the cutch-producing acacias,[6] as evident from a direct comparison between the catechin from the cacao bean and *l*-acacatechin. Thus cacao catechin and *l*-acacatechin melt at 229° and rotate in aqueous solution $[\alpha]_D$ −69°; they both give penta-

[1] Ultée and van Dorssen, "Bijdrage tot de kennis der op Java gecultiveerde Cacaosoorten," reprint no. 33, 2d series of Mededeelingen van het Algemeen-proefstation op Java te Salatiga, 1909.

[2] Trojanowsky, "Beiträge zur pharm. u. chem. Kenntnis des Cacao," Dorpat, 1875.

[3] Hilger, *Apoth.-Ztg.*, **7**, 469 (1892).

[4] Schweizer, *Pharm. Ztg.*, **43**, 380 (1898).

[5] Although the Trinidad cacao bean is supposed to be derived from Criollo stock, it has more characteristics of the Forostero than of the Criollo.

[6] Nierenstein, *J. Indian Chem. Soc.*, **7**, 279 (1930).

acetyl derivatives which melt at 151° and rotate $[\alpha]_D$ −12° in tetrachloroethane. Furthermore, neither the catechins themselves nor their acetyl derivatives, respectively, show depression in their melting points on admixture.

The importance of catechin in the production of the red and brown coloring matters and the tannins of the cacao bean have been dealt with in a previous communication, which describes a quantitative method for the estimation of catechin in the cacao bean. From the results with cacao beans from West Africa, Java, Guayaquil, Trinidad, Costa Rica and Bahia it is evident that the catechin content of the cacao bean is about 0.8%.[7]

Experimental

The beans used in the investigation were freshly collected, immersed in boiling water so as to destroy enzymes and sun dried. After removal of the shells, the raw nibs were ground in a mechanical mortar and exhaustively extracted in a large Soxhlet apparatus with petroleum ether. The material was then removed from the extraction apparatus, re-ground, mixed with acid-treated white sand and again extracted for several days with petroleum ether. The product was then freed from petroleum ether by exposure to air, powdered and extracted for a week with chloroform. This treatment was found to be necessary in order to remove completely the last traces of fat and the xanthine bases. No trace of catechin was found in the petroleum ether and chloroform extracts. The dried product was then treated as before and exhaustively extracted for several weeks with ether. The solid left on evaporation was practically pure *l*-acacatechin. It was obtained in colorless, anhydrous needles by purification with lead acetate, and crystallization from water slightly acidulated with acetic acid.[8] This process of purification was also found necessary in the case of Dr. Ultée's specimen. The acetylation was carried out by heating with acetic anhydride. The acetyl derivative crystallized in beautiful thick needles from alcohol, a few drops of acetone being added. The following table summarizes the analytical data obtained for the products dried at 160° (catechin) and 110° (pentaacetyl derivative), respectively.

TABLE I

ANALYTICAL DATA

Source of cacao bean	Catechin, calcd. for $C_{15}H_{14}O_6$: C, 62.06; H, 4.82 Found, % C	H	Pentaacetyl derivative, calcd. for $C_{15}H_9O_6[CO.CH_3]_5$: C, 60.02; H, 4.82 Found, % C	H
West-Africa [*Accra*]	61.92, 62.13	5.07, 5.15	59.72, 60.01	4.97, 4.89
Java	61.97, 62.00	4.99, 5.12	60.03, 59.83	5.03, 4.93
Trinidad	62.09, 61.84	5.02, 4.87	59.76, 59.89	5.12, 5.19
Java [Dr. Ultée's specimen]	61.87, 61.92	5.09, 5.11	59.83	5.02

Summary

It is shown that the catechin of the cacao bean is identical with one of the three catechins present in the heartwood of the cutch-producing acacias, namely, *l*-acacatechin.

BRISTOL, ENGLAND

[7] Adam, *Analyst*, **53**, 369 (1928)

[8] Nierenstein, *J. Chem. Soc.*, **121**, 608 (1922).